

Chemical Test Measurements for Potable Water Quality: A Preliminary Test Correlation Study in the Umgeni Water Catchments, Kwazulu-Natal, South Africa

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Abstract

In the potable water sector, many decisions are based on the actual test measurement results. It is thus critical that such test results are consistently accurate, valid and reliable. From the various drinking water quality tests data, four chemical tests results and ratios, collected over a 2-year period, were evaluated for any significant correlation: Alkalinity (total) vs. Hardness, Total dissolved solids (TDS) vs. Conductivity (EC), Conductivity vs. Sodium $[Na^+]$, and Conductivity vs. Chloride $[Cl^-]$. Of the 9 water works investigated in this preliminary study, 3 sites showed a significant correlation for all 4 comparisons, two other sites had 3 significant water quality relationships, one other site had 2 significant water quality relationships, and two other sites had 1 significant water quality relationships. The average (range) ratios were: Alkalinity/Hardness = 0.9 (0.7-1.1), TDS/EC = 6.3 (5.5-8.5), EC/ $[Na^+]$ = 1.1 (0.7-2.0) and EC/ $[Cl^-]$ = 0.8 (0.5-1.3). The derived regression equations were used to calculate the water quality parameters (Hardness using Alkalinity, Conductivity using: TDS, $[Na^+]$ and $[Cl^-]$), which were evaluated for accuracy; the percentage error was generally within $\pm 10\%$ for 91% of the calculated water quality test parameters. The observed trends (ratios), per site, can be used as an additional accuracy check for the individual, analytically measured, regulatory drinking water quality tests data to facilitate decision making.

Keywords: Drinking water quality • Measurement accuracy • Tests • Method validation • ISO/IEC 17025 accreditation • Correlation

Introduction

Umgeni Water's (UW) core business is to treat raw water to potable standards as per the national water quality guide for drinking water, South African National Standards (SANS 241: 2015) [1], which is aligned to the World Health Organization (WHO) guide for drinking water quality [2]. Currently its main operational area is KwaZulu-Natal (KZN), comprising catchments as raw water source.

KwaZulu-Natal has a total geographical area of 94 359 km² and is home to 11.1 million people and 2.9 million households. It has a total of 54 municipalities of which 14 are Water Services Authorities (WSAs): 1 is a Metro; 10 are District Municipalities (DM); and 43 are Local Municipalities (LM) of which 3 are WSAs. UW has at least 18 potable water works (WW), which treat raw water to potable standards. According to Figure S1b (Supplementary Information), the treated water is supplied, currently, to six local municipalities; there are plans to extend its area of bulk potable water supply to the northern KZN region.

The national drinking water quality guide (SANS 241, 2015) [1] also stipulates that the required analyses/test methods performance, with regard to trueness, precision and limit of quantification, must be able to offer the necessary level of performance in order to comply with the requirements of the guide. The latter technical competence in testing laboratories is evidenced by achieving ISO/IEC 17025 accreditation [3,4]. For test methods to be accredited to ISO/IEC 17025 standard, method validation, as per the guide is mandatory [3,5]. This ensures that test results are consistently reliable, valid and accurate.

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In the water sector, many decisions are based on the actual results of the test measurements. It is thus critical that such results are accurate and reliable. According to Magnusson and Koch [6], the required measurement quality can be achieved by validating that the test method is deemed fit for the intended purpose, by establishing traceability of the measured test results to stated references and an estimate of the measurement uncertainty (MU) [7,8]. Additionally the on-going quality control (QC), both internal and external (generally proficiency testing, interlaboratory), assures that the measurement result (including uncertainty) are of the same quality as at the time of validation. Measurement quality should include both sampling and analysis [9].

The UW Head Office (HO) laboratory is ISO/IEC 17025-accredited, by the national accrediting body, South African National Accreditation System (SANAS), to carry out the required physico-chemical tests, as per the drinking water national regulations (e.g., turbidity, pH, anions, etc.) [10]. In addition to the main pillars for measurement quality in an analytical laboratory: validation, metrological traceability, MU and QC, we additionally have an internal standard operating procedure (SOP 21) for manually verifying the validity and accuracy of the test results [11]. The latter procedure applies certain observed trends (correlations) between water quality tests, for example: Turbidity versus Suspended Solids, Turbidity versus Iron, Manganese and Aluminium, Conductivity (electrical conductivity (EC)) versus Total Dissolved Solids (TDS).

We have, in general, noted the following test relationships (ratios) for our produced drinking water analyses: Alkalinity (total) = Hardness (Alkalinity/Hardness = 1: 1), TDS = $\pm (7 \text{ to } 9) \times$ Conductivity (TDS/Conductivity = 1: 7-9), Conductivity = [concentration of Na^+] (Conductivity/ $[Na^+]$ = 1: 1), Conductivity = [concentration of Cl^-] (Conductivity/ $[Cl^-]$ = 1: 1). The latter trends are documented in our internal Standard Operating Procedure (SOP) 21: SOP 21 – Integrity of data, verification and authorization of test results on LIMS [11]. In accordance with our findings relating Conductivity to $[Na^+]$, $[Cl^-]$ and TDS, the relationship between conductivity and ion strength (m) was initially proposed by Debye-Hückel [12]. Moreover, Langelier, in 1936, suggested the relationship between ionic strength and TDS [13].

The recent updated 2017 version of the ISO/IEC 17025 guide highlights

risk. This is one area that the new guide addresses. All accredited testing laboratories must have a procedure for monitoring the validity of test results. The latter can be done, for example, by detecting trends, and the prior reviewing of the test results before they are reported or released to the customer [14,15].

Whilst various reports have appeared on the use of multivariate, geostatistical analyses, water quality index, and correlation studies regarding the assessment of ground, and surface water quality physico-chemical properties, most of these studies focus on the determination of the initial Pearson's correlation values, the correlation matrix, and/or the use of other models, with no further significant application, like extension to additional, supplementary accuracy checks for facilitating decision-making on drinking water quality [16,17].

Thus, the objectives of this study were to:

- Compare a selected, four pairs of measured water quality tests data: Alkalinity (total) vs. Hardness, Total dissolved solids (TDS) vs. Conductivity (EC), Conductivity vs. Sodium $[Na^+]$, and Conductivity vs. Chloride $[Cl^-]$, for any significant correlation.
- Determine the actual trend (ratios) for the following paired comparisons: Alkalinity/Hardness, TDS/Conductivity, Conductivity/ $[Na]$, Conductivity/ $[Cl]$.
- Check the accuracy of the derived regression equations to calculate water quality test data.
- Investigate the usefulness of the actual ratios noted as an additional accuracy check for measured drinking water quality tests.

Materials and Methods

Study area

Due to this being a preliminary study and the extensive data available for analysis, the preliminary study area (Figure 1) was randomly chosen: namely the following 9 potable water works (Umgeni Water unique sample site identification: raw water source): Durban Heights Final 3 (TDH010: Nagle Dam), Amanzimtoti Final (TAM010: Mixture of treated raw water from Nungwane Dam and the South Coast Pipeline (SCP); SCP is fed from the Wiggins WW and the source of raw water at Wiggins WW is Inanda Dam), DV Harris Final (TDV006: Midmar Dam), Midmar Final (TMM007: Midmar Dam), Hazelmere Final (THM008: Hazelmere Dam), Mtwalume Final (TMT004: Mtwalume River), Mzinto Water Works Final (TUZ010: EJ Smith Dam Raw and Umzinto River Raw), and Quarry Reservoir (TMPI005: Mixed output of Toti WW and SCP), Toti WW Reservoir 1 (TAM020: Nungwane Dam) (Table 1).

Climate and underlying geology of the study area

Umgeni Water has three climatic zones: The Köppen classification Cwb – the alpine-type, as in the Drakensberg Mountains; the Köppen classification Cfb, a more temperate summer rain climate, typical of the Midlands region; the Köppen classification Cfa, a subtropical perennial rainfall pattern, typical of the coastal areas [18]. The mean annual precipitation (MAP) (450 mm) within the Umgeni Water catchment area ranges from 700-1000 mm. Rains fall during the summer months of October to March, peaking during December to February for the inland areas, and November to March for the coastal areas [18]. The prevailing weather patterns are predominantly orographic Rain shadows occur in the interior valley basins of the major rivers; the annual rainfall can drop to less than 700 mm.

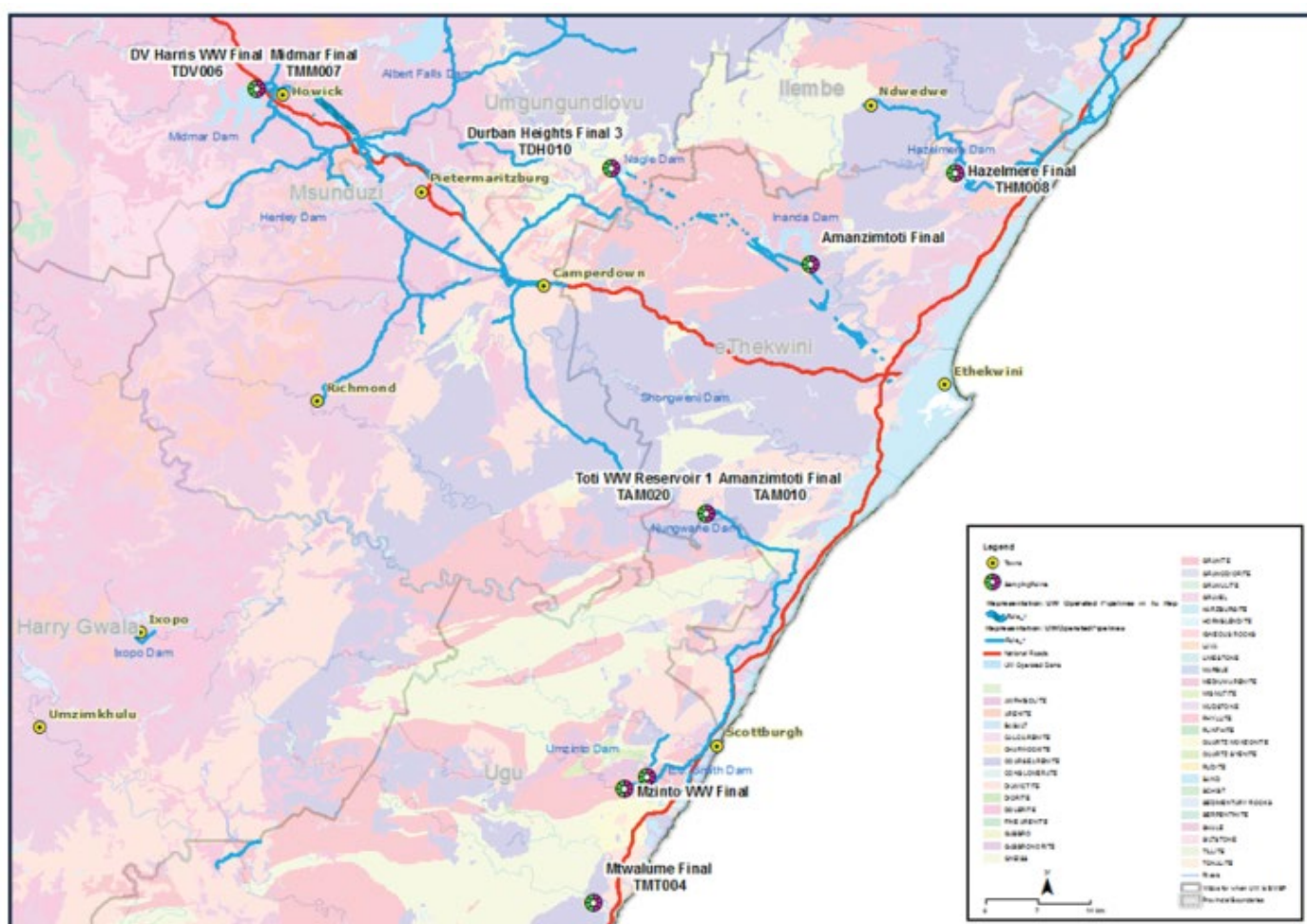


Figure 1. Geographical location of the nine potable water works, and underlying geology, used in this study area.

A relatively high humidity is experienced in summer. The daily means peak in February, ranging from 68% in the inland areas to greater than 72% for the coast and are low in July, ranging from 60% in the inland areas to greater than 68% at the coast. The mean annual gross evaporation ranges from 1600 mm to 1800 mm in the west, and from 1400 mm to 1600 mm in the coastal areas [18].

The mean annual temperature ranges from 12°C to 14°C in the west, and from 20°C to 22°C at the coast. The maximum temperatures are experienced in summer, from December to February and the minimum temperatures are during winter from June to July. There are snowfalls on the Drakensberg Mountain between April and September, which have an influence on the climate. Frost occurs over the same period in the inland areas, averaging 31-60 days per annum for the inland areas, to nil for the eastern coastal area [18]. The geology map (Figure 1) (Umgeni Water, GIS) of the study area (Table 1) was provided by Umgeni Water [19].

The UW resource regions are shown in Figure S1c (Supplementary Information) [18]. The Mooi Mgeni Region comprises Midmar Dam, Nagle Dam and Inanda Dam. Hazelmere Dam is part of the Mdloti Region. The geology [18] is: Sandstone, tillite, mudstone/shale supporting fractured groundwater regimes, dolerite intrusions and granite/gneiss supporting fractured and weathered groundwater regimes. Mtwalume River and EJ Smith Dam is part of the Middle South Coast Region. The geology is: Natal Group sandstone, Dwyka Formation, Shales of the Pietermaritzburg Formation, dolerite sills, and Rocks of the Natal Metamorphic Province. Nguwane is a part of the Mlazi/Lovu Region: the geology is Sandstone, tillite and granite/gneiss.

Sample collection

UW follows a risk-based sampling protocol for all its catchments, aligned to the national standards. Umgeni Water's Sampling Services (SS) Department is ISO 9001-accredited. All grab, water samples, from the Umgeni Water potable water works sample collection sites, were collected as per the documented

Table 1. Geographical study area and source water information.

System	Potable Water Works/ reservoir	Raw/ source water	Raw/Source water: GPS coordinates	2 year average Annual rainfall mm Mean $\pm$ SD (Range)	2-year % full Mean $\pm$ SD % RSD (Range)	Potable water works: Test and Sampling frequency							
						pH	Turbidity	Alkalinity	EC	Hardness	Na/ Sodium	Cl/ Chloride	TDS
Central: Nagle/ Durban Heights WW	TDH010 Durban Heights Final 3	Nagle Dam	-29.591919° 30.627642°	663.0	74.0 $\pm$ 9.3 12.6 (58.0-99.6)	daily	daily	monthly	daily	quarterly	quarterly	quarterly	quarterly
North: Hazelmere WW & Reservoirs	THM008 Hazelmere Final	Hazelmere Dam	-29.598256° 31.042256°	585.9	76.7 $\pm$ 23.7 30.9 (43.9-121.1)	daily	daily	monthly	daily	-	quarterly	quarterly	quarterly
Inland: DV Harris	TDV006 DV Harris WW Final	Midmar Dam	-29.496481° 30.201571°	780.3	87.2 $\pm$ 10.7 12.3 (70.4-101.2)	daily	daily	monthly	daily	quarterly	quarterly	quarterly	quarterly
Inland: Midmar WW	TMM007 Midmar Final	Midmar Dam	-29.496481° 30.201571°	780.3	87.2 $\pm$ 10.7 12.3 (70.4-101.2)	daily	daily	monthly	daily	quarterly	quarterly	quarterly	quarterly
South Coast	TMT004 Mtwalume Final	Mtwalume River	-30.476920° 30.606407°	-	-	weekly	weekly	monthly	weekly	quarterly	quarterly	quarterly	quarterly
South Coast	TAM020 Toti WW Reservoir 1	Nungwane Dam	-30.007131° 30.742589°	919.8	99 $\pm$ 4.6 4.6 (8.21-103.9)	3 per week	3 per week	monthly	3 per week	quarterly	quarterly	quarterly	quarterly
South Coast	TUZ010 Mzinto WW Final	EJ Smith Dam Raw	-30.324518° 30.671183°	1029.3	92.9 $\pm$ 10.1 10.9 (61.4-106.1)	weekly	weekly	monthly	weekly	quarterly	quarterly	quarterly	quarterly
		Umzinto River Raw	-30.339419° 30.643867°										
South Coast	TMPI005 Quarry Reservoir	Toti WW and SCP	-	-	-	fortnightly	fortnightly	not monitored	fortnightly	not monitored	annually	annually	annually
South Coast	TAM010 Amanzim =toti Final	Nungwane Dam; South Coast Pipeline, Wiggins WW: Inanda Dam)	-30.007131° 30.742589°	919.8	99 $\pm$ 4.6 4.6 (8.21-103.9)	3 per week	3 per week	monthly	3 per week	quarterly	quarterly	quarterly	quarterly
			-29.707612° 30.867598°	644.7	65.8 $\pm$ 4.9 7.4 (57.3-77.0)								

procedures, and frequencies and transported to the HO laboratory (Table 1). Samples were either analyzed immediately, or were preserved and stored as per the analytical test methods, in line with agreed the laboratory SLAs (service level agreements) with its customers.

Analytical test methods

All testing on drinking water, except for the on-site pH, by Sampling Services (SS), was done at the Head Office laboratories (Pietermaritzburg), which is ISO/IEC 17025-accredited for the bulk of the legislated tests, as per the national water quality guide, SANS 241: 2015 requirements. New, and current tests, are fully validated in line with the ISO/IEC 17025 quality management system for testing laboratories, and any other technical or reference documents, like the SANAS TR 26-03, and requirements by the national accrediting body SANAS. The various test method validation performance criteria is summarized in Table 2.

The pH was determined with a Cyberscan pH 300, and Hach meter. The turbidity was determined on a HACH TU5200 turbidimeter [20]. Alkalinity was determined on a Mettler Toledo T90 instrument [20]. The Electrical Conductivity (EC) [20] was measured on an InoLab Cond 7310 meter. Sodium, calcium and magnesium were determined by ICP-OE on an Agilent Technologies 700 Series spectrometer. Chloride [20] was determined by ion chromatography-conductivity detection [20], on a Waters HPLC (Waters 515 Pump, Waters 432 Conductivity detector, Waters 717 plus Auto Sampler). The total hardness of an aqueous solution containing either calcium, magnesium or both, is expressed as the number of equivalent mg/L of calcium carbonate (CaCO_3), and was calculated from the concentration of calcium and magnesium. The Total Dissolved Solids (TDS) was determined by gravimetry [20].

Suitable quality controls were prepared fresh, internally, from chemical standards, in ultrapure water, and was monitored by AQC charts with warning and control limits. For the validation of external accuracy, the laboratory participated in the South African Bureau of Standards (SABS) Proficiency Testing Scheme (Water Check) [21]; 2-4 samples were received in 4 cycles

per annum; PTS data for the pH test (Supplementary Information), was provided by SS.

Water quality data

The test result for water testing is captured on the LIMS (Lab Ware). The captured data is then auto-validated. The Auto Approve utility then tests results against standards and warning limits, logic tests, 5th and 95th percentile statistical limits. The status of all results that pass the above tests and limits is changed to 'Authorized' by the Auto Approve utility. The authorized results are now available to all Data users. If a result falls outside a standard or warning limit, it is flagged by Auto Approve utility and must be authorized manually by the appropriate Technical Signatory. In the latter instance, The Technical Signatory verifies the result using the correlations and other process to ensure the integrity of the result. Where samples are reanalyzed with dilutions, the Technical Signatory is responsible to authorize the required result. After validation, all captured data is accessible to all internal customers, for example Water Quality, Operations, etc.

The raw test measurement data, for drinking water, for: pH, turbidity, Alkalinity, Hardness (total), Conductivity, Sodium, Chloride, and TDS was extracted and downloaded off the Umgeni Water LIMS (Lab Ware) for the 2-year period: 01 March 2017 to 28 February 2019, thus covering the seasonal variation for a 2-year period. This data retrieval was also repeated, but only for the 3-month period: 01 March to 31 May 2019, for the accuracy check.

Rainfall data

The rainfall data for the water sources in this study were extracted using the WRMDSS reports, from the Umgeni Water Intranet server, for the 2-year period: 01 March 2017 to 28 February 2019. The system records daily rainfall data (Table 1).

Experimental design

A total of nine sample sites, from the corresponding potable water works,

Table 2. Method validation performance data for the water quality tests.

Status/ parameter	pH	Turbidity	Alkalinity	Hardness	TDS	Na	Ca	Mg	Cl	EC
ISO 17025-accredited	no	yes	yes	yes	yes	yes	yes	yes	yes	yes
Sample scope (matrix)	-	Drinking water, Source water	Drinking water, Source water	-	surface water (river/dam), sewage (waste water), borehole (ground water), potable waters	Drinking water, Source water	Drinking water, Source water	Drinking water, Source water	Drinking water, source water	Drinking water, Activated sludge, Untreated water
Linear range	-	0.2-600 NTU	n/a	-	-	2.5 - 50.0 mg/L	0.1 – 4 mg/L	0.01– 2 0.02 mg/L	25-100 mg/L: 5-20 mg/L low 55-100 mg/L high	1-141.2 uS/m
LOQ	-	0.2 NTU	10 mg/L	-	50 mg/L	2.12 mg/L	0.1 mg/L	0.01	0.31 mg/L	1 uS/m
Recovery (%)	-	111-115 (mean)	93-104	-	90-97	86-108	92-103	98-102	90-103	93-101
Repeatability precision (% RSD)	-	2.85%	0.08-0.45	-	3.28	0.15-0.75	0.81-10.42	0.80-10.36	1.1-2.2	0.04-0.24%
Standard/AQC Real samples	-	1.46-1.87	1.74-3.22	-	0.65-1.41	0.11-0.14	1.05-1.98	1.72-2.15		0.24
Reproducibility (% RSD)	-	2.43	2.11	-	-	3.1%	1.98%	2.12%	2.19%	0.15-0.29
QC: internal: standard concentration	-	0.80 NTU	40 mg/L Na ₂ CO ₃	-	100 mg/L NaCl	25 mg/L	10 mg/L	5 mg/L	10 mg/L; 50 mg/L	14.7 mS/m (KCl)
Bias (%)	-	6.16	-	-	-	+0.08	-1.44	-0.10		-0.12%
MU (± %)	-	8.09	8.54	-	10.8	3.2	15.10%	14.17%	5.40	3.78
QC external: PTS: March 2016-December 2018	92.3	100.0	100.0%	-	100.0%	88.9%	90.6%	88.2%	88.2%	100.0%
Z-scores: % Compliance										

were randomly chosen for this initial study. All test measurement data were processed to determine the mean, SD and % RSD, for the four tests that were being compared.

Statistical data analysis

Correlation tests for the different pairs of parameters were done using SPSS statistical package (SPSS). The physicochemical parameters were analyzed by calculating Pearson's correlation coefficient (*r*). Correlation for significance was further tested by applying the *p* value. The variations are significant if *p* < 0.05, *p* < 0.01, and non-significant if *p* > 0.05. The significance is considered at the level of 0.01 and 0.05 (2-tailed analysis).

Literature review

The main key word used for the search in Science Direct was "water quality tests correlation" over the period 2008 to 2019. The search returned 44 articles of this total, only 13 articles dealt with specific water quality tests correlation studies Table 6.

Results and Discussion

Rainfall patterns

The average daily rainfall, in mm (mean ± SD, range), was: 1.6 ± 5.9 (0-

Table 3. Analytically measured potable water quality tests: 2-year data summary and ratios.

Potable Water Works	pH Mean ± SD, % RSD, Range	Turbidity (NTU) ^a Mean ± SD, % RSD, Range	Alkalinity (mg CaCO ₃ /L) Mean ± SD, % RSD, Range	Hardness (mg CaCO ₃ /L) Mean ± SD, % RSD, Range	Alkalinity/ Hardness ^b Mean ± SD, % RSD, Range	TDS (mg/L) Mean ± SD, % RSD, Range	EC ^c (mS/m) Mean ± SD, % RSD, Range	TDS/ EC ^b Mean ± SD, % RSD, Range	[Na ⁺] ^d (mg/L) Mean ± SD, % RSD, Range	EC/ [Na ⁺] ^b Mean ± SD, % RSD, Range	[Cl ⁻] ^d (mg/L) Mean ± SD, % RSD, Range	EC/ [Cl ⁻] ^b Mean ± SD, % RSD, Range
SANS 241: 2015 limits	≥ 5 to ≤ 9.7	≤ 1 ≤ 5	-	-	-	≤ 1200 mg/L	≤ 170 mS/m	-	≤ 200	-	≤ 300	-
WHO limits	6.5-9.2	-	≤ 500	200-500	-	-	-	-	≤ 200	-	250-600	-
TDH010 Durban Heights Final 3	7.78	0.19	41.60	52.04	0.9	120.33	19.74	6.2	16.25	1.2	22.82	0.9
	± 0.10	± 0.08	± 6.51	± 3.41	± 0.1	± 20.79	± 2.04	± 0.6	± 2.46	± 0.1	± 4.09	± 0.1
	1.53	39.98	15.64	6.54	5.97	17.28	10.34	(9.83)	15.17	5.99	17.93	11.77
	7.6-8.1	0.10-0.50	37.00-46.20	45.20-59.10	0.7-0.9	95.00-79.00	13.40-31.30	5.6-8.3	12.20-20.50	1.0-1.3	12.69-29.30	0.8-1.3
THM008 Hazelmere Final	7.86	0.23	43.35	50.48	0.9	134.58	21.41	6.3	19.46	1.1	31.23	0.7
	± 0.26	± 0.11	± 6.07	± 5.54	± 0.2	± 10.15	± 0.83	± 0.4	± 1.10	± 0.1	± 2.29	± 0.4
	3.35	47.92	13.99	10.97	20.53	7.55	3.89	7.16	5.67	6.19	7.34	0.53
	7.1-9.1	0.10-0.80	20.00-51.00	37.70-59.40	0.3-1.3	118.00-152.00	18.00-31.70	5.5-7.3	17.20-21.90	1.0-1.2	23.70-33.70	0.6-0.9
TDV006 DV Harris WW ^e Final	8.63	0.27	35.35	36.30	1.0	63.67	9.82	6.5	4.68	2.1	7.13	1.4
	± 0.30	± 0.11	± 2.97	± 3.18	± 0.1	± 8.52	± 2.30	± 0.9	± 0.40	± 0.2	± 0.56	± 0.1
	3.48	41.01	8.40	8.77	7.56	13.39	23.38	13.26	8.62	9.73	7.90	9.38
	7.7-9.5	0.10-0.70	30.80-41.80	29.30-42.40	0.8-1.2	50.00-84.00	7.47-69.40	5.0-8.7	4.18-5.77	1.8-2.6	5.73-8.80	1.2-1.7
TMM007 Midmar Final	8.61	0.26	32.50	35.33	0.9	62.64	9.48	6.6	5.06	2.1	7.42	1.3
	± 0.34	± 0.10	± 2.60	± 4.90	± 0.2	± 9.88	± 2.35	± 0.9	± 2.55	± 0.4	± 0.78	± 0.2
	3.92	39.56	7.99	13.86	19.44	15.77	24.77	13.14	50.33	21.18	10.52	18.21
	7.3-9.7	0.10-1.00	28.80-39.70	24.00-44.80	0.6-1.7	< 50.00-84.00	7.17-70.50	5.5-8.5	3.76-16.80	0.5-2.8	4.40-8.42	1.1-2.3
TMT004 Mtwalume Final	7.92	0.27	61.42	57.92	1.1	165.91	25.59	6.2	31.09	0.9	37.77	0.7
	± 0.21	± 0.12	± 6.15	± 6.51	± 0.1	± 25.62	± 2.96	± 0.5	± 3.70	± 0.1	± 4.84	± 0.0
	2.66	46.11	10.01	11.23	9.37	15.44	11.57	8.12	11.89	7.05	12.81	4.26
	7.5-8.5	0.10-0.80	52.40-71.20	45.20-66.50	0.9-1.2	144.00-238.00	19.30-33.30	5.5-7.1	24.80-36.40	0.7-0.9	30.60-47.80	0.7-0.8
TAM020 Toti WW Reservoir 1	7.82	0.24	63.90	63.15	1.1	184.38	30.44	6.0	28.29	1.1	40.06	0.8
	± 0.17	± 0.11	± 2.20	± 14.88	± 0.4	± 12.93	± 2.75	± 0.3	± 5.68	± 0.4	± 3.01	± 0.0
	2.21	43.23	3.44	23.56	40.20	7.01	9.04	4.73	20.10	31.18	7.52	2.94
	7.6-8.3	0.10-0.50	60.20-66.60	29.70-73.70	0.9-2.2	170.00-209.00	16.70-33.30	5.6-6.4	15.60-34.40	0.9-2.0	34.60-43.10	0.7-0.8
TAM010 Amanzim=toti Final	7.85	0.29	50.69	56.44	0.9	150.54	25.80	6.3	24.05	1.1	41.35	0.7
	± 0.21	± 0.13	± 11.48	± 12.82	± 0.1	± 26.23	± 4.89	± 0.7	± 11.95	± 0.1	± 0.35	± 0.1
	2.62	47.00	22.65	22.72	8.48	17.42	18.93	11.02	49.69	8.86	0.86	10.14
	7.2-8.5	0.10-1.10	24.70-68.70	26.6-7.57	0.8-1.1	107.00-192.00	12.90-33.10	5.6-8.3	15.60-32.50	0.9-1.3	41.10-41.60	0.5-0.9
TUZ010 Mzinto WW Final	7.85	0.32	69.94	76.48	0.9	193.92	32.14	6.0	33.84	1.0	46.80	0.7
	± 0.20	± 0.09	± 8.53	± 8.03	± 0.1	± 16.25	± 3.57	± 0.4	± 3.72	± 0.0	± 5.25	± 0.1
	2.50	27.13	12.20	10.50	9.55	8.38	11.10	7.34	11.00	4.41	11.22	10.88
	7.2-8.5	0.20-0.50	51.90-86.10	60.50-95.70	0.8-1.1	159.00-216.00	5.53-37.20	5.3-7.4	28.50-40.30	0.9-1.1	33.30-56.30	0.6-1.0
TMP1005 Quarry Reservoir	7.69	0.24	62.45	66.30	0.9	178.63	29.55	6.1	27.00	1.1	35.84	0.8
	± 0.15	± 0.09	± 3.91	± 4.68	± 0.1	± 28.56	± 1.40	± 0.9	± 1.73	± 0.06	± 6.45	± 0.2
	2.01	38.34	6.26	7.06	7.56	15.99	4.74	14.06	6.41	5.2	17.99	22.57
	7.4-8.3	0.10-0.40	57.20-70.20	55.70-70.10	0.9-1.1	151.00-243.00	26.60-32.70	5.5-8.1	23.10-28.60	1.0-1.2	21.30-42.80	0.7-1.3

^a Nephelometric Turbidity Units; ^b Ratios were rounded off to 1 digit after decimal point; ^c Conductivity; ^d Concentration; ^e Water works

65) for Hazelmere Dam, 1.8 ± 5.9 (0-58) for Inanda Dam, 1.8 ± 5.8 (0-76) for Nagle Dam, 2.1 ± 5.9 (0-50) for Midmar Dam, 2.5 ± 8.9 (0-110) for Nungwane Dam, 2.8 ± 9.8 (0-120) for Umzinto Dam, 2.8 ± 9.9 (0-120) for EJ Smith Dam. The overall average was 2.2 ± 0.5 (range: 0-120 mm) for all the water sources.

For the rainfall data, the 2-year averages, in increasing order, were 585.9 for Hazelmere Dam, 644.7 for Inanda Dam, 780.3 for Midmar Dam, 919.8 for Nungwane dam, 1029.3 for EJ Smith Dam and 1034.1 for Umzinto Dam. The average annual rainfall for S Africa is 464 mm, compared to the global average annual of 860 mm [22]. While the average annual for some of these sources exceed the global average, the overall average ($\pm$ SD) for these water sources, in the KZN province of South Africa, is 808.1 mm ($\pm$ 187.3), which is still less than the global average (860 mm).

Method validation and accuracy

The data covering the main pillars for measurement quality for the tests being compared, the method validation data, are summarized in Table 2.

The data do comply with the ISO 17025 accreditation requirements for method validation for testing laboratories, and also with our laboratory's internal SOP 19 (Umgeni Water, 2018) for method validation: for example: spike matrix recovery (90-110%), precision ($\leq$ 10% RSD), bias ($\pm$ 5%). The MU ranged from a minimum of 3.78%, for Conductivity, to a maximum of 15.10% for Ca. Some z-score outliers ($-2 > z > +2$) for the external accuracy assessment, via PTS, were noted for the following tests: Na (4 outliers), Ca (4 outliers), Mg and Cl.

Water quality data

The water quality data is summarized in Table 3.

pH: The mean pH was 8.0 and ranged from 7.1-9.7. Although it is compliant with the SANS 241 limits, the pH for the Inland Systems DV Harris and Midmar Dam were above the upper WHO limit of 9.2. The variation was minimal: the percentage RSD was 1.53-3.92% over the 2-year period, $<10\%$ for all sites.

Turbidity: The mean turbidity was 0.26 NTU, and ranged from 0.1-1.10 NTU, all within the SANS 241 limit of <1 , except for Amanzimtoti Final (range: 0.1-1.1). The 2-year variation was however large: the percentage RSD was 27.13-47.92, $>10\%$ for all sites.

Alkalinity: The mean alkalinity was 51.24 mg/L CaCO_3 , and ranged from 20.0-86.1, all < 500 , compliant with the WHO limit. It was noticeably the lowest for Inland Midmar Final (32.50) and for DV Harris Final (35.35). The percentage RSD ranged from 3.44-22.65. The variation was $<10\%$ RSD for all sites, except for 3 sites: which were $>10\%$: 13.99% for Hazelmere, 15.64% for Durban Heights Final 3, and 22.65% for Amanzimtoti Final.

Hardness: The mean was 54.94, and ranged from 22.7-95.7, all complaint with the WHO limit of 200-500. It was noticeably the lowest for Inland Midmar (35.33) and for DV Harris Final (36.30). The percentage RSD was 6.54-23.56. The variation was $\pm 10\%$ RSD for all sites, except for the following 3 sites, where it was $>10\%$: 13.86% for Midmar, 22.72% for Amanzimtoti Final, and 23.56% for Toti Reservoir.

Alkalinity/hardness: The mean ratio was 0.93 and ranged from 0.3-2.2. The percentage RSD ranged from 5.97-40.20. The percentage RSD was $<10\%$ for all sites, except for Hazelmere Final (20.53%), Inland Midmar Final (19.44%) and Toti Reservoir (40.20%).

TDS: The mean was 139 mg/L, range: <50 to 243 mg/L, all compliant with the SANS 241 limit of <1200 mg/L. It was noticeably lower for 2 sites: DV Harris Final (63.67 mg/L) and Midmar Final (62.64 mg/L). It was much higher for all the other sites: Durban Heights Final (120.33 mg/L), Hazelmere Final (134.58 mg/L), Amanzimtoti Final (150.54 mg/L), Mtwalume Final (165.91 mg/L), Quarry Reservoir (178.63 mg/L), Toti Reservoir (184.38 mg/L), and Mzinto Final (193.92 mg/L). The percentage RSD ranged from 7.01-17.42; it was $< 10\%$ for only 3 sites: Toti Reservoir (7.01%), Hazelmere Final (7.55%), Mzinto Final (8.38%), and $>10\%$ for all the other sites:

EC: The mean EC was 22.66 mS/m, range: 5.53-70.50, all compliant with the SANS 241 limit of <170 mS/m. It was the lowest for 2 sites: DV Harris

Final (9.82) and Midmar Final (9.48), but noticeably higher for all the other sites: Durban Heights Final (19.74), Hazelmere Final (21.41), Mtwalume Final (25.59), Amanzimtoti Final (25.80), Toti Reservoir (30.44), and Mzinto Final (32.14). The percentage RSD was 5.5-70.5%. It was $\pm 10\%$ for all sites, except for DV Harris Final (23.38%), Midmar Final (24.77%), and Amanzimtoti Final (18.93%).

TDS/EC: The mean ratio was 6.36, and ranged from 5-8.7. The percentage RSD ranged from 4.7-14.06%. The percentage RSD was $<10\%$ for all sites except for DV Harris Final (13.26%), Midmar Final (13.14%), and Quarry Reservoir (14.06%).

[Na⁺]: The mean concentration was 21.8 mg/L, and ranged from 3.7-40.3 mg/L, all sites compliant with the SANS 241 limit of ≤ 200 mg/L. It was noticeably the lowest for DV Harris Final (4.68) and for Midmar Final (5.06), but relatively higher for Mtwalume Final (31.09) and for Mzinto Final (33.84). The percentage RSD ranged from 6.4-49.6%. It was $<10\%$ for all sites except for Durban Heights Final 3 (15.17), Midmar Final (50.33), Toti Reservoir (20.10), and Amanzimtoti Final (49.69).

EC/[Na⁺]: The overall mean ratio was 1.29, and ranged from 0.5-2.6. It was 0.9-1.2 for all sites, except for two sites- DV Harris Final (2.1) and for Midmar Final (2.1). The percentage RSD ranged from 4.41-31.18.; it was $<10\%$ for all sites, except for Midmar Final (21.18%) and Toti Reservoir (31.18%).

[Cl⁻]: The overall mean was 30.05 mg/L, and ranged from 4.4 -56.3. The mean Values for all sites were compliant with the SANS 241 limit of ≤ 300 mg/L. It was noticeably the lowest for 2 sites: DV Harris Final (7.13) and Midmar Final (7.42), and relatively higher for Hazelmere Final (31.23), Mtwalume Final (37.77), Toti Reservoir (40.06), Amanzimtoti Final (41.35), Mzinto Final (46.80), Quarry Reservoir (35.84). The percentage RSD ranged from 0.86-17.99; it was $\pm 10\%$ for all sites, except for 12.81), Durban Heights Final 3 (17.93), Quarry Reservoir (17.99).

EC/[Cl⁻]: The overall mean ratio was 0.89, and ranged from 0.5-2.3. It was noticeably >1 for two sites: DV Harris Final (1.4) and Midmar Final (1.3); it was <1 for all the other sites. The percentage RSD ranged from 0.53-22.57; it was $\pm 10\%$ for all sites, except for Quarry Reservoir (22.57).

Significant water quality test relationships

The results of the correlation analyses are summarized in Table 4; all regression and overlaid graphs for the paired water quality test comparisons are in the Supplementary Information. Table 5 is a summary, extracted from Table 4, showing only the sites with significant water quality relationships.

Some regression plots and overlaid graphs are illustrated in Figures 2 - 10. The results shown in Table 5 indicate that for all the 4 current water quality test relationships that we use, or applied to all our drinking water sites in our current practice of water quality data: that is, Alkalinity (total) = Hardness, TDS = (7-9) $\times$ Conductivity, Conductivity = [concentration of Na], Conductivity = [concentration of Cl⁻], the latter ratios were, in general, applicable to these drinking water sites included in this preliminary study.

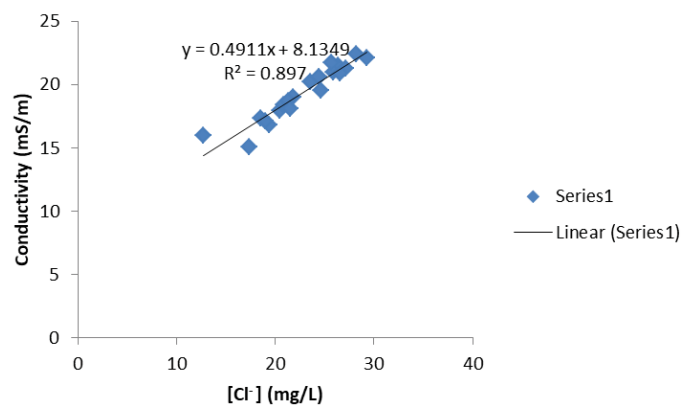
For these eight sites, the overall mean and range for the 4 water quality tests relationships (ratios) were: 0.9 (0.7-1.1) for Alkalinity/Hardness, 6.3 (5.5-8.5) for TDS/EC, 1.1 (0.7-2.0) for EC/[Na⁺], and 0.8 (0.5-1.3) for EC/[Cl⁻]. Regarding the general variance of the ratios across each of the 8 sites, the % RSD of the overall means ranged from a minimum of 0%, for Hardness/Alkalinity, to 3.2% for TDS/EC, up to a maximum of 11%, for EC/[Na⁺] and EC/[Cl⁻].

For Alkalinity/Hardness, these ratios can be as low as 0.7, for Durban Heights Final 3 and DV Harris WW Final, and as high as 1.1 (Mzinto WW Final, Amanzimtoti Final, Quarry Reservoir). The mean ratio was 0.9 for all the five sites: Durban Heights Final 3, DV Harris WW Final, Mzinto WW Final, Amanzimtoti Final, and Quarry Reservoir. For TDS/EC, these ratios can be as low as 5.3 (Mzinto WW Final), and as high as 8.5 (Midmar Final). The mean ratios for all six sites was < 7 ; the highest average ratio was 6.6, for Midmar Final. For EC/[Na⁺], these ratios can be as low as 0.7, for Mtwalume Final, up to a high of 2.0, for Toti Reservoir. The mean ratios for all five sites were fairly close to 1: 1, ranging from 0.9, for Mtwalume Final, to 1.2, for Durban Heights

Table 4. Pearson's correlation and p-value results for the water quality tests comparisons.

Potable Water Works/ reservoir	Hardness vs. Alkalinity		Conductivity vs. TDS		Conductivity vs. [Na]		Conductivity vs. [Cl]	
	Regression (r ²)	Pearson's r* (p-value)	Regression (r ²)	Pearson's r* (p-value)	Regression (r ²)	Pearson's r* (p-value)	Regression (r ²)	Pearson's r* (p-value)
TDH010 Durban Heights Final 3	$\hat{y} = 0.6048x + 24.377$ (0.4205)	0.648 (p = 0.001)*	$\hat{y} = 0.0777x + 9.6248$ (0.6674)	0.817 (p = 0.004)*	$\hat{y} = 0.4325x + 12.522$ (0.5279)	0.757 (p < 0.001)*	$\hat{y} = 0.4911x + 8.1349$ (0.897)	0.947 (p < 0.001)*
THM008 Hazelmere Final	$\hat{y} = -0.2746x + 62.39$ (0.0905)	-0.301 (p = 0.153)	$\hat{y} = 0.0216x + 18.569$ (0.1111)	0.333 (p = 0.111)	$\hat{y} = 0.0778x + 19.965$ (0.017)	0.130 (p = 0.544)	$\hat{y} = 0.0566x + 19.711$ (0.0388)	0.197 (p = 0.356)
TDV006 DV Harris WW Final	$\hat{y} = 0.6676x + 12.7$ (0.3877)	0.623 (p = 0.001)*	$\hat{y} = 0.0116x + 9.007$ (0.0352)	0.196 (p = 0.359)	$\hat{y} = 0.0799x + 9.4058$ (0.0037)	0.061 (p = 0.777)	$\hat{y} = 0.1719x + 8.5552$ (0.0355)	0.183 (p = 0.392)
TMM007 Midmar Final	$\hat{y} = -0.1627x + 40.621$ (0.0074)	-0.086 (p = 0.689)	$\hat{y} = 0.0356x + 7.2808$ (0.3259)	0.571 (p = 0.006)*	$\hat{y} = -0.3143x + 10.993$ (0.0697)	-0.264 (p = 0.224)	$\hat{y} = -0.112x + 10.363$ (0.0206)	-0.144 (p = 0.503)
TMT004 Mtwalume Final	$\hat{y} = 0.6258x + 19.482$ (0.35)	0.592 (p = 0.055)	$\hat{y} = 0.0971x + 10.631$ (0.7037)	0.839 (p = 0.001)*	$\hat{y} = 0.6205x + 7.4522$ (0.5975)	0.773 (p = 0.005)*	$\hat{y} = 0.587x + 4.5711$ (0.9168)	0.958 (p < 0.001)*
TAM020 Toti WW Reservoir 1	$\hat{y} = 1.454x - 24.858$ (0.2602)	0.510 (p = 0.242)	$\hat{y} = 0.0242x + 26.876$ (0.7656)	0.875 (p = 0.004)*	$\hat{y} = 0.6014x + 12.642$ (0.7995)	0.894 (p = 0.007)*	$\hat{y} = 0.5296x + 9.6459$ (0.8953)	0.946 (p < 0.001)*
TUZ010 Mzinto WW Final	$\hat{y} = 0.6191x + 33.177$ (0.433)	0.658 (p < 0.001)*	$\hat{y} = 0.1136x + 10.464$ (0.4401)	0.663 (p < 0.001)*	$\hat{y} = 0.6532x + 10.394$ (0.7625)	0.873 (p < 0.001)*	$\hat{y} = 0.3607x + 15.615$ (0.4727)	0.680 (p < 0.001)*
TAM010 Amanzimtoti Final	$\hat{y} = 1.0405x + 3.6946$ (0.8681)	0.932 (p < 0.001)*	$\hat{y} = 0.1891x - 4.2902$ (0.8279)	0.910 (p < 0.001)*	$\hat{y} = 0.8741x + 4.1141$ (0.8946)	0.946 (p < 0.001)*	$\hat{y} = 0.9764x - 7.9084$ (0.8979)	0.948 (p < 0.001)*
TMPI005 Quarry Reservoir	$\hat{y} = 0.5006x + 35.04$ (0.1748)	0.987 (p < 0.001)*	$\hat{y} = 0.0224x + 25.012$ (0.2475)	0.497 (p = 0.287)	$\hat{y} = 0.5005x + 15.5$ (0.4534)	0.673 (p = 0.067)	$\hat{y} = 0.1411x + 23.957$ (0.5007)	0.708 (p = 0.05)*

*Indicates a significant result at a 5% level of significance

**Figure 2.** TDH010 Durban Heights Final 3- Conductivity vs. [Cl⁻] regression analysis.

Final 3. For EC/ [Cl⁻], these ratios can be as low as 0.5, for Amanzimtoti Final, up to a high of 1.3, for Durban Heights Final 3 and Quarry Reservoir. The average ratios ranged from 0.7, for Mtwalume Final, Mzinto WW Final, and Amanzimtoti Final, to 0.9, for Durban Heights Final 3. The individual % RSD for each ratio for each site was within $\pm 10\%$, except for Toti WW Reservoir 1 (31% for EC/[Na⁺]) and for Quarry Reservoir (23% for EC/[Cl⁻]).

Out of a total of nine drinking water sites investigated, for only 3 sites: Durban Heights Final 3, Amanzimtoti Final, and Mzinto WW Final, all four water quality tests relationships, investigated in this study, have some significant relationship, fairly similar to the ones that we use for all our drinking water sites. For Durban Heights Final 3: Alkalinity/Hardness (Mean $\pm$ SD) = 0.9 ± 0.1 (range = 0.7-0.9), TDS/EC = 6.2 ± 0.6 (range = 5.6-8.3), EC/ [Na⁺] = 1.2 ± 0.1 (range = 1.0-1.3) and EC/ [Cl⁻] = 0.9 ± 0.1 (range = 0.8-1.3). For Amanzimtoti Final: Alkalinity/Hardness (Mean $\pm$ SD) = 0.9 ± 0.1 (range = 0.8-1.1), TDS/EC = 6.3 ± 0.7 (range = 5.6-8.3), EC/ [Na⁺] = 1.1 ± 0.1 (range = 0.9-1.3) and EC/ [Cl⁻] = 0.8 ± 0.2 (range = 0.7-1.3). For Mzinto WW Final, Alkalinity/Hardness (Mean $\pm$ SD) = 0.9 ± 0.1 (range = 0.8-1.1), TDS/EC =

6.0 ± 0.4 (range = 5.3-7.4), EC/ [Na⁺] = 1.0 ± 0.0 (range = 0.9-1.1) and EC/ [Cl⁻] = 0.7 ± 0.1 (range = 0.6-1.0). Two other sites had three significant water quality relationships: Mtwalume Final (TDS/EC, EC/ [Na⁺], EC/ [Cl⁻]), Toti WW Reservoir 1 (TDS/EC, EC/ [Na⁺], EC/ [Cl⁻]). One other site had two significant water quality relationships: Quarry Reservoir (Alkalinity/Hardness, EC/ [Cl⁻]). Two other sites had one significant water quality relationships: DV Harris WW Final (Alkalinity/Hardness) and Midmar Final (TDS/EC). The data indicated that for only one site: Hazelmere Final, the four water quality test relationships were not significant.

Current literature reports on correlation studies

Whilst various reports have appeared Table 6 on the use of multivariate, geostatistical analyses, water quality index, and correlation studies regarding the assessment of ground, and surface water quality physico-chemical properties [15,16,23-33], most of these studies focus on the determination of the initial Pearson's correlation values, the correlation matrix, and/or the use of other models, with no further significant application. Al Mamun et al. [23] reported a strong positive correlation of EC with TDS (0.994) for surface water. Kawo and Karuppannan [17] reported high correlation of EC with Na⁺ (0.75) and Cl⁻ (0.60) for ground water. Yousefi et al. [33] reported a Pearson value of 0.879 for Na⁺ vs. EC and 0.931 for Cl⁻ vs. EC. Masoud et al. [26] reported Pearson correlation values of 1.00 for TDS and EC, 0.96 for EC and Na⁺, 0.96 for EC and Cl⁻, for groundwater. Soleimani et al. [32] reported Pearson's correlation values of 0.685 for Na and EC, and 0.77 for Cl and EC, for ground water. Khanoranga [24] reported a very strong correlation of EC and TDS with each other and with Na⁺ and Cl⁻ for groundwater. Khatoo et al. [25] reported a significant positive Pearson's correlation for EC vs. Cl⁻ (0.877) and for EC vs. TDS (0.836), for river water. Shroff et al. [31] reported a strong positive Pearson's correlation value between EC and TDS (0.99), Cl⁻ (0.98) and Na⁺ (0.95), for groundwater. For two wetland beels in India, Alam et al. [16], a highly positive correlation was noted for TDS and conductivity.

There seems to be a lack of any significant study regarding potable water quality as well. This study is, to our knowledge, the first report where some hypothesized drinking water quality tests relationships are evaluated

Table 5. Significant correlation and regression for the water quality tests comparisons.

Potable Water Works/ reservoir	Hardness (y) vs. alkalinity	Alkalinity/ Hardness Mean $\pm$ SD (% RSD) Range	Conductivity (y) vs. TDS	TDS/EC Mean $\pm$ SD (% RSD) Range	Conductivity (y) vs. [Na]	EC/[Na] ^b Mean $\pm$ SD (% RSD) Range	Conductivity (y) vs. [Cl]	EC/[Cl] Mean $\pm$ SD (% RSD) Range
TDH010 Durban Heights Final 3	$\hat{y} = 0.6048x + 24.377$	0.9 ± 0.1 (5.97) 0.7-0.9	$\hat{y} = 0.0777x + 9.6248$	6.2 ± 0.6 (9.83) 5.6-8.3	$\hat{y} = 0.4325x + 12.522$	1.2 ± 0.1 (5.99) 1.0-1.3	$\hat{y} = 0.4911x + 8.1349$	0.9 ± 0.1 (11.77) 0.8-1.3
TDV006 DV Harris WW Final	$\hat{y} = 0.6676x + 12.7$	0.9 ± 0.1 (5.97) 0.7-0.9	-	-	-	-	-	-
TMM007 Midmar Final	-	-	$\hat{y} = 0.0356x + 7.2808$	6.6 ± 0.9 (13.14) 5.5-8.5	-	-	-	-
TMT004 Mtwalume Final	-	-	$\hat{y} = 0.0971x + 10.631$	6.2 ± 0.5 (8.12) 5.5-7.1	$\hat{y} = 0.6205x + 7.4522$	0.9 ± 0.1 (7.05) 0.7-0.9	$\hat{y} = 0.587x + 4.5711$	0.7 ± 0.0 (4.26) 0.7-0.8
TAM020 Toti WW Reservoir 1	-	-	$\hat{y} = 0.0242x + 26.876$	6.2 ± 0.5 (8.12) 5.5-7.1	$\hat{y} = 0.6014x + 12.642$	1.1 ± 0.4 (31.18) 0.9-2.0	$\hat{y} = 0.5296x + 9.6459$	0.8 ± 0.0 (2.94) 0.7-0.8
TUZ010 Mzinto WW Final	$\hat{y} = 0.6191x + 33.177$	0.9 ± 0.1 (9.55) 0.8-1.1	$\hat{y} = 0.1136x + 10.464$	6.0 ± 0.4 (7.34) 5.3-7.4	$\hat{y} = 0.6532x + 10.394$	1.0 ± 0.0 (4.41) 0.9-1.1	$\hat{y} = 0.3607x + 15.615$	0.7 ± 0.1 (10.88) 0.6-1.0
TAM010 Amanzimtoti Final	$\hat{y} = 1.0405x + 3.6946$	0.9 ± 0.1 (8.48) 0.8-1.1	$\hat{y} = 0.1891x - 4.2902$	6.3 ± 0.7 (11.02) 5.6-8.3	$\hat{y} = 0.8741x + 4.1141$	1.1 ± 0.1 (8.86) 0.9-1.3	$\hat{y} = 0.9764x - 7.9084$	0.7 ± 0.1 (10.14) 0.5-0.9
TMPI005 Quarry Reservoir	$\hat{y} = 0.5006x + 35.04$	0.9 ± 0.1 (7.56) 0.9-1.1	-	-	-	-	$\hat{y} = 0.1411x + 23.957$	0.8 ± 0.2 (22.57) 0.7-1.3
Overall Mean	-	0.9	-	6.3	-	1.1	-	0.8
Overall Range	-	0.7-1.1	-	5.5-8.5	-	0.7-2.0	-	0.5-1.3

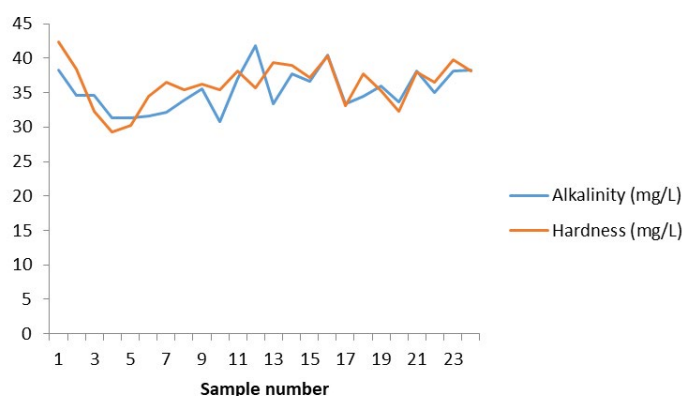


Figure 3. TDV006 DV Harris WW Final- Hardness vs. Alkalinity overlaid graph.

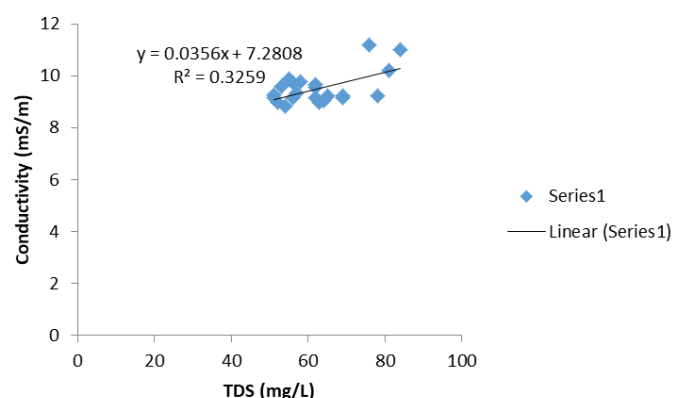


Figure 4. TMM007 Midmar Final- Conductivity vs. TDS regression analysis.

for correlation, then back-checked for accuracy using the linear regression equations.

Accuracy check of the derived regression equations

The water quality tests data for the 3-month period, for the sites which showed a significant relationship only, is summarized in Table 5. To check the accuracy of the derived relationships (summarized in Table 5), the corresponding water quality tests results were calculated using the measured values and the relevant regression equations listed in Table 5; the percentage error was calculated based on the actual, laboratory-measured water quality tests data. The data is summarized in Table 7. Aside from the 3 entries, where the percentage error was greater than 10%: Entry 10, Mtwalume Final site (19.39%, 14.10%), Entry 11, Mtwalume Final site (-58.92%), and Entry 12, Toti

WW Reservoir (-13.96%, 13.90%), the percentage error ranges from: -6.08 to +1.89% for Hardness (calculated using the measured Alkalinity), -9.82 to +8.80% for Conductivity, calculated using the measured TDS, -2.44 to +5.66% for Conductivity, calculated using the measured [Na⁺], and -0.63 to +8.10% for Conductivity, calculated using the measured [Cl⁻]. For Entry 11, the measured [Na⁺] was 5.08 mg/L, for this site, Mtwalume Final (TMT 004). The latter value is also noted to be outside the calculated Mean $\pm$ SD (31.09 $\pm$ 3.70), and Range (24.80-36.40 mg/L) for this site (Table 3). The resultant measured EC/[Na⁺] ratio of 5.1 was also out of the derived limits for this site, which was: Mean $\pm$ SD = 0.9 $\pm$ 0.1 and the Range = 0.7-0.9 (Table 3). The apparent inaccuracy of this measured [Na⁺] value may also be related to the observed PT compliance of being less than 100% (88.9%, or 11.1% inaccuracy) (Table 7) for this test. However, the overall percentage of the calculated water quality

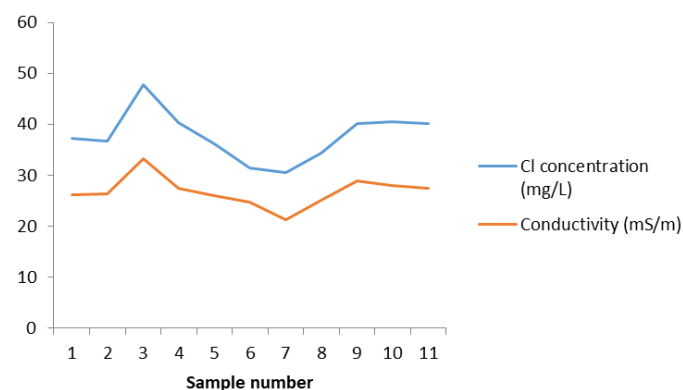


Figure 5. TMT004 Mtwalume Final- Conductivity vs. [Cl] overlaid graph.

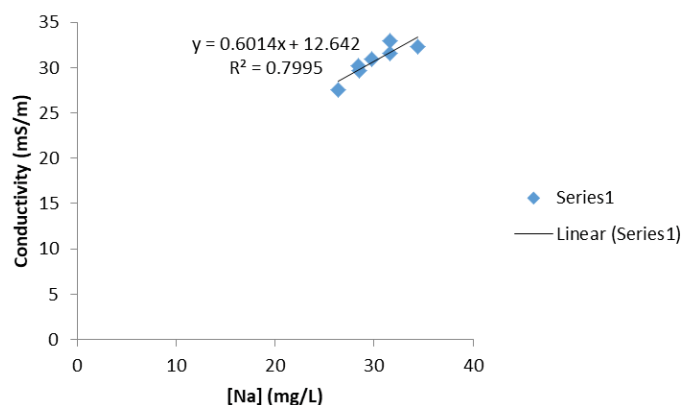
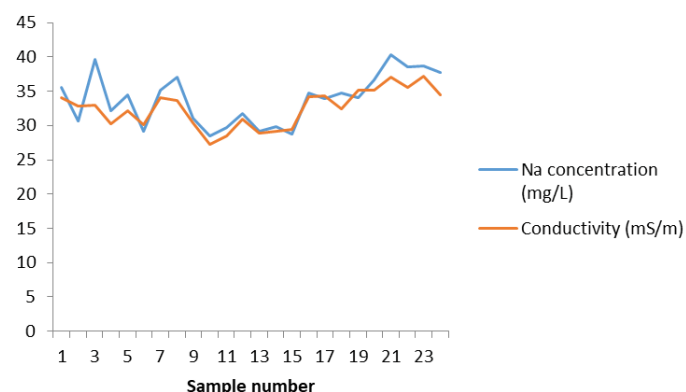
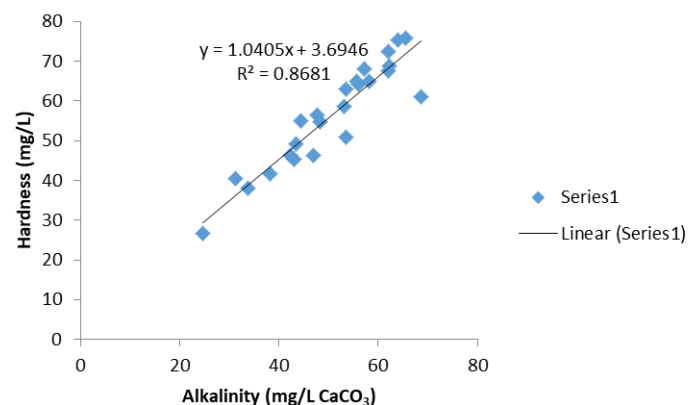
Figure 6. TAM020 Toti Reservoir 1- Conductivity vs. [Na⁺] regression analysis.Figure 7. Tuz010 Mzinto WW Final- Conductivity vs. [Na⁺] overlaid graph.

Figure 8. TAM010 Amanzimtoti Final: Hardness vs. Alkalinity regression analysis.

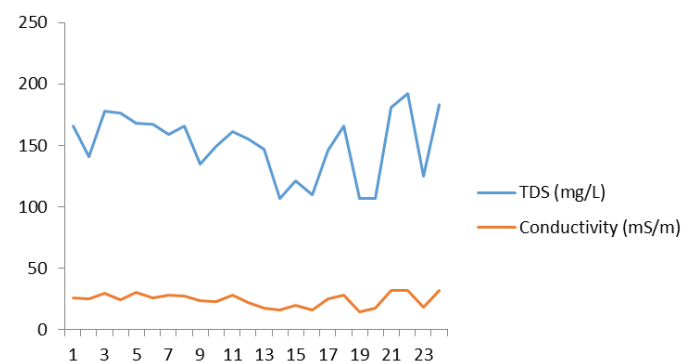


Figure 9. TAM010 Amanzimtoti Final: Conductivity vs. TDS overlaid graph.

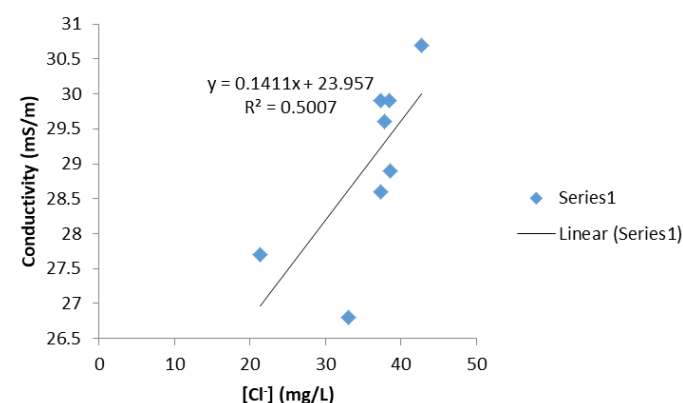


Figure 10. TMPI005 Quarry Reservoir- Conductivity vs. [Cl] regression analysis.

Table 6. Current literature reports on water quality tests correlation studies.

Number reference to Table S2	Journal	Water quality variable modelled besides Correlation	Reported Correlation/Pearson tested pairs/outcome (+ = positive correlation; - = negative correlation)					
19	Groundwater for Sustainable Development (2019) https://doi.org/10.1016/j.gsd.2019.03.002 .	Surface water; Water quality index; Fuzzy water Quality Index	EC with Alkalinity (0.919), Hardness (0.909), TDS (0.994)	TA with TH (0.867), TDS (0.901) Na (0.856)	-	-	-	-
1	Journal of African Earth Sciences, 147 (2018) 300-311	Groundwater; Water quality index; GIS technique	EC and TDS (0.99)	EC with: Ca ²⁺ , (0.66) Na ⁺ , (0.75) K ⁺ , (0.72) HCO ₃ ⁻ , (0.95) SO ₄ ²⁻ , (0.61) Cl ⁻ (0.60)	TDS with: Ca ²⁺ , (0.70) Na ⁺ , (0.74) K ⁺ , (0.74) HCO ₃ ⁻ , (0.95) SO ₄ ²⁻ , (0.66) Cl ⁻ (0.55)	Na ⁺ with HCO ₃ ⁻ (0.68), HCO ₃ ⁻ (0.68)	K ⁺ and HCO ₃ ⁻ (0.71)	Ca ²⁺ and HCO ₃ ⁻ (0.78)
3	Journal of African Earth Sciences, 138 (2018) 309-318	Groundwater; Water quality index; Multi-criteria decision making models	EC vs. TDS 0.999	Na ⁺ vs. EC 0.879	Na ⁺ vs. TDS 0.875	Cl ⁻ vs. TDS 0.925	Cl ⁻ vs. EC 0.931	Anions vs. Cations 0.999

7	Journal of African Earth Sciences, 142 (2018) 64-81	Groundwater; Multivariate and geostatistical analyses: Factor analysis; Hierarchical cluster analysis	TDS and EC (1.00), Ca ²⁺ (0.94), Mg ²⁺ (0.80), Na ⁺ (0.96), K ⁺ (0.52), SO ₄ ²⁻ (0.89), Cl ⁻ (0.96), Fe ²⁺ (0.54), Mn ²⁺ (0.74)	EC and Ca ²⁺ (0.94), Mg ²⁺ (0.80), Na ⁺ (0.96), K ⁺ (0.52), SO ₄ ²⁻ (0.89), Cl ⁻ (0.96), Fe ²⁺ (0.54), Mn ²⁺ (0.74)	Ca ²⁺ and Mg ²⁺ (0.75), Na ⁺ (0.86), K ⁺ (0.53), SO ₄ ²⁻ (0.90), Cl ⁻ (0.86), Mn ²⁺ (0.66)	Mg ²⁺ and Na ⁺ (0.71), SO ₄ ²⁻ (0.85), Cl ⁻ (0.73), Mn ²⁺ (0.58)	Na ⁺ and SO ₄ ²⁻ (0.82), Cl ⁻ (0.97), Fe ²⁺ (0.57), Mn ²⁺ (0.70)	SO ₄ ²⁻ and Cl ⁻ (0.77), Fe ²⁺ (0.51), Mn ²⁺ (0.67); Cl ⁻ and Fe ²⁺ (0.53) Mn ²⁺ (0.69); Fe ²⁺ and Mn ²⁺ (0.53))
9	Science of the Total Environment, 584-585 (2017) 131-144	Surface Water; Water quality index; GIS	Cl ⁻ and SO ₄ ²⁻ (0.951), Na ⁺ (0.897), COD (0.995), NO ₃ ⁻ (0.567), NO ₂ ⁻ (0.873), Cr (0.982), Mn (0.570)	SO ₄ ²⁻ and COD (0.966), NO ₃ ⁻ (0.976), NO ₂ ⁻ (0.460), Cr (0.950), Na (0.937), Mn (0.735)	Na with COD, (0.918) NO ₃ ⁻ , (0.446) NO ₂ ⁻ , (0.892) Cr, (0.880) Mn (0.712)	COD with NO ₃ ⁻ , (0.565) NO ₂ ⁻ , (0.895) Cr, (0.983) Mn (0.626)	HCO ₃ with Cl ⁻ , (0.856) SO ₄ ²⁻ , (0.800) Na ⁺ , (0.838) COD, (0.834) NO ₃ ⁻ (0.453) NO ₂ ⁻ , (0.726) Cr (0.817)	Ca and Mg, (0.736); NO ₃ ⁻ and Cr, (0.884) Mn (0.770) NO ₃ ⁻ and Cr (0.565); Cr and Mn (0.581)
10	Journal of Geochemical Exploration 112 (2012) 118-130	Hydrogeo=Chemical; Bottled water; Multivariate statistical analyses	Ca ²⁺ and Cl ⁻ (0.858), HCO ₃ ⁻ (0.515), K ⁺ (0.643), Mg ²⁺ (-0.947), NO ₃ ⁻ (0.847), SiO ₂ (-0.959), SO ₄ ²⁻ (0.799)	Cl ⁻ and Mg ²⁺ (-0.839), NO ₃ ⁻ (0.999), SiO ₂ (-0.764), SO ₄ ²⁻ (0.773)	HCO ₃ ⁻ and K ⁺ (0.959), Na ⁺ (0.964), SO ₄ ²⁻ (0.506)	K ⁺ and Na ⁺ (-0.850), SiO ₂ (-0.540), SO ₄ ²⁻ (0.727)	Mg ²⁺ and NO ₃ ⁻ (-0.816), SiO ₂ (0.984), SO ₄ ²⁻ (-0.582)	NO ₃ ⁻ and SiO ₂ (-0.740), SO ₄ ²⁻ (0.793); SiO ₂ and SO ₄ ²⁻ (-0.596)
21	Environmental Pollution 244 (2019) 575-587	Surface water; Water quality Index	Turbidity with TSS (0.62)	-	-	-	-	-
26	Heliyon 5 (2018) e01123, 1-36.	Ground, surface water; Multivariate statistics: Water quality index; Factor-principal component analysis; Cluster analysis; Hazard quotient and index	0.815-0.981 for pairs of Mg-K, Cu-P, Al-Y, Ca-Mg	Median relevance (0.500-0.791) for: Ca-K-Na-Mg Cr-Mn Al-Ca Mg-Al Na-Al	Median positive (0.703-0.740) between TDS and Ca, K, Mg	Na and TDS with high relevance (0.879)	Hg and Y had median positive (0.407, 0.611)	
56	Data in Brief 20 (2018) 375-386.	Groundwater; Water quality index	pH and Ca (-0.437) HCO ₃ ⁻ (-0.473) TH (-0.362)	Na and K (0.681) SO ₄ ²⁻ (0.82) Cl (0.658) TDS (0.69) EC (0.685); TDS and HCO ₃ ⁻ (0.619) TH (0.69)	K and Mg (0.383) SO ₄ ²⁻ (0.71) Cl (0.373) TDS (0.594) EC (0.591); EC and HCO ₃ ⁻ (0.625) TH (0.696)	Ca and Mg (0.615) Cl (0.328) TDS (0.629) EC (0.635) HCO ₃ ⁻ (0.698) TH (0.961)	Mg and SO ₄ ²⁻ (0.325) Cl (0.308) TDS (0.629) EC (0.634) HCO ₃ ⁻ (0.66) TH (0.808)	SO ₄ ²⁻ and Cl (0.816) TDS (0.798) EC (0.793) HCO ₃ ⁻ (0.118) TH (0.25); Cl and TDS (0.774) EC (0.77) TH (0.353); HCO ₃ ⁻ and TH (0.752)
57	Journal of Geochemical Exploration 197 (2019) 14-26.	Groundwater; Water quality index; Multivariate statistical approaches: Principal Component Analysis; Cluster Analysis	Positive between pH, fluoride and As	pH with Fe, Cd, Cu, Cr, Mn; pH with As and F-	pH and SO ₄ ²⁻	EC and TDS with one another and with: Na ⁺ , Ca ²⁺ , Mg ²⁺ , HCO ₃ ⁻ , SO ₄ ²⁻ , Cl ⁻ , F-	Among HCO ₃ ⁻ , SO ₄ ²⁻ , As, pH	Among F ⁻ , HCO ₃ ⁻ , SO ₄ ²⁻ , pH, Na ⁺ ; Na ⁺ and Cl ⁻
58	Journal of Geochemical Exploration 197 (2013) 14-26.	River water; quality assessment; Correlation	Various physicochemical parameters	Temperature vs. BOD (0.99); EC vs. Nitrate (0.846)	EC vs. Cl (0.877) vs. TDS (0.836)	TA vs. DO (0.842)	pH vs. Mg (-0.79); DO vs. BOD (-0.94); DO vs. TDS (-0.838)	TA vs. TDS (-0.88)
59	Journal of Fundamental and Applied Sciences 7(3) (2015), 340-349.	Groundwater quality; Correlation	Various physicochemical parameters	EC and TH 0.88 Ca 0.97 TA 0.84 TDS 0.99 Cl 0.98 SO ₄ ²⁻ 0.94 Na 0.95 SAR 0.90	Moderate EC and Ca 0.74	Moderate TH and SAR 0.61 and Na 0.71	Moderate Ca and TA 0.64 TDS 0.74 Cl 0.69 SO ₄ ²⁻ 0.70	
60	Ciencia e Tecnica Vitivinicola 30(3) (2015) 463-489. ISSN: 0254-0223.	Two Wetland beels; water quality; Correlation	Kumari beel Positive: Temperature and pH, hardness Nitrite nitrogen and ammonia, turbidity	Kumari beel Positive: pH and alkalinity, hardness, Turbidity and Ammonia	Kumari beel Positive: TDS and Transparency, conductivity	Kumari beel Negative: Conductivity and transparency	Hilna beel Positive: Temperature and CO ₂ Turbidity and ammonia, conductivity	Hilna beel Negative: Temperature and pH

Table 7. Accuracy check using the significant water quality tests correlations and regression equations.

Potable Water Works	Entry	Hma	Amb	H ^{cc} using Am	% Error On Hc	ECm ^d (y)	TDSme	EC ^{cf} using TDSm	% Error On ECc	ECm ^g (y)	[Na]mh	EC ^e using [Na]m	% Error On ECc	ECm (y)	[Cl]m	EC ^e using [Cl]m	% Error On ECc
TDH010 Durban Heights Final 3	1	52.0	45.6	51.96	-0.08	18.8	106.00	17.86	-5.00	18.8	15.2	19.10	1.60	18.8	22.4	19.14	1.81
	2	49.2	42.0	49.78	1.19	18.9	118.00	18.79	-0.58	18.9	14.8	18.92	0.11	18.9	23.4	19.63	3.86
	3	51.0	45.4	51.83	1.63	18.6	116.00	18.64	0.22	18.6	14.5	18.79	1.02	18.6	22.1	18.99	2.10
TDV006 DV Harris WW Final	4	39.8	37.0	37.38	-6.08	-	-	-	-	-	-	-	-	-	-	-	-
	5	38.2	36.6	37.13	-2.80	-	-	-	-	-	-	-	-	-	-	-	-
	6	38.5	37.2	37.53	-2.52	-	-	-	-	-	-	-	-	-	-	-	-
TMM007 Midmar Final	7	-	-	-	-	9.94	58.00	9.35	-5.94	-	-	-	-	-	-	-	-
	8	-	-	-	-	9.05	55.00	9.24	2.10	-	-	-	-	-	-	-	-
	9	-	-	-	-	9.41	69.00	9.74	3.51	-	-	-	-	-	-	-	-
TMT004 Mtwalume Final	10	-	-	-	-	19.8	134.00	23.64	19.39	19.8	21.7	20.92	5.66	19.8	30.7	22.59	14.10
	11	-	-	-	-	25.8	-	-	-	25.8	5.08	10.60	-58.92	25.8	38.7	27.29	5.77
TAM020 Toti WW Reservoir 1	12	-	-	-	-	32.8	157.00	30.68	-6.46	32.8	25.9	28.22	-13.96	32.8	35.1	28.24	-13.90
	13	-	-	-	-	30.5	176.00	31.14	2.10	30.5	30.5	30.99	1.61	30.5	41.2	31.47	3.18
	14	-	-	-	-	30.5	180.00	31.23	2.39	30.5	31.5	31.59	3.57	30.5	40.3	30.99	1.61
TUZ010 Mzinto WW Final	15	73.7	67.7	75.09	1.89	32.8	206.00	33.87	3.26	32.8	34.3	32.9	0.31	32.8	52.7	34.62	5.56
	16	72.7	62.2	71.69	-1.40	30.5	190.00	32.05	5.08	30.5	32.5	31.6	3.61	30.5	47.5	32.75	7.37
	17	67.5				30.5	200.00	33.18	8.80	30.5	31.2	30.8	0.10	30.5	48.1	32.97	8.10
TAM010 Amanzimtoti Final	18	68.7	59.6	65.71	-4.36	30.7	170.00	27.86	-9.26	30.7	30.1	30.43	-0.90	30.7	39.8	30.95	0.82
	19	69.3	63.6	69.87	0.82	30.0	175.00	28.80	-3.99	30.0	31.0	31.21	4.04	30.0	40.6	31.73	5.78
	20	71.4	62.2	68.41	-4.19	31.1	171.00	28.05	-9.82	31.1	30.0	30.34	-2.44	31.1	40.1	31.25	0.47
TMPI005 Quarry Reservoir	21	67.9	59.6	64.88	-4.45	-	-	-	-	-	-	-	-	30.2	42.9	30.01	-0.63

^aHm = Hardness measured; ^bHc = Hardness calculated; ^cAm = Alkalinity measured; ^dECm = Conductivity measured; ^eECc = Conductivity calculated; ^fTDSm = Total Dissolved Solids measured; ^g[Na]m = Sodium concentration measured; ^h[Cl]m = Chloride concentration measured

tests data, which had calculated values with less than 10% error, is 100% for Hardness (using Alkalinity), 94% for Conductivity (using TDS), 80% for Conductivity (using [Na⁺]), and 87% for Conductivity (using [Cl⁻]). Overall, 91% of the calculated values were noted to have an error of only $\pm 10\%$.

Conclusion

The aim of the current study was to evaluate the following four observed trends (ratios) via statistical data analysis, in particular, correlations for measurement quality of our drinking water quality test results: Alkalinity/Hardness = 1: 1, TDS/Conductivity = (7-9): 1, Conductivity/[Na⁺] = 1: 1, Conductivity/[Cl⁻] = 1: 1, as documented in our internal SOP 21. As per our current practice, this study has shown that, in general, the water quality test relationships (ratios) do exist, and are significant. This study has shown that the resultant trends (ratios) do vary from site to site, in the Umgeni Water catchments, and they only apply to the specific potable water works investigated: for the 8 sites, the average (range) ratios were: Alkalinity/Hardness = 0.9 (0.7-1.1), TDS/EC = 6.3 (5.5-8.5), EC/[Na⁺] = 1.1 (0.7-2.0) and EC/[Cl⁻] = 0.8 (0.5-1.3). These observed ratios could serve as an additional accuracy check for drinking water quality test results that are initially obtained by analytical test measurement, to facilitate decision-making. Additionally, in situations

where some laboratory equipment are not functional, the water quality test regression equations, noted in this study, can be applied to that specific site, in order to obtain the calculated, water quality test values (Hardness using measured Alkalinity, Conductivity using: measured TDS, measured [Na⁺] and measured [Cl⁻]), for the purpose of establishing drinking water quality. Umgeni Water has approximately 23 potable water works (sites). Future studies will consider extension of this current work to all the other potable water sites of the Umgeni Water catchments that were not included in this preliminary study. Globally, potable water treatment works can apply these findings to establish their own specific ratios/trends for their use in supplementing and confirming the accuracy of the observed, regulatory drinking water quality tests data, for facilitating subsequent decision-making.

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