Macrothink Institute™

Aquatic Science and Technology
ISSN 2168-9148
2018, Vol. 6, No. 1

Assessment of Anthropogenic Impact on Surface Water Quality, South Africa

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Received: March 18, 2017 Accepted: April 17, 2018 Published: June 19, 2018

doi:10.5296/ast.v6i1.12837 URL: https://doi.org/10.5296/ast.v6i1.12837

Abstract

This article investigates the impact of anthropogenic activities on an important surface water from physico-chemical, chemical and microbial perspectives. The surface water, referred to as Blesbokspruit is in the West Rand District of South Africa. Potential impactors include wastewater treatment plant, mines, farmlands and informal settlements. Water samples were collected from nine purposively selected sampling points and analysed in 2014. The mean values of analysed variables across sampling sites and periods ranged from pH: 7.4-8.4; EC: 93.0 - 146.6 mS/m; TSS: 11.3 – 39.0 mg/L; TDS: 590.3 - 1020.3 mg/L; COD: 15.6- 34.8 mg/L. Those for anions varied from NO_3^-: 0.2- 2.1 (mg/L) N; PO_4^{3-} : 0.4-0.9 mg/L and SO_4^{2-}: 118.6 - 379.5 mg/L. The metallic variables ranged from As: 0.01-0.06 mg/L; Cd: 0.02-0.06 mg/L; Fe: 0.04-0.73 mg/L; Cu: 0.02 – 0.05 mg/L and Zn: 0.05 – 0.15 mg/L. The Faecal coliform varied from 15.9-16878.5 cfu/100 ml; Total coliform: 92.9-430294 cfu/100 ml and HPC from 4322.5-39776 cfu/1ml. Detection of toxic metals and pathogenic organisms above target safety limits indicate unsuitability of the water for domestic use with impact on the health of aquatic ecosystem. The study generally revealed the impact of anthropogenic activities on the surface water quality.

Keywords: Trace metals, pathogens, anthropogenic, water quality, South Africa

1. Introduction

Continual monitoring and protection of the quality of water resources is usually strategic especially in arid and semi-arid countries such as South Africa. Hence, activities that may negatively impact and diminish the quality of these resources should be prevented. Surface waters such as rivers, lakes and streams are major sources of water utilised for irrigational, industrial, recreational as well as domestic activities including the informal settlers where there is no access to potable water supply. The quality of natural water resources can be impacted because of rapid economic development, urbanisation and anthropogenic activities (Masere et al., 2012). Factors such as run-offs from agricultural farmland, discharges from wastewater treatment plants and industrial effluent and illegal dumping of wastes into the water systems are among major sources of concern on quality of surface waters (Nartey et al., 2012).

Polluted water is one of the major causes of human disease and health problems. Incidences of contamination of aquatic resources by bacteria pathogens in South Africa (Pitman, 2011) and elsewhere (Keddy et al., 2011; NICD, 2016) have been reported. In addition, incidences of diarrhoea-associated illnesses can be attributable to unsafe water, inadequate sanitation and insufficient hygiene. The bacteria commonly found in polluted water are coliforms mostly from animal and human wastes and improperly treated effluent from sewage treatment plants. Some local authorities in South Africa were reported to capacity for effective sewage treatment because of the increase in population among other factors (Wall, 2006).

The Blesbokspruit drains into the Vaal River; downstream of the Vaal Dam. It forms part of the Ekurhuleni municipality in the East Rand and extends to the Lesedi Municipality in Heidelberg. The spruit is one of the water resources that are under constant threat in the Upper Vaal Water Management Area. Water pollution in this catchment has witnessed steady increase over time and the impact of anthropogenic activities on surface waters has been source of concern to the government (DWAF, 2006).

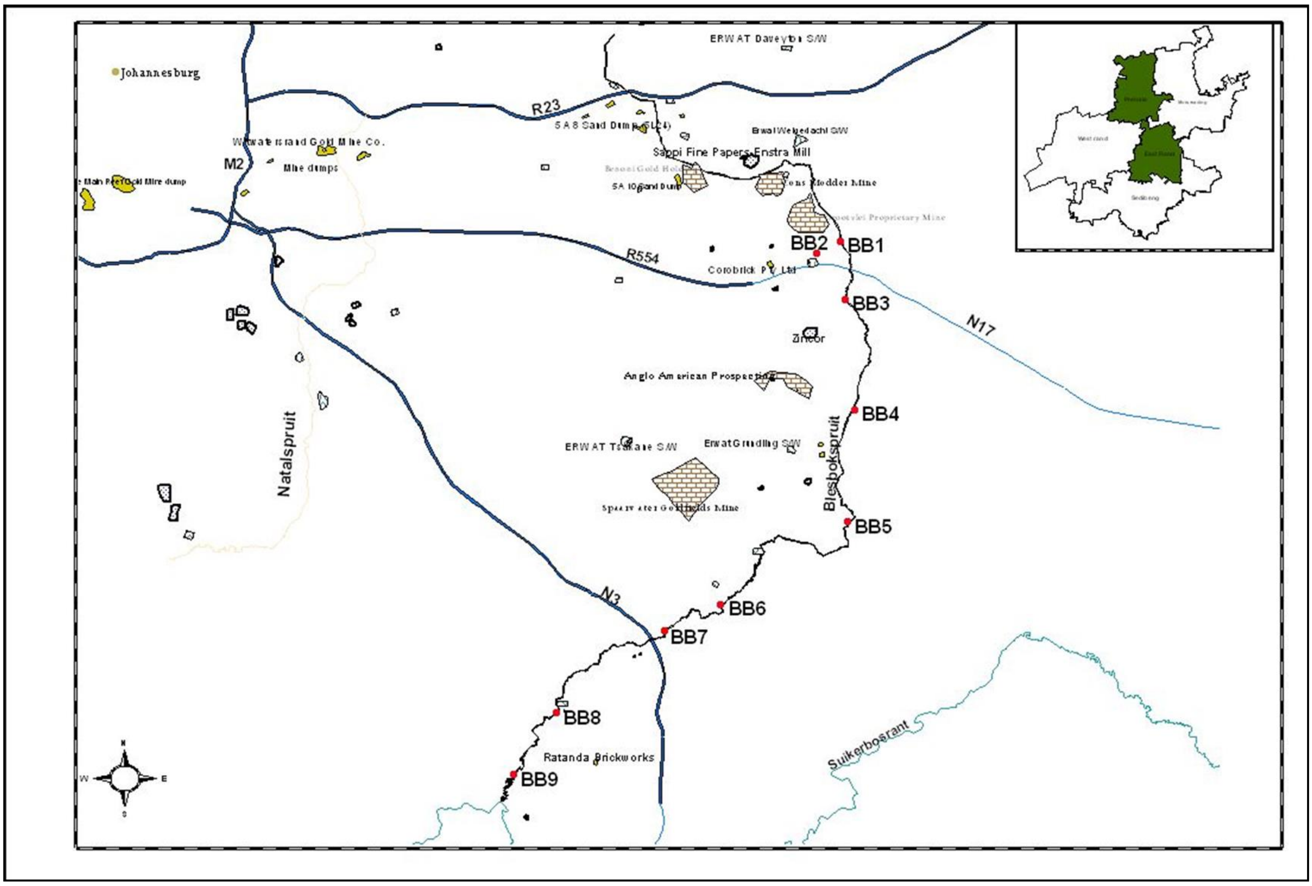
High level of trace metals such as Cd, As and Pb in surface waters are of major concern to the health of aquatic ecosystem and that of human (Sanjay et al., 2010). These metals have no physiological benefits to man (Duruibe et al., 2007). Cadmium is of concern due to its carcinogenic and possible endocrine disrupting effects (Bernhoft, 2013). Environmental sources of Cd include wastes from Cd-based batteries, incinerators and runoff from agricultural soils where phosphate fertilizers are used. Zinc toxicity in human has been regarded as mild, however continual or prolonged ingestion of large doses can result in health complications such as fatigue, dizziness, and neutropenia (Hess and Schmid, 2002). Although, copper (Cu) has been classified as essential element due to its involvement in some physiological processes, elevated levels have however been found to be toxic to gastrointestinal tract and the kidney (Gamakaranage et al., 2011).

The aim of the research therefore, was to investigate the impact of anthropogenic activities on the quality of the surface water commonly referred to Blesbokspruit. This was with a view of assessing possible human exposure to water as well as safety of the aquatic ecosystem.

2. Materials and Methods

2.1 Study Area

The study site is the Blesbokspruit which drains into the Vaal River at Vereeniging, downstream of the Vaal dam and upstream of the barrage. The Vaal dam and the Barrage are water abstraction points by one of the major bulk water treatment and supplier in the country. Water abstracted at these points is treated for potable use and further distribution to consumers. The Blesbokspruit is within the Vaal River Water Management Catchment Area (WMCA) and have become highly altered due to urban, industrial and mining developments. These activities are most likely to have impact on the flow, level, morphology and quality of the water (Warburton et al., 2012). All these impacts may further have effects on the health of the ecosystem and various end users for domestic, irrigational and recreational activities. The map of the study area is as shown below.



The ecology of the spruit consists of Highveld Grassland which is fast disappearing due to land use practices such as agriculture and mining. Terrestrial vegetation consists of a variety of flowering plants such as the Orange River lily (*Crinum bulbispermum)*, plough breaker (*Erythrina zeyheri)* and *Aloe ecklonis*. The geological formation of study area is characterised by dolomitic formation as well as sedimentary rocks with sandstones and shales as the most common rock types (Hoares et al., 2008). The region is considered semi-arid with a temperate climatic condition typified by short winter period. The region also falls with the summer rainfall period with an average rainfall of between 670-735mm per annum. However, for the Upper Vaal Area i.e. upstream of the Vaal Barrage, the mean annual temperature varies between 16^{o}C to 12^{o}C with an average of 15^{o}C for the catchment (DWAF, 2004).

2.2 Samples, Sampling and Sample Treatment

Water samples were collected along the Blesbokspruit using purposive sampling technique based on identified potential impactors (i.e. anthropogenic events) along the channel of the surface water. Samples were collected once a month from nine (9) points within the vicinity of identified potential impactors. The sampling points and their co-ordinates are as presented in Table 1.

Table 1. Sample collections points on the Blesbokspruit and their co-ordinates

Sampling Points	Co-ordinates	Site description
B1	26 °15'20"S; 28 °29' 56" E	Upstream section, located around the Grootvlei Mine.
B2	26 °15'47"S; 28 ° 29' 03" E	Located on Klein Blesbokspruit downstream of Erwat Ancor Sewage Works.
B3	26 °17'28"S; 28 °30'06" E	Located at the Daggafontein mines. Tailing dams and old mine surrounds this point with visible pipes indicating river diversion.
B4	26 °21'33"S; 28 °30'27" E	Near Marivale Bird Sanctuary; the northern point is another shaft of Grootvlei mine.
B5	26 °25'41.03"S; 28 °30'11.92" E	Located on R51 road to Balfour which is also close to mine dumps.
B6	26 °28'43"S; 28 °25'32" E	Located downstream of Erwat Herbert Bickley Sewage Works.
B7	26 °30'30"S; 28 °25'32" E	Located downstream of Heidelberg town and its residential areas.
B8	26 °32'43"S; 28°19'28" E	Located downstream of Erwat Heidelberg Sewage Works.
B9	26° 35’07"S; 28°17'54" E	Downstream section located near Erwat Ratanda Sewage Works.

Water samples were collected into cleaned acid washed 1-L Nalgene plastic containers at about 12 cm below the water surface from various sampling points. These were kept cool in a cooler box and transported to the laboratory for analyses. Water samples for microbiological investigations were collected in 2-L sterile glass bottles and taken immediately to the laboratory for refrigerating. Analyses were carried out within 12h of sample collection.

2.3 Sample Analysis

2.3.1 Physico-chemical Variables

The pH and temperature of the water samples were determined directly on site with the pH meter 330 supplied by Merck NT Laboratory (Pty) Limited. EC was also determined on site using the Radiometer Conductivity Meter Model CDM83. All on-site instruments were properly calibrated before use. Total Dissolved Solids (TDS) was determined using the vacuum, evaporating, drying and weighing method; Total Suspended Solids (TSS) in mg/L was determined using the vacuum, filtering, drying and weighing method while the COD was determined using the digestion block (148 ℃ ± 5℃) and measured using UV-Visible Spectrophotometer at 445 nm as previously described by Clesceri et al. (1998).

2.3.2 Nitrate (NO_3^-), Phosphates (PO_4^{3-}) and Sulphates (SO_4^{2-}) Analysis in Water Samples

Nitrate determination in water samples was carried out using the TRAACS 800 equipment fitted with a 10-mm x 0.5 mm diameter flow cell using 520 nm filter. Phosphate (PO_4^{3-}) and sulphate (SO_4^{2-}) analyses were also conducted using the TRAACS 800 equipment also fitted with 10 mm x 0.5 mm diameter flow cell but using a 660-nm filter as described by Clesceri et al. (1998).

2.3.3 Metal analysis, Quality Assurance and Metal Limits of Detection (LOD)

Mineral acid digestion (MAD) following previously described method (Awofolu et al., 2005) was applied for the isolation of metallic content in water samples. Quality assurance of the applied method was carried out through metal standard addition procedure of double-distilled water at fortification levels of 0.05 mg/L of As and Cd, 5.0 mg/l of Fe, Cu and Zn was applied. Triplicate analyses of each metal together with a blank were carried out.

Metal limits of detection were carried out as three times the standard deviation (3α) of their lowest detectable concentrations from the mean of six replicate analyses. Good linearity was obtained from the calibration curves prepared from 1,000 mg/L of each metal standard purchased from Hanna Inc. Johannesburg, South Africa. Iron (Fe), Cadmium (Cd), Copper (Cu), Zinc (Zn), and Arsenic (As), were determined using the Perkin Elmer dual View Model (optima) 4300 DV Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) as described by Clesceri et al. (1998).

2.3.4 Analyses of Microbial Entities in Water Samples

This was conducted to assess the health of the surface water from microbiological point of view since the surface water is utilised for domestic activities by informal settlers along the banks of the surface water. Heterotrophic (HT) bacteria count is usually carried out to reveal the general microbial quality of water while the Total Coliform (TC) bacteria analysis is conducted to show the general hygienic quality and integrity of the water. Faecal coliform/*Escherichia coli* analysis provides a reflection or presence of faecal pollution of the water. Hence, determination of these microbial indicators in water samples were carried out following the APHA (1992) standard methods.

2.4 Statistical Analysis

The Pearson Correlation Coefficient was applied to data to verify the relationship between some of the evaluated variables in water samples. The Accumulation Factor (AF), expressed as the ratio of the average level of a given variable downstream to the corresponding average level upstream (Fakayode, 2005; Bhat et al., 2014) was used to estimate the degree of contamination due to anthropogenic inputs. The magnitude of AF value of a variable relative to others indicates extent of accumulation. In this study, the upstream average value was based on values from BB1-BB4 (designated and used for deduction due to relatively fewer and moderate impactors within this section of the sampling points) while downstream average was based on values from BB5-BB9 (high impactors and used for deduction) along the stretch of the stream. The river recovery capacity (RRC) was calculated based on the previously described mathematical equation (Ernestova and Semenova, 1994; Fakayode, 2005; Bhat et al., 2014) as shown below:

$$RRC = \frac{X_o - X_1}{X_o} \times 100$$

X_o is the value of variable downstream and X_1 is the corresponding value at upstream of the surface water where pollution is assumed to be relatively lower.

To verify whether significant differences exist between the sampling sites with respect to analysed variables, all data were analysed using one-way analysis of variance (ANOVA) at $P < 0.05$. Possible differences between analysed variables were also checked using 2-tailed t-test. All statistical analysis was performed using MS Excel data analysis.

3. Results

3.1 Method Quality Assurance

Result of the quality assurance of analysed trace metals as reflected by their recoveries as well as their detection limits are presented in Table 2.

Table 2. Detection limits (μg/l) and *mean % recoveries (±SD) of metal standards in deionised water

Metals	Detection limits	Spiked amount	Recoveries
Cd	0.003	0.05	91.5 ± 0.004
As	0.001	0.05	93.2 ± 0.005
Fe	0.002	5.0	95.5 ± 0.002
Zn	0.002	5.0	98.2 ± 0.003
Cu	0.003	5.0	90.5 ± 0.002

***Mean of triplicate analyses; DL = 3 x S.D (3σ) of least detection; n =6**

Recoveries from metal standard addition varied from 90.5 ± 0.002 - 98.2 ± 0.003 μg/L while metal detection limits ranged from 0.001, 0.003, 0.002, 0.002 and 0.00.3 μg/L for As, Cd, Fe, Zn and Cu respectively. These are the various concentration levels at which each of the analysed trace metals can be determined.

3.2 Physico-chemical Parameters

Results of the physico-chemical variables in analysed water samples are presented in Table 3.

Table 3. Level of the physico-chemical variables (mean ± SD) in analysed water samples

Sampling points	**pH values**	**EC (mS/m)**	**TSS (mg/L)**	**TDS (mg/L)**	**COD (mg/L)**
BB1	7.4 ± 0.4 (6.8 - 7.9)	146.6 ±26.7 (100 - 182)	19.3 ± 23.0 (10 -80)	1001.3 ± 214.7 (740 -1308)	15.8 ± 8.5 (10-31)
BB2	7.4 ± 0.3 (7.0 - 7.6)	93.0 ± 24.0 (52 - 127)	12.9 ± 2.1 (10-16)	590.3 ± 153.0 (336-824)	34.8 ±2 2.3 (10-81)
BB3	7.7 ± 0.3 (7.3 - 8.1)	137.3 ± 21.4 (99 - 171)	28.8 ± 28.6 (10 - 95)	952.2 ± 137.0 (718 - 1174)	21.9 ±15.5 (10 - 58)
BB4	8.0 ± 0.2 (7.6 - 8.3)	142.6 ± 19.5 (116 - 179)	11.3 ± 3.30 (10 - 20)	970.3 ± 153.5 (800 - 1260)	15.6 ± 7.8 (10 - 30)
BB5	8.3 ± 0.2 (7.7 - 8.2)	141.8 ± 20.1 (120 - 181)	18.1 ± 11.7 (10 - 44)	1020.3 ± 147.6 (828 - 1220)	18.6 ±10 (10 - 35)
BB6	8.1 ± 0.1 (7.8-8.5)	134.4 ±14.6 (115 – 156)	22.5 ± 19.2 (10 - 60)	912.5 ± 133.3 (632 - 1070)	16.1 ± 9.4 (10 - 34)
BB7	8.1 ± 0.2 (7.9 - 8.4)	122.5 ± 12.0 (106 - 140)	31.0 ± 33.4 (10 - 112)	853.0 ± 81.1 (730 - 962)	20.1 ± 10.8 (10 - 42)
BB8	8.2 ± 0.1 (7.8 - 8.5)	120.0 ± 13.0 (103 - 138)	30.5 ± 28.9 (10 - 100)	787 ± 92.4 (676 - 908)	24.3 ±13.6 (10 - 51)
BB9	8.4 ± 0.3 (7.6 - 8.7)	123.0 ±13.5 100 - 140	39.0 ± 43.1 (10 - 147)	796.5 ± 123.7 (554 - 970)	21.1 ±12.5 (10 - 44)

NB: Values in parentheses are range of variables; BB = Blesbokspruit; 1-9 = sampling point; Values are mean of triplicate analysis

The mean pH values across the sampling periods ranged from 7.4 – 8.4 with overall mean of 8.0. The lowest pH was recorded at sites BB1 and BB2, both at the upstream section of the sampling sites while the highest was recorded at BB9. The electrical conductivity (EC) values of water samples across sampling points varied from 93.0 – 146.6 mS/m while that of the Total Dissolve Solids (TDS) was 590.3 – 1020.3 mg/L. Mean values for the chemical oxygen demand (COD) obtained across the sampling points was 15.6 – 34.8 mg/L while the total suspended solids (TSS) ranged from 11.3 – 39.0 mg/L.

Results of the anionic variables in analysed water samples are as shown in Table 4 below.

Table 4. Level of anionic variables analysed in water samples of the Blesbokspruit

Sampling points	**NO_3^- (mg/L) N**	**PO_4^{3-} (mg/L)**	**SO_4^{2-} (mg/L)**
BB1	0.3 ± 0.2 (0.1- 0.5)	0.8 ± 0.70 (0.1-2.3)	379.5 ± 99.3 (198 - 520)
BB2	1.0 ± 0.8 (0.1 - 2.3)	0.9 ± 1.0 (0.1 - 3.6)	118.6 ± 49 (74 - 222)
BB3	0.3 ± 0.3 (0.1- 0.2)	0.6 ± 0.5 (0.1 - 1.4)	337.8 ± 52.6 (224 - 398)
BB4	0.2 ± 0.4 (0.1- 0.5)	0.6 ± 0.3 (0.2 - 1.8)	353.1 ± 52.0 (272 - 440)
BB5	0.2 ± 0.1 (0.1 - 0.3)	0.5 ± 0.6 (0.1 - 1.9)	369 ± 93.1 (305 - 600)
BB6	2.1 ± 3.9 (0.1 - 12.3)	0.5 ± 0.4 (0.1 - 1.2)	326.3 ± 34.6 (289 - 386)
BB7	1.0 ± 0.4 (0.3 - 1.8)	0.6 ± 0.3 (0.1 - 1.4)	297.8 ± 45.1 (222 - 357)
BB8	0.8 ± 0.3 (0.2 - 1.3)	0.6 ± 0.4 (0.1 - 1.6)	284.8 ± 39.4 (220 - 345)
BB9	1.4 ± 0.4 (0.8 - 1.8)	0.4 ± 0.3 (0.3 - 1.3)	261.1 ± 92.7 (31 - 333)

NB: Values in parentheses are range of variables; BB = Blesbokspruit; 1-9 = sampling point; Values are mean of triplicate analysis

The mean values of nitrate varied from 0.16 - 2.01 mg/L across all sampled sites while that of phosphate and sulphate varied from 0.50-0.96 mg/L and 118.63 - 379.5mg/L respectively.

3.3 Level of Trace Metals in Surface Water

The concentrations of trace metals in analysed water samples are as shown in Table 5.

Table 5. Concentration (mean ±SD) of heavy metals (mg/L) in analysed water samples from the Blesbokspruit

Sampling points	**As**	**Cd**	**Fe**	**Cu**	**Zn**
BB1	0.03 ±0.02 (0.03 - 0.05)	0.04 ±0.03 (0.02 - 0.07)	0.08 ±0.06 (0.01- 0.19)	0.04±0.01 (0.01 - 0.04)	0.07 ±0.01 (0.06 - 0.07)
BB2	0.02 ±0.01 (0.02 - 0.05)	0.05 ±0.03 (0.02 - 0.07)	0.73 ±0.6 (0.03 - 1.47)	0.04 ±0.02 (0.01 - 0.04)	0.08 ±0.01 (0.06 - 0.07)
BB3	0.05 ±0.01 (0.01 - 0.05)	0.04 ±0.02 (0.02 - 0.08)	0.12 ±0.1 (0.01 - 0.39)	0.03 ±0.02 (0.01 - 0.04)	0.12 ±0.1 (0.06 - 0.50)
BB4	0.04 ±0.01 (0.04 - 0.07)	0.06 ±0.03 (0.02 - 0.06)	0.04 ±0.02 (0.01 - 0.10)	0.02 ±0.01 (0.01 - 0.04)	0.06 ±0.01 (0.05 - 0.07)
BB5	0.05 ±0.03 (0.02 - 0.8)	0.04 ±0.03 (0.01 - 0.08)	0.13 ±0.22 (0.01 - 0.70)	0.03 ±0.02 (0.02 - 0.05)	0.07 ±0.02 (0.06 - 0.07)
BB6	0.05 ±0.01 (0.05 - 0.06)	0.03 ±0.02 (0.03 - 0.07)	0.10 ±0.09 (0.01 - 0.31)	0.04 ±0.02 (0.01 - 0.04)	0.05 ±0.01 (0.05 - 0.07)
BB7	0.01 ±0.02 (0.01 - 0.03)	0.02 ±0.04 (0.02 - 0.07)	0.18 ±0.1 (0.01 - 0.39)	0.02 ±0.02 (0.01 - 0.04)	0.15 ±0.05 (0.06 - 0.17)
BB8	0.04 ±0.02 (0.04 - 0.05)	0.06 ±0.03 (0.02 - 0.08)	0.25 ±0.3 (0.01 - 0.91)	0.04 ±0.03 (0.01 - 0.12)	0.08 ±0.01 (0.06 - 0.08)
BB9	0.06 ±0.02 (0.02 - 0.06)	0.05 ±0.03 (0.02 - 0.07)	0.19 ±0.1 (0.01 - 0.49)	0.05 ±0.03 (0.01 - 0.14)	0.06 ±0.01 (0.05 - 0.07)

NB: Values in parentheses are range of variables; BB = Blesbokspruit; 1-9 = sampling point; Values are mean of triplicate analysis

The mean level of Arsenic (As) ranged from 0.01 – 0.06 mg/L across the sampling periods while those for Cd varied from 0.02 - 0.06 mg/L. Lowest and highest values of 0.02 and 0.06 mg/L Cd was obtained at sampling sites BB7 and BB8 respectively. Mean values of Fe varied from 0.04 - 0.73 mg/L while that of Cu ranged from 0.02 - 0.05 mg/L. The lowest value of Fe was recorded at BB4 (upstream) while the highest value was at BB8 (downstream). The mean concentration of Zn in analysed water samples varied from 0.06 - 0.15 mg/L.

3.4 Level of Microbial Entities in Analysed Surface Water

The mean values of microbial parameters in analysed water samples from the Blesbokspruit are shown in Table 6 below.

Table 6. Concentration of microbial variables analysed in water samples of the Blesbokspruit

Sampling points	**Faecal coliform (cfu/100ml)**	**Total coliform (cfu/100ml)**	**Heterotrophic plate (cfu/1ml)**
BB1	20.6 ± 13.0 (2.0 - 44)	92.9 ±143.7 (7.0 - 470)	7266.3 ± 5033.2 (1820 -17100)
BB2	44021 ± 11957.1 (140 - 340000)	430294 ± 506913.5 (26000 -1200000)	39776 ± 49 (74 - 222)
BB3	52.9 ± 109 (0 - 340)	674.9 ± 1635.4 (4.0 - 5000)	10190 ± 7384 (1600 - 25700)
BB4	15.9 ± 18.4 (1.0 - 59)	48.1 ± 52.1 (13 -180)	4322.5 ± 3760.7 (930 - 14000)
BB5	61.8 ± 84.3 (8.0 - 280)	162.4 ± 192.9 (20 - 620)	9560 ± 12096.4 (1980 - 41200)
BB6	772 ± 988 (10 - 2900)	5205 ± 5835.5 (180 - 18000)	20350 ± 25128.6 (1410 - 83000)
BB7	1035.4 ± 1303.9 (24 - 3600)	8633.8 ± 12208.4 (250 - 39000)	22712.5 ± 19243.4 (3900 - 68000)
BB8	16878.5 ± 3072.5 (0 - 9700)	16018.5 ± 20339.8 (28 - 66000)	39365.7 ± 53054.1 (3160 - 213800)
BB9	1936.3 ± 4003.6 (10 - 12500)	18403.8 ±29383.3 (110 - 92000)	36800 ± 33563.0 (6000 - 105000)

The level of *Faecal coliform* (FC) obtained across sampled sites ranged from 20.63 - 44021 cfu/100ml, Total coliform (TC) varied from 92.88 cfu/100ml - 430, 294 cfu/100 ml while the Heterotopic Plate Count (HPC) also varied from 10,190 cfu/100ml – 397,775 cfu/100ml.

3.5 Correlation Analysis, ANOVA and Accumulation Factor

Results of the correlation analysis for the physico-chemical parameters are presented in Table 7a. Correlation of 0.99 was obtained between EC and TDS; 0.51 between pH and TDS and strong negative correlation between E.C and COD

Table 7a. Correlation analysis of physico-chemical variables in water samples

	pH	*EC (mS/m)*	*TSS (mg/L)*	*TDS (mg/L)*	*COD (mg/L)*
pH	1				
EC (mS/m)	0.16	1			
TSS (mg/L)	0.51	-0.07	1		
TDS (mg/L)	0.18	0.99	-0.10	1	
COD (mg/L)	-0.34	-0.92	-0.04	-0.89	1

Results of the correlation analysis of trace metals in water samples are as shown in Table 7b.

Table 7b. Heavy metals correlation analysis in water samples

	As	*Cd*	*Fe*	*Cu*	*Zn*
As	1				
Cd	0.36	1			
Fe	-0.33	0.20	1		
Cu	0.50	0.25	0.30	1	
Zn	-0.47	-0.52	0.07	-0.53	1

Correlation of 0.36 was recorded between As/Cd; 0.50, As/Cu while negative correction of -0.47 was obtained between As/Zn; -0.33 As/Fe; -0.53 Cu/Zn

Results of the correlation analysis of microbial variables are presented in 7c.

Table 7c. Correlation analysis of microbial variables in water samples

	FC (cfu/100ml)	*TC (cfu/100ml)*	*HPC (cfu/1ml)*
FC (cfu/100ml)	1		
TC (cfu/100ml)	0.94	1	
HPC (cfu/1ml)	0.68	0.53	1

From this table, (r= 0.94) was obtained between FC and TC while an average correlation was recorded between FC and HPC as well as TC and HPC.

ANOVA: Assessment of the relationship between sampling sites and the analysed variables using one-way ANOVA test revealed P- values of 0.49, 3.29 $\times 10^{-30}$, 0.002, 1.31$\times 10^{-13}$ for the microbial, physico-chemical, metallic and anionic variables. Possible relationship among some variables within each of these groups using the t-test gave values of 0.05 between (TC and HPC); 0.06 (FC and HPC) and 0.34 (FC and TC) for the microbial group. Values of 1.97 $\times 10^{-11}$ (EC and TDS); 2.27 $\times 10^{-12}$ (TDS and COD) and 2.46 $\times 10^{-13}$ (pH and EC) were obtained for the physico-chemical group while Cd and Zn (0.004); Cu and Zn (0.0006); Fe and Cu (0.03) and Cd and Cu (0.13) were recorded for the metallic group. Values for the anionic group include those between NO_3^- and SO_4^{2-} (4.29 $\times 10^{-9}$); PO_4^{3-} and SO_4^{2-} (4.25 $\times 10^{-9}$) and NO_3^- and PO_4^{3-} (0.38). All data were processed at ($P < 0.05$)

Results of the accumulation factor and the river recovery capacity of the spruit are presented in Table 8 below.

Table 8. Accumulation factor (AF) and river recovery capacity (RRC) of analysed variables in water samples the Blesbokspruit

	Physico-chemical parameters						**Trace metals**			
	pH	**EC**	**TSS**	**TDS**	**COD**	**As**	**Cd**	**Fe**	**Cu**	**Zn**
AF	1.01	0.99	1.56	1	0.91	1.03	0.8	0.71	1.16	0.98
RRC	9.4	-5.6	53.6	-10.1	-4.31	41.7	4	-26.3	38	-36.7

AF = Accumulation factor; RRC = River recovery capacity (%)

A range of 0.99 – 1.56 (AF) was obtained for the physico-chemical parameters while the range obtained for the trace metals was from 0.71 – 1.16. The RRC obtained ranged between -5.6 – 9.4 for the physico-chemical parameters and between -36.7 – 4 for the trace metals.

4. Discussion

4.1 Quality Assurance of Analytical Protocol

The high recovery of analysed metals from the quality assurance experimental process confirmed method applicability, hence reliability of the analytical process. The detection of metals at the low parts per billion (ppb) ranges ensures the detection of analysed metals in water samples.

4.2 Physico-chemical Parameters

The pH is an important indicator of water quality and health due to the influence it exerts on the solubility, biological and chemical activities of water constituents. The result showed that pH values across the sampling sites and periods remained steady from BB1-BB2, increased marginally up to site BB5, remained steady thereafter between BB6-BB7 and with a marginal increase again up to site BB9. This pattern might possibly be due to cumulative upstream contribution. This gradual trend towards alkalinity could be because of contributions from sewage effluents as well as possible erosional activities from agricultural farmlands. However, the pH values obtained were within the Target Water Quality (TWQ) range of 6.0 - 9.0 for drinking water purposes (DWAF, 1996a). At this pH level, no significant effects on health due to toxicity of dissolved metal ions and protonated species or on taste are expected.

The electrical conductivity (EC) gives a measure of water conductivity as well as an indication of the level of inorganic constituents. It also has a direct relation with the total dissolve solids (TDS) in water. TWQ value of 45mS/m and 300 mg/L were recommended for EC and TDS respectively (DWAF, 1996a). By these, all analysed water samples exceeded the recommended values. The high level of inorganic constituents may be due to erosional phenomenon of soil nutrients from agricultural farmlands along the spruit as well as effluents from sewage treatment plants. From the correlation analysis, the strong correlation obtained between EC and TDS revealed common source of contaminants and also reflects direct proportionality between the two variables. Average correlation ($r = 0.51$) was obtained between pH and TSS. Strong negative correlation ($r = -0.92$) was however obtained between EC and COD. Chemical Oxygen Demand (COD) provide a measure of the level of oxidisable organic matter and an indication of dissolve oxygen level. It is not so much a variable of concern with respect to water for domestic use. However, a permissible level of 250 mg/L of COD in inland surface water for the protection of aquatic ecosystem was recommended (MoEF, 2005). All the COD values obtained in this study were below this limit.

Although, there is no recommended value for TSS (i.e. particles in water > 2 microns) for human health protection, however, a value of 100 mg/L has been prescribed for safe aquatic ecosystem (DWAF, 1996b). The highest value of 39.0 mg/L of TSS obtained in the study was much less than the prescribed value for safe aquatic ecosystem, hence no adverse effect is expected on aquatic organisms. High level of TSS has been reported to cause acute and chronic physiological effects in aquatic organisms, affect fish habitat, breeding and survival (kjelland et al., 2015).

The presence of nitrate (NO_3^-) in water is beneficial to some aquatic plants; excess level can lead to eutrophication and loss of dissolved oxygen. Target Water Quality range of 0 - 6 mg/L of nitrate in surface water was specified by DWAF (1996a). The highest mean value of 2.1 mg/L was obtained at site BB6 (Table 3) was well within the TWQ range, hence no adverse human health effect is expected upon consumption of the surface water. However, the range (0.1-12.3 mg/L) obtained specifically at this site BB6 was higher than the recommended TWQ range for the protection of human health. High level of nitrate in water consumed by infants may result in illness with symptoms such as shortness of breath and blue-baby syndrome which could result in death if untreated (USEPA, 2009).

As with nitrate, excess amount of phosphate in aquatic medium is not desirous and may lead to proliferation of algae with consequential impact on aquatic health. An acceptable limit of 5.0 mg/L of phosphate for the protection aquatic ecosystem was recommended (DWAF, 1996b). The mean levels of obtained in this study were within the limit hence, the propensity of algal and other plants growth is minimal. However continuous medium to long-term release of nitrogen and phosphate-rich irrigation water from integrated agricultural practices may initiate negative effects (Xiao-e et al., 2008).

Sulphates play an important role in water hardness and affect the aesthetics of water in terms of taste as odour due to the action of sulphur reducing bacteria. A range of 0 - 200 mg/L of SO_4^{2-} in water for domestic use was recommended (DWAF, 1996a). All the mean values across sampled sites except for the value (118. 6 mg/L) obtained at site BB2 were above this range. Upper range values of 222 (BB2) - 600 mg/L (BB5) were also recorded which revealed that the water is highly laden with this salt. High level of sulphate in water may initiate the development of diarrhoea in sensitive and some non-adapted individuals as well as slight taste if consumed. This high sulphate level could have emanated due to run-off of top soil, especially those from agricultural land.

4.3 Level of Trace Metals in Water Samples

Trace metals are natural constituents of the earth's crust; however anthropogenic activities have contributed to their environmental prevalence (Tchounwou et al., 2012). Highest mean value of 0.06 mg/L of arsenic (As) was obtained in this study which was higher than the recommended TWQ value of 0.01 mg/L (DWAF, 1996a) for safe domestic water use as well as the 0.01 mg/L value for the protection of aquatic ecosystem (DWAF, 1996b). A range of 0.02 - 0.8 mg/L of arsenic (As) obtained at (BB5) was quite worrisome since continual exposure has been reported to lead to long-term health fatality (USEPA, 2006). Cd also recorded highest mean value of 0.06 mg/L in analysed water samples with the upper range of 0.08 mg/L at BB3 and BB8 which were higher than the recommended value of 0.005 mg/L for water intended for domestic use (DWAF, 1996a). This value was however lower than 0.15 mg/L prescribed for the safety of aquatic ecosystem (DWAF, 1996b).

Continual consumption of the water could result in acute or irreversible effects of Cd associated with kidney failure (Jaishankar et al., 2014). Iron (Fe) is regarded as an essential element due to the role it plays in human physiology. Excess in human has been attributed to a condition called hemochromatosis as well as hemosiderosis (Turlin and Deugnier, 1998). The highest mean value of 0.73 mg/L (BB3) of Fe obtained was higher than the recommended TWQ range of 0.001 – 0.5 mg/L (DWAF, 1996a) and higher than the value of 0.32 mg/L reported in a similar study (Huser et al., 2011). Six out of nine sampling sites recorded values above this range hence; the surface water can be regarded as unsafe for domestic use. Copper (Cu) is also considered as essential to life but could become toxic at elevated levels. Low concentration in water has been linked to brain damage in some mammals (DWAF, 1996a). The highest mean value of 0.04 mg/L of Cu obtained in this study was within the TWQ range of 0-1.0 mg/L (DWAF, 1996a) recommended for Cu in water intended for domestic use and is also within the recommended value of 0.3 mg/L (DWAF, 1996b) for the protection of aquatic ecosystem.

Although, Cu is regarded as an essential element, ingestion at higher concentrations can lead to gastrointestinal problems with possible damage to the liver, kidney and red blood cells (DWAF, 1996a). Zinc (Zn) generally is considered to possess low toxicity in human due to usage in food supplements. Higher amount however has been linked to gastrointestinal disturbance, dizziness and fatigue (Boreiko, 2010). TWQ range of 0-3 mg/L of Zn has been recommended (DWAF, 1996a). At this level, no aesthetic or human health effect is expected. The highest mean value of 0.15 mg/L of Zn obtained across the sampled sites and period as well as the highest range of 0.06-0.50 mg/L obtained at site BB3 was lower than the recommended value. Hence, no health effect associated with domestic use of the surface water is expected. The TWQ value of Zn in water for safe aquatic ecosystem was 0.002 mg/L (DWAF, 1996b). By this value, the water is not fit for the sustenance of aquatic ecosystem.

In terms of possible relationship between the analysed metals, the correlation indicator revealed low correlation between the metals. This possibly indicates varied sources of the metals in water samples. Different industries and entities are located along the spruit and they may all be releasing trace metals into the water body.

4.4 Level of Microbial Entities in Water Samples

Escherichia. coli, comprising of about 97 % of coliform bacteria is normally used to confirm the presence of faecal pollution by human and animal in several aquatic media. These bacterial pathogens are known to cause diseases such as salmonellosis, dysentery, gastroenteritis and typhoid fever (Crum-Cianflone, 2008). TWQ value of 0 cfu/100 ml has been recommended for water intended for domestic use (DWAF, 1996a). Highest mean value of 16878.5 cfu/100 ml as well as highest range of 140 – 340000 cfu/100 ml (BB2) were obtained in this study. Possible sources of this group of coliforms include municipal effluent and run-off from agricultural activities. Faecal coliform greater than 20 cfu/100ml pose a significant and increasing risk of infectious disease transmission. Prevalence of faecal coliform bacteria have been reported in the South African water system (Pitman, 2011).

Total coliform (TC) is normally used to assess water hygiene, water treatment efficiency and integrity of the distribution system. Ideally, TC bacteria should not be present in any water intended for consumption. However, a TWQ range of 0-5 counts/100 ml was recommended (DWAF, 1996a). At this range, the risk of microbial infection is deemed negligible. The mean values and range of TC obtained in this study were above this recommended range. Possible sources of this high contamination include improperly treated sewage, poor sanitary practices by informal settlers along the water channel and erosional effects from agricultural land. Significant and increasing risk of infectious disease transmission is highly expected from consumption of this water. The Heterotrophic Plate Count (HPC) is used to assess the general microbial quality of water and efficiency of disinfection processes. It is utilised in detecting certain bacteria amenable to growth under specific conditions. Bacteria such as *Klebsiella, Citrobacter, Aeromonas* and *Yersinia spp.* fall under this category. A TWQ range of 0 – 100 count/1 ml has been recommended (DWAF, 1996a). Risk of microbial infection and disease transmission is very high considering the mean values and ranges (Table 5) obtained in this study. Correlation analysis however, revealed strong association between FC and TC while average correlation was shown between TC and HPC. These correlations could indicate similar sources of the microbial variables in the water body.

4.5 Accumulation Factor (AF), River Recovery Capacity (RRC) and ANOVA

The AF and RRC of the physico-chemical and trace metal variables are presented in Table 8. Results of the AF showed that there was no significant difference in the values of analysed variables at both up- and downstream section of the water channel. This however, indicated the prevalence of the variables across the sampled points. This could also be due to continual release of variables by impactors from the upstream section of the study area. Of concern were the AF values of 1.56 (TSS) and 1.16 (Cu) obtained which could impact negatively on the health of the aquatic system. Low recovery values were obtained for As (42%) and Cu (38%) while average recovery was obtained for TSS (54%). This indicated the released of analysed variables at a rate that was beyond the capacity of the aquatic system. These variables (EC, TDS, COD, Fe and Zn) recorded negative recovery values. This indicate high burden of the aquatic system with respect to these variables as they are present/released at the rate that was beyond the recovery capacity of the system.

The sampling sites were not significantly different ($P > 0.05$) with respect to microbial variables in analysed water samples. However, significant difference was observed between the sites and physico-chemical, metallic and anionic ($P < 0.05$) variables. T-test between the variables TC and HPC; FC and HPC and FC and TC were not significant at ($P < 0.05$) while significant differences were found between EC and TDS; TDS and COD and pH and EC all at ($P < 0.05$). Significant difference also occurs between Cd and Zn; Cu and Zn; Fe and Cu ($P < 0.05$) while the interaction between Cd and Cu was not significant all at ($P > 0.05$). Interaction between the anions shows significant difference between NO_3^- and SO_4^{2-} and PO_4^{3-} and SO_4^{2-} ($P < 0.05$) while that between NO_3^- and PO_4^{3-} was not significant at ($P > 0.05$). In generally, the sampling sites were significantly different with respect to the physico-chemical, elemental and anionic variables except for the microbial variables that were not significantly different. The post-hoc analysis showed no significant difference between the sampling points for both the factor and block levels.

5. Conclusion

The study revealed the need to conduct assessment of the quality of natural water resources on a regular basis, identify potential impactors on water quality and institute mitigating measures. The Blesbokspruit is important especially when the water is utilised for domestic and other purposes. The detection of toxic trace metals such as Cd and As above target water quality limits as well as high level of faecal pollutants was quite worrisome in view of the health implications on human. The high conductivity values will also have serious impact on aquatic life. Water plays a major role in economic development and if this resource is not protected, the consequences are innumerable especially for a semi-arid country. Hence, monitoring of the activities of various impactors on the stream regular monitoring of the quality of the surface water is recommended.

Acknowledgement

The authors would like to thank the Department of Water Affairs, Resource Quality Services, South Africa for the assistance with sample analysis.

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