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ORIGINAL PAPER

Characterisation of the physicochemical qualities of a typical rural-based river: ecological and public health implications

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Abstract The physicochemical qualities of a typical rural-based river were assessed over a 12-month period from August 2010 to July 2011 spanning the spring, summer, autumn and winter seasons. Water samples were collected from six sampling sites along Tyume River and analysed for total nitrogen, orthophosphate, biochemical oxygen demand (BOD), temperature, pH, dissolved oxygen (DO), electrical conductivity (EC), total dissolved solids (TDS) and turbidity. BOD regimes did not differ significantly between seasons and between sampling points and ranged from 0.78 to 2.76 mg/L across seasons and sampling points, while temperature ranged significantly ($P < 0.05$) between 6 and 28 °C. Turbidity varied significantly ($P < 0.05$) from 6 to 281 nephelometric turbidity units while TDS (range 24–209 ppm) and conductivity (range 47.6–408 mg/L) also varied significantly ($P < 0.05$) across sampling points with a remarkable similarity in their trends. Orthophosphate concentrations varied from 0.06 to 2.72 mg/L across seasons and sampling points. Negative correlations were noted between temperature and the nutrients, DO and temperature ($r = -0.56$), and TDS and DO ($r = -0.33$). Positive correlations were noted between TDS and temperature ($r = 0.41$), EC and temperature ($r = 0.15$), and DO and pH ($r = 0.55$). All nutrients were positively correlated to each other. Most measured parameters were within prescribed safety guidelines. However, the general trend was that water quality tended to deteriorate as the river flows through settlements, moreso in rainy seasons.

Keywords Environment · Parameters · Pollution · Sampling · Seasons

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Introduction

Rivers are self-sustaining ecosystems that, without any human interference and natural disasters, could be able to indefinitely support both themselves and all life forms within them. They are vital but vulnerable freshwater systems that are critical for the sustenance of all life (Venkatesharaju et al. 2010). The declining quality of water in these systems threatens their sustainability and is therefore a cause for concern. Since most rural communities around the world traditionally take their water supply from rivers, dams, springs or from shallow dug wells (Sun et al. 2010; Aneck-Hahn et al. 2009; WHO and UNICEF 2006), increasing pollution from urban, industrial and agricultural sources is making available resources unusable and dangerous to health (Contaminated surface water 2008). Globally, about 1.6 billion children under the age of 5 years die annually due to unsafe drinking water, coupled with a lack of basic sanitation (WHO and UNICEF 2006). In the developing world alone, almost 5 million deaths annually are due to water-related diseases as water quality problems are affecting virtually all of the developing world's major rivers (Contaminated surface water 2008). Even where pollution levels in the main stem of a river are in acceptable levels, serious problems are often seen in the tributaries, usually local streams that have become "urban drains". Unfortunately, these "urban drains" are also the main source of water for drinking and daily use for downstream poor communities along their banks (Contaminated surface water 2008). Compared with assumed pristine conditions, rivers and streams worldwide have doubled their content of nitrogen and phosphorus as a consequence of human activities (Camargo et al. 2004). Severe pollution levels can cause rivers to become biologically dead and poisonous to drink from.

Causes of surface water pollution are diverse though anthropogenic activities are the major contributors to freshwater pollution. For example, continued discharge of nutrient-rich wastewater effluent into surface water resources leads to eutrophication problems. While statistics show Cambodia, Indonesia, the Philippines and Vietnam all have abundant internal freshwater resources per capita, they nevertheless suffer from significant freshwater pollution from human activities (Hutton et al. 2007). In Vietnam, for example, 13 % of households dispose of solid waste to water courses (Hutton et al. 2007). In agriculture, while the application of organic manure and/or inorganic fertilisers will boost the production of food crops and so make food affordable to even the low socio-economic class, nutrient application in excess of plant needs has a potential to pollute surface and groundwater (Bhumbla 2011). Apart from wastewater effluents and agriculture, storm water run-off from the built-up environment is another source of nutrient enrichment in rivers (Bhumbla 2011).

Surface water pollution also has economic consequences. A serious problem impacting on communities relying on polluted water sources for the production of potable water is the eventual costs of potable water. Treatment costs may become so excessive that water becomes available only to those who can afford it (Hutton et al. 2007). Pollution of surface waters by agricultural run-offs like sediment, nutrients, pesticides, salts and pathogens can impose costs on water users (Water quality impacts of agriculture 2012). Pesticides are especially difficult to remove from freshwater and thus can be found in municipal or bottled water, even after conventional treatment (Maria 2003). Eutrophication of surface waters may accelerate algal production, resulting in clogged pipelines, fish kills, which may result in loss of revenue, and reduced recreational opportunities (USEPA 1998). Sediment is the largest contaminant of surface water by weight and volume (Koltun et al. 1997). Besides increasing the cost of water treatment for municipal and industrial water uses, sediment can also destroy or degrade aquatic wildlife habitat, reducing diversity and damaging commercial and recreational fisheries. In addition, many toxic materials can be bound to silt and clay particles that are carried into water bodies, including nutrients, pesticides, industrial wastes and metals (Osterkamp et al. 1998).

In addition to anthropogenic activities, meteorological events are also major determinants of physicochemical parameters such as temperature, pH and turbidity of the water (Zamxaka et al. 2004). These parameters greatly influence the biochemical reactions that occur within the water and drastic changes in their levels may be indicative of changing conditions in the water. The imbalance between the construction of settlements (formal and informal) and sanitary infrastructure to carter for such increases in population growth poses a serious threat to the existing water resources, both through increased demand in terms of increased abstraction and storage, and through pollution by disposal, dilution and transportation of effluents. Hence, the need for a better understanding of the qualities of water resources becomes imperative in the management and mitigation of problems that may arise, such as pollution. Major pollutants in surface waters can be classified into two categories, viz physicochemical pollutants and the microbiological pollutants. In this paper, we report for the first time that the physicochemical qualities of the Tyume River in the Eastern Cape Province of South Africa were assessed in the period between August 2010 and July 2011.

Materials and methods

Description of study site

The Tyume River is located in the Nkonkobe local municipality, under the Amathole District Municipality, in the Eastern Cape Province, South Africa. It flows from the upper part of the Amathole Mountains in Hogsback, passing through the lower coastal escarpment down to Alice through several rural settlements and finally joins the Keiskamma River at Manqulweni community. Close proximity of the river to its host communities makes it ideal for utilisation for domestic activities where piped potable water is not available. The Tyume River also feeds the Binfield Park Dam that serves as a source of raw water for several water treatment plants in the area where water is treated and reticulated to Alice Town and surrounding rural settlements. Tyume River water samples were collected from six sampling sites that include Hala, Khayalethu, Sinakanaka, Alice, Drayini and Manqulweni communities. Table 1 shows the morphometric details of the sampling sites.

Sampling and analytical procedures

Water samples from the six sampling points were collected over a 12-month period starting from August 2010 and ending in July 2011 to shed light on the effect of season on the parameters. During sampling, the bottles were triple-rinsed with sample water before being filled with the

Table 1 Morphometric details of the sampling sites along Tyume River

Sampling site	Description	Coordinates
Hala	Hala is a community immediately downstream the source of Tyume River in Hogsback. The river source at Hogsback is inaccessible. At this point, the river is a source of drinking water for livestock and wild animals	32°36′39″S and 26°54′34″E
Khayalethu	Located in a major rural community, upstream the Binfield Park Dam. The inhabitants of this settlement use the river for irrigation, recreation, stock watering and domestic purposes	32°38′22″S and 26°56′10″E
Sinakanaka	Sinakanaka is a rural community on the banks of the Tyume River further downstream of Khayalethu and comprises several densely populated settlements. The Tyume River is very important to the inhabitants of this community as it is used for drinking, fishing, irrigation, recreation and other domestic purposes	32°45′37″S and 26°51′27″E
Alice	Alice is a semi-urban settlement comprising several suburbs that include Golf Course to the north-west; Happy Rest to the west; and Gaga, Gqumashe and Ntselamantsi to the north. Adding to the population of Alice is the student population at the University of Fort Hare to the east, which alone has a population of over 6,000. The combined population of Alice is over 48,000 according to UFH Interstudy (2012). The river is extensively used for irrigation, fishing and domestic purposes, as well as a source of drinking water for livestock	32°47′17″S and 26°50′31″E
Drayini	Drayini is a rural town further downstream the banks of the Tyume River after Alice. The sampling site is located downstream of Fort Hare farmlands and Alice Town. Its water is perpetually turbid with green aquatic plants covering its surface. The river serves as drinking water for domestic animals	32°48′37″S and 26°52′20″E
Manqulweni	Manqulweni is located further downstream the Tyume River after Drayini, just before the confluence of Tyume River with the Keiskamma River	32°54′50″S and 26°56′13″E

sample. The actual samplings were done midstream by dipping sample bottles at approximately 20–30 cm below the water surface, projecting the mouth of the container against the flow direction. Samples were transported in cooler boxes to the Applied and Environmental Microbiology Research Group (AEMREG) Laboratory at the University of Fort Hare, Alice, for the analyses. Processing and analysis of samples was done within 6 h of sample collection, following the procedure recommended by American Public Health Association (APHA 2005).

A total of ten physicochemical parameters in water quality control and pollution studies were determined. Temperature (°C), pH, electrical conductivity (EC) (μs/cm) and total dissolved solids (TDS) (mg/L) were determined using a digital multi-parameter system (Hanna; HI 9828). Turbidity [NTU (nephelometric turbidity units)] was determined using a digital turbidimeter (HACH; 2100P). Phosphate (mg/L $PO_4^{-}P$), nitrite (mg/L $NO_2^{-}N$) and nitrate (mg/L $NO_3^{-}N$) were determined using a spectrophotometer (Merck; Spectroquant NOVA 60). Dissolved oxygen (DO) (mg/L) and 5-day biochemical oxygen demand (BOD_5) were determined using a BOD metre (HACH; HQ 40d).

Statistical analysis

All data were subjected to descriptive statistical analysis (95 % confident limit). The generalised linear model (GLM) of SAS was used to generate analysis of variance (ANOVA), means, standard errors and ranges. Tukey's studentized range (HSD) test was used to test differences among all possible pairs of treatments. Correlation was performed using Proc Corr procedure of SAS (SAS version 8, SAS Institute, Cary, NC).

Results and discussion

Physicochemical data were pooled according to the four climatic seasons of South Africa as follows: summer (November to January), autumn (February to April), winter (May to July) and spring (August to October). Table 2a, b shows the summary of the seasonal variations in physicochemical parameters of Tyume River. Collectively, the BOD levels observed in this study ranged as follows: Hala (0.78–1.36 mg/L), Khayalethu (1.03–2.73 mg/L), Sinakanaka (0.98–1.46 mg/L), Alice (1.33–2.14 mg/L), Drayini (1.26–2.44 mg/L) and Manqulweni (1.44–2.76 mg/L), and fell within the stipulated BOD guidelines of 10 mg/L for surface waters where full contact use is allowed and $\leq$30 mg/L where public access is prohibited, restricted or infrequent (EPA 2004).

Table 2 Statistical comparisons of the mean values of physicochemical parameters in Tyume River water

Parameter	Season	Sampling sites						*P* value
		Hala	Khayalethu	Sinakanaka	Alice	Drayini	Manqulweni	
a								
BOD (mg/L)	Summer	$1.25 \pm 0.91_{a}^{A}$	$2.73 \pm 0.9_{a}^{A}$	$0.98 \pm 0.0_{a}^{A}$	$1.39 \pm 0.3_{a}^{A}$	$1.83 \pm 0.5_{a}^{A}$	$2.33 \pm 1.1_{a}^{A}$	0.22
	Autumn	$1.36 \pm 0.8_{a}^{A}$	$1.28 \pm 0.6_{a}^{A}$	$1.44 \pm 0.6_{a}^{A}$	$2.14 \pm 1.3_{a}^{A}$	$2.44 \pm 1.2_{a}^{A}$	$2.76 \pm 1.0_{a}^{A}$	0.05
	Winter	$1.18 \pm 0.3_{a}^{A}$	$1.03 \pm 0.3_{a}^{A}$	$1.46 \pm 0.4_{a}^{A}$	$1.33 \pm 0.3_{a}^{A}$	$1.26 \pm 0.8_{a}^{A}$	$1.72 \pm 1.1_{a}^{A}$	0.47
	Spring	$0.78 \pm 0.4_{a}^{A}$	$1.72 \pm 1.1_{a}^{A}$	$1.32 \pm 0.7_{a}^{A}$	$1.47 \pm 0.6_{a}^{A}$	$1.95 \pm 0.6_{a}^{A}$	$1.44 \pm 0.3_{a}^{A}$	0.28
	P value	0.59	0.33	0.28	0.26	0.15	0.15	
pH	Summer	$7.2 \pm 0.4_{b}^{B}$	$7.2 \pm 0.6_{b}^{B}$	$7.4 \pm 0.5_{c}^{B}$	$7.7 \pm 0.7_{c}^{B}$	$8.6 \pm 0.5_{bc}^{A}$	$8.8 \pm 0.7_{b}^{A}$	<0.001
	Autumn	$10 \pm 0.3_{a}^{A}$	$10.1 \pm 0.4_{a}^{A}$	$9.5 \pm 0.61_{b}^{AB}$	$9.1 \pm 0.9_{b}^{B}$	$9.8 \pm 0.1_{a}^{AB}$	$9.9 \pm 0.1_{a}^{A}$	0.0008
	Winter	$9.6 \pm 1.0_{a}^{AB}$	$9.5 \pm 1.2_{a}^{AB}$	$10.4 \pm 0.8_{a}^{A}$	$10.6 \pm 0.4_{a}^{A}$	$8.8 \pm 1.2_{b}^{B}$	$8.95 \pm 1.2_{ab}^{B}$	0.001
	Spring	$7.7 \pm 0.5_{b}^{AB}$	$7.2 \pm 0.5_{b}^{AB}$	$7.1 \pm 0.2_{c}^{B}$	$7.3 \pm 0.4_{c}^{AB}$	$7.8 \pm 0.8_{c}^{A}$	$7.7 \pm 0.6_{c}^{AB}$	0.01
	P value	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	
Temperature (°C)	Summer	$15.6 \pm 1.7_{a}^{B}$	$17.8 \pm 2.0_{ab}^{B}$	$23.1 \pm 1.4_{a}^{A}$	$21.3 \pm 1.7_{a}^{A}$	$21.8 \pm 2.2_{a}^{A}$	$23.4 \pm 0.9_{a}^{A}$	<0.001
	Autumn	$16.6 \pm 2.8_{a}^{B}$	$18.5 \pm 4.0_{a}^{B}$	$22.8 \pm 4.5_{a}^{A}$	$20.9 \pm 3.7_{a}^{AB}$	$22.4 \pm 3.9_{a}^{A}$	$23.8 \pm 4.6_{a}^{A}$	0.002
	Winter	$9.2 \pm 2.9_{b}^{B}$	$10.1 \pm 2.7_{c}^{AB}$	$12.3 \pm 2.3_{b}^{AB}$	$12.2 \pm 2.5_{c}^{AB}$	$13.1 \pm 2.4_{b}^{A}$	$13.0 \pm 2.4_{c}^{A}$	0.006
	Spring	$11.0 \pm 4.3_{b}^{B}$	$13.8 \pm 4.8_{bc}^{AB}$	$16.4 \pm 4.5_{b}^{AB}$	$16.3 \pm 3.8_{b}^{AB}$	$15.9 \pm 3.4_{b}^{AB}$	$17.5 \pm 3.8_{b}^{A}$	0.02
	P value	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	
Conductivity (µs/cm)	Summer	$62.2 \pm 10_{ab}^{C}$	$51.2 \pm 4_{a}^{CD}$	$176 \pm 41_{a}^{BC}$	$246 \pm 70_{a}^{B}$	$368 \pm 99_{a}^{A}$	$374 \pm 157_{a}^{A}$	<0.001
	Autumn	$57 \pm 2_{ab}^{D}$	$47.6 \pm 8_{a}^{D}$	$144 \pm 11_{b}^{C}$	$263 \pm 57_{a}^{B}$	$396 \pm 56_{a}^{A}$	$417 \pm 86_{a}^{A}$	<0.001
	Winter	$50.6 \pm 3_{b}^{D}$	$50 \pm 5.4_{a}^{D}$	$144 \pm 19_{b}^{C}$	$253 \pm 38_{a}^{B}$	$345 \pm 51_{a}^{B}$	$237 \pm 41_{b}^{A}$	<0.001
	Spring	$69 \pm 8_{a}^{E}$	$64.8 \pm 7_{b}^{E}$	$128 \pm 2_{b}^{D}$	$222 \pm 7_{a}^{C}$	$351 \pm 10_{a}^{B}$	$408 \pm 15_{a}^{A}$	<0.001
	P value	0.005	<0.0001	0.004	0.49	0.38	0.002	
TDS (mg/L)	Summer	$32.1 \pm 6.2_{ab}^{C}$	$25.1 \pm 2.0_{b}^{C}$	$108 \pm 56_{a}^{B}$	$117 \pm 37_{a}^{B}$	$188 \pm 59_{a}^{A}$	$187 \pm 78_{a}^{A}$	<0.001
	Autumn	$29.6 \pm 5.5_{bc}^{D}$	$23.7 \pm 4.2_{b}^{D}$	$72 \pm 5_{ab}^{C}$	$133 \pm 27_{a}^{B}$	$199 \pm 28_{a}^{A}$	$209 \pm 43_{a}^{A}$	<0.001
	Winter	$25.3 \pm 1.7_{c}^{D}$	$25.1 \pm 2.6_{b}^{D}$	$73 \pm 8.4_{ab}^{C}$	$143 \pm 48_{a}^{AB}$	$172 \pm 26_{a}^{A}$	$118 \pm 21_{b}^{B}$	<0.001
	Spring	$36.2 \pm 1.6_{a}^{E}$	$32 \pm 2.4_{a}^{E}$	$65 \pm 2_{b}^{D}$	$109 \pm 3_{a}^{C}$	$170 \pm 10_{a}^{B}$	$194 \pm 17_{a}^{A}$	<0.001
	P value	<0.0001	<0.0001	0.02	0.15	0.27	0.001	
DO (mg/L)	Summer	$8.57 \pm 0.1_{c}^{A}$	$8.45 \pm 0.03_{c}^{AB}$	$7.77 \pm 0.33_{c}^{C}$	$8.13 \pm 0.37_{c}^{B}$	$7.56 \pm 0.28_{c}^{C}$	$7.55 \pm 0.02_{c}^{C}$	<0.001
	Autumn	$9.69 \pm 0.7_{b}^{B}$	$9.54 \pm 0.75_{b}^{B}$	$9.17 \pm 1.02_{b}^{B}$	$9.3 \pm 0.98_{b}^{B}$	$8.78 \pm 0.63_{b}^{B}$	$8.9 \pm 0.91_{b}^{B}$	0.18
	Winter	$10.42 \pm 0.6_{a}^{A}$	$10.28 \pm 0.49_{a}^{A}$	$10.25 \pm 0.47_{a}^{A}$	$10.27 \pm 0.88_{a}^{A}$	$9.6 \pm 0.7_{a}^{A}$	$10 \pm 0.77_{a}^{A}$	0.15
	Spring	$8.73 \pm 0.2_{c}^{A}$	$8.55 \pm 0.11_{c}^{A}$	$7.74 \pm 0.21_{c}^{BC}$	$7.98 \pm 0.5_{c}^{B}$	$7.54 \pm 0.13_{c}^{C}$	$7.47 \pm 0.06_{c}^{C}$	<0.001
	P value	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	
Turbidity (NTU)	Summer	ND	ND	ND	ND	ND	ND	ND
	Autumn	$24.16 \pm 1_{a}^{A}$	$20.39 \pm 18_{a}^{A}$	$61.2 \pm 61_{a}^{A}$	$99.9 \pm 115_{a}^{A}$	$158 \pm 21_{a}^{A}$	$112 \pm 123_{a}^{A}$	0.09
	Winter	$19.72 \pm 8_{a}^{B}$	$17.38 \pm 8_{a}^{B}$	$76.3 \pm 56_{a}^{AB}$	$77.1 \pm 58_{a}^{AB}$	$83.8 \pm 63_{a}^{AB}$	$281.1 \pm 36_{a}^{A}$	0.008
	Spring	$11.81 \pm 3_{a}^{C}$	$6.48 \pm 1_{a}^{C}$	$22.3 \pm 4_{a}^{B}$	$22.2 \pm 4_{a}^{B}$	$12.63 \pm 3_{a}^{C}$	$33 \pm 3_{a}^{A}$	<0.001
	P value	0.07	0.11	0.16	0.20	0.15	0.13	
b								
Nitrate (mg/L)	Summer	$2.27 \pm 0.9_{a}^{A}$	$2.02 \pm 0.4_{a}^{A}$	$2.10 \pm 1.0_{a}^{A}$	$2.29 \pm 0.8_{a}^{A}$	$2.29 \pm 0.7_{ab}^{A}$	$2.65 \pm 0.8_{a}^{A}$	0.67
	Autumn	$0.25 \pm 0.1_{b}^{C}$	$0.81 \pm 0.1_{b}^{BC}$	$0.54 \pm 0.3_{b}^{C}$	$1.31 \pm 0.1_{b}^{AB}$	$1.54 \pm 0.8_{a}^{A}$	$0.58 \pm 0.4_{b}^{C}$	<0.001
	Winter	$0.93 \pm 0.4_{c}^{B}$	$0.95 \pm 0.4_{b}^{B}$	$2.34 \pm 2.0_{a}^{AB}$	$1.48 \pm 0.6_{b}^{AB}$	$2.52 \pm 0.9_{bc}^{A}$	$1.96 \pm 1.0_{a}^{AB}$	0.006
	Spring	$3.23 \pm 0.1\ _{d}^{B}$	$3.64 \pm 0.1_{c}^{AB}$	$3.67 \pm 0.2_{a}^{AB}$	$3.52 \pm 0.4_{c}^{AB}$	$3.46 \pm 0.3_{c}^{AB}$	$3.91 \pm 0.3_{c}^{A}$	0.01
	P value	<0.0001	<0.0001	0.0003	<0.0001	0.0006	<0.0001	
Nitrite (mg/L)	Summer	$0.64 \pm 0.5_{a}^{A}$	$0.59 \pm 0.5_{a}^{A}$	$1.54 \pm 1.2_{a}^{A}$	$1.53 \pm 1.3_{a}^{A}$	$1.22 \pm 0.7_{a}^{A}$	$0.83 \pm 0.5_{a}^{A}$	0.06
	Autumn	$0.03 \pm 0.0_{b}^{B}$	$0.02 \pm 0.0_{a}^{B}$	$0.05 \pm 0.0_{b}^{B}$	$0.13 \pm 0.1_{b}^{AB}$	$0.17 \pm 0.2_{b}^{A}$	$0.09 \pm 0.0_{b}^{AB}$	0.001
	Winter	$0.47 \pm 0.5_{ab}^{A}$	$0.51 \pm 0.5_{a}^{A}$	$0.48 \pm 0.6_{b}^{A}$	$0.47 \pm 0.5_{b}^{A}$	$0.48 \pm 0.5_{b}^{A}$	$0.53 \pm 0.6_{ab}^{A}$	0.99
	Spring	$2.34 \pm 0.1_{c}^{AB}$	$1.65 \pm 0.7_{b}^{B}$	$2.19 \pm 0.0_{a}^{AB}$	$2.03 \pm 0.5_{a}^{AB}$	$2.35 \pm 0.1_{c}^{A}$	$2.04 \pm 0.3_{c}^{AB}$	0.04
	P value	<0.0001	<0.0001	<0.0001	0.0001	<0.0001	<0.0001	

Table 2 continued

Parameter	Season	Sampling sites						P value
		Hala	Khayalethu	Sinakanaka	Alice	Drayini	Manqulweni	
Orthophosphate (mg/L)	Summer	$0.77 \pm 0.5_{a}^{B}$	$0.77 \pm 0.4_{a}^{B}$	$0.92 \pm 0.4_{a}^{AB}$	$0.79 \pm 0.5_{a}^{B}$	$0.92 \pm 0.3_{a}^{AB}$	$1.43 \pm 0.6_{a}^{A}$	0.02
	Autumn	$0.06 \pm 0.0_{b}^{C}$	$0.08 \pm 0.0_{b}^{C}$	$0.13 \pm 0.1_{b}^{BC}$	$0.16 \pm 0.1_{b}^{BC}$	$0.63 \pm 0.5_{a}^{A}$	$0.44 \pm 0.3_{b}^{AB}$	<0.001
	Winter	$0.15 \pm 0.1_{b}^{B}$	$0.15 \pm 0.1_{b}^{B}$	$0.32 \pm 0.2_{b}^{AB}$	$0.26 \pm 0.1_{b}^{B}$	$0.61 \pm 0.5_{a}^{A}$	$0.25 \pm 0.2_{b}^{B}$	0.0003
	Spring	$1.51 \pm 0.3_{c}^{CD}$	$1.48 \pm 0.3_{c}^{CD}$	$2.72 \pm 0.1_{c}^{A}$	$1.07 \pm 0.1_{a}^{D}$	$2.13 \pm 0.1_{b}^{B}$	$1.60 \pm 0.4_{a}^{C}$	<0.0011
	P value	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	

Along the rows, different upper case letters show significantly different readings ($P < 0.05$) of the parameters per given season in sampling sites while across the rows, different subscript letters show significantly different readings ($P < 0.05$) of the parameters per site in different seasons

Also, DO concentrations which generally ranged from 7.47 to 10.42 mg/L were well within the criteria standard of 5–6 mg/L for warm-water biota and 6.5–9.5 mg/L for cold-water biota (Enderlein 1996). BOD and DO results imply that Tyume River is clean with respect to organic pollution (Bhutiani and Khanna 2007; Kannel et al. 2007).

Dissolved oxygen concentrations were not significantly different when compared by sampling point in autumn and winter probably because of high rainfall activity that resulted in high water volumes and thorough water mixing throughout the river course. In spring and winter when sampling coincided with extended dry weather conditions, significantly higher DO concentrations ($P < 0.05$) were observed at upstream sampling points (Hala and Khayalethu) where the stream gradient is steeper compared to the downstream points (Alice, Drayini and Sinakanaka). DO levels are important in determining the natural self-purification capacity of a river (Mukherjee et al. 1993). Good levels of DO in all the sampling sites of the river may also be indicative of high re-aeration rates and rapid aerobic oxidation of biological substances (Suthar et al. 2010).

Besides the use of temperature, BOD and/or COD to explain DO concentrations in surface waters, other determinants of DO concentrations include the stream gradient and the nature of the river bed as well as the rate of primary productivity. When the stream gradient is steep, combined with a rocky outcrop on the river bed, mixing of water with atmospheric oxygen is highly encouraged resulting in high concentrations of DO in the water (Chang 2008). Low DO concentrations (below 70 % saturation), when combined with the presence of toxic substances, may lead to stress responses in aquatic ecosystems because the toxicity of certain elements, such as zinc, lead and copper (not covered in this study), is increased by low concentrations of DO (EPA 1986). Low concentrations of DO, associated with high water temperature, also increase the adverse effects on biota (Enderlein 1996). The water quality criterion for DO, therefore, cannot be taken independently of other water quality determinants.

The temperature range for Hala was 6–20 °C, while those for Khayalethu, Sinakanaka, Alice, Drayini and Manqulweni were 8–23, 10–28, 9–25, 10–27 and 10–25 °C, respectively. Temperature regimes varied significantly ($P < 0.05$) by season, and whereas there were also significant differences in the temperature regimes by sampling point, it was mainly at Hala and, in summer and autumn, Khayalethu also, where temperature varied with that of the other sampling points. Water temperature at Hala, which is located at the foot of the Hogsback Mountains, was always lower than at the other points. This point receives the least insolation because of the high mountains casting shed on this part of the river till very late in the afternoon and even then, riparian vegetation still shields this part of the river from receiving much sunshine. As has been pointed above, temperature generally drives the chemical reactions in an aquatic system and warmer temperatures (>25 °C) may influence the toxicity of some substances like ionised ammonia that may be found dissolved in water (Hargreaves and Tucker 2004; Knepp and Arkin 1973). However, in this study, the temperature regimes for most sampling sites were within the acceptable limit of no risk (≤25 °C) for domestic water uses (DWAF and WRC 1995).

Electrical conductivity (EC) data which generally ranged from 47.6 to 408.2 µs/cm showed significant variability among sampling points but, when compared by season, EC results for Alice and Drayini did not show significant variation at the 95 % confidence level. These two sites are impacted by sewage disposal from Alice Town and the University of Fort Hare, respectively, which could explain why their electrical conductance was more or less the same. Previous findings indicate that sewage disposal tends to increase the EC levels of the receiving water body because of the high concentrations of salts and ions in the sewage (Suthar et al. 2010). EC estimates the amount of total dissolved salts, or the total amount of dissolved ions in the water and is controlled by, among other factors; the geology of the catchment area determines the chemistry of the watershed soil and ultimately the water (Chang 2008). The size of the catchment relative to the size of the river also has a significant impact on the EC of the water since a bigger catchment area means relatively more water draining into the river, and more contact with soil before reaching the river only when stream flow is low, otherwise high flow volumes will result in dilution (Ouyang et al. 2006). A quick glance at the mean values for EC in Table 2a shows that the mean values become progressively bigger from Hala to Manqulweni (upstream to downstream), contrary to the most commonly held notion that pollute concentration becomes progressively lower as we go downstream due to the effect of dilution and self-purification capacity of the river (Osode and Okoh 2009). A combination of factors can be used to explain the observed trend and these include dispersed (non-point) pollution sources, the water's increased contact with soil with time and distance of flow and also the cumulative effect of ions, as more and more tributaries/rivulets discharge their loads into the main stream (Brainwood et al. 2004). Sewage disposal and urban surface run-off in the downstream stretch of the river may also have contributed to the observed pattern. Similar findings have been observed elsewhere (Igbinosa and Okoh 2009). High EC levels can be damaging to aquatic life because of increased salinity in the stream and possible smothering of the stream bottom, especially if the stream is deep (DWAF 1996a). The target water quality limit of no risk for domestic water uses with respect to EC is set at 700 µs/cm (DWAF 1996b), and results obtained in this study suggest that with respect to EC, the river water could be suitable for domestic use.

The pH regimes in this study showed significant seasonal variability in each of the six sampling sites. The pH of river water is affected by a number of factors among them the geology and mineral content of the catchment area, acid mine drainage, agricultural run-off, carbon dioxide concentration in the atmosphere, and accumulation and decomposition of organic detritus in the water producing weak carbonic acids that impact on pH. However, there is no mining activity in the Tyume River catchment while agricultural activity and the use of fossil fuels are limited. Again, the observed pH ranges (Table 2a) were either in the neutral or alkaline range, ruling out the accumulation and decomposition of organic detritus in the river as possible causes of pH fluctuations since that would have resulted in pH values below 7 being observed. The most likely cause of the observed fluctuations in river water pH could be the bedrock and soil composition of the catchment, which could be containing some limestone deposits. River water levels were higher in winter and autumn than they were in summer or spring (data not available). This could have caused the river to have greater erosive power in autumn and winter (as compared to either summer or spring), possibly contributing to higher pH in autumn and winter as more soil and bedrock were eroded. Other unknown factors, though, could be responsible for the observed trend in pH. DWAF (1996b) set the target water quality for pH in water for domestic use between 6 and 9, same as that of the European Union tolerance limit for pH in water for the support of fisheries and aquatic life (Chapman 1996). pH values in this study ranged from 7.2 to 10.6 across seasons and sampling points.

Turbidity was assessed for only three seasons, viz. autumn, winter and spring, and the results revealed that the turbidity of the river water did not differ significantly by season at all the sampling sites. However, when analysed by sampling point, the turbidities of upstream sampling points (Hala, and Khayalethu) were significantly lower ($P < 0.05$) than the turbidities of downstream sampling points in winter and spring. In autumn, turbidity did not significantly differ from one sampling site to another. Suspended silt and clay, organic matter, and plankton can contribute to turbidity; hence, turbidity in a stream will fluctuate before, during and after storm flow (Igbinosa and Okoh 2009). Highly turbid water has an altered odour, taste and its visual properties are negatively impacted and will significantly increase water treatment costs due to the amount of flocculants needed to clarify the water (Osode and Okoh 2009). The overall turbidity range for this study was 6–281 NTU and fell short of the target water quality range (0–1 NTU) of no risk for domestic water uses as proposed by DWAF (1996b). Increased turbidities also interfere with the normal workings of sanitisers by forming a chemical "shield" around bacteria, algae and other substances normally attacked by chlorine (Hoko 2005) in addition to shielding enteric bacteria from photooxidation. Highly turbid water will therefore present a microbiological hazard to consumers of raw river water.

Total dissolved solid (TDS) levels ranged from 23.7 to 209 mg/L across seasons and sampling points. TDS is the sum total of all of the dissolved substances in a given body of water and includes hardness, alkalinity, chlorides, bromides, sulphates, silicates and all manner of organic compounds. Although elevated TDS concentration may not mean that the water is a health hazard, it however does mean the water may have aesthetic problems or cause nuisance problems. These problems may be associated with staining, taste, or precipitation. With respect to trace metals, elevated TDS may suggest that toxic metals may be present at an elevated level. DWAF (1996b) has set the water quality guidelines for TDS at 0–450 mg/L as applied to domestic uses. TDS values for this study fell within stipulated DWAF guidelines.

Nitrate, nitrite and orthophosphate concentrations are remarkably similar in that significantly higher values ($P < 0.05$) were obtained in summer and spring compared to those obtained in autumn and winter. The higher rainfall in autumn and winter could have significantly increased the flow volume and resulted in a dilution effect. Low-flow situations increase the concentrations of water quality stressors. Concentrations of substances that are continuously added, but in low doses (e.g. from sewage treatment plants), will increase and might reach levels toxic to organisms, or concentrations might exceed bathing and recreational water directives (Nilsson and Renöfält 2008). Agricultural activities can result in high levels of these nutrients due to run-off. However, there is little agricultural activity in the Tyume catchment. In this case, nutrient loadings typically arise from non-point source run-off from flash storms, particularly in urban areas (Brainwood et al. 2004). In summer and spring when there was less rainfall, and hence low flow, the effects of sewage discharge into the river were evident from the higher nutrient concentrations observed at Alice and Drayini sampling points. Similar trends have been observed elsewhere (Jarvie et al. 2006; Ferrier et al. 2001; Castillo et al. 2000).

All three nutrients are naturally present in the environment and natural nutrient cycling processes prevents accumulation of very high concentrations of the nutrients. However, human activities have increased environmental nitrate and nitrite concentrations, with agriculture being the major source (Ferrier et al. 2001; Castillo et al. 2000). This includes increased use of nitrogen-containing fertilisers as well as concentrated livestock and poultry farming; the latter two produce millions of tons of nitrate-containing manure each year (EPA 2007). Nitrate and nitrite compounds are very soluble in water and quite mobile in the environment (Blanchard and Lerch 2000). They have a high potential for entering surface water during rainfall events, as nitrates in applied fertilisers can dissolve in run-off that flows into streams (Brainwood et al. 2004). Nitrates themselves are relatively non-toxic and normal individuals have low levels (0.5–2 %) of methemoglobin in their blood (EPA 2007). When in excess, nitrates may also result in excessive nutrient enrichment in water systems (eutrophication) leading to the loss of diversity in the aquatic biota and overall ecosystem degradation through algal blooms, excessive plant growth, oxygen depletion and reduced sunlight penetration (Odjadjare and Okoh 2010). Water quality guidelines for nitrate concentration consider the effect of this compound on the health of infants and pregnant women, and thus DWAF (1996b) has set the safety limit for water meant for human consumption at 6 mg NO_3^- as N/L. The nitrate concentrations in this study all fell within this target water quality range.

Nitrite levels ranged from 0.02 to 2.35 mg/L across seasons and sampling points (Table 2b). However, in spring alone, mean values for nitrite levels were as follows: 2.34, 1.65, 2.19, 2.03, 2.35 and 2.04 mg/L at Hala, Khayalethu, Sinakanaka, Alice, Drayini and Manqulweni, respectively. These levels were clearly above the limit associated with oligotrophic conditions (<0.5 NO_2^- as mg N/L) (DWAF 1996a) and also above the drinking water limits of 0.5 mg N/L and 1 mg N/L for the EU and USA, respectively. However, nitrite easily changes to nitrate as the end product of the oxidation of organic nitrogen and ammonia. The detected nitrite concentrations may therefore not have posed a health risk in the case of people imbibing the raw water since the detected nitrate levels in the same season were within the safety guidelines of 6 mg NO_3^- as N/L set for water meant for human consumption.

Orthophosphate (as P) concentrations in this study varied from 0.06 to 2.72 mg PO_4^{3-}/L across seasons and sampling points (Table 2b). However, like nitrite, in spring alone, mean values of orthophosphate concentration were as follows: 1.51, 1.48, 2.72, 1.07, 2.13 and 1.60 mg/L at Hala, Khayalethu, Sinakanaka, Alice, Drayini and Manqulweni, respectively. These values were clearly above the standard limit (0.1 mg/L) of the US Public Health Standards (Solaraj et al. 2010) in water systems that will not encourage the growth of algae and other plants. Since municipal wastewater contains substantial amount of phosphorus contributed by human urine and detergents (Ekholm and Krogenus 1998), disposal of municipal sewage into the river may account for the observed trend in spring. Because spring season was dry compared to other seasons, the dilution effect on the sewage disposed into the river could have been less in this season, hence the higher concentrations of nutrients in this season than in other seasons. In the presence of sufficient available phosphorus as was the case in the spring season of this study, nitrogen-fixing organisms will be able to fix atmospheric nitrogen, thereby compensating for any deficit caused by low inorganic nitrogen concentrations culminating in aquatic eutrophication.

Correlation analysis output is shown in Table 3. Correlation analysis revealed a significant negative correlation between temperature and the nutrients (NO_3^-, NO_2^- and PO_4^{3-}) at the 99 % confidence level. This result concurs with the findings of Badran (2001) and Manasrah et al. (2006) which they explained to be the result of increased nutrient consumption by primary producers in favourable temperature conditions. DO was also negatively correlated to temperature ($r = -0.56$) while TDS and EC showed positive correlation to temperature at 99 and 95 % confidence levels, respectively. This trend is expected since high water temperatures result in less DO in the water while low water temperatures will also result in high DO concentration in the water (Papafilippaki et al. 2008; Rounds 2002; Vega et al. 1998). Results also show that the dissolution of solids in the water is temperature-dependant while EC is also a function of TDS, hence its positive correlation to temperature. TDS assumed an inverse correlation to DO ($r = -0.33$). All nutrients were positively correlated to each other at the 99 % confidence level indicating that they

Table 3 Correlation analysis output for microbiological and physicochemical data of Tyume River

Parameters	pH	WT	TDS	TBD	EC	NO_3^-N	NO_2^-N	$PO_4^{3-}P$	BOD	DO
pH	1									
WT	0.014	1								
TDS	0.077	0.412[a]	1							
TBD	0.021	−0.052	−0.052	1						
EC	0.037	0.150[b]	0.593[a]	0.101	1					
NO_3^-N	−0.046	−0.223[a]	−0.078	0.135[b]	0.288[a]	1				
NO_2^-N	−0.004	−0.320[a]	−0.125	0.240[a]	0.154[b]	0.747[a]	1			
$PO_4^{3-}P$	−0.013	−0.387[a]	−0.047	0.266[a]	0.223[a]	0.717[a]	0.701[a]	1		
BOD	−0.110	−0.016	−0.481[a]	0.006	−0.278[a]	0.032	0.086	−0.101	1	
DO	0.550[a]	−0.562[a]	−0.333[a]	−0.003	−0.246[a]	0.088	0.166[b]	0.271[a]	0.088	1

WT water temperature, *EC* electrical conductivity, *TDS* total dissolved solids, *TBD* turbidity, *DO* dissolved oxygen, *BOD* biochemical oxygen demand

[a] Correlation is significant at the 0.01 level (two-tailed). [b] Correlation is significant at the 0.05 level (two-tailed)

probably come from the same source. The highly significant positive correlation between DO and pH ($r = 0.55$) is an interesting observation, which seems to indicate that the bacteria responsible for the decomposition of organic material, and hence utilisation of DO in water, do not thrive in alkaline conditions. This will suggest that as the pH is increased, more and more bacteria die out and the oxygen concentration is maintained at a high level. Similar results have been reported elsewhere (Araoye 2009; Swaminathan 2005). The positive correlation between DO and nutrients observed in this study is in agreement with the findings of Morgan et al. (2006) and that of Arheimer and Liden (2000) who attributed this trend to the fact that nutrient input promotes primary productivity during day, largely contributing to the water's DO concentrations during day though this trend is likely to reverse in the night when these primary producers are respiring.

Conclusion

Physicochemical parameters are the major determinants of water quality that directly or indirectly affects its use. All physicochemical parameters were within recognised water quality guidelines for the duration of the study period. This has major health, ecological and economic implications for a water scarce country like South Africa where every flowing river is a precious natural resource that needs to be safeguarded against pollution. Since Tyume River is the source water for a drinking water treatment plant (DWTP), its relative purity in respect of physicochemical pollutants means that water treatment costs will be kept at a minimum. Water quality investigations are carried out to provide information on the health of water bodies and for developing strategies that help in better management of catchment and water resources. Though the levels of all physicochemical parameters were within certain prescribed levels, the general trend was that water quality tended to deteriorate as the river flows through settlements, moreso in rainy seasons.

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