PHYSICO-CHEMICAL ASSESSMENT OF POLLUTION IN THE CALEDON RIVER AROUND MASERU CITY, LESOTHO

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Water quality around the cities is a global concern owing to the impact of the population density and industrial activities. Assessment of the Caledon River (Mohokare), which flows along the periphery Maseru City, was carried out using a number of physico-chemical properties. The data obtained shed considerable light to the effect of the textile industry on the water quality. There was generally much higher increase in most parameters up to 900% at sampling site where textile effluents joins the river water (Tikoe-Thetsanae) compared to 'Maliemere (a sampling site upstream of the city). There was however a slight decrease in other parameters (dissolved oxygen, pH) while other parameters (silicates, nitrates and phosphates) did not seem to change or follow any particular pattern. Principal component analysis indicated conductivity, turbidity and total dissolved solids as the most prominent variants accounting for major difference in the PC1 in agreement with the comparison of relative amounts as a percentage of the 'Maliemere sampling site. The major contributor along the PC2 was found to be the silicates. However, only the concentrations of phosphates were above the maximum contaminant level (0.74 compared to 0.1 mg L^{-1} respectively) at all sampling points. Hence it is concluded that the water quality assessment shows a detrimental impact on the quality of the water.

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Introduction

In recognition of the importance of the valuation of water resources to the country, the Government of Lesotho established the Division of Hydrological Survey under the Ministry of Public Works in the 1970's which later metamorphosed to Department of Water Affairs under the Ministry of Natural Resources. This Department is responsible for the integration of water resources management through water quality and quantity monitoring, updating and maintaining the water resources database as well as liaising with the international organisations in which Lesotho is a member while being guided by the Water Act of 2008.[1,2]

Lesotho is highly endowed with fresh water resources leading to the sale of the water to the Republic of South Africa through a multi-billion project called Lesotho Highlands Water Project earning closer to 25 % of its export and 5 % of the GDP.[3] This has led to a saying that water is Lesotho's white gold.[4,5] Despite this, access to clean water is still a challenge in the cities in Lesotho, such as Maseru, the situation which has led to the dependence of the city on Mohokare (Caledon) river for the municipal water supply owing to the lack of infrastructure to collect relatively cleaner water from the mountains. This however, is about to become history in that a multi-billion project to catch water at one rural area called Metolong and channel it to supply the Maseru City and neighbouring towns through the support of United States Millennium Challenge Corporation with between US$ 362- 400 million in cash injection.[6,7]

Trans-boundary river pollution is one of the critical issues between neighbouring countries especially for those countries with upstream/downstream configuration. This is the situation between Lesotho and its sole neighbour South Africa. Lesotho lies upstream and its rivers converge to Caledon, Makhaleng and Orange Rivers that flow into South Africa. Despite the generally clean water from the mountains, there are concerns about the quality of water in rivers that traverse through the highly dense and industrialised areas such as Maseru with some textile industries owned by Chinese companies due to the AGOA agreement that allows Lesotho and other African countries to export textile products to American markets without paying any 'tariff barriers'.[8] Since the introduction of AGOA in 2001, exports from Lesotho to the US have increased considerably, and Lesotho has become one of the largest exporters of apparel in Africa to the American market.[9]

In recognition of importance of clean water, there are arguments that by 2025, the World could face wars about water and not oil.[10] Cookley reported the first war over water in 1967 between Israel and its Arab neighbours Syria and Egypt after the latter tried to divert the River Jordan.[11] Gleick and Heberger argue that the conflicts over water resources are continuing despite the studies into prevention of such.[12] Gizelis and Wooden argue that most studies have focused on proving or disproving a direct deterministic relationship between scarcity of resources and conflict.[13] Katz on the other hand argues that the prediction of war over water is an over exaggeration of those seeking incentives for conserving water hence questioned the merits of such arguments.[14] Whatever the case, there seems to be some contention that warrants a study of trans-boundary water especially in the upstream/downstream setting to maintain peace and harmony between neighbouring countries.

There are many parameters that are used in river pollution monitoring such as using fresh water algae.[15,16] Other techniques especially at trace quantitative level require highly sophisticated and expensive analytical instrumentation such as spectrometers. The price and level of investment depends on the level of the pollutant being considered. Some attributes are considered of primary while others are of secondary importance. The primary drinking water standards regulate organic and inorganic chemicals, microbial pathogens, and radioactive elements that may affect the safety of drinking water. These standards set limits - the maximum contaminant level (MCL) - on the highest concentrations of certain chemicals allowed in the drinking water supplied by a public water system. The most prominent agencies for setting these standards is United States Environmental Protection Agency (US-EPA)[17] and the World Health Organisation (WHO).[18]

Water quality analysis and monitoring usually generate a large volume of data. Multi-variate statistics is therefore used extensively in high volumes of data to reduce the data multiplicity to identify only a few parameters that are responsible for the variations within the system,[19] while preserving the relationships in the original data.[20] Due to its robustness multi-variate statistics has been reported in a number of areas ranging from medical diagnostics,[21] plant pathology,[22] engineered structures[23] to environmental monitoring.[24]

This study presents the analysis of a number of physico-chemical properties of the Caledon (Mohokare) River water which is an important source of potable water for the city of Maseru. The river flows along the periphery of the city and forms the national border with the Republic of South Africa. The study assesses the perceived impact of the indiscriminate discharge of domestic waste and industrial wastewater at various stages of treatment and uncontrolled inflows of urban surface run-offs on the quality of this river water. The data generated was analysed using conventional statistics and principal component analysis to identify the major contributors to the pollution from these multiple of the parameters.

Experimental

Sample collection and handling

The five sampling sites were selected at strategic locations with reference to key industries and human activities, which are potential sources of surface water pollution. The other deciding factor for selecting the sampling locations was the ease of accessibility of the sites. The sampling points from upstream to downstream as per the designation by the Department of Water Affairs are 'Maliemere, Seapoint, LEC, Ratjomose and Tikoe-Thetsane. The satellite image in Figure 1 shows the sampling sites designated with flags with the river flowing from top right corner to the bottom left corner of the picture. The sampling points are designated with small flags.

The collection, handling and preservation of samples were consistent with standard principles.[25,26] Some of the parameters, conductivity, dissolved oxygen, pH, temperature and turbidity were measured in the field at the sampling points to reflect the true values.

Figure 1. The Caledon River in Maseru showing the sampling points

Samples were collected on the same day at all sampling points to avoid possible momentary fluctuations in some of the target parameters as a result of surface run-off from rain or any other discharges into the river from the communities.

Determination of the selected physico-chemical parameters

Most of the analysis followed the New South Wales guidelines for sampling and analysis of water pollutants.[27] The field measurements were made using the Mettler-Toledo GmbH MX 300 multi-meter (Giessen, Germany) equipped with the temperature, pH, Dissolved Oxygen and Conductivity probes. The other parameters were determined in the laboratory by spectrophotometric methods using HACH DR/2400 Spectrophotometer (Düsseldorf, Germany), which has prescribed programmes and reagents/kits for each parameter. A 25-mL volume of each of the samples was used for the determination of each parameter using a set of specified reagents and programme for each parameter.[28] Total nitrogen was determined according to the US-EPA Method 1688.[29]

Data analysis

Other than a normal comparison of the data using normal replicates (*n*=3) for individual parameters, the data was subjected to the principal component analysis using the SIMCA P 13.0 Software (Umetrics, Umea Sweden).

Results and discussions

Determination of physical parameters

The quantities of the physical parameters determined were as presented in Table 1.

A clear comparison of the changes in the abundance of these parameters downstream was plotted relative to 'Maliemere sampling site and presented in Figure 2.

Table 1. Some physical parameters determined at different sampling sites

Sampling site Parameter	'Maliemere	Seapoint	L.E.C	Ratjomose	Tikoe-Thetsane
pH	7.34	7.77	7.54	8.20	7.95
Temperature, °C	20.5	19.6	18.4	20.8	21.2
Conductivity, µS cm^{-1}	257	286	355	367	458
Total dissolved solids, mg L^{-1}	88	90	123	126	157
Total suspended solids, mg L^{-1}	10	16	47	54	65
Turbidity, NTU	12	17	38	46	78
Dissolved oxygen, mg L^{-1}	0.95	0.87	0.72	0.84	0.69

Table 2. Chemical parameters determined at different sampling sites

Sampling site Parameter	'Maliemere	Seapoint	L.E.C	Ratjomose	Tikoe-Thetsane
NH_3 , mg L^{-1}	0.30	0.29	0.34	0.38	0.32
Cl_2, mg L^{-1}	0.02	0.04	0.15	0.14	0.19
Total chlorine, mg L^{-1}	0.05	0.07	0.19	0.20	0.25
SiO_4^{4-}, mg L^{-1}	18.7	30.6	20.5	37.7	40.5
SO_4^{2-}, mg L^{-1}	14	17	12	15	13
Fe, mg L^{-1}	0.08	0.12	0.16	0.24	0.31
Total Fe, mg L^{-1}	0.17	0.25	0.31	0.42	0.50
Mn, mg L^{-1}	0.2	0.4	0.7	0.5	0.3
PO_4^{3-}, mg L^{-1}	0.57	0.64	0.71	0.68	0.74
NO_3^-, mg L^{-1}	1.7	1.6	1.3	1.6	1.4
NO_2^-, mg L^{-1}	0.003	0.005	0.004	0.003	0.007
Total Kjeldahl nitrogen, mg L^{-1}	35	23	19	29	21

An inspection of Figure 2 clearly shows that most parameters were increasing from Maliemere to Tikoe-Thetsane with suspended solids and turbidity increased to higher 600 % in Tikoe-Thetsane relative to 'Maliemere. Temperature is the only parameter that did not seem to change between the sampling sites ranging between 18.4 °C and 21.2 °C. Water temperature is important in water quality because it affects the rates of biological and chemical processes in the water as well as influencing the volume of dissolved oxygen in the water. Dissolved oxygen on the other hand seemed to decrease (1.5 to 0.65 mg L^{-1}) albeit not considerably as compared to other parameters such as suspended solids. The drop in dissolved oxygen can however not be totally be attributable to the noted temperature increase although this is a known fact the higher the temperature the less the dissolved oxygen, since the decrease in oxygen content is more marked than the increase in temperature. Dissolved oxygen is one of the most important water quality parameters for freshwaters, because aquatic organisms cannot survive without oxygen. Generally, dissolved oxygen levels lower than 5.0 mg L^{-1} are stressful to aquatic organisms.[30] Thus this indicates that this river is not habitable to most aquatic life.

The pH values fall within a narrow range of 8.20 to 7.15 units indicating neutral to slightly alkaline conditions for all the five sampling points. The highest pH values were measured at the Ratjomotse sampling point with the mean pH of 8.20 units. However the variation is not significant. The conductivity values fall within a wide range from 252 µS cm^{-1} ('Maliemere) to 490 µS cm^{-1} (Tikoe-Thetsane). Freshwater sources usually have a low conductivity and there is no set standard for the conductivity of water. Despite the lack of standards and the effects of the surrounding environment and local geology on conductivity, there are approximate values for freshwater sources in the range of 600 – 2000 µS cm^{-1}.[31]

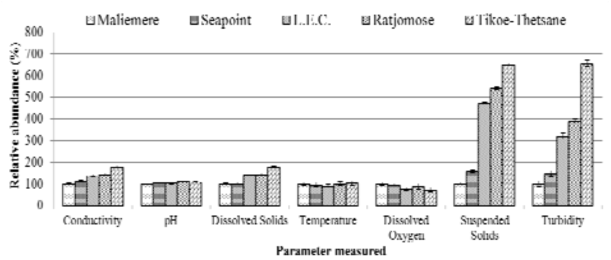

Figure 2. The abundances of the physical parameters relative to 'Maliemere sampling site

Total dissolved solids (TDS) give a general indication of the level of dissolved solids in the stream or lake that are smaller than 2 microns.[32] This includes all of the disassociated electrolytes that make up salinity concentrations, as well as other compounds such as dissolved organic matter. A high concentration of dissolved ions is not necessarily an indication of pollution of the stream. It is normal for streams to dissolve and accumulate fairly high concentrations of ions from the minerals in the rocks and soils over which they flow.

Table 3. Comparison of Maximum Contaminant Levels of Some Domestic Water Quality Parameters with the values obtained in the study

Parameter	*RSA (1996)	§ USA (2009)	#WHO (2008)	Obtained values from Caledon River Samples Minimum	Maximum
pH value	6.0 – 9.0	6.5 – 8.5	6.5 – 8.5	7.34	8.20
TDS, mg L^{-1}	450	500	-	257	458
Turbidity, NTU	10	2	-	12	87
NO_2^- nitrogen, mg L^{-1}	-	0.1	0.5	0.003	0.007
NO_3^- nitrogen, mg L^{-1}	-	10.0	50	1.3	1.7
NH_3 nitrogen, mg L^{-1}	1.0	0.1	0.5	0.32	0.38
Phosphates (PO_4^{3-}), mg L^{-1}		0.1		0.57	0.74
Sulfate (SO_4^{2-}), mg L^{-1}	200	250	250	12	17
Total chlorine, mg L^{-1}	-	4.0	-	0.02	0.19
Iron, mg L^{-1}	0.1	0.3	0.2	0.17	0.50
Manganese, mg L^{-1}	0.05	0.05	0.05	0.2	0.7

Sources: #WHO, 2008; §US-EPA, 2009; * South African Quality Standards – Domestic use, 1996

A variety of human activities may contribute to elevated levels of TDS in river water. A few examples are fertilizers and urban runoffs during storm and wastewater and septic system effluents can add a variety of ions to a stream.[33] Dissolved solids are also important to aquatic life by keeping cell density balanced.[34] However, depending upon the ionic properties, excessive TDS can produce toxic effects on fish and fish eggs.[31]

The TDS values increase downstream from 'Maliemere to Tikoe-Thetsane sampling points. The values ranged between 75.85 and 185.20 mg L^{-1} 156.70 to 88.50 mg L^{-1} mean values respectively (See Table 1). The DO levels decrease downstream as the river flows along the industrial area where different industrial and domestic wastewaters, urban run-offs, storm waters and other discharges are discharged into it, which increase the amount of nutrients, i.e. phosphorus, nitrogen as ammonia, nitrate, and nitrite and organics. This can result in the increased growth of algae and flora and fauna that together use up oxygen, thus reducing the DO. The presence of oxidisable species and increased salinity further reduces DO as observed downstream.[35]

Total suspended solids (TSS) concentrations and turbidity both indicate the amount of solids suspended in the water, whether minerals or organic. While TSS measures the actual weight of solids per unit volume of water, turbidity measures the amount of light scattered from a water sample as the result of the suspended particles. High values for TSS and turbidity decreases light penetration and productivity and increases water temperature because suspended particles absorbs more heat. This will in turn decrease DO as warm water dissolves less oxygen.

The mean TSS values ranged from a maximum of 65 mg L^{-1} at the lowest downstream sampling point at Tikoe-Thetsane to a minimum of 10 mg L^{-1} at the uppermost upstream sampling point at 'Maliemere. The corresponding turbidity values are 78 NTU and 12 NTU respectively. TSS combined with storm water discharges play a crucial role in wet-weather pollution in urban areas and TSS during rain events can have toxic effects of aquatic organisms, because major potential toxic substances, such as heavy metals, organic matter can be absorbed onto TSS that would latter settle down into the sediments.[36]

Interestingly, there was a significant correlation between the conductivity and total dissolved solids (R^2 = 0.9839) as well as with the total suspended solids (R^2 = 0.9451) indicating the cause-effect relationship between these parameters.

Determination of Chemical Parameters

Chemical properties are those elements that can come from the chemical weathering of the rocks or washed into the river water from other activities. The chemical parameters analysed are as in Table 2. A graphical representation of the amounts at different sampling sites relative to 'Maliemere is shown in Figure 3.

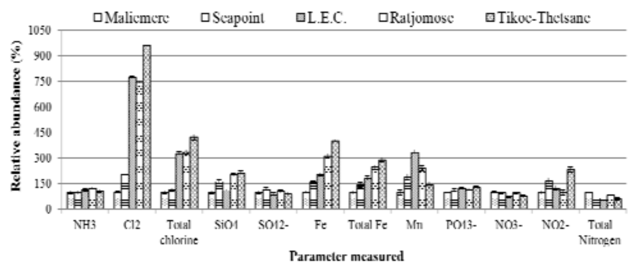

Figure 3. Some relative amounts of chemical parameters downstream of the river

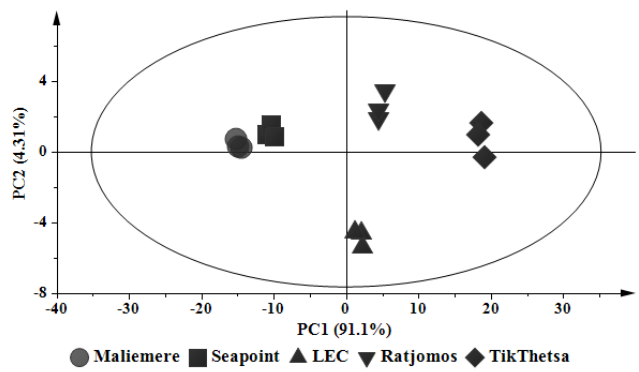

Figure 4. PCA scores plot: the scores plot (PC1 vs PC2) showing sample clustering.

Elements such as phosphorus and nitrogen are important plant nutrients. However excessive amounts in water can cause eutrophication which upsets the ecosystem through the reduction of light penetration capacity thus affecting other aquatic flora and fauna. Nitrates and phosphates levels vary within a narrow range 1.30 to 1.70 mg L^{-1} for nitrates and 0.57 to 0.74 mg L^{-1} for phosphates. The highest levels for nitrates were recorded at the ‘Maliemere sampling point with a mean of 1.74 mg L^{-1}. This could be attributable to the surface run-off from fertilizers coming from the fields across the river in the South African side. The recommended levels for nitrates and nitrites to sustain the aquatic life and human consumption are 10 mg L^{-1} and 1.0 mg L^{-1} respectively. Typical levels of phosphorous in natural waters 0.02 mg L^{-1}.[37]

A guideline limit for phosphorus is 0.1 mg L^{-1} for surface waters. However, the range for the mean of total Kjeldahl nitrogen is 19-35 mg L^{-1}, which is much higher than the sum of nitrates, nitrites and ammonia indicating that there could be another significant source of nitrogen besides these three forms.

The levels of most parameters studied were within the maximum contaminant levels (MCL) as shown in Table 3. The value for phosphates was found to be more than 5 times the MCL values, at all the sampling sites including ‘Maliemere which is has limited human activity. The decreasing amounts downstream could be attributable to dilution as other water streams and/or discharges join the river. Chlorine seemed to be the most dominant chemical species whose variation was about 10 times that in ‘Maliemere. This could be attributable to the use and disposal of the chlorinated water in the munipality as well as bleaching processes in the textile industries.

The samples from the Tikoe-Thetsane point have the highest concentrations for the all the parameters investigated and a sharp increase in the concentrations was observed between Ratjomose and Tiko-Thetsane sampling points. This could be due the fact that the effluent from the wastewater treatment plant, which receives and treats the effluent from all the industries (mostly partially treated or totally untreated) in the Thetsane industrial area, is discharged into the river upstream to this sampling point.

Principal Component Analysis for potential markers for major differences

Examination of data in Tables 1 and 2, in comparison with Figure 2 and 3 creates some confusion as to which of the components account for the major pollution and that can be used as markers in this respect. Hence a principal component analysis of the complete raw data was used to determine the relationship between the sampling points. A five-component model, explaining 99.6 % of the variance (with the accuracy of prediction of 95.4 %), was computed.

The resulting scores and loadings plots are presented in Figures 4 and 5. A scores plot was constructed from PC1 and PC2 [R^2X (cum) of 0.954, Q^2 (cum) of 0.875 and 95 % confidence] and explains 95.4 % of the variation, and shows a differential clustering of the samples (sampling sites).

Clearly each of the sites seems to form its own cluster differentially from the rest with ‘Maliemere and Seapoint sites closer to one another that the other sites. This makes sense in that ‘Maliemere site comes prior to the city area and the Seapoint area is just on the northern tip of the city where not much effluent from the populated area is discharged. This suggests that the two sites are more similar (in the detected/measured variables) in comparison to the rest of the sites. The perpetual increase along PC1 demonstrates the continual increase of the contribution of the component as the river traverses the sampling sites. Interestingly, the LEC site seems to drift away from the rest of the sites and seems to be different in the PC2. However, it is still in line with the rest of the sites on the PC1. There are few industries around this side so the difference could be brought by the nature of the chemicals discharged into the river.

To understand more the underlying variables responsible of the clustering and the deviations observed on scores plot, a loadings plot was computed as shown in Figure 5.

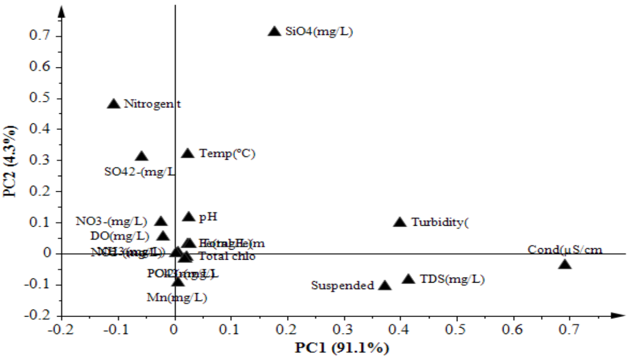

Figure 5. PCA loadings plot showing variables responsible clustering on the scores plot

From the loadings plot in Figure 5, it could be seen that variables that contribute significantly to the clustering are SiO_4^{4-} content and conductivity. The other variables that contributed to the shift of the LEC site from the rest of the sampling sites were nitrogen, temperature and sulphates; while those along the PC1 axis are those that generally change as the river flows downstream. The clustering along the PC1 was expected given that as the river traverses along the city, there are a number of areas that possible could lead to some increased level of pollution. What was surprising was the expression of variability in PC2.

A close inspection of the components drifting along the PC2 (those responsible for L.E.C. site deviation), namely, SiO_4^{4-}, SO_4^{2-}, temperature and Nitrogen, it was observed that these components break the trend of increasing levels of the other analytes from ‘Maliemere down to Tikoe-Thetsane site as shown in Figure 4. The values did not conform to any trend as opposed to those values along the PC1 axis. It is however difficult to attribute the observed deviation along the PC2 to anything, except noting that there are some textile factories around that area as shown in Figure 4. Soluble silica in natural waters is usually not ionized, but present as the orthosilicic acid H_4SiO_4 or $Si(OH)_4$. The chemical transformation of silica in freshwaters is complex and it is influenced by the biological activity aquatic organisms such as diatoms. There is also an important relationship between silicon and the major nutrients, phosphorus in particular.[38]

Figure 6. The sampling point L.E.C and factories within close distance to the river

As can be seen from the map, the factories lie up-stream (towards the right with flow towards the left) of the L.E.C. sampling site marked with a flag since their discharge goes in the north direction. Some key parameters responsible for the PC2 variation were identified and their trends are presented in Figure 5. Only four of these, SiO_4^{4-}, nitrogen, temperature and SO_4^{2-} that can be picked from the loadings plot in Figure 3, are presented for the ease of scaling.

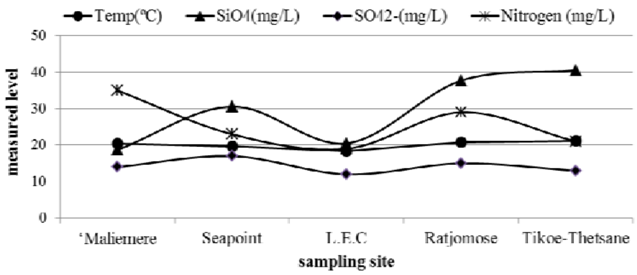

Figure 7. Some parameters responsible for the deviation in PC2 of the scores plot

On the other hand Figure 6 represents some of the parameters responsible for the shift of the different sampling sites along the PC1; notably conductivity, turbidity, total dissolved solids (TDS) and total suspended materials (denoted as 'suspended' in the loadings plot – Figure 6).

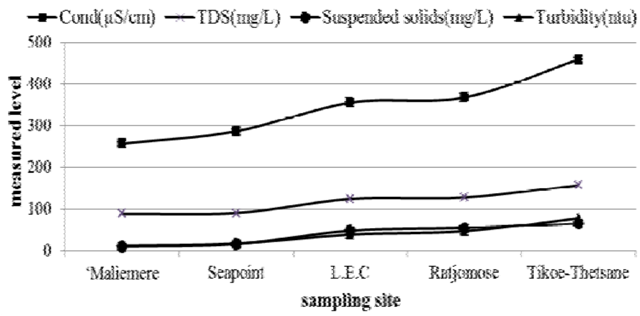

Figure 8. A chart showing some of the parameters responsible for the trend along PC1

Notably there was a significant jump for all the values from the LEC sampling site onwards. And there are not the only parameters that showed this dramatic jump, others as well, although they could not be included in Figure 8 due to their significantly lower numerical levels to fit on this scale (See Tables 1 and 2).

Conclusion

The water quality assessment of the Caledon River along Maseru City was carried out and principal component analysis was used to identify major role players in the observed trends. The levels of all most of the samples determined showed the expected increasing trend from 'Maliemere as shown on the PCA analysis. However, L.E.C. site shows some interesting break in the trends. Since the levels of most of the parameters assessed in this study peak up considerably around the factories, their respective levels could be attributed to the factory waste. Thus one of the ways in which to identify the responsible sources would be to identify the nature of waste from the factories, a very difficult task given the hostility of the factory owners and the relaxed regulation and law enforcement framework in the country. Other insignificant levels of chemicals such as phosphates and nitrates whose levels do not generally increase downstream could be attributable to the agricultural activities taking place across the border in the South African side of the river. In the follow-up study, the other elements responsible for general parameters such as high levels of conductivity as well as those responsible for the L.E.C. sampling site will be covered.

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