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Land Use Impacts on Water Quality of Rivers draining from Mulanje Mountain: A Case of Ruo River in the Southern Malawi

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Abstract

A research study was carried out to determine the effects of different land uses on the water quality of Ruo River. Water sampling was done both in the upper and the middle sections of the river. The water samples were analysed for pH, total dissolved solids (TDS), electrical conductivity (EC), dissolved oxygen (DO), sulphates, chloride, bicarbonates, nitrates, phosphates, fluoride, sodium, potassium, cadmium and Escherichia coli using standard methods.

Land uses in the area significantly affected the concentration of EC, TDS, sulphates, potassium and sodium ($p \leq 0.05$) while pH, dissolved oxygen, chloride, bicarbonates, nitrates, phosphates and E-coli did not significantly fluctuate with land use changes in the area ($p \geq 0.05$). The effect of seasons was significant on pH, dissolved oxygen, phosphates, chloride, bicarbonates and sodium ($p \leq 0.05$) but not on electrical conductivity, total dissolved solids, sulphates, nitrates, lead, potassium and e coli in Ruo River. The research recommends an integrated water resources management approach where all users and relevant stakeholders should take an active role in the conservation of Ruo River catchment in order to avoid further degradation of the catchment through different land uses.

Keywords: *Ruo River, Mulanje Mountain, Land use changes, Water quality, smallholder farmers, Estate farmers*

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Introduction

Land use has for a long time been considered a local environmental issue, but has become a force of global importance. Worldwide changes to forestry, farmland, waterways and air, are being driven by the need to provide food, shelter, fibre and water to more than six billion people (Foley, *et al*., 2005). The changes in land use reflect the history and perhaps the future of humankind as they are linked with economic development, population growth, technology and environmental change (Houghton, 1994). Sala *et al*. (2000) showed that global plant and animal diversity has been changing at unprecedented rate in response to several human induced changes in the global environment. It is evident that global croplands, pastures, plantations and urban areas have continued to expand in recent decades, accompanied by large increase in energy, water and fertilizer consumption along with considerable losses to biodiversity (Foley, 2005). Such changes in land use have resulted in man consuming an increasing share of the planet's resources, further creating challenges of maintaining tradeoffs between immediate human needs and maintaining the capacity of the biosphere to provide goods and services in the long term.

Africa has a total land area of about 29.6 million sq km which represents 20% of the earth's surface (FAOSTAT, 2006). About 60% of the population live in rural areas and 55% of the economic active population is dependent on agriculture (FAOSTAT 2006). Africa has an urban growth rate averaging almost 5% per year for the past two decades, the most rapid in the world, and nearly twice the global average (Satterthwaite, 2002). Africa as other developing countries, population is heavily dependent on fresh water, forests, croplands and fisheries (Homer-Dixon and Blitt, 1998). Increased demand for fresh water resources associated with these trends is expected to be especially intense in rapidly urbanizing regions (Taylor, *et al*., 2004), and in the agricultural sector in order to boost food production (Carter, *et al*., 2009; MacDonald, *et al*., 2009). The population growth has put pressure on the Africa's environment to sustainably provide goods and services to an increasing population with the current technologies, resulting in the loss of forests, animals, plant species, land degradation, increasing water shortages and declining water quality.

Over the years forest cover in Malawi has declined from 47% in 1975 to 30% in 2010 (FAOSTAT, 2010; MSOER, 2010) representing the highest deforestation rate in SADC (CURE, 2010).Generally natural resources face deterioration that results in social and economic losses. For instance, Yaron *et al*., (2010) showed that wildlife and forestry contribute 2.7% and more than 5.3% of the GDP respectively. Considering that over 90% of Malawi's exports have their source in natural resources, the economic cost of the major forms of degradation, which include soil erosion, deforestation, water resources degradation, fisheries depletion and biodiversity loss is likely to be more (GoM, 2010). Poverty estimated at 39% (UNDP, 2010) and increasing population growth in Malawi are considered major factors contributing to the escalating deterioration of natural resources. Water quality is often used as a measure of the state of degradation of natural resources since the quality of water in an ecosystem is a reflection of its water and air shed. This study, therefore, endeavoured to link the water quality of Ruo river at various points to associated land uses in order determine the impact of various land uses.

Materials and Methods

A reconnaissance survey of the area was done from the upper course of the river that represented the source, followed by a transect walk along the river profile up to the middle course where the river cuts through tea estates by both smallholder and estate farmers to the confluence between Ruo and Muloza Rivers (Figure 1).

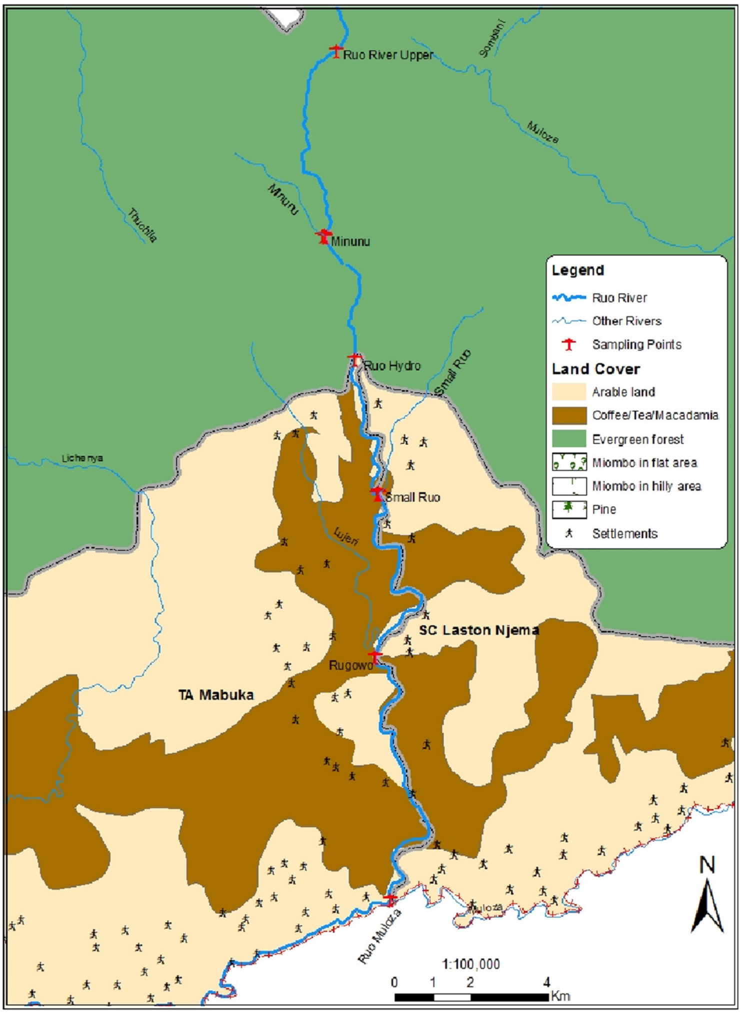

Figure 1: *Land Use Map for the study area*

In the upper section, two land uses observed were grassland at the very top of the Mulanje Mountain Forest Reserve where the Ruo River has its source and rain forest. The sampling points that represented the specific land uses were chosen. GPS coordinates for the water sampling points were taken and recorded in a field book and a mark was put as an identity for subsequent water sampling (Table 1).

Table 1: Water sampling points along the Ruo River.

No.	Catchment	River/Tributary	GPS Way Points	Elevation
1	Upper	Ruo River	(x) 783739 (y)8240746	2081 m
2	Upper	Minunu River	(x) 783455 (y)8235885	1404 m
3	Upper	Ruo River	(x) 783376 (y)8235905	1419 m
4	Upper	Ruo River	(x) 783440 (y)8235939	1395 m
5	Upper	Ruo River	(x) 784229 (y)8232685	876 m
6	Middle	small Ruo River	(x) 784819 (y)8229214	696 m
7	Middle	Ruo River	(x) 784850 (y)8229173	703 m
8	Middle	Ruo River	(x) 784795 (y)8229165	689 m
9	Middle	Rugowo River	(x) 784764 (y)8224897	601 m
10	Middle	Ruo River	(x) 784751 (y)8224889	606 m
11	Middle	Ruo River	(x) 784749 (y)8224896	604 m
12	Middle	Ruo River	(x) 785161 (y)8218562	601 m

The middle section land use is predominantly agriculture. However, it was necessary to differentiate between the anthropogenic effects of smallholder farmers and those of tea estate farmers in relationship to water quality. Small Ruo River, a tributary of Ruo River, was therefore identified as representing the smallholder farmers' anthropogenic activities because from its source to the point of joining Ruo River, it only flowed through fields of smallholder farmers. Similarly, another tributary of Ruo River, Rugowo River was chosen to represent tea estate land use because from its source it only flowed through tea estates before it joined the main Ruo River. Specific points were identified as sampling points to represent smallholder, tea estates and combined (smallholder and estates) land uses. GPS points were used to locate the sampling points in a land use map for the area (Figure.1).

The sampling was done during a period of six months from the month of October, 2010 to end of March, 2011 at two week intervals. Thus samples were collected during the second and fourth week of every month. The first three samples collected represented the dry season before the onset of the rains whereas the rest of the collection represented the rainy season. The water samples was analyzed for the following biochemical constituents; electrical conductivity, pH, dissolved oxygen, total dissolved solids, sulphates, chloride, fluoride, carbonates, bicarbonates, nitrates, phosphates, lead, cadmium, sodium and *Escherichia coli*.

Dissolved oxygen was measured in-situ using Dissolved Oxygen Meter, Hanna Instruments, Model DO H1 9145. Electric conductivity and total dissolved solids were measured in- situ using EC/TDS Meter, Martin Instruments, EC59 and pH was measured using pH Meter, Martin Instruments, PH 55.Levels of Sulphates were determined using turbidimetric method. Barium sulphate turbidity was formed by measuring 100 ml sample into a 250-ml Erlenmeyer flask. 5 ml conditioning reagent was added and stirred in the stirring apparatus. While the solution was being stirred, a spoonful of $BaCl_2$ crystals were added and timing began immediately. Stirring was done for 1 minute at a constant speed. Measurement of barium sulphate turgidity was done by pouring some of the solution immediately after stirring period had ended into the absorption cell of the photometer and measures the turbidity at 30 sec interval for 4 minutes. Sulphate concentration in the sample was finally calculated using the a standard calibration curve. The calibration curve was done using standard solutions of concentration between 5, 10, 15, 20, 30 and 40 mg/l.

Chloride was measured using argentometric method. 100-ml sample was transferred to a conical flask, and 1.0 ml of K_2CrO_4 indicator solution added. The solution was titrated with standard silver nitrate titrant to a pinkish yellow end point. Silver nitrate titrant was standardized to establish the reagent blank value by using the titration method above. The concentration of the sample chloride in the sample was calculated as follows:

Mg/l Cl = (A-B) × N × 35.450/ml sample, where

A = ml titration for sample

B = ml titration for blank

N = Normality of $AgNO_3$

Fluoride concentration was measured using electrode method. Fluoride standards in the ranges of 0.5, 1.0, 2.0, 5.0 mg/l were prepared. To the standards 50mls of pH 5.0 to 5.5 TISAB solution was added. The concentration of the sample is reduced by half by the addition of TISAB solution, as such doubling the standard's true concentration enables the analyst to read the samples' original concentration directly. 50 mls of the each sample was put to a 100-ml volumetric flask, and diluted to the mark with TISAB and mixed them well. The samples were made in triplicates. Both the sample and the standards were subjected the same room temperature. Each standard and sample were transferred to a 150-ml beakers. Measurements were taken by immersing the electrodes in both the standards and then the samples while stirring the test solution on a stirrer. Stirring the solution before immersing the electrodes was avoided as the entrapped air around the crystal could produce erroneous readings or needle fluctuations. The electrodes were left for 3 minutes before taking a final millivolt reading. The electrodes were rinsed with distilled water and blot dry between readings. The electrodes were recalibrated frequently by checking the potential reading of 1.00- mg/l F standard and adjust the calibration control until the meter reads as before. The calibration was confirmed after each unknown and also reading each standard when preparing the standard curve. The potential measurement of fluoride standards were plotted graphically in a standard curve. Using the potential measurement for each unknown sample, the corresponding fluoride concentration was read from the standard curve

Alkalinity was measured using sulphuric acid and phenolphthalein indicator method. Transfer 10 ml of sample was transferred to a 100 ml conical flask and added 2 drops of phenolphthalein indicator. Pink colour showed the presence of carbonate; the sample was then titrated against 0.01N H_2SO_4 until it was colourless. The reading was denoted as volume "Two drops of methyl orange indicator was added, yellow colour appearing. Titration continued until the yellow colour changed to red. The volume was denoted as "B";

Calculation

$$CO_3^{2-}\ \text{me/l} = \frac{2 \times N \times A}{\text{Ml of sample}} \times 1000.$$

$$CO_3^{2-}\ \text{mg/l} = \frac{2 \times N \times A}{\text{Ml of sample}} \times 1000 \times 30.$$

$$HCO_3\ \text{me/l} = \frac{N \times (B - A)}{\text{Ml of sample}} \times 1000$$

$$\text{HCO}_3 \text{ mg/l} = \frac{\text{N} \times (\text{B} - \text{A})}{\text{Ml of sample}} \times 1000 \times 61$$

Where,

N = Normality of acid

2 = Valance of carbonate

B = Volume of titrant against methyl orange indicator

30 = Equivalent weight of CO_3

61 = Equivalent weight of HCO_3

Phosphate was determined via vanadomolybdophosphoric colorimetric method at 470 nm wavelength on Jenway UV/V Spectrophotometer according to standard procedure (ALPHA, 1989). Standards of concentration between 0.1 and 0.5 mg/l were used for calibration to maintain quality control. Standards used for plotting a standard curve were in the following ranges 0.5, 1, 2, 4, 5 mg/l. The potential reading of the concentration of sample solutions were calculated from the standard curve.

Nitrate was determined using an Ion Selective electrode, Ellit 8021; reference electrode, Ellit 003N (NICO, USA) on a pH Seven Multimeter ion analyzer (Mettler Toledo, Switzerland). The electrode was first calibrated with appropriate standards prepared from the standard stock solution. The nitrate sample concentrations were then read directly from the meter and corrected for dilution due to the addition of ISAB at 2% per volume of the sample. Standard curve was then plotted using the readings from standard solutions that were made as follows; 1, 10, 50, 100 mg/l. The concentrations of the sample solutions were then read from the standard curve.

Cadmium using AAS Unicam 969 at 283.3nm wavelength and slit width 0.7nm. Cadmium standard stock solution (1000 µ/l) was prepared by dissolving cadmium metal (0.1 g) (dried at 105oC for 2 hours), in 12 ml of 1 +1 HNO3 of water (v/v) and diluting the resulting solution to 1000 ml with deionised water. Standard working solutions containing, 0.5, 0.8, 1.0, 1.5, 2.0, 3.0 and 5.0 mg/L were used in the final determination. The standard solutions (100 ml) and samples were mixed with 25 ml lanthanum solution before aspiring them on AAS Unicam 969 at 283.3 nm wavelength and slit width of 0.7 nm. The gas mixture used for flame was air/acetylene. The sample concentrations were read directly from the AAS (Clesseri *et al*., 1989)

Sodium was measured using flame photometer Sodium standard stock solution (100 µg/ml) was prepared by dissolving 0.2542 g sodium chloride (dried at 140 degrees Celsius for 2 hours) in 200 ml deionised water and made up to 1000 ml. Working sodium standard solutions of 0.5, 1.0, 1.5 2.0, 2.5, 3.0 mg/l Na were prepared from the standard stock solution. Standardisation of the flame photometer was done by aspirating the Sodium standards. The emission of the sample and standards was read after aspirating sample and standards into a Sherwood 410 Flame Photometer at a wavelength of 589 nm which uses air/propane gas mixture as fuel. Concentration of the sample was read from the flame photometer (Horwitz, 1980). A standard curve was made using solutions from which the real concentration of samples was read.

Potassium standard solution (100 µg/ml) was prepared by dissolving 0.1907 g potassium chloride (dried at 110 degrees Celsius for 2 hours) in 200 ml deionised water and made up to 1000 ml. Potassium standard solutions of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 and 5.0 mg/l were prepared from the standard stock solution. The samples and standards were aspirated into a Sherwood 410 Flame Photometer and their emissions were read at 766.5nm using air/propane gas mixture as fuel. Concentration of the sample was read from the flame photometer. (Horwitz, 1980). A standard curve was then prepared from the standard solutions from which the actual concentrations of the samples were read

Escherichia coli contamination was determined using incubator based standard method. The membrane filtration method was used to determine the presence of faecal coliforms. A measure volume of 1 ml was filtered under vacuum through a cellulose acetate membrane of uniform pore size diameter. Bacteria were retained on the membrane given media for culturing bacteria and incubated at 44.5 degrees Celsius for 24 hours. Faecal coliforms were identified by the development of characteristic colonies which were counted manually with the help of magnifying glasses (Clesseri *et al*, 1989).

Data Analysis

Analysis of variance (ANOVA) was conducted on TDS, EC, DO, sulphates, chloride, fluoride, carbonates, bicarbonates, nitrate, phosphates, cadmium, sodium, e coli and lead concentrations in order to compare the mean concentrations of biochemical constituents from different land uses where water samples were taken. The mean concentrations were compared at 95% level of significance to find out if there existed any significant differences on how land uses affected the mean concentration of the biochemical constituents along the Ruo River. Similarly in order to investigate if seasonal changes had an effect on the mean concentration of the biochemical constituents of the water from Ruo River, analysis of variance was done to compare mean biochemical constituents from different land uses between the two seasons, dry and wet.

Post hoc analysis was done where the results of the analysis showed significant differences. Post hoc tests are designed for situations in which the researcher had already obtained a significant omnibus F-test with a factor that consisted of 3 or more means and additional exploration of the differences among means is needed to provide specific information on which means are significantly different from each other. In the study Least Significant Difference (LSD) was used. LSD explored all possible pair-wise comparisons of means comprising a factor using equivalent of multiple t-tests.

Results

Mean Biochemical Constituents Variation due to Land Use Changes

The table below summarises the mean concentrations of EC, pH, DO, TDS, sulphates, chlorides, bicarbonates, nitrates, phosphates, cadmium, sodium, potassium and e coli and their variations with land uses

Table 2: Summary of Mean Concentration and Variation due to Land Use

Chemical	**Mean Concentration**	**P- Value**
EC ((µs/cm)	5.915	0.000
pH	6.640	0.181
DO (mg/l)	9.077	0.551
TDS (mg/l)	3.211	0.000
Sulphates (mg/l)	9.407	0.036
Chloride (mg/l)	1.0156E1	0.755
Flouride (mg/l)	Below detectable limit	
Bicarbonates (mg/l)	1.5201E1	0.461
Nitrates (mg/l)	0.462	0.536
Phosphates (mg/l)	0.346	0.483
Cadmium (mg/l)	Below detection limit	
Sodium (mg/l)	1.202	0.037
Potassium (mg/l)	0.913	0.00

E coli (colonies per 100ml)	1.6666E2	0.237

Analysis of Variance (ANOVA) showed that EC and TDS were significantly affected by changes in land uses along the Ruo River while DO and pH were not significantly affected by changes in land use in the study area ($p \leq 0.05$) (Table 2) (Figure 2).

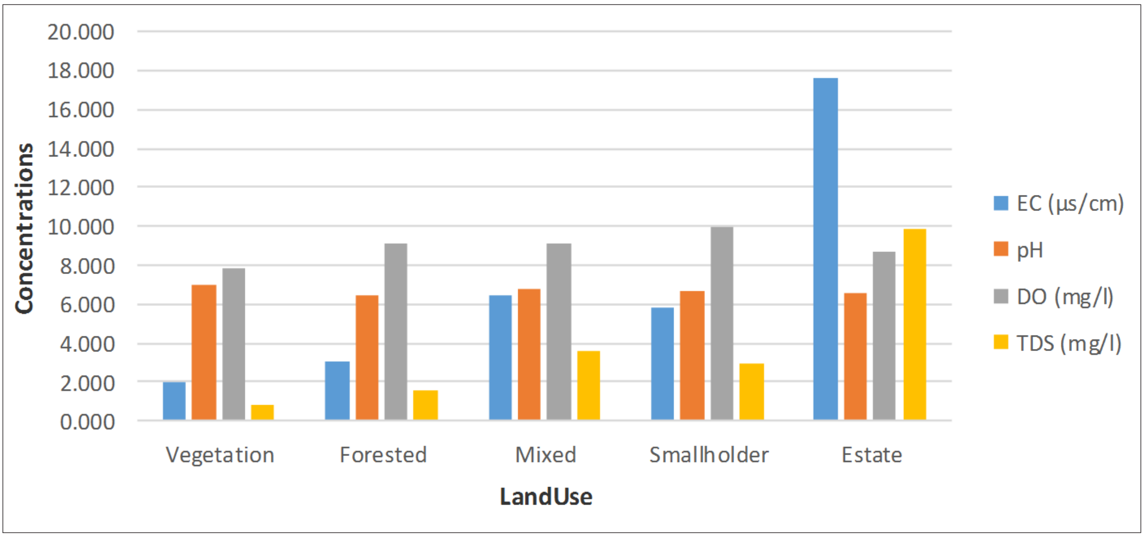

Figure 2: *Variations of EC, DO, pH, TDS with Land Use changes along the Ruo River*

The post hoc analysis for EC (Table 3) showed that significant differences existed among the following pairs of land uses; grassland vegetation and mixed land use; Grassland vegetation and Estate Farmers land use; forested land use and mixed land use; forested land use and estate farmers; mixed land use and estate farmers and smallholder farmers and estate farmers ($p \leq 0.05$).

Table 3: Post Hoc Analysis for Electric Conductivity

Dependent	**Land Use Category**		**P value**
Variable	**Main Category**	**Sub Category**	
Electric Conductivity	Grassland	Forested	0.602
		Mixed	0.03
		Smallholder Farmers	0.137
		Estate Farmers	0.001
	Forested	Mixed	0.004
		Smallholder Farmers	0.157
		Estate Farmers	0.001
	Mixed Land Use	Smallholder Farmers	0.724
		Estate Farmers	0.001
	Smallholder	Estate Farmers	0.001

Post hoc analysis for TDS (Table 4) showed that significant differences occurred among the following land uses; grassland vegetation land use and mixed land use; grassland land use and estate farmers land use; forested land use and mixed land use; forested land use and estate farmers' land use and between smallholder farmers' land use and estate farmers' land use ($p \leq 0.05$). There was, however, no significant differences among the following land uses: grassland vegetation and forested vegetation; grassland vegetation and smallholder farmers land use; forested land use and smallholder farmers' land use and mixed land use and smallholder farmers' land use ($p \geq 0.05$). Grassland vegetation had the lowest concentration of electrical conductivity, pH, dissolved oxygen, total dissolved solids, sulphates, chloride, fluoride, carbonates, bicarbonates, nitrates, phosphates, lead, cadmium, sodium and *Escherichia coli* compared to forested land probably because of the ground cover provided by grasses near the source which resulted in less erosion of top soil.

Table 4: Post Hoc Analysis Results for TDS

Dependent	**Land Use Category**		**P value**
Variable	Main Category	Sub Category	
Total Dissolved	Grassland	Forested	0.478
Solids		Mixed	0.011
		Smallholder Farmers	0.108
		Estate Farmers	0.001
	Forested	Mixed	0.001
		Smallholder Farmers	0.169
		Estate Farmers	0.001
	Mixed Land Use	Smallholder Farmers	0.528
		Estate Farmers	0.001
	Smallholder	Estate Farmers	0.001

Land uses significantly affected sulphate concentration along the Ruo River ($p \leq 0.05$) (Figure 3), (Table 2). Post hoc analysis results (Table 5) showed significant differences occurred between estate farmers' land use and the rest of the land uses ($p \leq 0.05$). Comparison of other land uses except estates did not show significant differences on the variation of concentration of sulphates with associated land uses ($p \geq 0.05$).

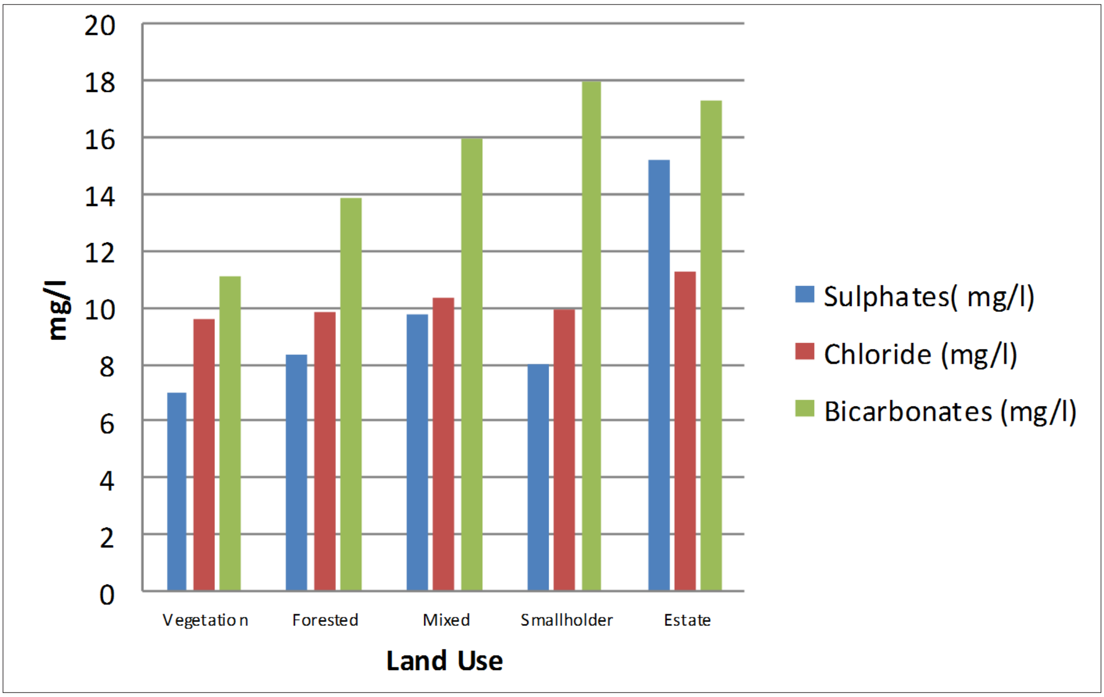

Figure 3: *Variation of sulphates, chloride an bicarbonates with land use*

Table 5: Post Hoc Analysis Results for Sulphates

Dependent	**Land Use Category**		**P value**
Variable	Main Category	Sub Category	
Total Dissolved	Grassland	Forested	0.578
Solids		Mixed	0.251
		Smallholder Farmers	0.747
		Estate Farmers	0.008
	Forested	Mixed	0.303
		Smallholder Farmers	0.864
		Estate Farmers	0.004
	Mixed Land Use	Smallholder Farmers	0.420
		Estate Farmers	0.018
	Smallholder	Estate Farmers	0.015

Sodium and potassium concentrations significantly varied with changes in land use along the Ruo River ($p \leq 0.05$) (Table 2) (Figure 4). The significant differences were evident between estate farmers land use and other land uses however, potassium concentrations showed significant differences between mixed farmers land use and forested land use (Table 6 and 7). Mean chloride, nitrate, phosphate, bicarbonate and *Escherichia coli* concentrations were not significantly affected by changes in land use ($p \geq 0.05$) (Table 2). Flouride and cadmium were below detection limits (Table2).

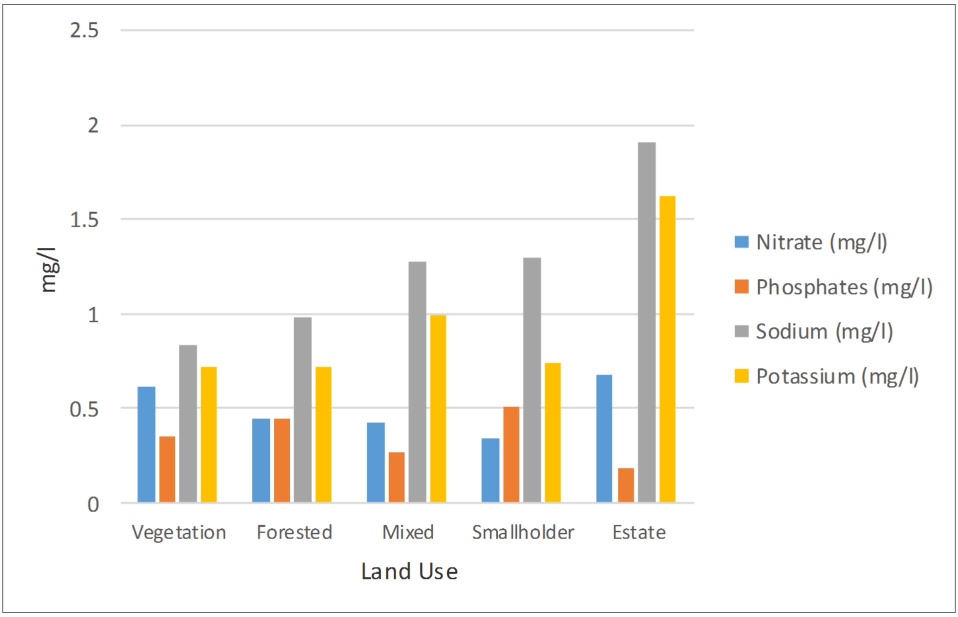

Figure 4: *Variation of, Cadmium, sodium and potassium with land use changes along the Ruo River*

Table 6: Post Hoc Analysis Results for Sodium

Dependent	**Land Use Category**		**P value**
Variable	Main Category	Sub Category	
Total Dissolved	Grassland	Forested	0.658
Solids		Mixed	0.184
		Smallholder Farmers	0.267
		Estate Farmers	0.011
	Forested	Mixed	0.122
		Smallholder Farmers	0.318
		Estate Farmers	0.004
	Mixed Land Use	Smallholder Farmers	0.948
		Estate Farmers	0.042
	Smallholder	Estate Farmers	0.124

Table 7: Post Hoc Analysis Results for Potassium

Dependent	**Land Use Category**		**P value**
Variable	Main Category	Sub Category	
Total Dissolved	Grassland	Forested	0.971
Solids		Mixed	0.064
		Smallholder Farmers	0.939
		Estate Farmers	0.001
	Forested	Mixed	0.001
		Smallholder Farmers	0.889
		Estate Farmers	0.001
	Mixed Land Use	Smallholder Farmers	0.057
		Estate Farmers	0.001
	Smallholder	Estate Farmers	0.001

Mean Biochemical Constituents Variation due to Seasonality

Table 8 shows that seasonality significantly affected the following biochemical constituents: pH, dissolved oxygen, phosphates, chloride, bicarbonates and sodium ($p \leq 0.05$). The concentration of other biochemical constituents such as; TDS, EC, sulphates, nitrates, fluoride, potassium, and *Escherichia coli* were not significantly affected by changes in seasons.

Table 8: Biochemical Constituents Variation due to Seasonality

Parameter	**Mean Dry Season**	**Mean Wet Season**	**P-Value**
EC	6.42	5.40	0.457
pH	6.45	6.84	0.004
DO	7.73	10.00	0.001
TDS	3.83	2.57	0.091
Sulphates	9.20	9.62	0.735
Nitrates	0.55	0.37	0.053
Phosphates	0.03	0.67	0.001
Chloride	9.41	10.93	0.012
Bicarbonates	19.98	10.29	0.001
Potassium	0.98	0.84	0.136
Sodium	1.46	0.93	0.001
E Coli	120	305	0.441

Discussion

Electrical conductivity measures the ability of water to pass an electric current and is affected by the presence of inorganic dissolved solids. EC was lowest in the grassland and forested land use because in the grassland the water was slow and had less material dissolved in it, while in the forested land use, the river was mostly passing through rocky surfaces surrounded by trees which acted as buffer to materials falling into the river. In both land uses, there are no agricultural activities taking place and therefore no disturbances to the soil, and no application of chemical fertilizers and pesticides. The sharp increase in electrical conductivity in the estate farmers land use was as a result of increase in chemical fertilizers and pesticides being applied by estate farmers as opposed to smallholder farmers. The concentration for TDS showed the same trend sharply increasing in the estate farmers' land use.

The lower pH in the forested area agreed with Dow and Zampella (2000); Hunchak – Kariouk and Nicholson, (2001); Coulter and Kolka *et al*. (2004), who reported that streams draining from forested watersheds were usually acidic and nutrient poor, whereas streams draining from upland agriculture and developed lands display elevated pH values. Decomposition of soil organic matter releases acids leading to decrease in pH in forested land use (Killman, 1994). However in the study area, pH values were also lower in the middle section of the river. This agreed with Wang Hui and Xu Ren-Kou (2010), who reported tea growing well in acidic soils and cultivation of tea plants caused soil acidification and soil acidity increased with the increase of tea cultivation period. Tea in the study area has been grown commercially since the 1880s.

The lack of significance in how DO was affected by land use in the study area was as a result of the fact that in the grassland the Ruo River was flowing in shorter vegetation and therefore well aerated, whereas in the forested the river was flowing in a rocky surface and with a higher discharge, thus increasing the mixing up of water with atmospheric oxygen. Cunningham (2003), reported that fast moving water, rushing water is aerated by bubbles as it churns over rocks and other barriers thereby falling down hundreds of tiny waterfalls that facilitated mixing with the atmospheric oxygen.

The high levels of sulphate concentration in the estate farmers' land use was as a result of higher application rates of fertilizers rich in sulphates as compared to smallholder farmers. Although this research did not capture the types of fertilizers being used, ammonium sulphate is one of the fertilizers commonly used as an alternative to urea. Others include single super phosphate, muriate of potash and CAN. Mean chloride concentration followed a similar pattern to that of sulphates increasing from grassland vegetation to estate farmers land use, except in smallholder farmers land use where it slightly decreased (Figure 4). Phillips (1994) found chloride concentration as largely controlled by point sources. The results therefore indicated the absence of point sources of chloride along the river profile.

The lower nitrate concentration in the forested land use, support the findings of Vanderbilt *et al*. (2003); Cassalli and Gimenez *et al*. (2010), who reported that overall, forests in catchments limit nitrate delivery to streams. Hayakawa *et al*. (2006); Cassalli and Gimenez *et al*. (2010) attributed this to the relatively high denitrification potential of the soils in the forested catchments. The higher mean value in the grassland agree with Lovette *et al*. (2000); Cassalli and Gimenez *et al*. (2010); Emmett (1993) who attributed forest type and maturity of the forests to differences in nitrate export to streams. It may also be suggested that some vegetation in the grassland are leguminous in nature and help fix nitrogen into the soil which later gets denitrified to inorganic nitrates. There is therefore a need to investigate the vegetation types to find out if really there are some vegetation leguminous in nature.

In much agricultural land use, ploughing increased the concentration of nitrates in surface and ground waters, as oxygenation of the soil caused nitrification (Falkenmark and Chapman, 1989). In the tea cultivation, there was almost zero tillage practised except where they were replacing the crop. The relatively higher value under estate farmers would be attributed to higher levels of fertilizer application in the estate land use as compared to smallholder farmers.

The relatively higher concentration in the smallholder farmers' land use might not only be as a result of fertilizers rich in phosphates but also as a result of detergents from domestic water use. Mvunguti *et al*. (2003) reported principal sources of phosphates as being inorganic chemical fertilizers from agricultural fields, diffuse sources and sewage effluents from point sources and detergents from domestic waste water. People in the surrounding villages used the Ruo River and small Ruo River to wash their clothes as well as bathing. The detergents from such uses influenced the increase in phosphate concentration in the rivers. In smallholder farmers' land use, apart from tea farming, some farmers grew annual crops such as maize and these increased soil disturbances and consequently phosphate loss from such soils. Gray (2008) reported an increased generation of phosphates as the proportion of disturbed land cover such as mixed small scale agriculture and bare land cover increased.

The concentration of fluoride was below detection limit. The natural concentration of the fluoride was either too low to be detected or it might have been as a result of bauxite minerals. Mulanje Mountain is believed to contain bauxite minerals. The Mulanje Mountain Bauxite Study undertaken in 1993 through African Development Bank funding showed the probable and indicated reserves of bauxite amounting to 25.6 million tonnes using a cut-off grade of 30% Al203 (MET-CHEM, Canada Inc., 1994). LONRHO, (1969, 1974, unpublished) conducted bauxite feasibility studies in Mulanje Mountain to ascertain the availability of bauxite. Sajidu *et al* (2008) reported occurrence of bauxite as having deflouridation capacity attributed to its gibbsite and kaolinite minerals. This may have lead to the non detection of the fluoride.

The concentration of sodium in the grassland represented natural sources as the area has no human settlements as it is high on top of the Mulanje Mountain. There is very minimal anthropogenic pressure in that area that is exerted by tourists visiting the mountain, watchmen guarding temporary shelters for tourists and some encroachers who steal Mulanje cedar. However the increase in the concentration of sodium in the middle section of the river where farming activities were more pronounced was as a result of anthropogenic activities from both smallholder and estate farmers. These ranged from non point source pollution from household waste as people washed their clothes and household utensils closer to the river. The comparative higher concentration of potassium in estate farmers' land use would be as a result of high application rates for NPK fertilizers as compared with smallholder farmers' land use.

Cadmium mean concentrations were found below detection limits. Cadmium is naturally found in the earth's crust and is relatively a rare metal, ranking 67th in abundance among the 90 naturally occurring elements on earth. Major anthropogenic activities that play an important role in its release to the environment included mining, fossil fuel burning, waste incineration and steel products among others. Anthropogenic sources of cadmium in cultivated soils include phosphorus fertilizers, atmospheric deposition, animal manures, and sewage sludge among others. There was no enough anthropogenic pressure to stimulate the release of cadmium to the environment and that natural sources were extremely very low for detection.

The significance of seasonality on the concentration of dissolved oxygen agreed with the findings of Kwanjana (2009) who studied biochemical constituent levels in the water of the upper catchment of Lilongwe River in Malawi and found mean DO values for dry season lower than those in the wet season. The decreased water levels in the dry season led to decreased flow of the river, thereby reducing the rate at which the water mixed with atmospheric oxygen. The pH values were higher during the rainy season due to an increase in common pollutants from both the agricultural fields and the rain forested vegetation. Phiri *et al*. (2005) reported that common pollutants that can affect the pH of water were the effluents from commercial and industrial activities and agricultural fields run off that may contain chemical fertilizers and pesticides. The significant effect of seasonality on the concentration of chloride in Ruo River would be as a result of other non point sources of pollution within the study area that drained into the river by running water. Phillips (1994) noted that chloride levels generally declined with increasing discharge and that there would be elevated chloride concentration during high flows being attributed to other sources such as runoff from roads. In the study, it was difficult to categorically distinguish the source of the pollution as BGS etal. (1996) noted that in rural areas it was difficult to distinguish between agricultural pollution and pollution by untreated sewage. The significant effect of seasonality on the concentration of phosphates might be attributed to land use disturbances in the smallholder farmers' land use thereby increasing the generation of phosphates to the river after the rains. In smallholder farmers' land use, apart from tea farming, some farmers grew annual crops such as maize, thereby increasing soil disturbances and consequently phosphate loss from the soil. Cassalli and Gimenez *et al*. (2010) attributed soil conditions as a dominant factor in the loss of phosphates in run off. The significant effect of seasonality on the concentration of sodium in the study area was due to the fact that during the rainy season, there was more discharge leading to dilution of the concentration of the sodium. In the dry season, there was low river discharge coupled with high evaporation leading to higher concentration of the sodium

Conclusions

Land uses in the area affects the water quality of rivers draining from the Mulanje Mountain. Levels of total dissolved solids, electrical conductivity, sulphates, potassium and sodium in Ruo River are significantly affected by changes in land use while pH, dissolved oxygen, chloride, bicarbonates, nitrates, phosphates and e coli are not significantly linked to land use changes in the area. The concentration of fluoride, carbonates and cadmium were found to be below detection limits.

Change in seasons is a significant factor in the variability of pH, dissolved oxygen, chloride, bicarbonates, phosphates and sodium in the Ruo River. However, variations in levels of electrical conductivity, total dissolved solids, sulphates, nitrates, lead, potassium and e coli in Ruo River are not significantly dependent on changes in seasons.

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