Journal of Scientific Research & Reports
6(1): 1-12, 2015; Article no.JSRR.2015.126
ISSN: 2320-0227

SCIENCEDOMAIN *international*
www.sciencedomain.org

Characterisation of Distillery Molasses Stillage and Assessment of Water Quality of a River Running through a Sugar Cane Plantation in Southern Zimbabwe

A. Kanda[1*], G. Nyamadzawo[1] and J. Gotosa[1]

[1]Department of Environmental Science, Bindura University of Science Education, P. Bag 1020, Bindura, Zimbabwe.

Authors' contributions

This work was carried out in collaboration between all authors. Author AK designed the study, collected data and managed the experimental process. Author JG managed the literature searches. AK and GN performed the analyses of the study. Author AK wrote the first draft which was reviewed by authors GN and JG. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/JSRR/2015/13732
Editor(s):
(1) Luis H. Alvarez Valencia, Laboratory of Environmental Biotechnology and Microbiology, CIIBAA Instituto Tecnológico de Sonora(ITSON), México.
Reviewers:
(1) Małgorzata Krzywonos, Department of Bioprocess Engineering, Wrocław University of Economics, Poland.
(2) Anonymous, China.
(3) Suntud Sirianntapiboon, Department of Environmental Technology, School of Energy Environment and Materials, King Mongkut 's University of Technology Thonburi, Thailand.
Complete Peer review History: http://www.sciencedomain.org/review-history.php?iid=754&id=22&aid=7966

Original Research Article

Received 1st September 2014
Accepted 14th October 2014
Published 31st January 2015

ABSTRACT

The aims of this case study were to characterise partially-treated distillery molasses stillage, determine river pollutant loading and its self purification capacity during the dry season (April to September) in 2012 in southern Zimbabwe. Monthly water and stillage samples were analysed in triplicate for BOD_5, DO, NO_3-N and PO_4-P using standard procedures for water and wastewater analysis. Discharge was estimated using the area-velocity method. River pollutant loading was determined as the product of pollutant concentration and discharge. River self-purification was determined using the upstream and downstream approach. Normality-tested data were subjected to analysis of variance and the least significant difference post-hoc procedure at 95% confidence limit using GENSTAT statistical package. Pearson correlation test was used to determine the

---

*Corresponding author: Email: alzkanda@gmail.com;

strength of associations among parameters. Average monthly values for pond stillage (4 559±9.01 $mgBOD_5/l$; 3 647±2.31 mgTDS/l; 876±2.08 $mgNO_3$-N/l; 729.40±1.15 $mgPO_4$-P/l; 40.35±1.61°C, pH: 4.50±0.06 and 0.46±0.06 mgDO/l) were outside the Zimbabwean permissible limits for safe surface discharge. Average monthly concentrations of parameters upstream differed from those at the first point downstream by between 1.76 and 725.00%, but decreased further downstream (except for DO and pH). Trends of loading rates were: TDS (SP4<SP3=SP1<SP2); BOD_5 (SP1<SP4<SP3<SP2); NO_3-N (SP1=SP4<SP3<SP2) and PO_4-P (SP1=SP3=SP4<SP2). Distillery pond stillage was found to be acidic with high organic matter, nutrients and total dissolved solids for surface discharge. The characteristics of the river upstream were not sufficient for its self-purification within the studied stretch prompting the need for further pre-treatment of stillage. The variation of pollutant concentrations was attributed to uncharacterised watershed and in-stream non-point sources of pollution.

Keywords: Fertigation; molasses stillage; pollutant load; non-point source pollution; river self-purification; river water quality; Southern Zimbabwe.

1. INTRODUCTION

The use of sugarcane for ethanol production may result in the reduction of fuel imports for Zimbabwe as a result of the recent large volume of car imports from Japan. Ethanol has been used in blending petrol. However, the production of ethanol through fermentation-distillation of sugar cane is associated with the generation of large amount of waste including stillage. A hectare of land with a yield of 82tonnes of sugar cane can produce about 7 000litres of ethanol [1]. For every litre of ethanol that is produced, between 10 and 20 L of stillage are generated [2-5]. Molasses stillage is usually characterised by low pH, a dark brown colour, high BOD and high TDS [4,6-9]. Uncontrolled surface discharge or land application of stillage may cause environmental pollution [10]. This presents to fermentation distilleries, potential challenges of disposing large quantities of pollutant-laden stillage.

There is need to increase fertilisation in order to achieve high levels of crop productivity. However, this may result in nutrient enrichment in water bodies, a major threat to freshwater ecology, leading to water pollution [11-15]. Rivers have competing and conflicting uses in catchments [16-19]. They receive pollutants in amounts that may exceed their natural purification capacities or that may be accommodated into the overall balance of the river system. Not readily detectable changes in river water quality may occur. The total pollutant loading of a river consists of direct, diffuse and background contributions from both natural and artificial sources [12,20,21]. Non-point sources of pollution need more recognition than point sources as they may contain harmful contaminants and receive less continuous effort to reduce [21]. Their influence is less obvious due to poorly defined origins, volume and frequency of loading [17]. Fertigation and river discharge are commonly practised methods of molasses stillage disposal [7,9,22]. Fertigation offers double benefit in water pollution control and utilisation for agricultural production [5]. Stillage disposal has been a subject for research for a long time. Earlier studies demonstrated the beneficial and detrimental effects of land application or river disposal of molasses stillage [1,3,4,6,7,10,23]. In some cases data is not readily available as companies may want to protect their corporate image if they are poorly managing their environmental footprint.

The impairment of water quality of a river that is not directly receiving stillage within a stillage-irrigated sugar cane plantation, especially in the dry season, seems to have received little attention. Such rivers may receive pollutants through irrigation return flows, surface runoff, sub-surface flow and burst stillage distribution pipes or flooded canals, in concentrations that may impact water quality of the receiving rivers. In this work we selected some physico-chemical parameters to characterise partially treated molasses stillage that is used for irrigation. We then used the upstream-downstream approach [21] to determine the pollutant loading, thus self purification, of a river which runs through a sugar cane plantation which is periodically irrigated with molasses stillage. There were no gauging stations along the river for real-time data.

No attempt was made to quantify both watershed and in-stream processes that contributed to river pollutant loading. This study may provide invaluable information on the disposal and use of stillage considering the commissioning of a newly built US$600 million-dollar ethanol distillery plant in Chisumbanje in the south eastern lowveld of Zimbabwe. There may be potential stillage disposal or usage challenges especially in the dry season where very little-to-no flows are experienced in most of the rivers of the Runde catchment.

2. MATERIALS AND METHODS

2.1 Description of the Study Area

Triangle Estates are characterised by low, erratic mean annual rainfall (469 mm) that is received between November and March [24]. The temperature ranges from 23°C (June) to 36°C (October). The mean evaporation rate is 1751 mm annually. The rain fed growing season is <90 days, making the region unsuitable for dry land cropping. These conditions make irrigation inevitable for successful crop production. Cheche River, which is approximately 14.71 km long, originates from shallow in-field and surface drainage systems of Triangle estates (20°2' 0" S and 31°27' 0" E) in the Runde catchment in southern Zimbabwe. It is a tributary of Mutirikwi River which experiences dry areas upstream in the dry season. The river flows through sugar cane estates that are fertilised and irrigated with stillage.

The studied river stretch had sparsely vegetated river banks which are dominated by *Typha latifolia, Cyperus articulates* and *Panicum repens*. The river channel widens downstream but due to heavy siltation and water abstractions, it experiences low flows within a narrow channel with water. Water quantities that were abstracted were not ascertained during the study. Water uses downstream included irrigation of sugar cane, domestic uses and livestock watering. However, the organic loading and stream flow downstream of the irrigated plantation in the dry season, assumed to be most affected, are unknown. The ethanol distillery produces about 4.0×10^4 m^3 of fuel-grade ethanol from the fermentation of sugar cane molasses and generates approximately 4.8×10^5 m^3 molasses stillage annually. Distillery stillage is temporarily retained in a pond for about two days before being periodically used for the irrigation of sugar cane as a disposal option.

2.2 Sampling and Sample Analysis

River water and pond stillage were collected monthly from April to September, 2012 using polythene bottles that had been previously washed with non ionic detergent, rinsed with de-ionised water and three times with sample water at the point of sampling [19]. Samples were preserved on ice at about 4°C [25] and transported to the laboratory. Water samples were collected along the river at established sampling points: A reference point which was located 200 m upstream of the sugar cane plantation edge (SP1); downstream sampling points that were located 200 m (SP2), 1000 m (SP3) and 1500 m (SP4) from the boundary of the sugar cane plantation. Molasses stillage was sampled at the holding pond outlet. All samples were analysed in triplicate for BOD_5, DO, NO_3-N and PO_4-P using standard procedures for water and wastewater analysis [25] (Table 1). Temperature, pH and TDS were measured *in situ*. The results were presented as means of the triplicate measurements. Dissolved oxygen for the pond stillage was then converted to percent saturation [26] for ease of comparison with local discharge standards. Stream flow was estimated at the four sampling sites along Cheche River using the area-velocity method [11] at the time of water sampling. The float method was used to estimate mean stream velocity. River pollutant loading was determined as the product of pollutant concentration and water flow [11,21,27]. The degree of river self-purification that occurred between sampling sites was determined [27].

2.3 Statistical Analysis

River water quality normality-tested data were subjected to analysis of variance (ANOVA) to compare means for months and sites. The least significant difference (lsd) post-hoc procedure was used to separate treatment means at $P<.05$ using GENSTAT statistical package [28]. Pearson correlation test was used to determine the strength of associations between physico-chemical parameters of stillage, and between stream water quality parameters and flow rates.

3. RESULTS AND DISCUSSION

3.1 Characterisation of Pond Molasses Stillage

Results show that stillage from the holding pond had low pH, high organic strength, high TDS and high nutrient content with mean parameter values higher ($P<.05$) than Zimbabwean surface discharge limits. The stillage treatment processes in the holding pond could not reduce parameter levels to within permissible national discharge limits [29] implying that the stillage could not be directly discharged into surface watercourses. Common stillage treatment methods that were recommended in literature include dilution with fresh irrigation water [7] and anaerobic methods [2]. The disposal of the stillage by river water dilution is an option. The required dilution factors for stillage parameters to fall to within acceptable discharge levels [29] for the parameters ranged from 1.3 (temperature) to 1 459 (PO_4-P) (Table 2). Dilution for safe disposal with respect to the evaluated parameters would require very large volumes of fresh water which cannot be supplied by the Cheche River during the dry period. Land application (sugar cane irrigation) becomes the only stillage disposal option.

The characteristics of partially treated molasses stillage (Table 2) satisfactorily agree with values that are reported from literature with respect to pH, DO, BOD_5, TDS, NO_3-N and PO_4-P [7,8]. Variations in the characteristics of distillery stillage have been attributed to the varying types of feedstock and the distillation process [2] and possibly to the degree of treatment that was accorded by the stillage holding pond.

High temperature and high BOD_5 of stillage (Table 2) may account for the low concentration of DO that was observed in pond stillage. Molasses stillage leaves the distillation column at high temperature. Surface discharge of distillery effluent would alter the physico-chemical parameters of water, negatively impacting aquatic life [7,8]. Nutrients released by sugar cane processing that remained in molasses could have contributed to the observed high concentrations of PO_4-P and NO_3-N in stillage. Stillage still contained the dark reddish-brown colour reminiscent of the burnt or caramelised sugar [2,7] and the presence of melanoidin [5]. Obnoxious odours were also produced by stillage in the holding tank. These could be attributed to volatile fatty acids [6].

3.2 River Water Quality Assessment

Average water quality parameters at the reference site (SP1) were lower than those measured downstream at SP2 (except for temperature), nearest to the sugar cane plantation (Table 3). These values increased (except for pH and DO which decreased) by between 1.76 and 725.00%. This may suggest the existence of inputs from a diffuse source of pollution, probably irrigation return flows, surface runoff from burst pipes, flooded canals from sugar cane plantations or subsurface flow of infiltrated stillage. Non-point sources of river water pollution could be due to agricultural activities, remobilisation from or entrainment of contaminated bottom sediments, groundwater contributions or a combination of these factors [21]. There were no direct discharges of stillage into the river that were observed during the study period. Bursting of stillage pipes averaged twice per month during the study period. The measured average water quality parameter values decreased ($P<.05$) downstream from SP2 to SP4 except for pH and DO which increased, while temperature showed no significant ($P>.05$) changes. The observed decrease could be attributed to the dilution effect of river water. However, at the furthest point downstream (SP4) the concentrations of BOD_5, NO_3-N and PO_4-P remained higher than those at the reference site (SP1) (Table 3). Within this stretch, Cheche River could not effectively reduce the high strength organic material (stillage) that had high nutrient content.

Table 1. Physico-chemical parameters, units and methods of analysis that were used in evaluating water and effluent quality and flow in the south eastern lowveld of Zimbabwe, April – September, 2012

Parameter	Unit	Method of analysis [25]	Instrumentation
TDS	mg/l	Electrochemical	TDS meter (Hanna HI9835)
BOD_5	mg/l	Titrimetric (Winkler's)	Titrations apparatus and Incubator
pH	-	Electrochemical	pH meter (model: HI9835)
Temperature	°C	Instrumental	Hg -in glass thermometer (Alpha Technics 4500)
NO_3-N	mg/l	Cd reduction	Uv-Vis spectrophotometer (model: U-2900/2910)
PO_4-P	mg/l	Phosphomolybdate	Uv-Vis spectrophotometer (model: U-2900/2910)
DO	mg/l	Titrimetric (Winkler's)	Titrations apparatus
Stream flow	m/s	Float method	Float and stopwatch

3.2.1 Dissolved oxygen (DO) and biological oxygen demand (BOD_5)

The average monthly concentration of BOD_5 values ranged from 13.78±0.09 - 61.13±1.23 mg/l with site SP2 recording the highest value (Table 3). From SP2 to SP4 there was substantial increase in the concentration of DO downstream with decreasing BOD5. Similar observations were reported in a related study of estimating pollutant loading along a river stretch [21]. Higher BOD_5 levels were reported for a river in Jordan than the allowable limit until 33 km downstream of a sewage treatment plant [30]. The measure of the oxygen-absorbing capacity of a water body (BOD_5) has been reported to be both time and place specific [19]. This may be because the rate at which oxygen is supplied to the river water carrying an organic load is affected by site-specific factors such as the river's morphology and climate.

The average concentration of DO at SP1 (14.57±0.5 mg/l at 25.55°C and 1atm i.e. about 182% saturation) was within limits, but became critically low at SP2 (Table 3). The gradual increase in the concentration of DO observed at SP3 and SP4 (Table 3) could be attributed to photosynthetic activity by submerged aquatic flora [13,21] more than to contributions from surface aeration, further suggesting the reduction of nitrate levels by plant uptake [15]. Contributions of DO from surface water aeration due to prevailing currents and turbulence [9,13,] could have been minimal because of the low and decreasing stream flows coupled with the relatively gentle regional gradient. The concentration of DO of a water body defines the capacity of that water body to assimilate the imposed load by itself or with the help of aeration through absorbed atmospheric oxygen and photosynthesis [19]. The BOD_5:DO ratio decreased with distance downstream at sites SP2 (33.04), SP3 (13.96) and SP4 (4.45). This could be explained by the decreasing BOD_5 and increasing concentration of DO downstream. Aquatic systems with high BOD_5 tend to have low concentration of DO [12] as high organic matter in water uses up DO at rates that are higher than those of its atmospheric replenishment leading to reduced concentrations of DO. Low concentrations of DO in river water have been attributed to the decomposition of organic substances and nutrients [14,15]. River water at the furthest sampling point (1.5 km) downstream still showed the brown colour that is synonymous with stillage. Highly coloured effluents influence primary productivity, thus the concentrations of DO [31]. As the concentration of DO falls from the optimal levels to below 3%, mobile animals such as fish would flee [14].

High concentration of DO provides water with natural self purification capacity, and also indicates high aeration rate and rapid aerobic degradation of organic matter [32]. Concentrations of DO that are greater than 5 mg/l have been considered to promote proper growth of aquatic organisms while concentrations <2 mg/l may lead to death of most fish [13,33]. In some related work, falling concentrations of DO in river water were attributed to increasing temperature and decreasing flows [17]. Temperature has been known to influence the concentration of DO and biochemical processes of river water system [13,18]. In this study, no significant spatial variation in temperature was observed (*P*>.05) There was no direct effluent discharge that was observed. This may suggest that decreasing stream flows could have influenced the concentration of DO to some extent.

Table 2. Mean values for physico-chemical parameters (mean±SE) of pond-treated molasses distillery stillage and national limits for surface discharge. Data are mean monthly values of six months of a dry season for a sugar distillery in the south eastern lowveld of Zimbabwe. unless specified, units are mg/l

Parameter	Partially treated pond stillage	[1]EMA (2007) Effluent surface discharge maximum limits	Dilution factor for safe discharge
Colour	reddish brown	-	-
TDS	3 647±2.31	≤ 500	7.3
BOD_5	4 559±9.01	≤ 30	152.0
NO_3-N	1 876±2.08	≤ 10	187.60
PO_4-P	729.40±1.15	≤ 0.5	1458.8
Temperature (°C)	40.35±1.61	≤ 35	1.15
pH (units)	4.52±0.06	6 - 9	1.32
DO (%)	0.46±0.06	≥ 60 (about 5 mg/L at 25°C)*	10.89

*[1]Environmental Management Agency, Zimbabwe; *Recalculated [26]*

Table 3. Variation of mean physico-chemical parameters (mean±SE) for water samples collected at four sampling sites (SP1, SP2, SP3 and SP4) along the river. Data are mean monthly values for six months at a sugar distillery in the south eastern lowveld of Zimbabwe. unless specified, units are mg/l

Parameter	Parameter value (mean±SE) at river sampling sites				
	SP 1	SP 2	SP 3	SP 4	lsd
TDS	596.67 ± 7.83^{b}	820.76 ± 11.97^{d}	703.54 ± 9.82^{c}	551.55 ± 26.73^{a}	44.23
BOD_5	13.78 ± 0.90^{a}	61.13 ± 1.23^{d}	42.45 ± 1.27^{b}	31.28 ± 1.08^{c}	3.283
NO_3^-	3.08 ± 0.77^{a}	15.27 ± 0.74^{d}	8.50 ± 0.42^{c}	5.98 ± 0.06^{b}	1.372
PO_4^{3-}	0.24 ± 0.02^{a}	1.98 ± 0.22^{b}	0.39 ± 0.02^{a}	0.30 ± 0.01^{a}	0.337
Temp (^{o}C)	25.55 ± 0.63^{a}	26.00 ± 0.46^{a}	25.83 ± 0.59^{a}	25.47 ± 0.38^{a}	0.640
pH	7.74 ± 0.15^{d}	5.09 ± 0.11^{a}	6.07 ± 0.11^{b}	7.03 ± 0.07^{c}	0.377
DO	14.57 ± 0.50^{d}	1.85 ± 0.17^{a}	3.04 ± 0.10^{b}	7.03 ± 0.15^{c}	0.753
*DO (% saturation)	182	25	37	87	

*a, b, c ... different superscripts in the same row denote significant differences (P<.05) and same superscripts in the same row denote no significant differences (P>.05); * approximate calculated values at the given water temperature [26]*

3.2.2 Nutrients: NO_3-N and PO_4-P

Natural concentrations of nitrates from natural sources in surfaces waters often rarely exceed 0.1 mg/l but can be enhanced by human activities up to 5mg/l which indicate pollution [13]. High NO_3-N and PO_4-P levels that were observed at SP2 could be attributed more to watershed than in-stream processes. Natural sources of nitrates in surface waters which include igneous rocks, land drainage and plant or animal debris, and the remobilisation and re-suspension of settled pollutants, may be more pronounced in fast moving waters and high flows [13]. This may exclude nutrient addition by surface runoff as no precipitation was recorded during the study period. Fertilisers that were not used by plants or absorbed by the soil, remnants of organic matter degradation and/or stillage that were used for irrigation could have found their way into the river as subsurface flow or surface irrigation return flows. Sources of nitrogen and phosphorus which are essential components of healthy aquatic ecosystems [13,15] include in-stream and watershed processes [14,15,27]. However, high nutrient levels in water bodies have been linked to eutrophication [18]. The observed decrease in the concentration of NO_3-N between SP2 and SP3 may be attributed to limited nitrification (an aerobic process catalysed by bacteria) which has a tendency to increase the concentration of NO_3-N and reduce pH from the mineralisation of organic matter. Low concentrations of NO_3-N in river water were attributed to probably high levels of denitrification [21]. The low concentration of DO and a significant ($P<.05$) increase in pH from SP2 to SP3 (Table 3) may further support this. Spatial variation of NO_3-N concentration downstream was observed in a similar study [18].

The concentrations of PO_4-P at SP1 and SP4 were not different (*P*>.05). Although the concentration of PO_4-P increased for SP2 and SP3, Cheche River was able to return it to its background level at SP4 (Table 3). Low stream flow may have promoted the sedimentation of PO_4-P in the river bed. A similar observation was reported [4]. The concentration of PO_4-P is rarely found high in freshwaters (0.005 - 0.02 mg/l) as it is actively taken up by plants [13]. Without direct stillage discharge into the river, the observed high nutrient content may be attributed to watershed processes such as pipe bursts, irrigation return flows and subsurface drainage. Dry weather was observed to result in low stream discharges (<1.2 m^3/s) and inactive runoff from the watershed [15]. Under such conditions total phosphorus inputs are at natural background and non point sources from the watershed.

3.2.3 Water temperature

The average site water temperature values in Cheche River ranged from 24°C to 28°C during the study period (Table 3). Water temperature exhibited no differences (*P*>.05) both spatially and temporally (Table 3). The trend in temperature variation at all the sites followed that of the air temperatures recorded in the area with lowest observed in July (peak of winter) and highest in September (beginning of hot season). The mean maximum air temperatures in the area ranged between 26 and 33°C (http://www.worldweatheronline.com/Buffalo-Range-weather-averages). In a similar study [17] river water temperature was highly correlated with air temperature suggesting that local air temperature influenced water temperature.

A product of complex interactions influences stream temperature, among stream morphology, soil hydrology, riparian vegetation, climate and human activities [34]. Stream temperature was observed to increase following harvesting of riparian vegetation [35]. Surface runoff and tributary inflows could not have influenced stream temperature at the studied river sites as no precipitation was recorded during the study period. Any slight increase in stream temperature may have been modified by base flow which is assumed to be cooler than surface flow [35]. Water temperature has been shown to inversely vary with the concentration of DO [17]. In the present study the linear relationship observed was very poor (Table 4). Variations in stream temperature may be due to watershed and in-stream processes. Spatial variability in stream temperature has been suggested to be a result of the differences in elevation [13] but in this study, there was no spatial variation in temperature (*P*>.05). The gentle slope of the area may not have substantial variation in elevation.

3.2.4 Concentration of TDS

The concentration of TDS in Cheche River ranged from 551 to 820mg/l. The concentration and composition of TDS in natural waters are determined by the geology of the drainage, atmospheric precipitation and the water balance (evaporation-precipitation) [36]. The average concentration of TDS at SP1 was higher than SP4 (Table 2). However, the concentration of TDS was highest at SP2 for corresponding months. This may indicate that the river was able to return to its initial status (self purification) with respect to TDS within 1.5km. There was no significant variation in the concentration of TDS across the months at each site (*P*>0.05). The high concentration of TDS in stillage could be due to salts that are formed during pH adjustment, mixing of stillage with blow-down water, wash-water and cooling water [31]. Potential effects of high concentration of TDS in water have been given [13,33,36]. High concentrations of TDS are usually expected in hot weather and low flows due to high temperature that causes evapo-concentration of solutes in the water column [17]. The weather in the south eastern lowveld of Zimbabwe favours such increases in the concentration of TDS.

3.2.5 Water pH

The pH of river water was different at all sites with average site values ranging from 5.09±0.11 - 7.74±0.15 (Table 2) (*P*<.05). Water pH from 6.5 – 9.0 is suitable for aquatic life [32] and a range of 6.5 – 8.5 makes water suitable for potable use [33]. Site SP2 had the lowest pH in the acidic and unsafe range possibly due to pollution from molasses stillage irrigation of sugar cane. River processes failed to raise the pH of water to background values within the studied 1.5 km stretch downstream of the irrigated field. The increase in water pH from SP2 to SP4 may be explained by the presence of bicarbonates and carbonates of calcium and magnesium in the water [13,32]. Water that is slightly alkaline may be preferable to that which is acidic as heavy metals are removed as non toxic carbonates or bicarbonates which settle onto sediments and also promote primary productivity within the river system [32].

3.3 Correlation Coefficients for Measured River Water Quality Parameters

(Table 4) shows the correlation coefficients for measured river water quality parameters at the four sites along Cheche River. At SP1 strong positive correlations of association which were not significant (*P*>.05) were determined for NO_3-N/temperature and NO_3-N/DO while strong negative correlations of association were determined for flow/pH, flow/BOD_5, pH/DO, PO_4-P/temperature and NO_3-N/pH. The rest of the associations at SP1 were weak (r<0.50). At SP2 the PO_4-P/temperature couple was the only one with a significantly strong positive correlation of association (*P*<.05). Other correlations of association which were positive and strong were determined for the BOD_5/NO_3-N, BOD_5/DO, flow/PO_4-P and flow/TDS couples. Strong negative correlations of association were determined for the BOD_5/PO_4-P, BOD_5/temperature and the pH/flow combinations (Table 4). At SP3 all strong correlations of association were positive. Significant correlations of association were determined for the pH/PO_4-P and the DO/flow combinations. The other strong correlations of association were for the flow/TDS, flow/pH, TDS/PO_4-P, DO/NO_3-N and NO3-N/temperature combinations. The strong NO_3-N/TDS association at SP4 was the only one which was negative and significant. Other strong correlations of association that were negative and not significant were BOD_5/TDS, DO/PO_4-P, BOD_5/flow and NO_3-N/flow while the

BOD_5/temperature and TDS/flow couples were positive.

3.4 River Pollutant Loading and Self-purification Capacity

(Table 5) shows average monthly river discharges at four sampling sites during the dry period from May to September, 2012. Average river flows showed a unique pattern, with flows decreasing downstream (SP1>SP2>SP3>SP4) and ranging from 0.53±0.05 to 0.68±0.06m^3/s. River flow has commonly been reported to increase downstream [21]. Cheche River became wider but shallower downstream due to siltation which reduced its hydraulic radius, thus the stream flow. Siltation also promotes subsurface flow leading to an apparent 'reduction' in river flow downstream.

There was no precipitation that was recorded during the study period. This suggests that precipitation did not influence river flow, and thus the pollutant loading of the river. Precipitation provides the major source of energy for the transport of pollutants through its effect on soil erosion [15]. However, pipe bursts (two events per month), irrigation with stillage and water from overnight reservoirs drained down slope to Cheche River. The study was done during the dry season when river flow was assumed lowest. Low flows have been suggested to reflect the effect of dilution significantly [20]. During low flows the river carries low amounts of silt and sediment. Sedimentation may be enhanced whereas resuspension may be low. Stream velocity influences the kinds of microorganisms and habitats that can be found in a stream, the concentration of DO, and dilution effect and in-stream water temperature [12]. The low stream velocities of the river at the sampling sites may suggest a reduced capacity to attenuate and degrade wastes.

(Table 6) shows the average pollutant (TDS, BOD_5, NO_3-N and PO_4-P) loading rates of Cheche River at four sampling sites (SP1-SP4). Values represent the net effect of loading and any loss or generation within the water body [21]. Pollutant loading significantly varied with sampling sites ($p<0.05$). The variations of the loading rates at the various sampling sites were as follows: TDS (SP4<SP3=SP1<SP3); BOD_5 (SP1<SP4< SP3<SP2); NO_3-N (SP1=SP4<SP3<SP2) and PO_4-P (SP1=SP3=SP4<SP2). The TDS, BOD_5, NO_3-N and PO_4-P loading rates increased between SP1 and SP2 by 23.47, 301.18, 343.98 and 674.77% respectively.

Pollutant loading values then decreased with distance downstream up to SP4 similar to the observed variation in parameter concentration (Table 3). Slight variations could be attributed to disparities in river discharge at sampling sites. At SP4, BOD_5 and NO_3-N loadings were higher than corresponding values at SP1 except for TDS ($p<0.05$). There were no significant differences between PO_4-P loading at SP1 and SP4 ($p>0.05$). The PO_4-P load was however, still high. Very low concentrations of PO_4-P can cause eutrophication [15]. The reduction in pollution load is indicative of self river purification capacity [9].

Table 4. Pearson correlation and p-values for water quality parameters and daily mean flow at sampling sites along Cheche River, Zimbabwe, from April to September, 2012

Parameter and site	Variable						
	TDS	BOD_5	NO_3-N	PO_4-P	pH	Temperat.	DO
TDS	1						
SP1	1						
SP2	1						
SP3	1						
SP4							
BOD_5	0.109^{NS}	1					
SP1	-0.168^{NS}	1					
SP2	-0.148^{NS}	1					
SP3	-0.501^{NS}	1					
SP4							
NO_3-N	0.120^{NS}	0.017^{NS}	1				
SP1	-0.135^{NS}	0.579^{NS}	1				
SP2	0.363^{NS}	-0.304^{NS}	1				
SP3	-0.855*	0.413^{NS}	1				

Parameter and site	Variable						
	TDS	BOD_5	NO_3-N	PO_4-P	pH	Temperat.	DO
SP4							
PO_4-P	0.426^{NS}	-0.454^{NS}	-0.298^{NS}	1			
SP1	0.311^{NS}	-0.733^{NS}	-0.308^{NS}	1			
SP2	0.781^{NS}	0.082^{NS}	-0.012^{NS}	1			
SP3	-0.060^{NS}	0.097^{NS}	-0.134^{NS}	1			
SP4							
pH	-0.165^{NS}	0.106 ^{NS}	-0.843^{NS}	0.395^{NS}	1		
SP1	-0.671^{NS}	-0.180^{NS}	-0.499^{NS}	0.080^{NS}	1		
SP2	0.543^{NS}	0.271^{NS}	-0.021^{NS}	0.830*	1		
SP3	0.084^{NS}	0.369^{NS}	0.216^{NS}	-0.027^{NS}	1		
SP4							
Temp.	-0.163^{NS}	-0.124^{NS}	0.507^{NS}	-0.586^{NS}	-0.478^{NS}	1	
SP1	-0.036^{NS}	-0.670^{NS}	-0.119^{NS}	0.923*	0.210^{NS}	1	
SP2	0.172^{NS}	0.487^{NS}	0.603^{NS}	0.052^{NS}	0.006^{NS}	1	
SP3	-0.391^{NS}	0.613^{NS}	0.007^{NS}	0.356^{NS}	-0.451^{NS}	1	
SP4							
DO	0.316 ^{NS}	-0.278^{NS}	0.758^{NS}	0.200 ^{NS}	-0.592^{NS}	0.484^{NS}	1
SP1	-0.477^{NS}	0.506^{NS}	0.075^{NS}	0.299^{NS}	0.081^{NS}	-0.359^{NS}	1
SP2	0.437^{NS}	0.133^{NS}	0.579^{NS}	0.396^{NS}	0.714^{NS}	0.345^{NS}	1
SP3	0.443^{NS}	0.224^{NS}	-0.354^{NS}	-0.583^{NS}	-0.079^{NS}	0.231^{NS}	1
SP4							
Flow SP1	-0.116^{NS}	-0.563^{NS}	0.286^{NS}	-0.213^{NS}	-0.597^{NS}	0.123^{NS}	0.030^{NS}
SP2	0.656^{NS}	-0.091^{NS}	0.286^{NS}	0.619^{NS}	-0.609^{NS}	0.486^{NS}	-0.299NS
SP3	0.639^{NS}	0.198^{NS}	0.315^{NS}	0.403^{NS}	0.632^{NS}	0.141^{NS}	0.784*
SP4	0.864*	-0.592^{NS}	-0.933^{NS}	-0.076^{NS}	-0.401^{NS}	-0.126^{NS}	0.451^{NS}

*NS: not significant (P>.05); * significant (P<.05)*

Table 5. Mean monthly river discharge (m^3/s) at four sampling sites along Cheche River in the dry period of April to September 2012

Month	Sampling site			
	SP1	SP2	SP3	SP4
April	0.93	0.89	0.85	0.71
May	0.74	0.65	0.64	0.62
June	0.67	0.60	0.60	0.56
July	0.65	0.60	0.57	0.51
August	0.54	0.46	0.45	0.40
September	0.56	0.45	0.44	0.38
Mean	0.68±0.06	0.61±0.07	0.59±0.06	0.53±0.05

Table 6. Mean pollutant loading at four sampling sites along Cheche River running between sugar cane fields in the dry season (April- September 2012). Values are mean±SE in Kg/d and D is mean monthly river discharge at a sampling site estimated over six months in m^3/s

Parameter	Sampling site				lsd
	SP1	SP2	SP3	SP4	
TDS	35118.16±2994.79^{b}	43361.15±5120.08^{c}	36 131.43±4113.09^{b}	25776.06±3505.37^{a}	3762.4
BOD_5	798.88±55.44^{a}	3 210.02±331.77^{d}	2176.81±250.81^{c}	1 418.17±120.60^{b}	416.4
NO_3-N	182.09±17.97^{a}	808.45±99.84^{c}	438.09±61.45^{b}	272.41±24.33^{a}	126.8
PO_4-P	13.91±1.50^{a}	107.77±2.44^{b}	19.88±2.69^{a}	13.71±1.40^{a}	34.72

a,b,c,d: Different superscripts in the same row denote significant differences (p<0.05) and same superscripts in the same row denote no significant differences (p>0.05)

4. CONCLUSION

Results indicate that holding distillery stillage in a temporary tank for about two days did not treat molasses stillage to meet national maximum surface discharge limits. Anaerobic treatment or stabilisation ponds may be considered in order to reduce organic and nutrient levels. Dilution of pond stillage with fresh water was shown not to be feasible due to large volume of water required to meet discharge standards. The study has also showed that non-point source pollution which can go unnoticed and undetected may significantly contribute to the impairment of river water quality especially in the dry season when the river self-purification capacities are lowest. Cheche River could not effectively self purify pollutants (TDS, BOD_5, NO_3-N and PO_4-P) within a 1.5 km stretch immediately below the irrigated sugar plantations. Results showed no significant temporal variation in the measured water quality parameters but showed substantial spatial variations along sampling sites downstream, except for temperature. Changes could be associated with reduced stream flows due to abstractions. The poor pollutant assimilative capacity of Cheche River within the studied stretch may limit the multiple uses of water, aquatic ecosystem functions and services downstream. Best management practices in agriculture such as blocking pollutant pathways to the river by employing riparian buffers in order to minimise river water pollution may be encouraged. The determination of nutrient retention capacity of a river is important in determining the restoration of normal riverine ecosystem functions and river water uses further downstream. Watershed processes contributing to pollutant loading in Cheche River could be recommended for future studies, especially during the rainy season.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Hartemink AE. Growing sugar cane for bioenergy - Effects on the soil. In: Soil, energy and food security, Soil solutions for a changing world. Paper presented at the 19th World Congress of Soil Science*:* Symposium 4.2.1, 1- 6 August 2010. Brisbane, Australia. 2010;13-15.
2. España-Gamboa E, Mijangos-Cartes J, Barahona-Perez L, Dominguez-Maldonado J, Hernández-Zarate G, Alzate-Gavirira L. Vinasses: Characterisation and treatments. Waste Management and Research. 2011;29(12):1235-1250.
3. Karanam PV, Joshi HC. Application of distillery effluents to agricultural land: Is it a win-win option for soils and environment. Paper presented at the 19th World congress of Soil Science: Soil solutions for a changing world, 1-6 August 2010. Brisbane, Australia; 2010.
4. Matibiri B. The effects of stillage (Vinasse) on nine ratoon crops of NCo 367 receiving full irrigation in the south east lowveld of Zimbabwe. Proceedings of South African Sugar Technologists' Association. 1996;70:63-6.
5. Rajkishore SK, Vignesh NS. Distillery spent wash in the context of crop production- A review. The Bioscan. 2012;7(3):369-375.
6. Ansari F, Awasthi AK, Srivastava BP. Impact of distillery effluent and its leachate on groundwater (using lysimeter): An experimental approach (Part B). European Journal of applied Engineering and Scientific Research. 2012;1(4):99-112. (Accessed 5 January 2013). Available:http://scholarsresearchlibrary.com/archieve.html
7. Baskar M, Kayalvizhi C, Bose MS. Eco-friendly utilisation of distillery effluent in agriculture: A review. Agricultural Review. 2003;24(1):16-30.
8. Bhasin SK, Singh A, Oberoi J, Gupta KC. Evaluation of pollution load from physico-chemical parameters of the effluent from Haryana distillery, Yamuna Nagar (India). Journal of Environmental Research and Development. 2007;1(4):369-376.
9. Willington IP, Marten GG. Options for handling stillage waste from sugar-based fuel ethanol production. Resources and Conservation. 1982;8:111-129.
10. Chandra S, Joshi HC, Pathk H. Impact of distillery effluent and salts on hydraulic conductivity of a sand loam soil. Caspian Journal of Environmental Sciences. 2005;3(1):9-14.
11. Bere T. The assessment of nutrient loading and retention in the upper Chinyika River, Harare: Implications for eutrophication control. Water South Africa. 2007;33(2):279-284.

12. Carr GM, Neary GM. Water quality for ecosystems and human health. 2nd ed. United nations Environment Programme Global Environment Monitoring System (UNEP GEMS)/Water Programme: Ontario; 2008.
13. Chapman D. ed. Water quality Assessment- A Guide to use of biota, sediments and water in environmental monitoring, 2nd ed. Chapman and Hill: London; 1996.
14. Rabalais NN. Nitrogen in aquatic ecosystems. Ambio. 2002;31(2):102-112.
15. Zaimes GN. Phosphorus in agricultural watersheds: A literature review. Iowa State University: Iowa; 2002. (Accessed 23 May 2012).
    Available:http://www.worldweatheronline.com/Buffalo-Range-weather-averages
16. Akali NM, Nyongesa ND, Neyole EM, Miima JB. Effluent discharge by Mumias Sugar Company in Kenya: An empirical investigation of pollution of River Nzoia. Sacha Journal of Environmental Studies. 2011;1(1):1-30.
17. Bayram A, Onsoy H, Bulut VN, Akinci G. Influences of urban waters on the stream water quality: A case study from Gumushane Province, Turkey. Environmental Monitoring and Assessment. 2013;185:1285-1303.
18. Chigor VN, Sibanda T, Okoh AL. Variations in the physicochemical characteristics of the Buffalo River in Eastern Cape Province of South Africa. Environmental Monitoring and Assessment. 2013;185:8733-8747.
19. Longe EO, Omole DO. Analysis of pollution status of River Illo, Ota, Nigeria. Environmentalist. 2008;28:451-457.
20. Chandra SM, Sreenivasulu D. Modelling nutrients contributed by overland flow from the Krishna River basin, 1A: Water Resources Management. In: Bruen M. editor. Diffuse pollution and River basin management. Proceedings of the 7th International specialised IWA Conference. Dublin: Ireland; 2003. 1.20-3. (Accessed 22 July 2012). Available:http://www.Ucd.ie/dipcon/docs/theme01/theme01_04PDF
21. Jain CK, Singhal DC, Sharma MK. Estimating nutrient loadings using chemical mass balance approach. Environmental Monitoring and Assessment. 2007;134:385-396.
22. Gunkel G, Kosmol J, Sobral M, Rohn H, Montenegro S, Aureliano J. Sugar cane industry as a source of water pollution-Case study on the situation in Ipojuca River, Pernambuco, Brazil. Water Air and Soil pollution. 2006;180(1-4):261-269.
23. Van der Laan M, Van Antewerpen R, Bristow KL. River water quality in the northern sugar cane-producing regions of South Africa and implications for irrigation: A scoping study. Water South Africa. 2012;38(1):87-96. (Accessed 5 January 2013).
    Available:htt://dx.doi.org/0.4314/wsa.v38i1.11
24. Department of Meteorological Services. Climate Handbook of Zimbabwe. Supplement No.5, Harare: Government Printers. 1981;119-160.
25. American Public Health Association. Standard Methods for the Examination of Water and Wastewater. 20th ed. APHA: Washington D.C; 1998.
26. Murdoch TB, Cheo M, O'laughlin K. The streamkeepers' guide: Watershed inventory and stream monitoring methods. 3rd ed. Adopt-a-stream foundation; 1991.
27. Bourne A, Armstrong N, Jones G. A preliminary estimate of total nitrogen and total phosphorus loading to streams in Manitoba, Canada. Conservation Report No. 2002-04; 2002.
28. VSN International Ltd. Genstat Statistical Package, Release 14.1, 14th ed. Hemel Hempstead, UK; 2011. (Accessed 5 January, 2013). Available: www.vsni.co.uk
29. Environmental Management Agency. Effluent and solids waste disposal regulations. Statutory Instrument 6:2007, CAP 20:27, Supplement to the Zimbabwean Government Gazette. Harare. 2007;56-64.
30. Al-Zboon KK, Al-Suhaili RH. Improvement of Water Quality in a Highly Polluted River in Jorda. Jordan Journal of Civil Engineering. 2009;3(3):283-293.
31. Wilkie AC, Riedsel KJ, Owens JM. Stillage characterisation and anaerobic treatment of ethanol stillage from conventional and cellulosic feed stocks. Biomass and Bioenergy. 2000;19:63-102.
32. Sharma A, Bora CR, Shukla V. Evaluation of seasonal changes in physico-chemical and bacteriological characteristics of water from the Narmada River (India) using multivariate analysis. Natural Resources Research. 2013;22(4):283-296.

33. World Health Organisation. Guidelines for drinking water quality, First Addendum to 3rd ed. recommendations. Geneva; WHO. 2006;1.
34. Independent Multidisciplinary Science Team. Influences of human activity on stream temperatures and existence of cold-water fish in streams with elevated temperature. Report of a Workshop: Technical Report 2000-2 on the Oregon Plan for Salmon and Watersheds. Oregon: Oregon Watershed Enhancement Board, Salem; 2000.
35. Moore RD, Spittlehouse DL, Story A. Riparian microclimate and stream temperature response to forest harvesting: A review. Journal of the American Water Resources Association. 2005;813-834.
36. Weber-Scannell PK, Duffy LK. Effects of total dissolved salts on aquatic organisms: A review of literature and recommendation for salmonid species. American Journal of Environmental Sciences. 2007;3(1):1–6.

Peer-review history:
The peer review history for this paper can be accessed here:
http://www.sciencedomain.org/review-history.php?iid=754&id=22&aid=7966