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A multi-spatial scale assessment of land-use stress on water quality in headwater streams in the Platinum Belt, South Africa

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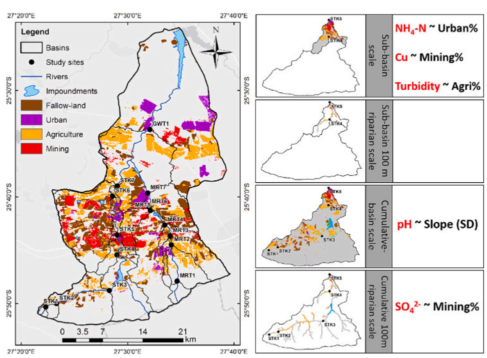
HIGHLIGHTS

- Multi-scale modeling disentangles multiple water quality stressors.
- Water quality reacts to various land uses at particular spatial scales.
- Study demonstrates need for scale-specific water quality management regimes.
- Study provides context for policies that address development and aquatic health.

GRAPHICAL ABSTRACT



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ABSTRACT

River water quality is affected by various stressors (land-uses) operating at different hydrological spatial scales. Few studies have employed a multi-scaled analyses to differentiate effects of natural grasslands and woodlands, agriculture, impoundments, urban and mining stressors on headwater streams. Using a multi-scaled modeling approach, this study disentangled the distinct spatial signatures and mechanistic effects of specific stressors and topographic drivers on individual water quality parameters in tributaries of the Gwathle River Catchment in the Platinum Belt of South Africa. Water samples were collected on six occasions from 15 sites on three rivers over 12-months. Physio-chemical parameters as well as major anions, cations and metals were measured. Five key water quality parameters were identified using principal components analysis: sulfate, ammonium, copper, turbidity, and pH to characterise catchment water quality conditions. Using class-level composition (PLAND) and connectedness (COHESION) metrics together with topographic data, generalized linear mixed models were developed at multiple scales (sub-basin, cumulative catchment, riparian buffers) to identify the most parsimonious model with the dominant drivers of each water quality parameter. Ammonium concentrations were best explained by urban stress, Cu increased with mining and agriculture, turbidity increased with elevation heterogeneity, agriculture, urbanisation and fallow lands all at the sub-basin scale. River pH was positively predicted by slope heterogeneity, mining cover and impoundment connectivity at the catchment scale. Sulfate increased with mining and agriculture composition in the 100 m riparian buffer. Hierarchical cluster analysis of

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water quality and scale-dependent parsimonious drivers separated the river sites into three distinct groups distinguishing pristine, moderately impacted, and heavily mined sites. By demonstrating stressor- and scale-dependent water quality responses, this multi-scale nested modeling approach reveals the importance of developing adaptive, targeted management plans at hydrologically meaningful scales to sustain water quality amid intensifying land use.

1. Introduction

Headwater streams are crucial for supplying appropriate water quality to support aquatic and adjacent terrestrial ecological functionality, while also ensuring socio-economic development. They provide refugia and dispersal corridors for aquatic biodiversity, ensure hydrological connectivity for the storage, processing and energy transfer downstream; all thereby supporting lowland aquatic ecosystem integrity (Wallace and Eggert, 2015). These streams are inherently coupled to the terrestrial biosphere, being reliant on allochthonous energy subsidies from run-off and the surrounding riparian zone (Vannote et al., 1980). Their high stream edge to surface area ratio, however, makes them susceptible to surrounding land-use activities, particularly those that generate mobile pollutants (Richardson and Danehy, 2007). Due to their comparatively smaller size relative to lowland systems, headwater streams are also often unprotected, with few resources allocated to their conservation in developing countries (Richardson and Danehy, 2007; Wallace and Eggert, 2015).

Surface water quality is influenced by natural processes and anthropogenic land-use activities (stressors). In undisturbed catchments, rivers contain seasonally-influenced dissolved substances, such as phosphorus, that support essential biogeochemical cycles and rarely constitute water quality concerns (Boyd, 2019). Globally, anthropogenic stressors modify surface water quality via point and/or diffuse pollution sources. As a result, the relationship between land-use and surface water quality has been investigated extensively (Johnson et al., 1997). Commercial agriculture and livestock farming are leading contributors to sediment loading as well as nitrogenous nutrient input in rivers worldwide through diffuse and point source pollution inputs (Saleh et al., 2000). Urban settlements also contribute diffuse pollution, through stormwater infrastructure and septic tank systems. Poorly maintained domestic bulk wastewater distribution networks and treatment facilities can become point sources of metals and nutrients entering aquatic systems (Paul and Meyer, 2001; Carey et al., 2013). Additional point source and diffuse pollutants are derived from industry and mining, originating from waste storage facilities as well as effluent discharges increasing concentrations of a wide range of pollutants (Erasmus et al., 2020).

To improve catchment water quality management of headwater streams, it is essential to assess the spatial pattern-process relationship between stressors and adjacent water quality (Shehab et al., 2021). Much of the research linking stressors to surface water quality has been conducted on lowland rivers in developed nations (Zhou et al., 2012; Xu et al., 2020; Liu et al., 2021), with fewer on headwater streams in developing nations (Ding et al., 2016). In assessing the effects of stressors on river water quality, the class-level composition metric, being the percentage cover of each land cover class (PLAND), is often integrated with additional class-level metrics, including those assessing connectivity (Ding et al., 2016; Giri and Qiu, 2016; Li et al., 2022). Using such, studies have determined that the predictive relationship between stressors at different spatial scales and aquatic water quality is often catchment and study specific (Allan, 2004).

Past investigations using a range of physico-chemical water quality parameters have identified the catchment scale to best explain water quality variability (Zhou et al., 2012), while other research indicated finer scales (e.g. sub-basin and riparian buffer) (Tran et al., 2010; Ding et al., 2016). For example, nutrient loading and retention has been found to occur at catchment scale (King et al., 2005; Ding et al., 2016; Xu et al., 2020), while across narrower extents rivers can exhibit natural filtering capacities and remove nutrients (Shen et al., 2015; Zhang et al., 2019). Few spatially-aligned studies have, however, examined multi-stressor interactions with mining activities on water quality in headwater streams, particularly within South African catchments. For example, chrome and platinum mining, which provide critical foreign currency revenue for the South African economy (Oranje et al., 2021), are major sources of mobile pollution that can interact with other stressors to influence aquatic water quality. Assessing metal mining contaminants in combination with other parameters like nutrients and suspended particles, can thus provide an important perspective on integrated stressor exposures in streams draining these heavily industrialized regions of the country.

While past studies sought optimal single scales for water quality management (Zhang et al., 2020), certain water quality parameters may respond to heterogeneous drivers operating at different spatial extents, necessitating multi-scaled modeling and management approaches tailored to the processes governing individual parameters (Mello et al., 2018; Wang et al., 2023). A multi-scale multi-parameter approach can capture the true complexity of multi-scale processes influencing river water quality. Importantly, this provides the ability to elucidate the distinct spatial signatures and mechanistic controls of specific stressors as well as catchment processes on individual water quality parameters. Such an approach can allow the development of more adaptive, targeted and scale-dependent management plans for specific problematic water quality parameters while providing a more nuanced understanding of the interplay with various controls on river water quality.

The Gwathle River Catchment in the North-West Province of South Africa, situated within the western lobe of South Africa's intensively mined Platinum Belt (Oranje et al., 2021), offers the ideal case study to assess the relationship between stressors and river water quality responses using different class-level metrics and potentially confounding topographic factors at the sub-basin, cumulative basin, as well as differing riparian scales. This catchment represents a natural experiment with longitudinally stepped mixed land-use activities drained by three low-order rivers, including fallow-land, agriculture, urban and mining activities. All water-usage activities associated with these stressors produce specific and often predictable step-changes in surface water quality through point and/or diffuse source inputs. This allows for individual stressors to be identified and untangled from one another within mixed-use catchments such as this.

This study sought to disentangle and identify dominant drivers influencing specific water quality responses across a land-use intensification gradient using a multi-scaled approach across sub-basin, cumulative, and riparian scales. Sub-basin scales are of particular interest to water resource management in South Africa, where multiple approaches to defining sub-quaternary catchment units have previously been employed for more effective hydrological modeling and water resource conservation (Driver et al., 2011; Nel et al., 2011; Maherry et al., 2013). The research objectives are to 1) determine the key water quality parameters that best characterise the surface water quality conditions of the Gwathle Catchment, 2) assess at which spatial scale water quality responses are best predicted, as a function of class-level metrics and topographic factors, and 3) assess the spatial similarities between river sites using spatially-explicit predictors and water quality variables.

2. Materials and methods

2.1. Study area

The Gwathle River Catchment (Quaternary Catchment A21K), part of the larger Limpopo Water Management Area, drains the northern slopes of the Magaliesberg Mountain range between the towns of Rustenburg and Mooinooi, before its confluence with the Crocodile (West) River at Roodekoppies Dam in the North West Province, South Africa. The catchment has minimum and maximum elevations of 986 m and 1843 m respectively. The semiarid catchment receives on average 629 mm of rainfall per year with the typical wet season being between November and March (wettest January) and the dry season between April and October (Funk et al., 2015). The average monthly air temperatures range between 4.94 °C and 31.76 °C, with June and February being the coolest and warmest months respectively (SAWS, 2023). The western part of the catchment is drained by the third-order Sterkstroom (sites STK1–7), and the eastern part by the third-order Maretlwane (sites MRT1–7), before the two form a confluence with the fourth-order Gwathle River (site GWT1) (Fig. 1).

The rivers fall within two aquatic ecoregions (level 1), the Western Bankenveld and Bushveld Basin. The upland reaches of the catchment are partially contained within the Magaliesberg Biosphere Reserve; an area designated for ecotourism and sustainable development under the UNESCO Man and Biosphere Programme (Pool-Stanvliet, 2013). The catchment lies on the western lobe of the Bushveld Igneous Complex, important for the platinum group elements (PGE) mining industry (Thormann et al., 2017) (Fig. 1; Fig. 2). The catchment is exposed to a stepped progression of stressors from the pristine headwater reaches, followed by commercial irrigated agriculture and livestock rearing (fallow-land), urban and informal settlements, chrome and platinum mining as well as mine supportive industry activities (e.g. smelters). The predominant land cover classes are natural grasslands (67.6 %), followed by agricultural lands (22.0 %), mining activities (4.4 %) and informal-formal urban cover (4.4 %).

2.2. Physico-chemical field sampling

Physico-chemical water quality data were collected during six separate sampling events, capturing individual points in time of wet, intermediate, and dry seasons, between May 2021 and March 2022. A total of 15 river sites were strategically selected, with seven on the Sterkstroom, seven on the Maretlwane and one on the Gwathle River below the confluence of the two main tributaries. Sites were placed immediately up- and down-stream of different land-use activities to capture these unique stressors. At each sampling event, electrical conductivity (μS/cm), total dissolved solids (mg/L), pH (units), dissolved oxygen (mg/L) and temperature (°C) were recorded every 30 s for 5 min in-situ, using a YSI-Professional Plus Handheld Multi-parameter meter. All probes were calibrated prior to field sampling as outlined by the manufacturer specifications. River water clarity (turbidity) was measured in triplicate at each site using a portable Hanna turbidity meter (HI98703–02).

For the chemical analyses, 400 mL water samples were collected from the top 30 cm of the active river channel and filtered through Supor® 0.45 μm 47 mm filters using a Thermo Scientific Nalgene reusable filter unit. Filtrate was stored in two separate one-litre acid rinsed polyethylene bottles and kept in cold storage until transported to the laboratories for further analyses (Akyildiz and Duran, 2021). Once at the laboratory, the sample was analysed for Cl^-, SO_4-S (sulfate), NO_3^--N (nitrate), NO_2^--N (nitrite), PO_4^{3-}-P (ortho-phosphate), NH_3-N (ammonia) and NH_4^+ (ammonium) using a Aquakem/Discrete Analyser (photometric analyser).

Major cations, heavy and trace metals were analysed using an Agilent 7800× inductively coupled plasma mass spectrometry (ICP-MS) with concentrations measured against external matrix-matched standards. Total dissolved solids were determined using a Thermo Scientific ORION STAR A322. Samples with dissolved solids exceeding 120 mg/L were then diluted with milipore water. Each sample had 0.1 m/L of ultrapure acid (HNO_3) added to 10 mL of filtrate. The limitations posed by the limit of detection (LOD) to further statistical analyses were overcome by using a substitution method, whereby the LOD was

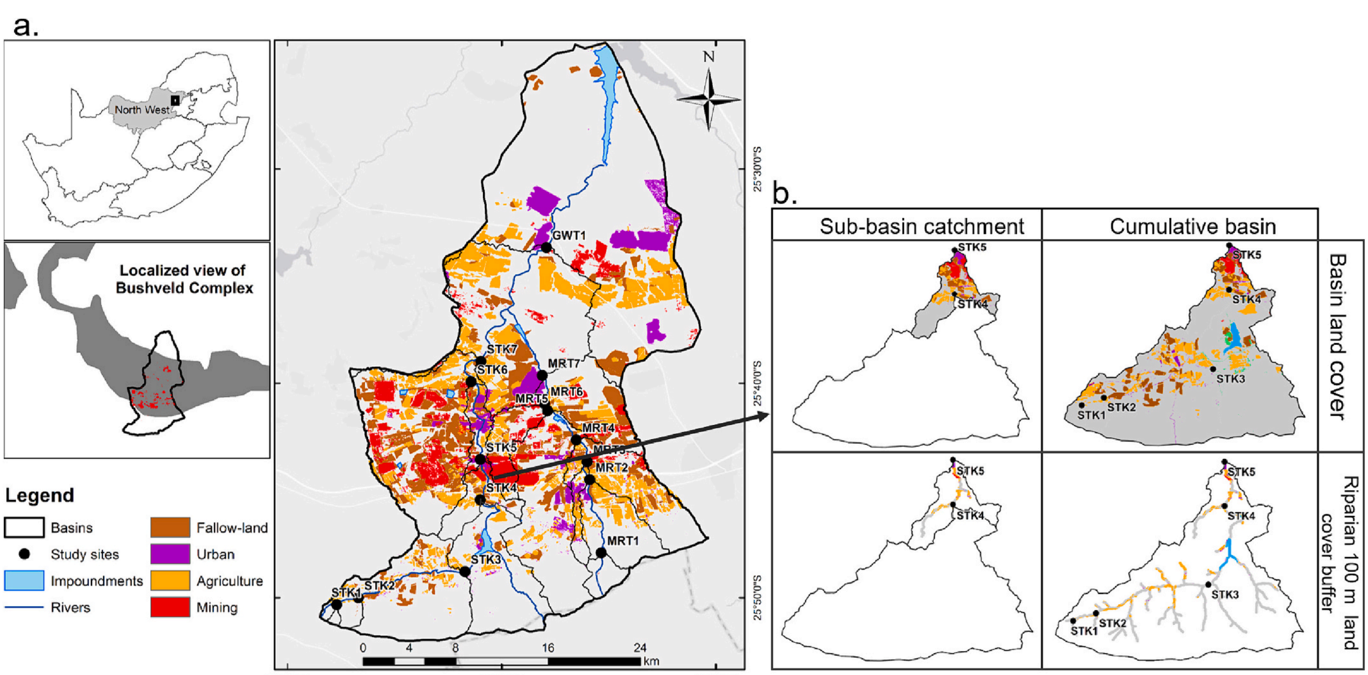

Fig. 1. The distribution of (a.) study sites across the Sterkstroom (STK), Maretlwane (MRT) and Gwathle (GWT) rivers draining an intensification gradient including natural (greyed area within), urban, agriculture and mining stressors in the Gwathle study catchment which lays across the Bushveld Complex. A diagram representing the four assessed spatial scales (b.) of sub-basin catchment, cumulative catchment as well as the riparian sub-basin 100 m buffer and riparian cumulative 100 m buffer spatial scales.

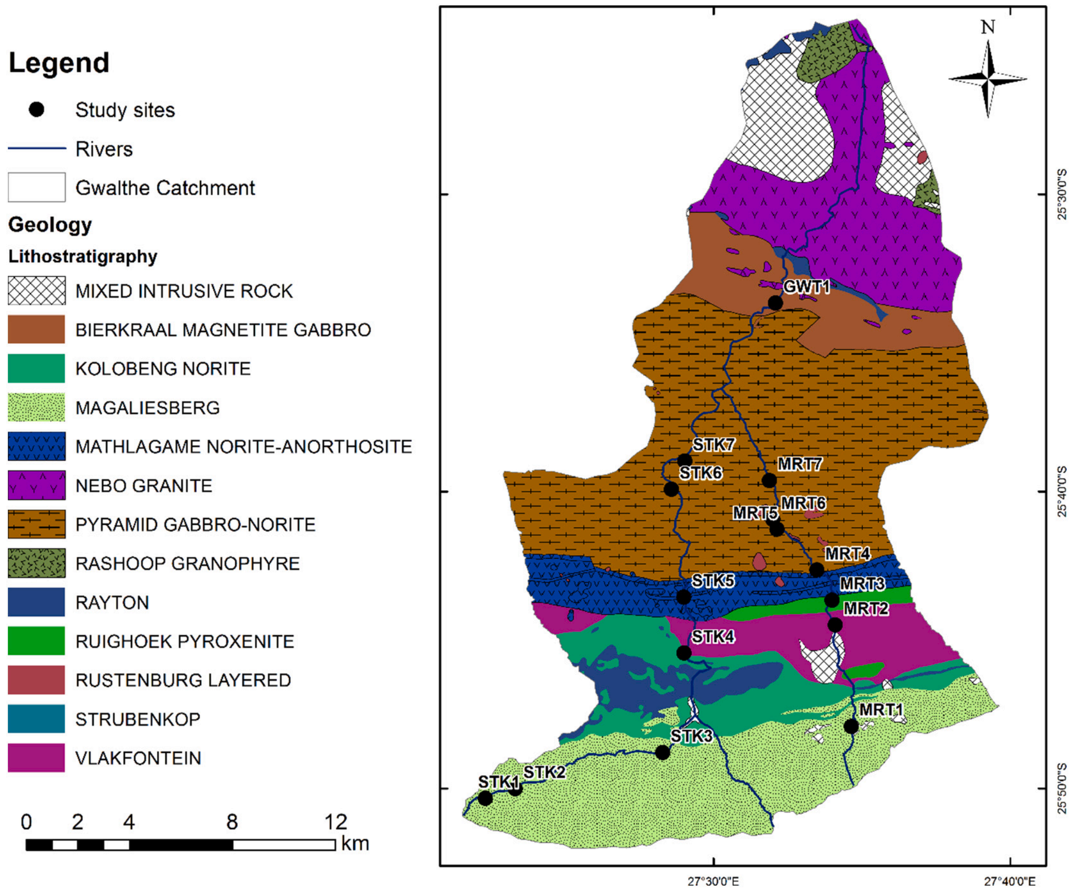

Fig. 2. Map of the Gwathle study catchment within the Bushveld complex as well as the sampling sites across the Sterkstroom (STK), Martlwane (MRT) and Gwalthe (GWT) rivers, draining an intensification gradient including natural (greyed area within), urban, agriculture and mining stressor activities.

replaced by an estimate of its division by two; following the assumption that data are uniformly distributed (Croghan and Egeghy, 2003).

2.3. Key land-cover class (stressor) determination

The landscape stressor data (land-cover) was obtained using the South African National Land Cover (SANLC) 2020 dataset released in June 2021 (Geoterraimage, 2021). The dataset was generated using ~20 m multi-seasonal Sentinel-2 satellite imagery and has a Kappa Index above 85 and an overall map accuracy >85 %. The Land-cover data were then interpreted using ArcGIS 10.5. The level 1 national database contains 73 land-cover classes, of which 53 classes occur within the bounds of the study catchment. The level 1 classes were reduced and reclassified into six key natural and stressor categories including (1) natural – woodland, shrubland and grassland, (2) cultivated land – all commercial annual crops, (3) fallow-land – altered range land for cattle grazing, (4) urban – residential formal and informal, commercial and smallholdings, (5) mining – extraction pits and tailing storage facilities and finally (6) dams – in-channel weirs and storage dams.

2.4. Study area and spatial-scale delineation

The river catchment, together with the investigated rivers, were delineated from the 30 m Shuttle Radar Topography Mission (STRM) digital elevation model (DEM) using the ArcSWAT (Soil & Water Assessment Tool) extension module in the ArcGIS software package (ESRI). Prior to their delineation, the DEM sinks were filled using the Spatial Analysis toolbox in ArcGIS. The spatially explicit nature of this study, was so that the stressor effects in the Gwathle Catchment on the aquatic ecosystems, could be assessed at a (1) cumulative catchment scale (i.e. draining entirely of one point upstream), (2) sub-basin and at (3) cumulative riparian and (4) sub-basin riparian scales (Table 1).

For the sub-basin scale, the extent was defined from the location study site (outlet location) and its upstream drainage area until the prior site (immediately upstream). The cumulative catchment extents of each study site were defined from the outlet location of each study site, and included the catchments/riparian zones of sites located upstream, thus creating a nested design (Xu et al., 2021). Each of the sub- and cumulative catchments were delineated using the Spatial Analyst tools in ArcGIS 10.5. The riparian buffers at the cumulative- and sub-basin scales were computed at 100 m using the Analyst Toolbox in ArcGIS 10.5. The 100 m buffer was selected based on the well-researched recommendation of at least a 50 m developmental buffer for South African 1:500000 mountain streams for most land-cover practices and features, which has been demonstrated to effectively mitigate sedimentation and reduce macronutrients in high-risk scenarios (Berliner and Desmet, 2007; Macfarlane and Bredin, 2017). The extended buffer, of 100 m, allows for

Table 1
The four spatial scales of water quality assessment and their descriptions.

Spatial scale		Description
1	Cumulative scale	The total upstream catchment area draining to a single downstream study site
2	Sub-basin scale	The area draining between the downstream and immediate upstream site
3	Riparian cumulative 100 m buffer	A 100 m riparian buffer draining the total upstream area to a single downstream study site
4	Riparian sub-basin 100 m buffer	A 100 m riparian buffer draining the area between the downstream and immediate upstream study sites

the capture of stressors adjacent to the riparian zone. The reclassified landscape stressor layers were clipped to each of the new spatial layers (i.e. scales) using the ArcGIS Data Management Tool.

2.5. Environmental driver determination

A combination of potential driver variables were used in the analysis to determine the most parsimonious drivers of catchment aquatic water quality (Table 2). For the topographic features, the mean and standard deviation for elevation and slope for each of the sites' respective four spatial scales were calculated in ArcGIS 10.5 using the conversion from raster to point tool and the Spatial Analyst Toolbox respectively. These variables exert strong controls on hydrologic flows and connectivity between upland areas and downstream water bodies, mediating impacts on aquatic ecosystems (Allan, 2004; Thompson et al., 2011; Ding et al., 2016). Using the SANLC dataset two class-level metrics, measuring composition and connectivity; PLAND (i.e., % landcover) and COHESION (i.e., connectedness to patches with the same landcover class) respectively were analysed in FRAGSTATS 4.2 for each of the six stressors in their four respective spatial scales (Table 1; Shi et al., 2017). Two class-level metrics were selected for as they provide spatial characteristics of each land cover class crucial for relating landscape structure to aquatic integrity while avoiding excessive redundancy (Uuemaa et al., 2007).

2.6. Statistical analysis

Principal Component Analysis (PCA) was employed as a dimensional reduction technique, as well as to visualize spatially explicit patterns among the data. The analysis reduced the high number of correlated water quality parameters to a few variables that best explain the catchment's overall river water quality variability in R (R Core Team, 2023). Prior to the analysis, data assumptions were tested using the Kaiser-Meyer-Olkin (KMO) and the Bartlett tests (Zhang et al., 2020). To avoid misinterpretations accompanied by variables of different units, the variables were standardized through z-scale transformation and centered. The Kaiser's rule was adhered to, in identifying the principal components for further use (Kaiser, 1960). One key uncorrelated, but significant contributing water quality parameter of the highest loading from each of the retained principal components was identified using the dimdesc function in the FactoMineR package, for use in further analysis (Lê et al., 2008).

Table 2
A summarized view of the specific stressor classes assessed, as well as the class-level metrics and topographic factors determined, with a description for each.

Variables		Description
Stressor classes	Agriculture	Agricultural land, containing irrigated and rain-fed cropland
	Fallow-land	Fallow-land used for cattle grazing and in crop rotation
	Urban	Settlement and commercial activities, both for the formal and informal
	Dams	On-stream impoundments, including dams and shallow weirs used for various purposes e.g. agriculture and mining
	Mining	Mine inclusive features, including tailing storage facilities (wet and dry), mining pits/strips and related industries (e.g. smelters)
	Natural	Natural land-cover inclusive of forests, rocky outcrops, grassland and shrubs
Class-level metrics	Percentage of landscape (PLAND - composition)	Percentage of the landscape belonging to a particular class
	Patch cohesion index (COHESION -connectedness)	Characterizes the connectedness of the patches belonging to a particular class
Topographic factors	Mean slope	The average slope of the assessed spatial scale measured in degrees
	Slope standard deviation	The standard deviation of the slope at the assessed spatial scale
	Mean elevation	The average elevation of the assessed spatial scale measured in meters
	Elevation standard deviation	The standard deviation of the elevation at the assessed spatial scale

Following the retention of the final water quality parameters as response variables, multi-spatial-scale generalized linear mixed effects models (GLMMs) were utilised to elucidate the dominant explanatory driver(s) of water quality within the catchment. Given the hierarchical data structure with river sites nested within repeated measurements over time, the utilisation of GLMMs enabled the incorporation of temporal and spatial effects, thus facilitating a robust analysis tailored to the complexities of the dataset. The predictor datasets, consisting of the FRAGSTATS class-level metrics for each of the six stressor classes and topographic factors, at the four spatial scales, were independently assessed for multicollinearity prior to model fitting. Variables where $r > 0.7$ were removed using the findCorrelation function in the caret package, before scale-specific model fitting, thus reducing model interpretability and overfitting issues (Kuhn et al., 2020). The glmer function from the lme4 package was used to fit the full GLMMs for each response variable at the different scales, and the scales' respective predictors as main effects with sample season and site as random effects (Bates et al., 2014). A Gamma distribution with a log link was fit to each model due to the continuous, skewed nature of the water quality response variables.

With the GLMMs created for each of the key water quality variables (responses) variables across the four spatial scales, a total of 20 models were fitted (Zuur et al., 2009). The most parsimonious GLMM for each response variable at each of the four scales was obtained through the step-wise dredge function in the MuMIN package (Barton, 2010). The step-wise analysis, based on Akaike's Information Criterion corrected for small sample size (AICc), allowed for the simplest yet most informative model to be identified that included predictors best explaining the variability of the responses (parameters). The final model selection, to determine at which spatial scale each response variable is best predicted, was determined by selecting the most parsimonious model among the four spatial scales with the lowest AICc. The goodness of fit for the final models was determined using the marginal R^2 (R^2_m; the variance explained by the fixed factors) and the conditional R^2 (R^2_c; the variance explained by both fixed and random factors) coefficients using the r.squaredGLMM function in the MuMIN package (Barton, 2010; Wanderi et al., 2022).

To isolate and visually assess the relationship between each water quality response variable and their most important predictor identified in the respective GLMM, reduced parsimonious models were created excluding the important variable while retaining the other predictors to account for their influence (Marshal et al., 2002). The log-transformed residuals of the reduced models were plotted against the respective important predictor with a trend line fit using ggplot2 (Wickham, 2016). Agglomerative hierarchical cluster analysis (HCA) was performed to assess environmental similarities among the river study sites. The analysis considered the five water quality response variables as well as the continuous class-level and topographic explanatory factors selected from the final fitted GLMM models. The analysis utilised the Euclidean distance metric and the suitable Wards clustering algorithm for the data determined using agnes and map_dbl functions from the cluster and purrr packages respectively (Maechler, 2018; Wickham and Henry, 2023). The optimal number of clusters (i.e. groups) for the cluster analysis was determined using the total within-sum of squares (WSS) in the Factoextra R package (Kassambara and Mundt, 2020). The resulting groups paired with respective sites, along with the response variables, the class-level metrics and topographic factors were represented for visual purposes on a final summary PCA biplot to visually discern drivers of the groupings.

3. Results

3.1. Class-level land use and topographic patterns between scales

The composition (percentage) of the agriculture, fallow-land, urban and mining predictors, tended to show higher proportions in the smaller headwater sub-basins and sub-basin riparian buffers than in the cumulative catchment and cumulative riparian buffers. The percentage of dam and natural land coverage conversely increased as the cumulative catchment and riparian scales increased area coverage. On average, the cohesion of agriculture and dams was higher with the cumulative catchment and cumulative riparian scales draining larger regions while decreasing with smaller scales draining less area. Both topographic factors including elevation and slope on average were higher in the cumulative catchment and riparian scales, decreasing as scale become smaller. Elevation and slope, however, on average remained higher in the mountainous sites' respective spatial scales.

3.2. Key response variable determination

The PCA analysis highlighted the high multi-collinearity between the water quality parameters measured across the Gwathle Catchment (Fig. 3). From the ordination, the first principal component (PC1) accounted for most of the datasets variation with 57.2 % followed by PC2 with 17.4 %. The first PC is the axes in which the sites are mostly separated according to land-use effects on water quality. Specifically, sites in the positive pole of PC1 were characterised by higher sulfates, electrical conductivity and major cations (e.g. Na^{+}, Mg^{+}), and are those positioned further down the mountainous catchment experiencing increased agricultural, cattle rearing and mining activities. Conversely those sites further up the catchment, experiencing small scale farming and a limited residential footprint, are negatively associated with these indicators. Having retained five principal components, accounting for 93 % of the datasets cumulative variance, following the Kaiser's rule, a reduced set of five water quality parameters, one from each PC (highest loading), were determined to be key variables that best characterise the overall water quality variation of the Gwathle river catchment during the study period. These included sulfate (mg/L), ammonium (mg/N-L), copper (ppb/mg/L), turbidity (NTU) and pH (units). These five variables would become the responses used in further model fitting and thereby achieving the first objective.

3.3. Optimal spatial scale for the catchment water quality prediction

Following the step-wise model selection to derive the most parsimonious models, it was determined that three of the four assessed spatial scales were important in predicting key water quality response variables. The final fitted models with the predictor variables are presented in Table 3, with the relationship between the water quality response variable and the models' most important predictor variables at their respective spatial scale presented in Fig. 4. At the sub-basin scale, ammonium, copper and turbidity were most accurately predicted. While at the cumulative catchment scale, river pH, and at the cumulative 100 m riparian buffer scale, sulfate concentrations, were most accurately predicted respectively. In the models with multiple determinants, mining land cover was the most important variable predicting elevated copper, pH and sulfate levels across the basin, while turbidity was strongly associated with the proportion of agricultural land cover at the sub-basin scale (Table 4).

3.4. Water quality responses to land-use metrics

For ammonium, the percentage of urban areas in the sub-basin exhibited a statistically significant positive relationship, where a 1 % increase predicted ~5.50 % rise in ammonium concentrations. Copper concentrations were predicted to increase by ~6.35 % and 1.36 % for every 1-unit rise in mining PLAND of mining and COHESION of agriculture respectively, where copper concentrations were predicted to increase by ~6.35 % and 1.36 % respectively, which both displayed significant positive associations. In contrast, PLAND of fallow-land displayed a significantly negative relationship, with a 1 % increase predicting a ~4.20 % decrease in copper concentrations in the sub-basin. Both COHESION of dams and PLAND urban displayed negative relationships with copper concentrations with a 1-unit change leading to a decrease of ~0.86 % and 2.84 % respectively.

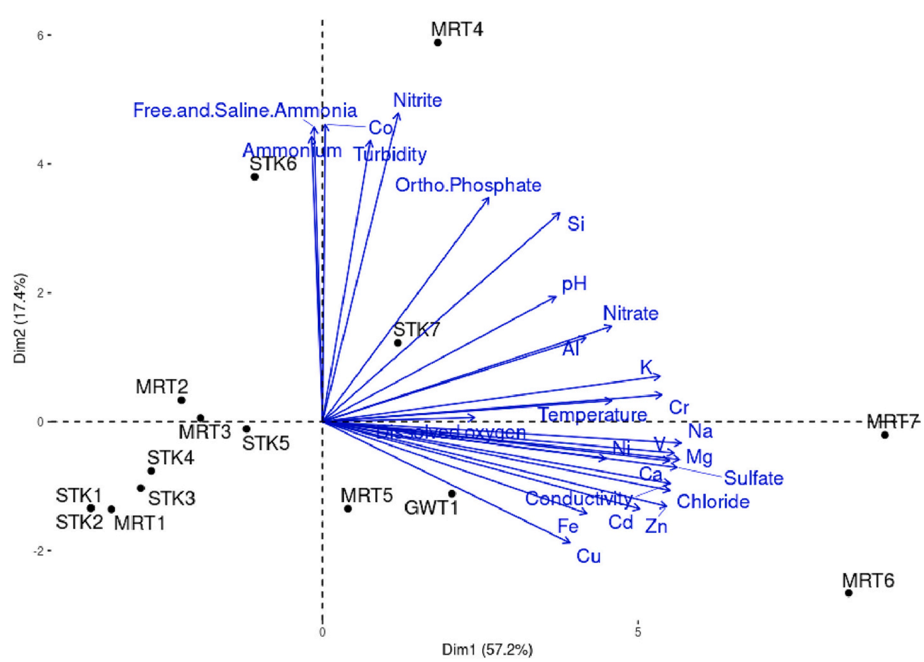

Fig. 3. A principal component analysis bi-plot showing the separation of individual study sites through their association with mean annual water quality parameters.

Table 3
The five most parsimonious generalized mixed effects models for each of the five water quality response variables the spatial-scale they best predicted at as well as each models respective explanatory/predictive variable(s).

Spatial Scale	Sub-basins			Cumulative basin	Cumulative 100 m riparian buffer
Response	Ammonium	Copper	Turbidity	pH	Sulfate
Model predictors	PLAND urban	COHESION agriculture COHESION dams PLAND fallow-land PLAND mining	Elevation (SD) PLAND agriculture PLAND urban PLAND fallow-land	COHESION dams Slope (SD) PLAND mining	PLAND agriculture PLAND mining
Model intercept	−2.18(±0.29)-7.41***	2.61(±0.36)7.79***	−1.49(±0.47)-3.19**	1.40(±0.11)12.64***	1.28(±0.39)3.28**
	Model Selection	Model Selection	Model Selection	Model Selection	Model Selection
Weight	0.05	0.05	0.18	0.19	0.03
AICc	-126.07	758.21	655.92	166.31	786.81
BIC	−114.35	779.0	674.0	182.3	804.4
	Goodness of fit	Goodness of fit	Goodness of fit	Goodness of fit	Goodness of fit
$R^2_{GLMM(m)}$	0.11	0.21	0.72	0.60	0.66
$R^2_{GLMM(c)}$	0.51	0.36	0.78	0.70	0.80
	Random effects	Random effects	Random effects	Random effects	Random effects
Site (SD)	0.66	0.01	0.39	0.04	0.60
Season (SD)	0.45	0.51	0.15	0.02	0.36
Residuals (SD)	0.89	1.04	0.83	0.08	0.85

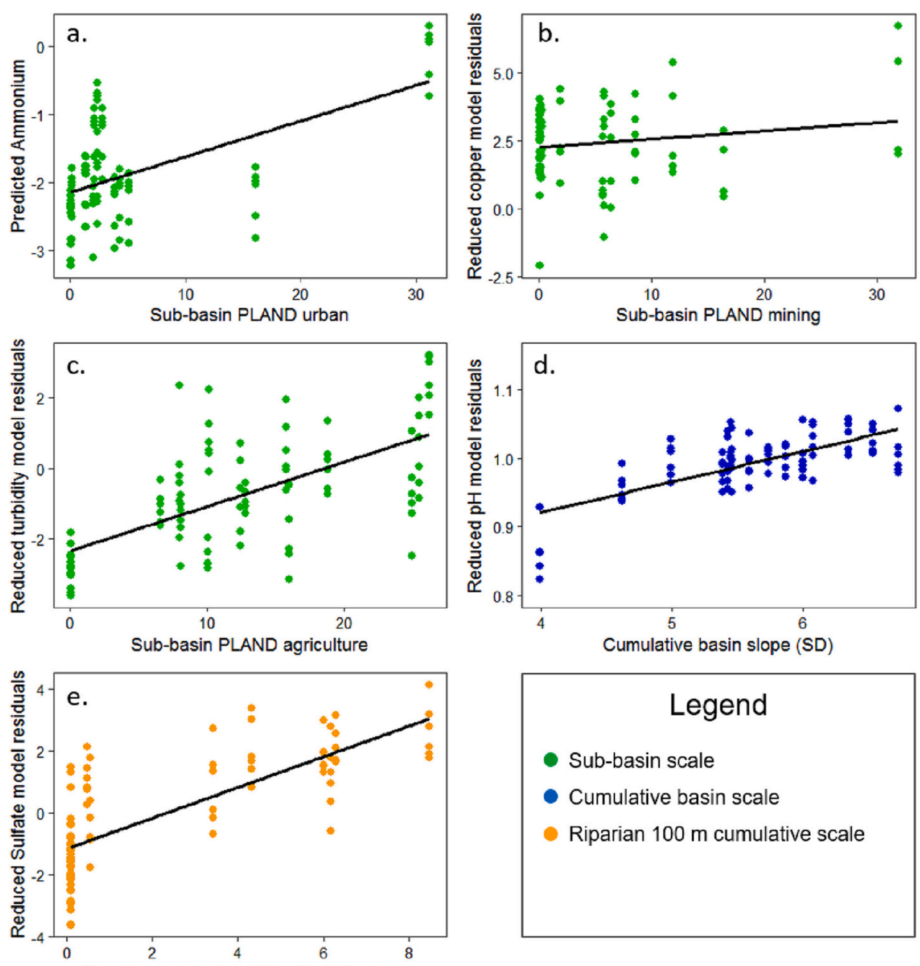

Fig. 4. Figures b – e present the visual relationships between each key water quality response variable and the most important predictor of each as identified in each respective generalized linear mixed effects model. Each figure represents the log-transformed residuals of the reduced parsimonious models plotted against the important predictor of each respective model. For figure a, no less important predictors were included in the parsimonious model, thus the predicted values from the full model were plotted against the expected values to provide a visual assessment of the relationship between response and predictor.

Table 4
The model average parameter estimates for each variable in the fitted models, as well as the variables importance representing the proportional effect of each variable in explaining the response variable. The greyed cells indicate the row the with predictor variable that has the greatest importance in each of the fitted models. Variables with asterisk (*) are significant at the 95 % level.

Parsimonious models spatial scale	Response	variable	Variable estimate	Lower 95% CI	Upper 95% CI	Variable importance
Sub-basin scale	Ammonium	PLAND urban*	0.05	0.01	0.10	1.00
	Copper	COHESION agriculture*	0.01	0.00	0.02	0.25
		COHESION dams	-0.01	-0.02	0.00	0.25
		PLAND fallow-land*	-0.06	-0.11	-0.02	0.23
		PLAND mining *	0.07	0.03	0.11	0.27
	Turbidity	Elevation (SD)*	0.02	0.01	0.02	0.23
		PLAND agriculture*	0.14	0.10	0.17	0.27
		PLAND urban*	0.04	0.00	0.07	0.24
		PLAND fallow-land*	0.08	0.04	0.12	0.25
Cumulative scale	pH	COHESION dams*	0.01	0.00	0.00	0.32
		Slope (SD)*	0.09	0.05	0.13	0.35
		PLAND mining*	0.01	0.00	0.02	0.32
Cumulative 100 m riparian scale	Sulfate	PLAND agriculture*	0.09	0.03	0.15	0.41
		PLAND mining*	0.45	0.33	0.57	0.59

Also at the sub-basin scale, turbidity was significantly predicted by class-level metrics and a topographic factor. Specifically, PLAND agriculture, PLAND fallow-land and PLAND urban, three class-level metrics, exhibited significant positive relationships with turbidity. For every 1 % increase in each of the three latter metrics, it was predicted that there was an associated increase of approximately 14.83 %, 7.95 % and 3.82 % in turbidity respectively. Furthermore, the topographic factor elevation (SD) had a statistically significant positive effect on turbidity. For every +1 standard deviation increase in elevation at the sub-basin scale, turbidity was predicted to rise by ~1.57 %.

At the cumulative basin scale, river pH was most accurately predicted. Two class-level metrics, PLAND mining and COHESION dams were significant positive predictors for river pH in the catchment, where a 1-unit increase led to a 0.80 % and 0.20 % increase in river pH respectively. This increase is observable in the longitudinal change in pH from upstream to downstream on both tributaries (see supplementary Fig. S1). Determined as the most important predictor, the slope (SD) topographic factor, was also a significant positive predictor of pH,

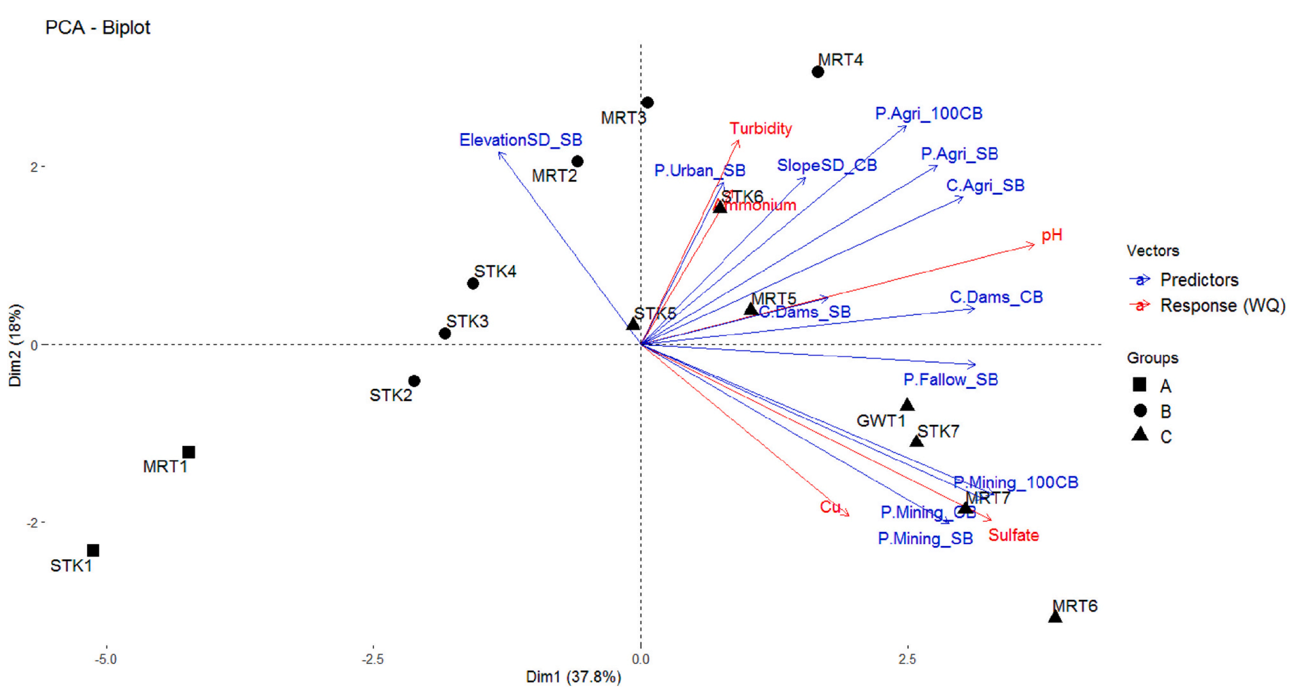

Fig. 5. A biplot with the sites clustered into three separate groups based upon all five river water quality (WQ) responses (red) as well as their respective parsimonious model responses to assess drivers of spatial change observed among the study sites. The FRAGSTATS derived predictors retained in the statistical models are denoted using the following abbreviations in the figure: P. = percentage of landscape (PLAND), C. = patch cohesion index (COHESION), Agri = agriculture, SD = standard deviation, SB = sub-basin, CB = cumulative-basin, 100CB = 100 m cumulative riparian buffer.

whereby an increase of 9.46 % in pH was experienced following every +1 standard deviation change in slope heterogeneity at the cumulative basin scale.

At the cumulative 100 m riparian buffer scale, the prediction of sulfate (mg/L) concentrations was most accurate. Notably, both PLAND agriculture and PLAND mining emerged as significant predictors, demonstrating their strong influence on sulfate levels. For every 1 % increase in agricultural and mining land cover, there was an associated increase of approximately 9.40 % and 56.20 % in sulfate concentration respectively. These findings emphasize the significant roles of agricultural and mining activities in shaping sulfate levels within the riparian buffer zone, particularly in the lower reaches where these activities are concentrated along the river continuum (see Fig. S1).

3.5. Cluster analysis and patterns

The sampled river study sites were grouped into three meaningful clusters, denoted A, B and C, determined from the HCA analysis. Integrated into a PCA for visual purposes together with the five water quality response variables and their respective parsimonious model predictors (e.g. PLAND etc.), the three groupings were distinguishable across PC1 (Fig. 5). In group A, the two pristine study sites were grouped, followed by sites experiencing lower-land-use stress in group B, and finally sites experiencing a range of the latter land-use activities with the addition of intensive mining activities in group C. The arrangement of these groups from negative to positive along PC1 reflects an upstream to downstream stressor intensification gradient apparent on both tributaries, with mining and urban land-use contributing to heightened water quality stress in their lower reaches (Fig. 1, also see Fig. S1).

Observing the water quality parameters, the pristine sites in group A were characterised particularly by lower pH as well as reduced turbidity, anion and metal concentrations compared to sites in the other groups (see supplementary Table S1, Fig. S1). Pertaining to the land-cover metrics, the group experienced low-level agricultural, limited urban land-cover as well as few to no impoundments.

The study sites in group B, downstream from group A, were characterised by higher differences in elevation standard deviation between the study sites (in the sub-basins), owing to this group being located both within and downstream of the slopes of the Magaliesburg mountain range. The group was also characterised by low copper and sulfate concentrations due to no mining activities present in the sites' sub-basin nor in the cumulative 100 m riparian buffers (Fig. 5; Table S1). The group did experience higher ammonium concentrations associated with higher urban and agricultural land-cover as well as rising pH levels as the COHESION of dams also rose.

Sites in group C, all located in the lower reaches of the catchment (Fig. 1, Fig. S1), were characterised by lower standard deviation of elevation, owing to being located on the flatlands, north of the Magaliesburg mountain range. They were also characterised by higher pH levels, associated with increased patch connectivity of dams in the cumulative basins. In addition, these sites experienced greater ammonium concentrations and turbidity levels, associated with higher PLAND urban land cover in the sub-basins. The sites were also characterised by higher copper and sulfate concentrations associated with increases in the PLAND mining land cover in the sub-basins and the cumulative 100 m riparian buffers. The PCA loadings are presented in Table S2.

4. Discussion

4.1. Scale-dependent relationships between land-use stressors and water quality

The parsimonious GLMM models derived from step-wise model selection indicated that water quality parameters, for the most part, responded best to land-use configurations (PLAND and COHESION) and less so to topographical factors (elevation and slope), owing to a higher frequency of the former in the fitted models. In the sub-basin scale, ammonium was significantly associated with positive increases in PLAND urban areas, which is consistent with previous findings linking increased urbanisation to ammonium loading in rivers (Drury et al., 2013; Levin et al., 2019).

The biological uptake and cycling characteristics of ammonium over relatively short distances support its optimal prediction at the sub-basin scale, when influenced by urban effects (Fig. 4). For example, localised inputs of NH_4^+ may become largely dissipated at larger scales due to the rapid biological uptake by plants and microorganisms within a few hundred meters (Peterson et al., 2001), as well as rapid nitrification to nitrate (NO_3^-) which can occur at localised well-oxygenated scales (Kemp and Dodds, 2002).

The built-up urban areas within the Gwathle catchment are primarily characterised by large expanses of both formal and informal residential development with some commercial districts. The urbanised impervious surfaces are known to provide an efficient pathway for mobile pollutants to enter rivers during rainfall events, leading to deteriorated urban river water quality (Paul and Meyer, 2001). This includes ammonium-rich grey-water entering rivers due to the use of urban-lawn fertilizers, ammonium-rich detergents and pet waste (Carey et al., 2013). In addition, sewerage infrastructure servicing urban areas in developing nations is often characterised by ill-maintained waste-water treatment works as well as blocked or leaky sewer systems allowing for raw sewage, high in ammonium, to be introduced into the aquatic environment (Carey et al., 2013; Levin et al., 2019). The informal areas in the catchment, however, frequently lack connections to the municipal sewerage network, leading communities to resort to bucket and pit latrine alternatives (Gqomfa et al., 2022). Anaerobic conditions inside filled pit latrines favour the conversion of nitrogenous compounds to ammonium, which can enter nearby systems via leachate or run-off during rainfall events. With inadequate wastewater infrastructure, ammonium-rich greywater can also be improperly disposed of on road surfaces, later entering the river as pollution (Gqomfa et al., 2022).

Copper was best predicted for at sub-basin scale. It was strongly associated with positive increases in the agricultural land-use connectivity (COHESION) as well as percent mining coverage, where PLAND mining had the highest variable importance in the fitted model (Fig. 4). In contrast, higher dam connectivity (COHESION), as well as the percent of fallow-land were negatively associated with copper. Although research exploring drivers of in-situ copper concentrations at differing spatial scales is limited, findings do support the sub-basin scale model prediction, where spikes in copper near pollution point sources such as mines have been found to rapidly dilute downstream (Navarro et al., 2008). Mining activities, including the extraction of Bushveld Complex platinum-group element (PGE) ore deposits, do contribute to riverine trace and heavy metal concentrations (Erasmus et al., 2020). Gangue rock, a characteristic component of the PGE deposits, is commonly associated with copper-bearing sulfide minerals (Thormann et al., 2017). The extensive strip and pit mining activities in the catchment thus likely result in the oxidation of improperly stored PGE-gangue minerals in tailing storage facilities, generating metalliferous drainage rich in dissolved copper (Mungall, 2014).

Globally, links have been identified between high agricultural land-cover (connectivity) and increased riverine trace metal concentrations. Copper-based bactericides and fungicides are commonly applied to cherry and blueberry plantations, such as those present in the upper catchment (Carroll et al., 2010; Oliver et al., 2022). A large proportion of such crop-applied chemicals, however, end up in soils (Aikpokpodion et al., 2010), and with high connectivity of agricultural land, characterised by modified hydrological pathways, it is likely that there is rapid and high copper-concentrated runoff, aided by copper desorption, into nearby streams.

The negative association between high dam connectivity across sub-basins and copper concentrations, suggests that impoundments act as pollution sinks, trapping trace metals at finer catchment scales. This entrapment is supported by geochemical processes, where Cu binds to the high sediment organic matter (e.g. fulvic acids) in dams through complexation reactions, producing stable Cu-ligand complexes, reducing potential desorption back into the water column (Shank et al., 2004; Tadini et al., 2020). In addition, anaerobic/anoxic sediments further promote Cu retention, since the lower redox potential under such conditions, leads to further Cu sorption (Sharma et al., 2022). Copper also decreased with respect to higher fallow land cover at the sub-basin scale. While no direct literature comparisons have been made between sources of copper in agriculturally cultivated versus fallow-lands, it is possible that leaving fields uncultivated for certain periods of time, raising fallow-land coverage, can mitigate possible prior copper runoff into adjacent streams as less chemical-ladened materials are applied to or on the land.

There was a significant positive association between the three PLAND class-level metrics, agriculture, urban and fallow-land on riverine turbidity at the sub-basin scale; with the agricultural predictor having the highest variable importance in the model (Fig. 4). It can be suggested that the turbidity input and removal processes operating at the sub-basin scale are more frequently predicted for than other scales. For example, local agricultural expansion and associated tillage practices, expose sediments and accelerates soil erosion; facilitated by wind and run-off, leading to sediment loading of nearby rivers (Jones et al., 2001). Due to this, turbidity is considered an indicator of catchment hardening, as impervious surfaces associated with urban development reduce infiltration, thereby providing an effective stormwater pathway for mobile anthropogenic waste and sediments to enter nearby streams (Levin et al., 2019). The agricultural impact is also often characterised by previous fallow-land and crop rotational areas experiencing extensive cattle grazing activities. Over-grazing can de-vegetate land expanses near rivers, reducing infiltration capacity and increasing runoff of loose sediment into nearby streams (Zaimes, 2004). In addition, cattle access to the rivers from adjacent grazing-land, delivers a major source of particulate organic matter through defecation while extensive trampling leads to erosional riparian and terrestrial landforms such as gullies, that concentrate overland flow and sediment into rivers (Belsky et al., 1999; Davies-Colley et al., 2004). Additionally, variation in elevation was a positive predictor of river turbidity, serving as an effective indicator of topographical heterogeneity in the Gwathle catchment. The diversity of catchments' slopes likely creates dynamic hydrologic connections throughout the watershed, delivering greater sediment loads into the rivers (Bracken and Croke, 2007).

At the cumulative catchment scale, the longitudinal rise in river pH across the Gwathle catchment was predicted for by the COHESION of dams, slope and mining. Besides for one deep water dam, the catchment has many smaller, shallow on-stream weirs and agricultural dams. The positive association between COHESION of dams and pH, indicates that the series of smaller dams had an overriding positive effect on downstream river pH, compared to the potential pH-reducing effects of a single deep dam (Wang et al., 2015). Shallow impoundments allow for high CO_2 concentrations to build up in the inundated zones via microbial and soil respiration as well as through enhanced dissolution of atmospheric CO_2 following the large water-air surface area (Kemenes et al., 2011). Under shallow, light-permitting conditions, enhanced photosynthesis can absorb high CO_2 concentrations and increase pH downstream (Wang et al., 2015).

Downstream mining activities on the catchment lowlands, with low variation in slope, also increase river pH (Fig. 4, Fig. S1). The slope (SD) may, in this case, act as a proxy for the catchments heterogeneous geology that may pose a confounding role in pH patterns. The quartzite-dominated mountain slopes may provide low acid buffering from soil material and plant activity, although chemically inert. In the lowlands, as the rivers flow into the mafic rocks of norite and gabbro that are enriched in Ca, Mg and Fe, sources of basic cations that can buffer and neutralize acidic inputs (Cawthorn, 2010; Mungall, 2014; Fig. 2).

Characteristic of the western lobe of the Platinum Belt are large pollution control dams (PCDs) supporting platinum and vanadium mining operations. There is substantial evidence from this study to support pollution leaching from these reservoirs, permeating into the adjacent environment before entering surface water, with other regionally relevant studies also identifying pollution leaching into ground and surface water (Skinner, 2018). Although high mine-derived sulfate concentrations are usually linked to acid mine drainage in rivers where gold and coal mining occurs, the opposite is found to be true in the Gwathle catchment like others with platinum, vanadium and chrome mines (McCarthy, 2011). The platinum group elements (PGE) mining belt, within the Gwathle catchment, is characterised by alkaline Gabbro and Norite rock materials (Fig. 2). Both are mafic to ultramafic igneous rocks with mineral compositions generally high in alkaline metals such as calcium and magnesium (Cawthorn, 2010). These rocks might host carbonate minerals such as calcite or dolomite, which possess inherent pH-buffering properties, potentially leading to elevated pH (Mungall, 2014). Furthermore, the composition of these rocks may include additional distinct minerals, such as calcium-rich plagioclase feldspars (e.g. anorthite) and pyroxenes (Cawthorn, 2010). Upon dissolution in water, such minerals release alkaline ions that can effectively counteract the acidic effect of decant water, while raising the pH.

Sulfate was the only water quality parameter best predicted for at the riparian 100 m cumulative buffer scale (Fig. 4). Within these boundaries, percentage mining and agricultural land-cover were positively associated with sulfate, indicating contributions from point and diffuse sources. The effectiveness of the buffer for predicting the anion is supported by its integration of multiple processes governing the fate and transport of sulfate inputs from such sources across successive riparian zones. These include the hydrological connectivity regulating delivery of such inputs from adjacent mining facilities and agricultural activities to streams, soil retention and microbial transformations moderating export (e.g. in wetland soils) enabling the cumulative riparian assessment to capture major river-scape interactions and patterns in the anion (Li et al., 2009; Ledesma et al., 2016). Other major anions (e.g. nitrite) have also shown strong positive associations with land-cover activities within similar-sized riparian buffers (Li et al., 2009; Li et al., 2022).

With western lobe PGE being highly concentrated in sulfide grains, the extensive mining activities within the catchment are the major point source contributor of sulfates in the Gwathle catchment (Cawthorn, 2010; Thormann et al., 2017; See Fig. S1). The sulfide minerals form part of the original composition of mafic and ultramafic igneous rocks such as norite, gabbros and pyroxenites that form the PGE ore bodies (Schouwstra et al., 2000; Cawthorn, 2010). Common sulfide minerals in these deposits include pyrrhotite, pentlandite, and chalcopyrite (Thormann et al., 2017). During mining and extraction activities, the crushing and grinding of the PGE-bearing sulfide ores exposes an abundance of fresh reactive mineral surfaces to oxidation (Nimick and Moore, 1994; Schouwstra et al., 2000). These reactive minerals come into contact with oxygenated water, releasing highly mobile dissolved sulfate, which then becomes collected and stored in large evaporation PCDs adjacent to tailing dumps and near the 100 m riparian buffer.

Upon permeating into the environment from unmaintained solid and liquid mine-waste storage facilities, the sulfate-rich mine water is then transported via small tributaries and decants into the major tributaries of the Gwathle Catchment. Notably, the presence of large tailing storage facilities (e.g. evaporative dams) were largely uncaptured in the GIS analysis by the cumulative 100 m buffer zones. This is owing to such facilities largely being aligned with the national regulations; stating no mine deposit, dam or reservoir may be positioned within the 1:100-year flood line or within a 100 m horizontal distance from a watercourse (DWAF, 2007). However, residual supporting mine classified infrastructure was captured, and served as a proxy indicator for such sulfate generating and storage features, resulting in its land-cover being a significant contributor to the parsimonious model. In addition, small-scaled unregulated artisanal mining operations target PGE (chromite) outcrops and process the ore within the Sterkstroom and Maretlwane

Rivers riparian zones. These activities occur within the riparian cumulative 100 m buffer zone and thus may provide additional point sources of sulfate entering the river system.

Percentage agricultural of land-cover was also a significant predictor of sulfate in the parsimonious model at the cumulative 100 m riparian scale. Such land-cover and its associated activities have been linked with elevated sulfate levels in adjacent rivers globally, through various pathways (Liu and Han, 2020). Vast expanses of the Gwathle catchment area are occupied by a variety of irrigated and rain-fed agricultural crops; many of which are planted adjacent to the rivers. The application of agrochemicals, including sulfur-containing inorganic fertilizers (e.g. ammonium sulfate [$(NH_4)_2SO_4$] and potassium sulfate; K_2SO_4) as well as fungicides (e.g. copper sulfate; $CuSO_4$) dissociate in water and oxidize in soil releasing SO_4^2, with the potential for diffuse sulfate pollution to enter rivers via erosional processes (Lodhi et al., 2006; Silva et al., 2018; Lwimbo et al., 2019; Zak et al., 2021). By identifying the key water quality parameters and their dominant landscape predictors at their respective spatial scales, objective two was fulfilled.

4.2. Spatial variations in water quality in response to land-use and topographic effects

This study assessed multiple river sites, traversing the Magaliesberg uplands to the lowlands of the Gwathle Catchment. The spatially explicit, nested nature of the study sites captured for different land-use stressors, allowing for the relationship between spatial scales, water quality, class-level metrics and topographical factors to be assessed. Integrating the outputs of an HCA analysis with a PCA, allows us to not only assess similarities between river sites, but visualize and summarize the key drivers of catchment water quality conditions and patterns.

The HCA analysis clustered the river study sites into three distinct groups based on similarities in the sites respective water quality responses, as well as associated class-level metrics and topographic factors. Following PCA analysis, these groups were best distinguished across PC1, accounting for most of the datasets variation (37.8 %). The pristine sites, located in the quarzitic Magaliesberg mountain headwaters, were characterised by only natural land-cover, with no stressor land-cover types. The sites were defined by the low pH river conditions ($\bar{x} = 6.50$ pH units), as well as natural physico-chemistry. The low pH of these sites is likely influenced by vegetation type (ferns), dissolved organic carbon from soils, atmospheric deposition of acids (surrounding smelters) as well as the underlying quarzitic sandstone geology (Arunachalam et al., 1999; Mompati et al., 2022).

The second group, consisting of the intermediately impacted river sites were characterised by higher standard deviations of elevation ($\bar{x} = 114.33$) at the sub-basin spatial scale. This group was also associated with built-up urban areas (PLAND urban), on-stream impoundments (COHESION dams) and agricultural activities. Consistent with these mixed land uses, the cluster exhibited elevated turbidity, ammonium concentrations, and pH levels compared to the pristine group (Levin et al., 2019). The nutrient enrichment is attributable to the well-researched effects of both urban and agricultural land covers as sources of nutrient pollution to aquatic systems. The third and final cluster was characterised by extensive mining-related activities, indicated by percentages of mining land cover in both the sub-basin as well as the riparian 100 m cumulative buffer. Among the water quality parameters, Cu as well as sulfate exhibited marked increases coinciding with mining activities within the Bushveld complex (Thormann et al., 2017; Erasmus et al., 2020). Having identified the similarities in the sampled river sites among the three clusters, objective three was achieved.

4.3. Implications of scale-specific assessment of land-use effects for catchment management

The step changes in land-cover across the Gwathle River Catchment during this study, have indicated that water quality parameters respond best at differing scales of spatial-assessment. It became clear that the macronutrient ammonium, the trace metal Cu, as well as river turbidity, were best predicted for at sub-basin scale. This suggests that targeting management efforts at the sub-basin level may be more effective, compared to current South African legislated mitigation measures, such as the 50 m riparian buffers for 1:500000 mountain streams, in controlling and improving water quality conditions for these parameters (Berliner and Desmet, 2007).

Catchment management agencies together with municipal stakeholders need to regulate urban-derived nutrient inputs regardless of their proximity to rivers. This is due to the improper disposal of ammonium-rich compounds as well as poorly maintained and inadequate wastewater infrastructure in the immediate drainage area, contributing to aquatic nutrient loading. During this investigation, free ammonia concentrations exceeded the chronic effect value (0.015 mg/L; DWAF, 1996) at urban impacted study sites, whereas the upper headwaters (inside the partially-protected Magaliesberg Biosphere Reserve) likely act as refugia from such toxic downstream inputs, especially for mobile organisms like aquatic insects and fish (Pringle, 2001; Orlinskiy et al., 2015). At the ammonia concentrations observed at the urban sites, fishes experience acute toxicity effects, impeding reproductive success, impaired growth and morphological development (DWAF, 1996). Targeted corrective measures are required and can be aided by implementing monitoring programs at the sub-basin spatial scale to identify priority hotspots for ammonium and ammonia pollution to limit aquatic ecosystem effects.

Urban, agricultural and mining activities should also be monitored at the sub-basin scale for the discharge of trace and heavy metal compounds to alleviate contamination in aquatic ecosystems. Being used in various sectors, for a variety of applications, Cu among other metal pollutants is widespread in other river catchments in South Africa, resulting in their bio-accumulation into the aquatic food web (Erasmus et al., 2020). Certain aquatic species have shown sensitivities to elevated concentrations of trace and heavy metals, where acute toxicity for Cu was reported in fishes at concentrations as low as 0.01–0.02 mg/L (NAS, 1977; DWAF, 1996). In this research, mining-affected study sites (e.g. MRT6) experienced Cu concentrations exceeding 0.17 mg/L. The National Water Act of South Africa (Act 26 of 1998), requires mining corporations to have effective water monitoring systems, which include providing routine monitoring of effluents from storage facilities e.g. spills (DWAF, 2007). The monitoring is necessary to identify deviation from compliance, to implement appropriate remedial actions as well as for regulatory enforcement purposes (DWAF, 2007).

The cumulative basin scale was effective at assessing changes in river pH where increased presence of mine- and dam-related stressors had a cumulative downstream influence. The catchments heterogeneous geology likely confounds distinguishing natural versus human effects on pH. Catchment management authorities should consider the cumulative scale when assessing the water quality implications of removing or adding impoundments to a river basin. In contrast, riparian buffer extents, specifically the riparian 100 m cumulative buffer, may better capture localised mining inputs across a river basin.

Sulfate is a key indicator of mining stress (strongly correlated with mine-related effluents) in the Gwathle River Catchment. The high concentrations are indicative of the poor operation or maintenance of tailing storage facilities (e.g. settling or evaporation PCDs), where underdrainage and seepage control measures are required by law to mitigate river pollution (DWAF, 2007). Without adequate controls on seepage/leaching of mine-derived mobile pollution from the storage facilities, pollution readily enters the main stem rivers within the catchment. Although spillage and/or leaching from PCDs is a possibility during storm events, this study found seepage and/or leaching from certain facilities occurred in both dry and wet seasons and, thus, urgent corrective actions are required to mitigate this chronic pollution of the surrounding freshwater resources. During the dry season sample, three river study sites downstream of PCD-related inputs, experienced sulfate concentrations in excess of 500 mg/L.

5. Conclusions

This study highlights the importance of a multi-spatial-scale approach in managing river water quality across an intensification gradient in a developing catchment. The investigation revealed that no single-scale model optimally predicted all water quality drivers. Holistic management is thus needed at different extents to capture and disentangle complex land-cover and eco-hydrological interactions influencing each constituent, to develop and inform adaptive spatially-optimized management plans. The sub-basin scale was shown in this case to better capture the stepwise intensification of stressors among three of the five water quality response variables, and should be considered in future landscape assessments of water-quality stress. For resource managers to track and forecast water quality threats across the land-use intensification gradient, a comprehensive river water quality monitoring network at ecologically meaningful scales would best target and identify pollution hotspots, allowing for focused corrective measures and enforcement. The synergistic integration of monitoring river water quality parameters across multiple spatial extents offers the most promising path for sustaining water quality amidst catchment intensification. Future research can include additional landscape metrics like edge density and/or shape complexity to provide supplemental context on land-water interactions beyond the current set.

CRediT authorship contribution statement

Jonathan C. Levin: Writing – review & editing, Writing – original draft, Visualization, Validation, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Christopher J. Curtis:** Writing – review & editing. **Darragh J. Woodford:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Darragh Woodford reports financial support was provided by Water Research Commission. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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References

Aikpokpodion, P.E., Lajide, L., Aiyesanmi, A.F., 2010. Heavy metals contamination in fungicide treated cocoa plantations in Cross River state, Nigeria. Am. Eurasian J. Agric. Environ. Sci. 8 (3), 268–274.
Akyildiz, G.K., Duran, M., 2021. Evaluation of the impact of heterogeneous environmental pollutants on benthic macroinvertebrates and water quality by long-term monitoring of the buyuk menderes river basin. Environ. Monit. Assess. 193 (5), 1–23.
Allan, J.D., 2004. Landscapes and riverscapes: the influence of land use on stream ecosystems. Annu. Rev. Ecol. Evol. Syst. 35, 257–284.
Arunachalam, K., Arunachalam, A., Melkania, N.P., 1999. Influence of soil properties on microbial populations, activity and biomass in humid subtropical mountainous ecosystems of India. Biol. Fertil. Soils 30, 217–223.
Barton, K., 2010. MuMIn: Multi-model Inference. R Package Version 0.13.17.
Bates, D., Mächler, M., Bolker, B., Walker, S., 2014. Fitting linear mixed-effects models using lme4. In: ar Xiv Preprint arXiv:1406.5823.
Belsky, A.J., Matzke, A., Uselman, S., 1999. Survey of livestock influences on stream and riparian ecosystems in the western United States. J. Soil Water Conserv. 54 (1), 419–431.
Berliner, D., Desmet, P., 2007. Eastern Cape Biodiversity Conservation Plan: Technical Report. Department of Water Affairs and Forestry (DWAF), Project No. 2005-012, Pretoria.
Boyd, C.E., 2019. Water Quality: An Introduction. Springer International Publishing, Switzerland.
Bracken, L.J., Croke, J., 2007. The concept of hydrological connectivity and its contribution to understanding runoff-dominated geomorphic systems. Hydrol. Process. 21 (13), 1749–1763.
Carey, R.O., Hochmuth, G.J., Martinez, C.J., Boyer, T.H., Dukes, M.D., Toor, G.S., Cisar, J.L., 2013. Evaluating nutrient impacts in urban watersheds: challenges and research opportunities. Environ. Pollut. 173, 138–149.
Carroll, J., Robinson, T., Burr, T., Hoying, S., Cox, K., 2010. Evaluation of pruning techniques and bactericides to manage bacterial canker of sweet cherry. N. Y. Fruit Q. 18, 9–15.
Cawthorn, R.G., 2010. The platinum group element deposits of the Bushveld Complex in South Africa. Platin. Met. Rev. 54 (4), 205–215.
Croghan, C.A.P.P.E., Egeghy, P.P., 2003. Methods of dealing with values below the limit of detection using SAS. Southern SAS User Group 22 (24), 22–24.
Davies-Colley, R.J., Nagels, J.W., Smith, R.A., Young, R.G., Phillips, C.J., 2004. Water quality impact of a dairy cow herd crossing a stream. N. Z. J. Mar. Freshw. Res. 38 (4), 569–576.
Ding, J., Jiang, Y., Liu, Q., Hou, Z., Liao, J., Fu, L., Peng, Q., 2016. Influences of the land use pattern on water quality in low-order streams of the Dongjiang River basin, China: a multi-scale analysis. Sci. Total Environ. 551, 205–216.
Driver, A., Nel, J.L., Snaddon, K., Murray, K., Roux, D.J., Hill, L., Swartz, E.R., Manuel, J., Funke, N., 2011. Implementation manual for freshwater ecosystem priority areas. In: Report No. 1801/1/11. Water Research Commission, Pretoria, South Africa.
Drury, B., Rosi-Marshall, E., Kelly, J.J., 2013. Wastewater treatment effluent reduces the abundance and diversity of benthic bacterial communities in urban and suburban rivers. Appl. Environ. Microbiol. 79 (6), 1897–1905.
DWAF, 1996. South African Water Quality Guidelines Volume 7 Aquatic Ecosystems: Second Edition, Pretoria, South Africa.
DWAF, 2007. Pollution Control Dams: Best Practice Guidelines for Water Resource Protection in the South African Mining Industry. Water Affairs and Forestry, Department.
Erasmus, J.H., Malherbe, W., Zimmermann, S., Lorenz, A.W., Nachev, M., Wepener, V., Sures, B., Smit, N.J., 2020. Metal accumulation in riverine macroinvertebrates from a platinum mining region. Sci. Total Environ. 703, 1–13.
Funk, C., Peterson, P., Landsfeld, M., Pedreros, D., Verdin, J., Shukla, S., Husak, G., Rowland, J., Harrison, L., Hoell, A., Michaelsen, J., 2015. The climate hazards infrared precipitation with stations—a new environmental record for monitoring extremes. Sci. Data 2 (1), 1–21.
Geoterraimage, 2021. 2020 South Africa National Land-Cover Dataset, Geoterraimage, viewed 10 February 2022, from. https://egis.environment.gov.za/sa_national_land_cover_datasets.
Giri, S., Qiu, Z., 2016. Understanding the relationship of land uses and water quality in Twenty First Century: a review. J. Environ. Manag. 173, 41–48.
Gqomfa, B., Maphanga, T., Shale, K., 2022. The impact of informal settlement on water quality of Diep River in Dunoon. Sustain. Water Resour. Manag. 8 (27), 1–18.
Johnson, L., Richards, C., Host, G., Arthur, J., 1997. Landscape influences on water chemistry in Midwestern stream ecosystems. Freshw. Biol. 37 (1), 193–208.
Jones, K.B., Neale, A.C., Nash, M.S., Van Remortel, R.D., Wickham, J.D., Riitters, K.H., O'neill, R.V., 2001. Predicting nutrient and sediment loadings to streams from landscape metrics: a multiple watershed study from the United States Mid-Atlantic Region. Landsc. Ecol. 16, 301–312.
Kaiser, H.F., 1960. The application of electronic computers to factor analysis. Educ. Psychol. Meas. 20, 141–151.
Kassambara, A., Mundt, F., 2020. Factoextra: Extract and Visualize the Results of Multivariate Data Analyses. R Package Version 1.0.7.
Kemenes, A., Forsberg, B.R., Melack, J.M., 2011. CO2 emissions from a tropical hydroelectric reservoir (Balbina, Brazil). J. Geophys. Res. Biogeosci. 116, 1–11.
Kemp, M.J., Dodds, W.K., 2002. The influence of ammonium, nitrate, and dissolved oxygen concentrations on uptake, nitrification, and denitrification rates associated with prairie stream substrata. Limnol. Oceanogr. 47 (5), 1380–1393.

King, R.S., Baker, M.E., Whigham, D.F., Weller, D.E., Jordan, T.E., Kazyak, P.F., Hurd, M. K., 2005. Spatial considerations for linking watershed land cover to ecological indicators in streams. Ecol. Appl. 15 (1), 137–153.
Kuhn, M., Wing, J., Weston, S., Williams, A., Keefer, C., Engelhardt, A., Cooper, T., Mayer, Z., Kenkel, B., Team, R.C., 2020. Package 'caret'. R J. 223 (7), 1–224.
Lê, S., Josse, J., Husson, F., 2008. FactoMineR: an R package for multivariate analysis. J. Stat. Softw. 25, 1–18.
Ledesma, J.L., Futter, M.N., Laudon, H., Evans, C.D., Köhler, S.J., 2016. Boreal forest riparian zones regulate stream sulfate and dissolved organic carbon. Sci. Total Environ. 560, 110–122.
Levin, J.C., Woodford, D.J., Snow, G.C., 2019. Evaluating the effectiveness of freshwater fishes as bio-indicators for urban impacts in the crocodile (west) catchment, South Africa. Water SA 45 (3), 477–486.
Li, S., Gu, S., Tan, X., Zhang, Q., 2009. Water quality in the upper Han River basin, China: the impacts of land use/land cover in riparian buffer zone. J. Hazard. Mater. 165 (1–3), 317–324.
Li, S., Zhang, J., Jiang, P., Zhang, L., 2022. Linking land use with riverine water quality: a multi-spatial scale analysis relating to various riparian strips. Front. Environ. Sci. 10, 1–15.
Liu, J., Han, G., 2020. Major ions and $\delta^{34}S$ SO_4 in Jiulongjiang River water: investigating the relationships between natural chemical weathering and human perturbations. Sci. Total Environ. 724, 1–12.
Liu, J., Xu, J., Zhang, X., Liang, Z., Rao, K., 2021. Nonlinearity and threshold effects of landscape pattern on water quality in a rapidly urbanized headwater watershed in China. Ecol. Indic. 124, 1–10.
Lodhi, H.S., Khan, M.A., Verma, R.S., Sharma, U.D., 2006. Acute toxicity of copper sulphate to fresh water prawns. J. Environ. Biol. 27 (3), 585–588.
Lwimbo, Z.D., Komakech, H.C., Muzuka, A.N., 2019. Impacts of emerging agricultural practices on groundwater quality in Kahe catchment, Tanzania. Water 11, 1–25.
Macfarlane, D., Bredin, I., 2017. *Buffer Zone Guidelines for Rivers, Wetlands and Estuaries Part 1: Technical Manual*. Report No. TT715-1-17, Water Research Commission, Pretoria, South Africa. Produced as part of Project No. K5/2463 Entitled Testing the Preliminary Guidelines for the Determination of Buffer Zones for Rivers, Wetlands and Estuaries.
Maechler, M., 2018. Cluster: Cluster Analysis Basics and Extensions. R Package Version 2.0. 7–1.
Maherry, A.M., Horan, M.J.C., Smith-Adao, L.B., van Deventer, H., Nel, J.L., Schulze, R. E., Kunz, R.P., 2013. Delineating river network quinary catchments for South Africa and allocating associated daily hydrological information. In: Report No. 2020/1/12. Water Research Commission, Pretoria, South Africa.
Marshal, J.P., Krausman, P.R., Bleich, V.C., Ballard, W.B., McKeever, J.S., 2002. Rainfall, El Nino, and dynamics of mule deer in the Sonoran Desert, California. J. Wildl. Manag. 1283–1289.
McCarthy, T.S., 2011. The impact of acid mine drainage in South Africa. S. Afr. J. Sci. 107 (5/6), 1–7.
Mello, K.D., Valente, R.A., Randhir, T.O., dos Santos, A.C.A., Vettorazzi, C.A., 2018. Effects of land use and land cover on water quality of low-order streams in Southeastern Brazil: watershed versus riparian zone. Catena 167, 130–138.
Mompati, M.K., Piketh, S.J., Aas, W., Van Zyl, P.G., Pienaar, J.J., Curtis, C.J., 2022. Rainwater chemistry and Total deposition of acidity from the northern savanna to the southern coastal fynbos of South Africa. Water Air Soil Pollut. 233, 1–18.
Mungall, J.E., 2014. 13.8 geochemistry of magmatic ore deposits. In: Turekian, K.K., Holland, H.D. (Eds.), Treatise on Geochemistry, 2nd edition. Elsevier Science, Toronto, Canada, pp. 195–218.
NAS, 1977. Copper. National Research Council, National Academy of Sciences, Washington DC.
Navarro, M.C., Pérez-Sirvent, C., Martínez-Sánchez, M.J., Vidal, J., Tovar, P.J., Bech, J., 2008. Abandoned mine sites as a source of contamination by heavy metals: a case study in a semi-arid zone. J. Geochem. Explor. 96 (2–3), 183–193.
Nel, J.L., Strydom, W.F., Maherry, A., Petersen, C., Hill, L., Roux, D.J., Nienaber, S., van Deventer, H., Swartz, E., Smith-Adao, L.B., 2011. Atlas of freshwater ecosystem priority areas in South Africa: maps to support sustainable development of water resources. In: Report No. TT500/11, Water Research Commission, Pretoria, South Africa.
Nimick, D.A., Moore, J.N., 1994. Chapter 19: stratigraphy and chemistry of sulfidic flood-plain sediments in the upper Clark Fork Valley, Montana. In: Alpers, C.N., Blowes, D.W. (Eds.), Environmental Geochemistry of Sulfide Oxidation ACS Symposium Series, American Chemistry Society, Washington. American Chemical Society, Washington DC, pp. 276–288.
Oliver, J.E., Cline, B., Curry, S., 2022. Evaluating organic fungicides for control of blueberry diseases in the southeastern. In: US Progress Report, Projects 2022 R-02 and 2022 R-03.
Oranje, M., Nel, V., van Huyssteen, E., Maritz, J., 2021. A brief history of platinum mining with a focus on the Rustenburg region. In: Marais, L., Campbell, M., Denoon-Stevens, S., van Rooyen, D. (Eds.), Mining and Community in the South African Platinum Belt a Decade After Marikana. Nova Science Publishers, New York, pp. 11–38.
Orlinskiy, P., Münze, R., Beketov, M., Gunold, R., Paschke, A., Knillmann, S., Liess, M., 2015. Forested headwaters mitigate pesticide effects on macroinvertebrate communities in streams: mechanisms and quantification. Sci. Total Environ. 524–525, 115–123.
Paul, M.J., Meyer, J.L., 2001. Streams in the urban landscape. Annu. Rev. Ecol. Syst. 32 (1), 333–365.
Peterson, B.J., Wollheim, W.M., Mulholland, P.J., Webster, J.R., Meyer, J.L., Tank, J.L., Marti, E., Bowden, W.B., Valett, H.M., Hershey, A.E., McDowell, W.H., 2001. Control of nitrogen export from watersheds by headwater streams. Science 292 (5514), 86–90.
Pool-Stanvliet, R., 2013. A history of the UNESCO man and the biosphere programme in South Africa. S. Afr. J. Sci. 109 (9–10), 1–6.
Pringle, C.M., 2001. Hydrologic connectivity and the management of biological reserves: a global perspective. Ecol. Appl. 11 (4), 981–998.
R Core Team, 2023. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria.
Richardson, J.S., Danehy, R.J., 2007. A synthesis of the ecology of headwater streams and their riparian zones in temperate forests. For. Sci. 53 (2), 131–147.
Saleh, A., Arnold, J.G., Gassman, P.W.A., Hauck, L.M., Rosenthal, W.D., Williams, J.R., McFarland, A.M.S., 2000. Application of SWAT for the upper North Bosque River watershed. Trans. ASAE 43 (5), 1077–1087.
SAWS, 2023. South African Weather Service, Precipitation Data for the Gwathle Catchment.
Schouwstra, R.P., Kinloch, E.D., Lee, C.A., 2000. A short geological review of the bushveld complex. Platin. Met. Rev. 44 (1), 33–39.
Shank, G.C., Skrabal, S.A., Whitehead, R.F., Kieber, R.J., 2004. Strong copper complexation in an organic-rich estuary: the importance of allochthonous dissolved organic matter. Mar. Chem. 88 (1–2), 21–39.
Sharma, N., Wang, Z., Catalano, J.G., Giammar, D.E., 2022. Dynamic responses of trace metal bioaccessibility to fluctuating redox conditions in wetland soils and stream sediments. ACS Earth Space Chem. 6 (5), 1331–1344.
Shehab, Z., Jamil, N.R., Aris, A.Z., Shafie, N.S., 2021. Spatial variation impact of landscape patterns and land use on water quality across an urbanized watershed in Bentong, Malaysia. Ecol. Indic. 122, 1–12.
Shen, Z., Hou, X., Li, W., Aini, G., Chen, L., Gong, Y., 2015. Impact of landscape pattern at multiple spatial scales on water quality: a case study in a typical urbanised watershed in China. Ecol. Indic. 48, 417–427.
Shi, P., Zhang, Y., Li, Z., Li, P., Xu, G., 2017. Influence of land use and land cover patterns on seasonal water quality at multi-spatial scales. Catena 151, 182–190.
Silva, V., Marques, C.R., Campos, I., Vidal, T., Keizer, J.J., Goncalves, F., Abrantes, N., 2018. Combined effect of copper sulfate and water temperature on key freshwater trophic levels–approaching potential climatic change scenarios. Ecotoxicol. Environ. Saf. 148, 384–392.
Skinner, S.J.W., 2018. Platinum tailings review-a comparison of the water quality in the tailings dam to the surrounding groundwater. IMWA 733–737.
Tadini, A.M., Mounier, S., Milori, D.M.B.P., 2020. Modeling the quenching of fluorescence from organic matter in Amazonian soils. Sci. Total Environ. 698, 1–9.
Thompson, S.E., Harman, C.J., Troch, P.A., Brooks, P.D., Sivapalan, M., 2011. Spatial scale dependence of ecohydrologically mediated water balance partitioning: a synthesis framework for catchment ecohydrology. Water Resour. Res. 47 (10), 1–20.
Thormann, L., Buchspies, B., Mbohwa, C., Kaltschmitt, M., 2017. PGE production in southern Africa, part I: production and market trends. Minerals 7 (11), 1–22.
Tran, C.P., Bode, R.W., Smith, A.J., Kleppel, G.S., 2010. Land-use proximity as a basis for assessing stream water quality in New York State (USA). Ecol. Indic. 10 (3), 727–733.
Uuemaa, E., Roosaare, J., Mander, Ü., 2007. Landscape metrics as indicators of river water quality at catchment scale. Hydrol. Res. 38 (2), 125–138.
Vannote, R.L., Minshall, G.W., Cummins, K.W., Sedell, J.R., Cushing, C.E., 1980. The river continuum concept. Can. J. Fish. Aquat. Sci. 37 (1), 130–137.
Wallace, J.B., Eggert, S.L., 2015. Terrestrial and longitudinal linkages of headwater streams. Southeast. Nat. 14 (7), 65–86.
Wanderi, E.W., Gettel, G.M., Singer, G.A., Masese, F.O., 2022. Drivers of water quality in Afromontane-savanna rivers. Front. Environ. Sci. 10, 1–20.
Wang, B., Liu, C.Q., Wang, F., Liu, X.L., Wang, Z.L., 2015. A decrease in pH downstream from the hydroelectric dam in relation to the carbon biogeochemical cycle. Environ. Earth Sci. 73, 5299–5306.
Wang, Y., Song, Z., Bai, H., Tong, H., Chen, Y., Wei, Y., Wang, X., Yang, S., 2023. Scale effects of land use on river water quality: a case study of the Tuojiang River Basin, China. Environ. Sci. Pollut. Res. 30 (16), 48002–48020.
Wickham, H., 2016. ggplot2: Elegant Graphics for Data Analysis. Springer-Verlag, New York.
Wickham, H., Henry, L., 2023. Purrr: functional programming tools. In: R Package Version 1.0.1.
Xu, S., Li, S.L., Zhong, J., Li, C., 2020. Spatial scale effects of the variable relationships between landscape pattern and water quality: example from an agricultural karst river basin, Southwestern China. Agric. Ecosyst. Environ. 300, 1–13.
Xu, Q., Wang, P., Shu, W., Ding, M., Zhang, H., 2021. Influence of landscape structures on river water quality at multiple spatial scales: a case study of the Yuan river watershed, China. Ecol. Indic. 121, 1–11.
Zaimes, G.N., 2004. Riparian Land-use Impacts on Stream and Gully Bank Soil and Phosphorus Losses With an Emphasis on Grazing Practices. Doctoral dissertation. Lowa State University.
Zak, D., Hupfer, M., Cabezas, A., Jurasinski, G., Audet, J., Kleeberg, A., McInnes, R., Kristiansen, S.M., Petersen, R.J., Liu, H., Goldhammer, T., 2021. Sulphate in freshwater ecosystems: a review of sources, biogeochemical cycles, ecotoxicological effects and bioremediation. Earth Sci. Rev. 212, 1–23.
Zhang, J., Li, S., Dong, R., Jiang, C., Ni, M., 2019. Influences of land use metrics at multi-spatial scales on seasonal water quality: a case study of river systems in the Three Gorges Reservoir Area, China. J. Clean. Prod. 206, 76–85.

Zhang, H., Li, H., Yu, H., Cheng, S., 2020. Water quality assessment and pollution source apportionment using multi-statistic and APCS-MLR modeling techniques in Min River Basin, China. Environ. Sci. Pollut. Res. 27 (33), 41987–42000.

Zhou, T., Wu, J., Peng, S., 2012. Assessing the effects of landscape pattern on river water quality at multiple scales: a case study of the Dongjiang River watershed, China. Ecol. Indic. 23, 166–175.

Zuur, A.F., Ieno, E.N., Walker, N.J., Saveliev, A.A., Smith, G.M., 2009. Mixed Effects Models and Extensions in Ecology With R. Springer, New York.