

Full Length Research Paper

Impact of Anthropogenic Activities on Diel Physico-Chemical Cycles in a Semi-Arid Zimbabwean River

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Using data from southeast Zimbabwe intensive agricultural zone we investigated diurnal changes in the Runde River to discover the variations that can occur in the control and test sites of agricultural development. This should predict how the aquatic ecosystem responds when 'stressed' by human activities, such as runoff from the land. Diurnal changes were studied at a resolution of 2 h intervals between 0500 and 0600 h in the control sites and test sites of an area with agricultural development in July 2005 and 2006. The observations gave same results. The diurnal fluctuations are characterized by sharp rises and gradual declines each day. The maximal and minimal points in diurnal changes can be useful biogeochemical signatures for describing the fluvial conditions of a river in a river basin. Significant associations ($R^2 = 0.64$, $y = -1.30x + 24.93$, $P = 0.03$) between measured dissolved oxygen concentration (mg/l) and temperature ($^{\circ}\text{C}$) were demonstrated during the daytime only in the site above the effluent outfall. Insignificant associations ($R^2 = 0.04$, $y = -0.32x + 13.94$, $P = 0.75$) between measured dissolved oxygen concentration (mg/l) and temperature ($^{\circ}\text{C}$) were demonstrated during the nighttime in the site above effluent outfall. This suggests that there was more dissolved oxygen concentration added during the day than at night at the site above the outfall. The coefficients of determination between dissolved oxygen concentration (mg/l) and temperature ($^{\circ}\text{C}$) for the daytime and nighttime were $R^2 = 0.35$ and $R^2 = 0.29$, respectively, for site below the outfall. There were almost identical regression lines demonstrated during the daytime and nighttime below the outfall, an indication that oxygen demanding wastes deplete dissolved oxygen concentration. No significant associations were found between dissolved oxygen and temperature during the daytime and nighttime below the outfall. This study indicates that fluvial conditions characterized by fluctuations in diurnal changes may be a strong signature to catchment activities but need to be looked at in conjunction with other fluvial measures such as flow rate, depth and channel discharge that may also be naturally challenging to aquatic organisms.

Key words: Zimbabwe, savanna semi-arid lowland river, diurnal changes, aquatic organisms.

INTRODUCTION

One of the most important processes governing the composition of the rivers on earth includes the diurnal cycles of freshwaters (Berg and Kautsky, 1997; Novotny et al., 2005). Stream studies (Brick and Moore, 1996; Jones et al., 2003; Roberts and Wilch, 2005) have indicated diurnal cycling of many hydrological parameters,

including pH, specific conductance, water temperature and turbidity (proxy for suspended solids). Diurnal changes have been shown to be robust and reproducible, having been documented in many streams (Scatena, 2001; Talling and Lemoalle, 2006). Chemical composition influence many micro-habitat changes under different environmental conditions that have aquatic organisms and aquatic vegetation. Many stream dwelling insects exploit the physical characteristics of streams to support themselves and this may be made difficult following sharp

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changes in diurnal cycles of temperature, conductivity and dissolved oxygen hereafter referred as DO. Species with larger diurnal migrations (e.g. *Daphnia* spp, *Acartia* spp) in the marine environment and lakes migrate into shallow water layers before sunrise and return to deeper layers around sunset (Ringelberg, 1999).

The phenomenon of diurnal variations has been the subject of considerable research interest in aquatic ecology before 1930 (Wiebe, 1929) and has been continued to present time (e.g. Jones et al., 2003, Marshall, 1997; Nimick et al., 2005; Tockner et al., 1999; Talling and Lemoalle, 2006). In the earlier studies attention was drawn to diurnal variations in ponds and this interest spread to cover swamps, ditches and streams in later years. Subsequent studies have explored the patterns of diurnal changes in streams (Lundquist and Cayan, 2002) and dams (Magadza, 1997; Marshall, 1997; Moyo, 1997) largely in upland regions. Lundquist and Cayan (2002) studied diurnal changes in the unimpaired rivers of western United States and suggested extending the studies to rivers impacted by human activities. Though, diurnal cycles are known to be important in controlling oxygen and carbon dioxide dynamics, the study of diurnal dynamics in tropical rivers has been fairly limited.

Lowland streams and rivers in semi-arid areas are little studied (Mazvimavi, 1998, 2003; Tafangenyasha and Dzinomwa, 2005; Thoms and Sheldon, 2000) and yet the concentration of human activities may have significant impacts on them. In the semi-arid areas of Zimbabwe, work on diurnal variations has been restricted largely to dams (Moyo, 1997) due to the need for maintaining drinking water quality. Thoms and Sheldon (2000) and Mazvimavi (2003) noted that contemporary ecosystem theories developed on temperate perennial streams may not explain river system functioning in semi-arid lowland river systems, hence, the need to conduct studies of a similar nature in a local condition. A lack of detailed information required to conceptualize structure and function and implications for management of lowland rivers has also been conceived (Mazvimavi, 1998, 2003; Mugabe et al., 2007, Tafangenyasha and Dzinomwa, 2005; Thoms and Sheldon, 2000).

Most lowland rivers in the semi-arid areas of Zimbabwe are threatened by siltation and in urgent need of conservation (Magadza, 1984, 1992). Like most rivers in the world the Runde River is a sink for sediment, organic matter and nutrients during flooding and runoff from agriculture. Previous studies have shown large and reproducible 24 h diurnal variations in temperature (Marshall, 1997), DO (Marshall, 1997), pH (Marshall, 1997), conductivity (Marshall, 1997), and nutrients (Marshall, 1997) for large dams. Diurnal variations in nutrients and physico-chemical variables have been observed to fluctuate significantly on a daily cycle but the extent of this phenomenon occurring in the lowland rivers has not been thoroughly investigated within Zimbabwe. The key questions in this study include: (1) How does agricultural development influence diurnal changes of a river in

in pristine conditions? (2) Can characteristics of the diurnal change be used to distinguish between reference conditions and impact areas below agricultural development? (3) Diurnal changes should provide a measure of a different type of information useful in predicting sensitivity of streams to land use changes, disturbance or restoration activities. Short-term variations in concentrations in stream chemistry due to day-night DO fluctuations could significantly affect a stream's capacity to transport nutrients.

It is unclear to what extent conditions in the river become more hospitable because of temperature changes during the day and night. Hypothesized causes of diurnal cycles include stream flow variation, ground-water exchange, temperature-and pH-dependent sorption reactions, precipitation and dissolution of solid phases, redox cycling and biotic uptake (Jones et al., 2003). Tockner et al. (1999) noted the role of temperature as a major determinant of floodplain ecology. The complexity of expansion-contraction events may have a bearing on habitat heterogeneity and functional processes (Tockner et al., 1999). Diurnal cycle's concentrations might fluctuate from low to high levels. Species capture roughly equally wide "slices" of environmental conditions, as illustrated by their "niche widths."

MATERIALS AND METHODS

Study area

The study area is situated within the Runde watershed an area of intensive commercial farming characterized by the Hippo valley and Triangle sugarcane estates, approximately 445 km south of the capital Harare (Figure 1). The sugarcane estates are located between 20°00'S and 32°00'E, 500 m a.s.l. in the southern lowveld of Zimbabwe. The Runde River catchment is approximately 41000 km² in area (Mugabe et al., 2003). The Runde River strongly influences the southeast lowveld and the nation's everyday life and long term economic development. The lowveld predominant land use is the intensive production of sugarcane under irrigation. Irrigation is facilitated by the use of canals and overnight storage dams that enable flood irrigation of the sugarcane. Chemical fertilizers, floodplain irrigation, canal irrigation and diesel-powered riverbed sand abstraction in the lowveld have enabled the expansion of intensive agriculture into zones with nutrient-limited soils and severe soil moisture deficits, effectively changing the distribution of high potential agricultural lands. The access and manipulation of the region's hydrologic resources has profound environmental consequences and may lead to unforeseen resource degradation. Lands traditionally used for grazing herds are now interrupted by islands of intensive agriculture and agricultural runoff to the rivers may be influencing water quality changes.

The Runde River captures agricultural runoff from the intensive agricultural areas and is thought to be influenced by fertilizers and sewage. The Runde catchment includes the area drained by the Chiredzi, Mtirikwi, Tokwe and Runde Rivers (Figure 1). The three tributaries, namely the Chiredzi, Mtirikwi and Tokwe enter the Runde River in areas impacted by agricultural development and constituting the test stations (Figure 2). Station 7 located on the upstream Runde River (Figure 2) constituted the control site. Station 4 (Figure 2), the test station was located within 5 m downstream of an outfall (discharge station) on the Runde River. Outfall may designate the point of release (discharge) of

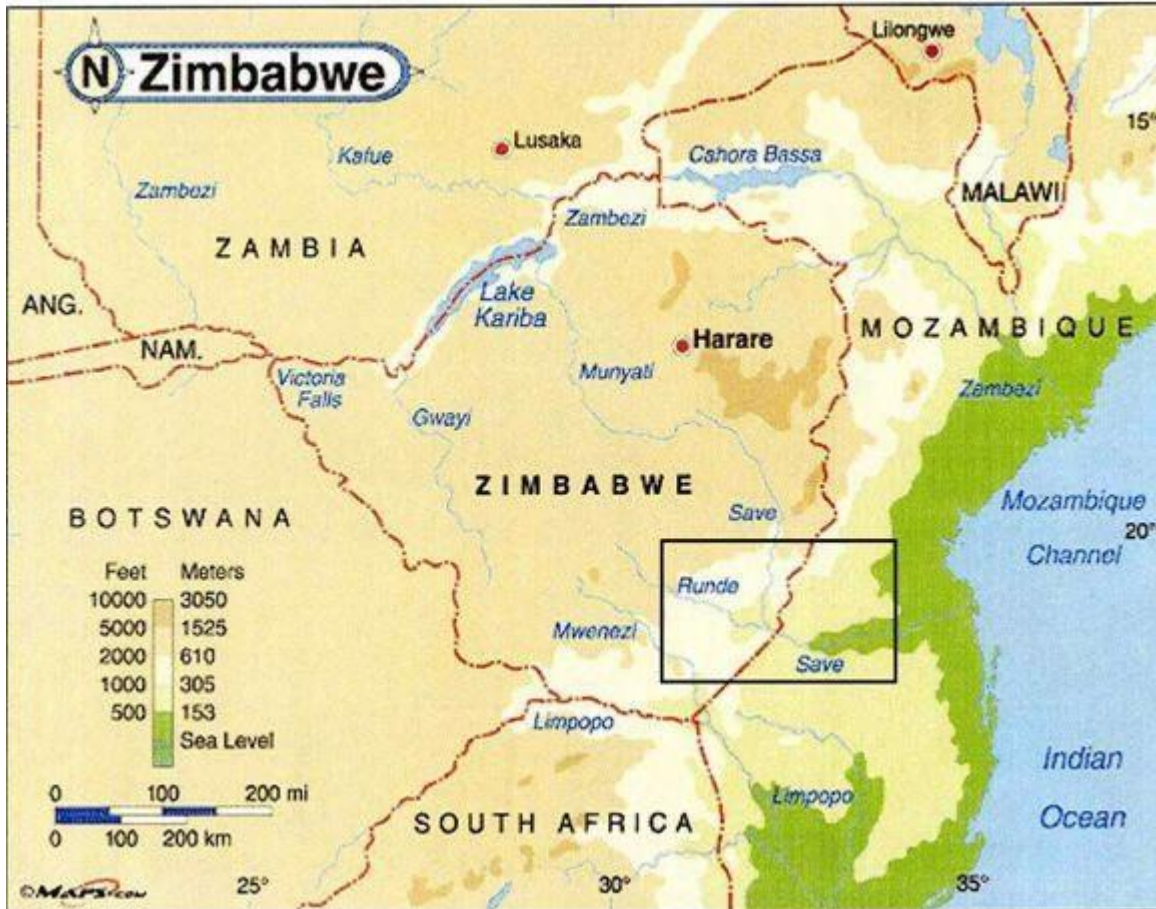


Figure 1. Map showing the situation of the study area in South east Zimbabwe.

wastewater to receiving Runde River water. The outfall conveys effluent discharged into the Runde River from the sewage treatment facilities and runoff from the sugarcane fields and comprises an unlined open trench that starts in the sewage treatment facilities and passes through the sugarcane fields before entering a natural wooded buffer zone at which point it empties into the Runde River. The drainage ditch is approximately 3 km long. The drainage ditch varies in width from 1.5 to 2 m. The depth of the drainage ditch varies from 0.5 to 1.0 m. The outfall is approximately 2 m wide and 2 m deep. Input from various environmental and regulatory agencies was a key component in the final selection of the final outfall location. Figure 3 shows that the Runde River mean monthly flows vary greatly between 0 m³/s in the dry months and 60 m³/s in the wet months and mean daily flows (at severe rain event) may be much larger. The study area is underlain by granite and gneiss, but in the east volcanics and rocks of Karoo age form the geological template. The tributaries of the Runde River start in areas where the substrate is predominantly sandy with some rocky outcrops. The Runde River is characterized by sandy and gravelly substrate. The riverbanks of the Runde River are lightly wooded with riparian vegetation of variable height. Water hyacinth and a variety of blooming algal species maybe seen in some of the most polluted sites of the Runde and lower sections of tributaries passing through the intensive agricultural areas. This study area was selected because it covers a wide range of typical Zimbabwean land uses, including sugarcane production at Triangle sugar estates and Hippo valley estates and sugarcane processing mills at Hippo valley and Triangle (Figure 2). Seasonal trends are clear in both the

precipitation and the flow regime (Magadza et al., 1993). Severe droughts have the effect of concentrating nutrients, shrinking and fragmenting aquatic habitats while excessive cyclonic rainfall has the effect of increasing river flows and diluting nutrients to trace levels. Drying up of the river waters is a natural variable hydrologic condition. Surface water levels vary dramatically over time, with dry periods characterized by extreme habitat shrinkage and fragmentation. The flow regime is characteristic of semiarid watercourses; extremes of discharge occur with low winter baseflows and occasional high summer flood flows. Dube (2002) and Dube and Jury (2000) have reported on the impacts of drought, drought forming processes and atmospheric circulation systems that affect the southeastern African region precipitation events.

The study area lies below the 600 m contour and is hot and semi-arid. The climate of the lowveld is hot and wet from mid-November to April, cool and dry from May to August and hot and dry from September to mid November. The temperatures range from 8.1°C in July to 50°C in January, with a mean of 24°C to 36°C (Figure 4). A significant feature of the rainfall is its unreliability, both in terms of quantity and duration. The variation from year to year is so great that the annual rainfall can range from 20 to 200% of normal. The rainfall varies considerably from a low level of 92.7 mm in 1991/92 to a high level of 834.0 mm in 1977/78 (Figure 5). Tropical depression and cyclone activity can produce unprecedented amounts of rainfall and floods as recorded in March 2000 across the eastern African subcontinent (Dube, 2002; Dube and Jury, 2000; Heritage et al., 2001). The variations in habitat conditions make the environment naturally challenging for organisms and this

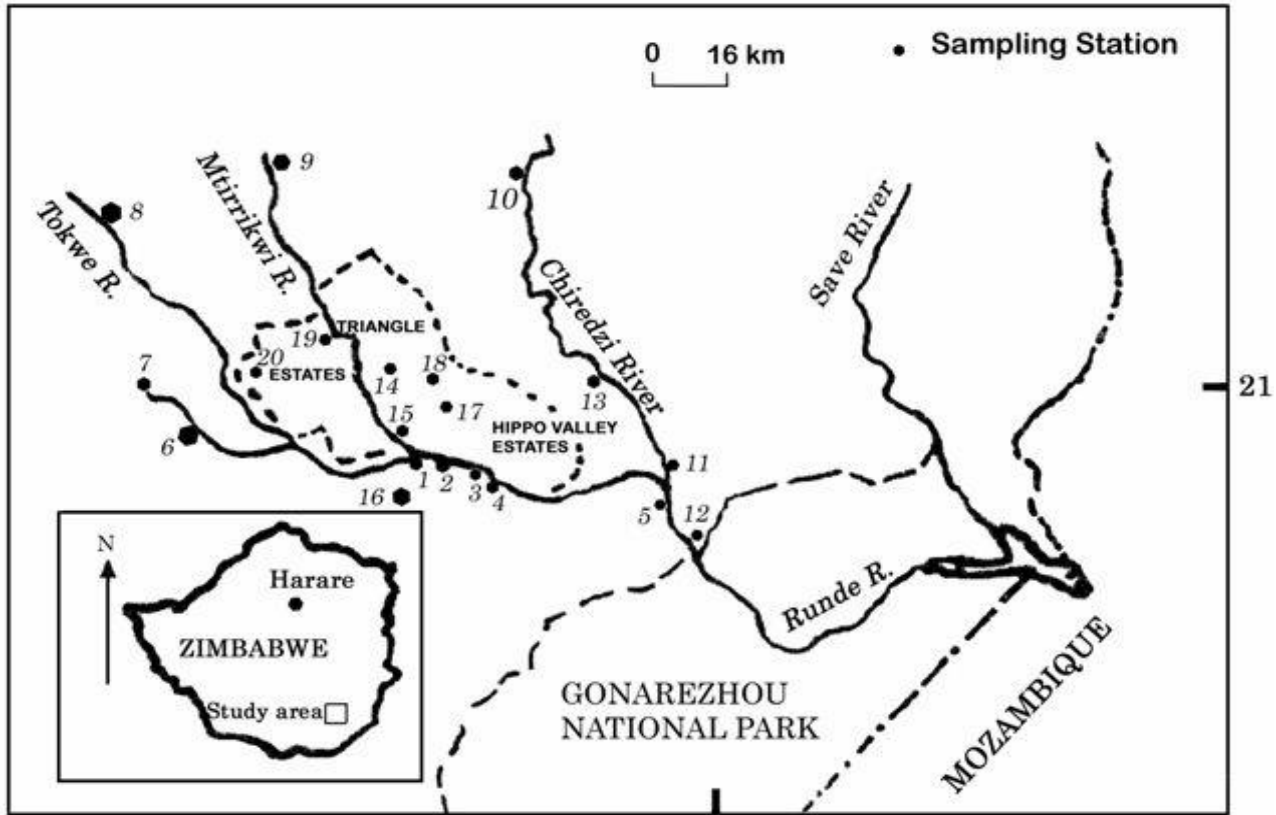


Figure 2. Simplified map of the southeast lowveld river system showing the different sampling stations along the studied watercourses. Diurnal change observations collected on the Runde River at stations 7 and 4, the remainder of the stations listed on the map were used in describing the hydrology of the study area.

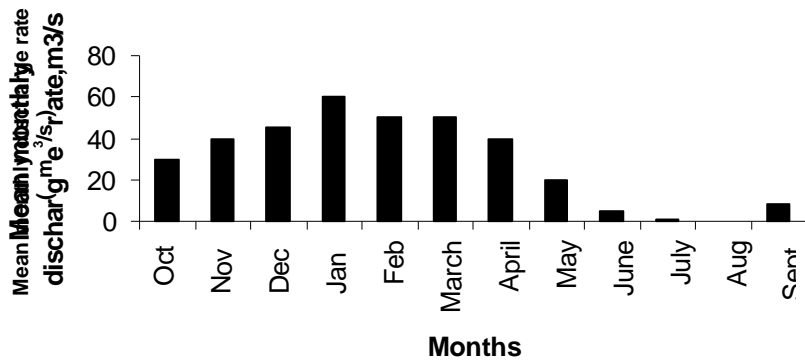


Figure 3. The change in mean daily discharge rate, m³/s in the Runde River.

situation may be exacerbated by the impacts of discharges of nutrients. Diurnal variations measure the living conditions of aquatic organisms by indicating magnitudes of variations of the physicochemical conditions in river water over 24 h.

Sampling

Stratified sampling in which the rivers were subdivided according to land use zones was undertaken. Diurnal cycles were monitored on

sites above and below outfall on the Runde River, respectively. This study was part of a wider project to study the influence of activities on the Runde River water quality. The investigation of diurnal variations was conducted on the Runde River on 7th July 2005 and this was followed by investigations of diurnal variations in both the reference station and test station on 7th July 2006 which gave almost similar results. Station 4 was the test station and station 7 was the control station (Figure 2). The stations situated above the outfall and below the outfall were chosen for their accessibility and

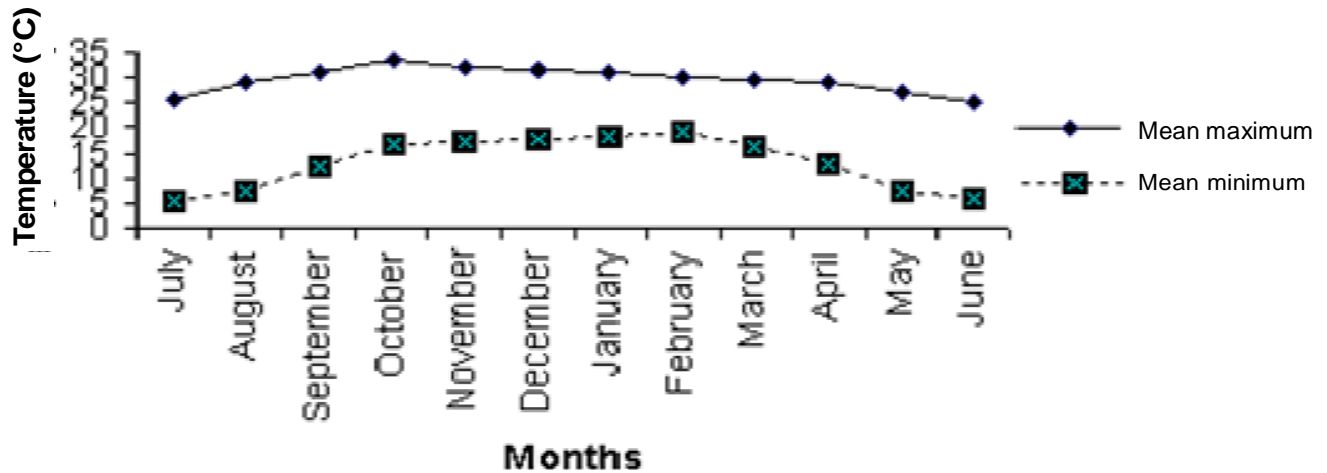


Figure 4. Mean maximum and minimum temperatures at Gonarezhou National Park (n = 11).

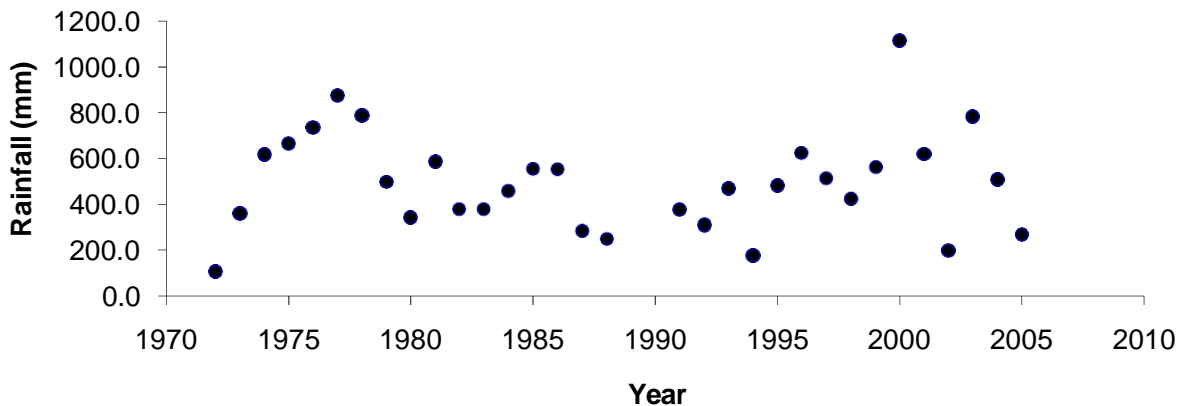


Figure 5. Long-term annual rainfall record for the Gonarezhou National Park (n = 31, CV = 50%).

condition. The test station was situated within 5 m of the outfall to enable effective mixing of outfall with river water. By measuring diurnal changes on one day in the hydrological year the data should provide links to the missing description of the aquatic ecology. Diurnal changes in the water temperature, pH, DO concentration, light penetration, conductivity and total dissolved solids (TDS) in the water column were determined by direct observations to investigate the relationship between agricultural development and river water quality at 2 h intervals for 24 h. At both study stations each variable was measured latitudinally at 0 - 15 cm at 3 spots around a site. By measuring diurnal changes on one day in the hydrological year the data should provide links to the missing description of the aquatic ecology.

The temperature of the water and the concentration of dissolved oxygen were measured with YSI DO meter. Measurements of water temperature, pH, DO concentration, light penetration, conductivity and TDS were undertaken with portable measuring devices (WTW). The data were organized into groups by putting the two study stations (7 and 4) into two groups (upstream and downstream) that can be interpreted more accurately. The first study station was located upstream of the effluent sources and was meant to be the control station indicating the unimpaired state of the rivers. The second study station was located downstream of the effluent

sources and was meant to indicate the effect of agriculture on the Runde River.

The maximal and minimal points critical in sustaining fish species in semi-arid lowland conditions has not been studied (Balarin, 1986). The maximal and minimal points on the daily DO concentration were chosen to represent the extremes of diurnal variation. Diurnal changes in the water column were determined by direct observations to investigate the relationship between land use and water quality at 2 h intervals for 24 h. Coefficient of determination was used to compare regression lines from night to day. A significance value $p < 0.05$ (two tailed) was used to test the data.

RESULTS

Diurnal variation of the many water quality variables measured on 7th July 2005 and 2006 at stations above and below outfall on the Runde River include temperature, DO concentration, DO saturation concentration, pH, conductivity and TDS (Figures 6 and 7) showed almost the same pattern of change.

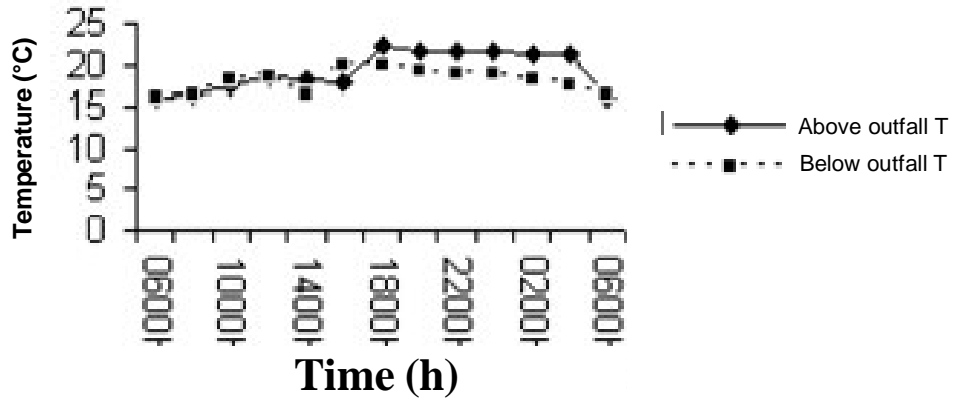


Figure 6a. Diurnal variation in temperature at sites above and below outfall on 7th July, 2005.

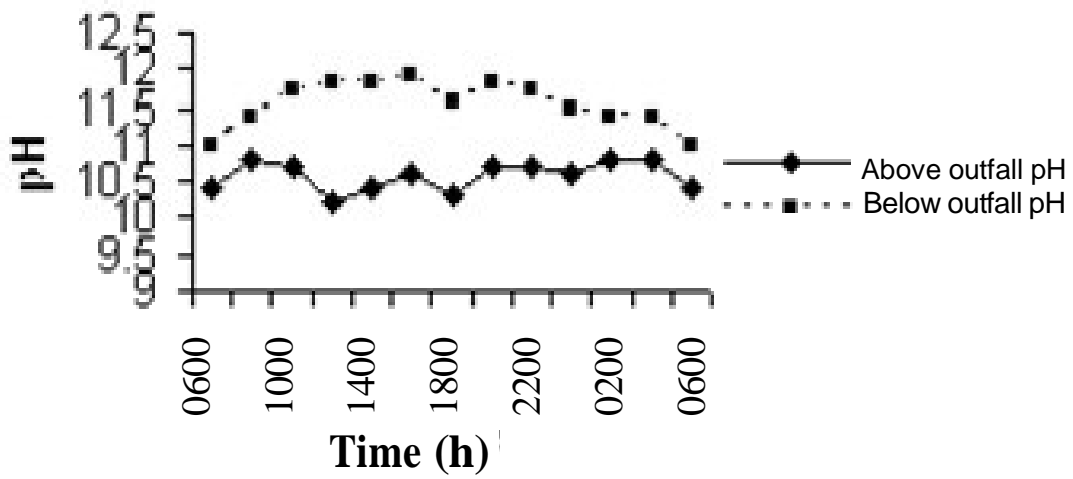


Figure 6b. Diurnal variation in pH at stations above and below outfall on 7th July, 2005.

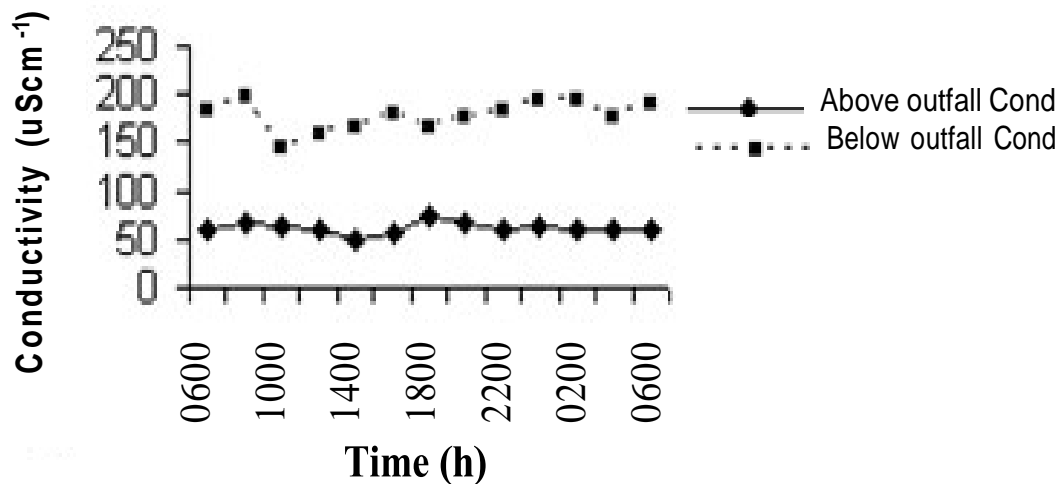


Figure 6c. Diurnal variation in conductivity at stations above and below outfall on 7th July, 2005.

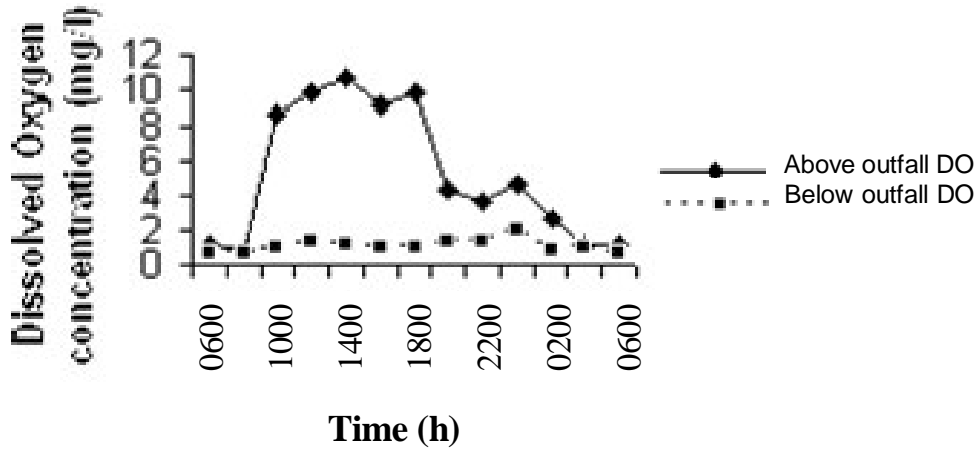


Figure 6d. Diurnal variation in DO concentration at stations above and below outfall on 7th July, 2005.

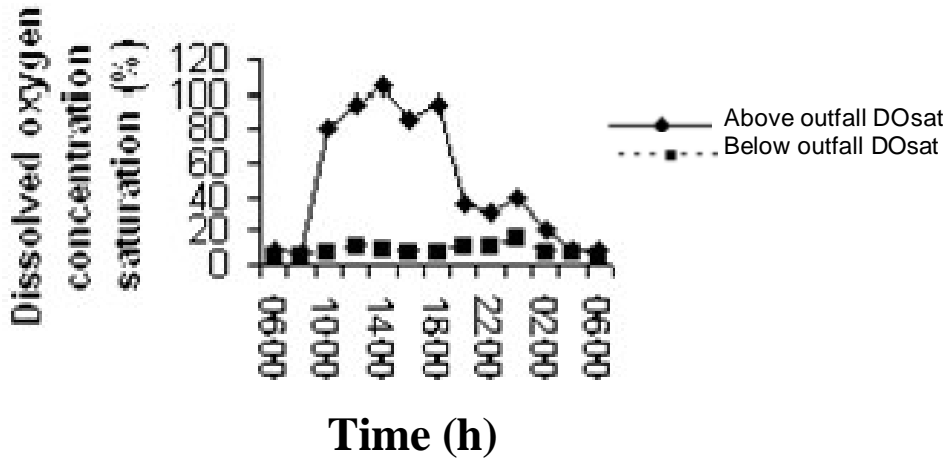


Figure 6e. Diurnal variation in DO concentration saturation at stations above and below outfall on 7th July, 2005.

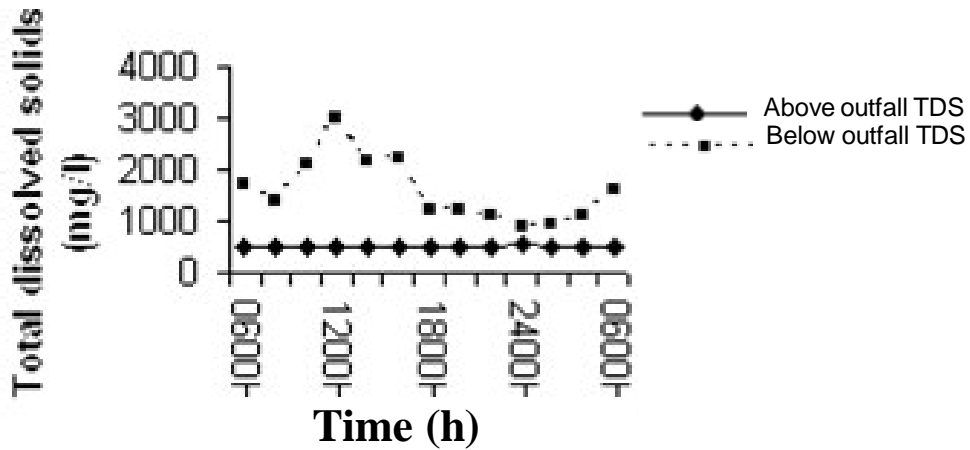


Figure 6f. Diurnal variation in total dissolved solids at stations above and below outfall on 7th July, 2005.

2005

Temperature

The station below the outfall shows a rapid increase in temperature and an early peak in temperature before the 1800 h (Figure 6a) time compared to above outfall temperature patterns.

Temperature measured between 1800 and 0600 h was almost the same at both outfalls. Separations in measured temperature at both outfalls were recorded between 0600 and 1800 h. The station below outfall recorded consistently higher temperatures than above outfall station.

PH

Measured pH levels fluctuate around 8.0 at the station below the outfall throughout the 24 h monitoring period (Figure 6b). At the station above the outfall measured pH fluctuate around 10.0 throughout the 24 h monitoring period. pH at the station below the outfall was consistently above that measured at the station above the outfall during the monitoring campaign.

Conductivity

Measured conductivity levels at the station below the outfall fluctuated between 150 and 250 uScm-1 at the station above the outfall (Figure 6c). Measured conductivity fluctuated between 100 and 40 uScm-1 at the station above the outfall.

DO concentration

Measured DO concentration showed a dramatic increase from 2.0 mg/l at 0800 h to 10 mg/l at 1400 h at the above outfall station (Figure 6d). The measured DO concentration declined dramatically from 10.0 mg/l at 1800 h to less than 2.0 mg/l at 0800 h at the above outfall station. Measured DO concentration below the outfall fluctuated around 2 mg/l during the 24 h monitoring campaign.

DO saturation concentration

The measured DO saturation concentration showed the same pattern as for the DO concentration fluctuation above the outfall (Figure 6e). DO saturation concentration increased from 20% at 0800 h to reach 100% saturation at 1400 h before declining dramatically to a saturation concentration of 20% at 0400 h at above the outfall station. DO saturation concentration fluctuated around 20% saturation concentration during the 24 h monitoring campaign at the station below the outfall.

Total dissolved solids concentrations

A spike in TDS concentrations was recorded at above the outfall station from 2000 uScm-1 at 0800 h to 3000 uScm-1 at 1200 h before it declined steadily to around 1500 uScm-1 at 0600 h (Figure 6f). TDS concentration fluctuated around 20 uScm-1 during the 24 h monitoring campaign.

2006

Temperature

Surface water temperature shows a tendency to increase from sunrise to a peak of 21.2°C at 1400 h at stations below the outfall (Figure 7a). At the station above outfall surface water temperature rises to a peak of 22.1°C before declining to 17°C and this is after surface water temperature below the outfall has peaked and declined. There is a decline in temperature after 1800 h to about sunrise. Above outfall waters have warmer conditions than after 1700 h.

pH

Below outfall pH level (Figure 7b) shows a tendency to rise from sunrise to a peak at 0900 h that stretches up to 2200 h and falling afterwards to 0600 h. Above outfall pH level is much lower than below outfall but shows a tendency to vary in wave-like pattern for the 24 h observation.

DO concentration

Above outfall DO concentration tends to rise at sunrise to a peak of 4.6 mg/l at 0800 h before falling to a low of 1.1 mg/l between 1100 to 1400 h (Figure 7c). DO tend to increase sharply from 0.9 mg/l at 1400 h to a high level of 9.9 mg/l at 2100 h before a drastic decline to 4.0mg/l at sunrise at stations above outfall. Slight variations are maintained at between 0.6 and 2.0 mg/l at stations below outfall.

DO saturation concentration

DO saturation concentration levels show the same pattern of dissolved oxygen variations between above outfall and below outfall as DO concentration levels (Figure 7d). DO saturation levels above outfall vary between 6.8 and 103.9% (Figure 7e). DO saturation levels below outfall vary between 4.5 and 15.6% (Figure 7e). DO concentration levels and DO saturation concentration showed the same patterns between the two years (Figures 7c-d and Figures 6 d-e).

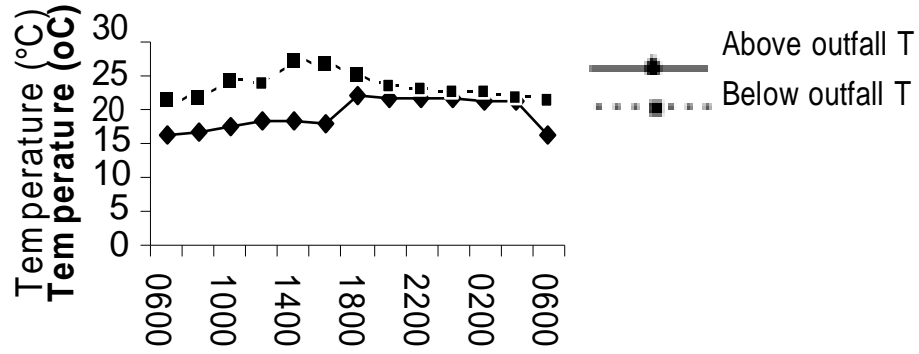


Figure 7a. Diurnal variation in temperature at stations above and below outfall on 7th July, 2006.

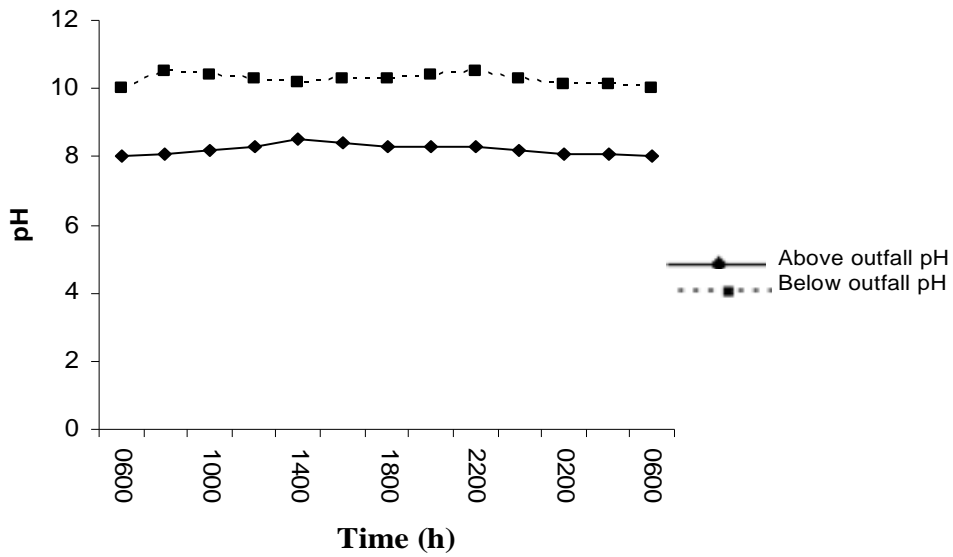


Figure 7b. Diurnal variation in pH at stations above and below outfall on 7th July, 2006.

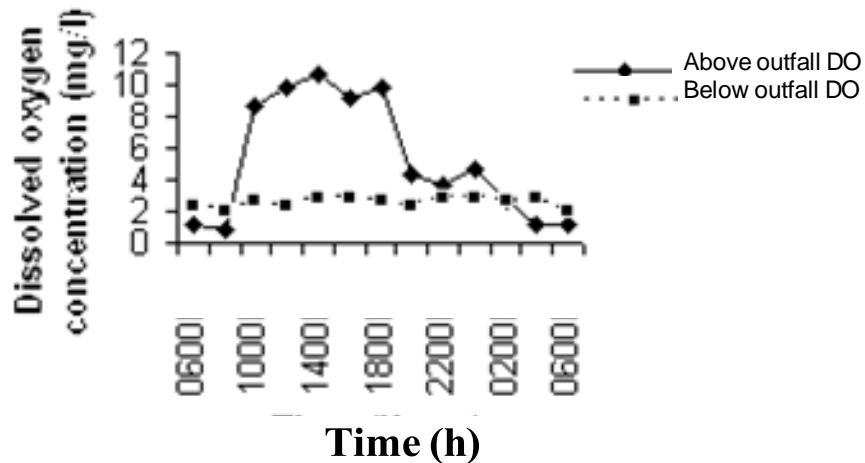


Figure 7c. Diurnal variation in DO concentration at stations above and below outfall on 7th July 2006.

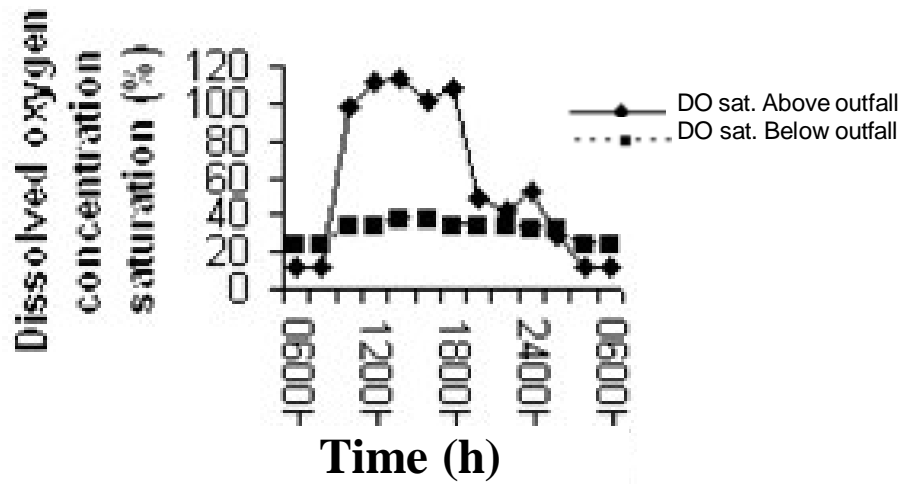


Figure 7d. Diurnal variation in DO concentration saturation at stations above and below outfall on 7th July, 2006.

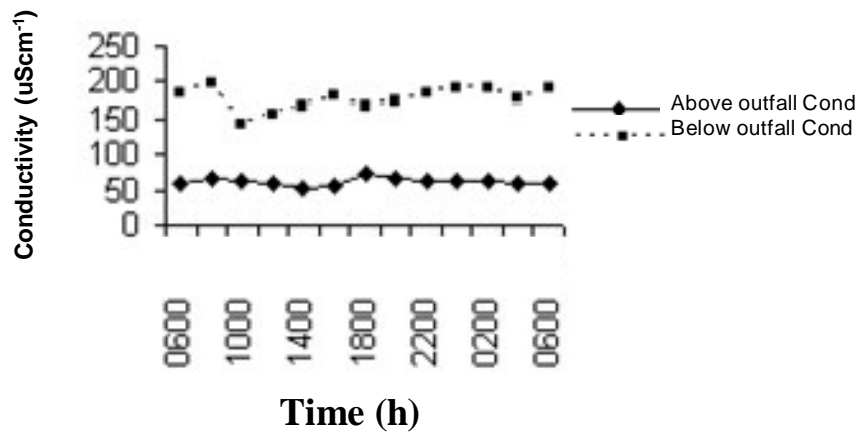


Figure 7e. Diurnal variation in conductivity at sites above and below outfall on 7th July, 2006.

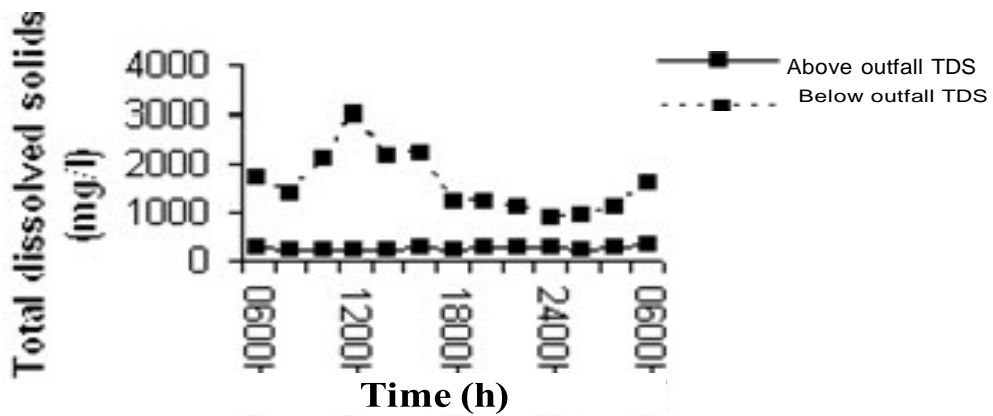


Figure 7f. Diurnal variation in Total dissolved solids (mg/l) concentration at stations above and below outfall on 7th July, 2006.

Conductivity

Above outfall conductivity (Figure 7e) rises from 184.4 μScm at sunrise to a peak of 200.0 μScm before falling to a low of 143 μScm at 1000 h. Conductivity levels below outfall shows a tendency to increase from 143.0 μScm at 1000 h to a high of 200.0 μScm at 2400 h that seems to be maintained to 0600 h. Above outfall conductivity levels tend to be maintained at 50.0 μScm for 24 h with slight variations of 66.9 and 73.8 μScm at 0800 and 1700 h, respectively. Below outfall conductivity levels are much higher than above outfall throughout the 24 h. Conductivity levels at station below the outfall in 2006 (Figure 7e) were greater than at station below the outfall and the same patterns were recorded in 2005 (Figure 6c).

TDS concentration

TDS maxima of 3000 mg/l at a station below the outfall occurs at 1200 and 0200 h and minima of 1800 mg/l occur at 2400 h (Figure 7f). TDS concentrations fluctuate daily around 500 mg/l (Figure 7f) at station above the outfall occur. Evening values show a gradual increase from sunset to midnight at stations below the outfall. Stations above outfall (Figure 7f) have TDS levels far below stations below the outfall (Figure 7f). The variations in the original measurements of the diurnal cycle above and below the outfall measured during 2005 and 2006 in the Runde River are shown in Tables 1 and 2.

Daytime and nighttime DO relationship

Marginal significant associations ($R^2 = 0.64$, $P = 0.03$, $n = 3$) between measured dissolved oxygen concentration (mg/l) and temperature ($^{\circ}\text{C}$) were demonstrated during the daytime only in station above effluent outfall (Figure 8). Insignificant associations ($P = 0.75$) between measured dissolved oxygen concentration (mg/l) and temperature ($^{\circ}\text{C}$) were demonstrated during the nighttime in the station above effluent outfall. This suggests that there was more DO concentration added during the day than at night at the station above the outfall. The coefficients of determination between DO concentration (mg/l) and temperature ($^{\circ}\text{C}$) for the daytime and nighttime were $R^2 = 0.35$ and $R^2 = 0.29$, respectively, below the outfall. The DO concentration addition to the daytime river water (Figure 8) may be explained by the process of photosynthesis. No significant associations were either found between dissolved oxygen and temperature and changes during the daytime and nighttime below the outfall.

DISCUSSION

Diurnal (24 h) fluctuations of temperature, DO

concentration, pH, conductivity and TDS measured at both control and test stations of the river (Figures 6 and 7) exhibited elevated levels at dawn and depressed levels overnight. Stations above the outfall show levels of pH, conductivity and total dissolved solids 2 - 3 fold lower than stations below the outfall. It is postulated that diurnal changes in the study area reflect complex interrelationships. The water temperature itself increases rapidly in the morning, peaks in the afternoon and decreases slowly overnight (Figures 6 and 7). Large variations in stream temperature occur probably due to the extreme annual range in air temperature and solar radiation typical of hot low-lying areas. DO concentration was greatest by day and least during the night. DO saturation concentration levels at the control station vary between

6.8 and 103.9% in July, 2006 and between 6 and 103% in July, 2005 during the day. DO concentration saturation levels at the test station outfall vary between 4.5 and 15.6% in July, 2006 and between 20 and 40% in July, 2005. The 24 h changes in the river water quality suggest fluctuations daily in response to cyclical environmental, biotic processes and anthropogenic factors. As a result, the chemical composition of the rivers may be variable, depending on time of day. Tockner et al. (1999) and Brick and Moore (1996) suggest that there is no one single factor responsible for diurnal variations.

At all stations, concentrations of DO concentration increased during the morning, reaching maximum values shortly after midday; concentrations then decreased to minimum values overnight. DO concentration is largely a measure of the eutrophic state of the river waters that may change during the day. Therefore, when taking oxygen measurements the time of day must be borne in mind because saturation can fall overnight when photosynthesis stops, or when the temperature rises as the higher the temperature the less the DO concentration water can hold in solution. The rates of supply of dissolved oxygen from the atmosphere and from photosynthetic inputs and hydromechanical distribution of oxygen may be counter balanced by consumptive metabolism of aquatic organisms.

DO levels may be reduced below those necessary for successful growth and reproduction of aquatic species. In extreme cases, the death of fish and other species and their subsequent decomposition can impose a further oxygen demand. The lethal conditions for aquatic life reported by Magadza (1997) and Marshall (1997) that occurred with high eutrophication status and complete depletion of DO concentration during the day time in Lake Chivero in Zimbabwe were not recorded in this study suggesting that the river conditions in the Runde River may not be severely threatened by organic loading. Oxygen supplies in the river water come from photosynthesis that requires light and is therefore most rapid in the surface water, and diffusion from the atmosphere. Morse (1981) suggests that temperature and DO concentration may be the most critical factors limiting the different distributions of the various species. However, the diurnal

Table 1. The variation in the original measurements (n = 3) for assessing the diurnal cycle above the outfall measured in the Runde River in 2005.

Time (h)	Above outfall T (°C)	Below outfall T (°C)	Above outfall DO (mg/l)	Below outfall DO (mg/l)	Above outfall Cond (mg/l)	Below outfall Cond (mg/l)
0600	16.1	21.1	2.3	1.1	58.4	184.4
	18.9	23.1	2.0	4.8	64.1	137.2
	13.3	19.1	2.6	2.6	52.7	137.2
0800	16.5	21.6	2.0	0.9	66.9	198.0
	19.3	23.6	2.3	1.3	67.4	245.2
	13.7	19.6	1.7	0.9	72.6	150.8
1000	17.4	24.1	2.7	8.7	61.7	143.0
	20.2	26.1	3.0	5.0	56.0	190.2
	14.6	26.1	2.4	12.4	67.4	95.8
1200	18.5	23.9	2.4	9.9	58.4	16.8
	21.3	25.9	2.7	13.6	64.1	30.4
	16.1	21.9	2.1	6.2	52.7	64.0
1400	18.2	27.1	2.8	10.6	50.7	165.8
	21.0	29.1	3.1	14.3	56.4	170.5
	15.4	25.1	1.8	11.9	45.0	118.6
1600	17.8	26.7	2.9	9.1	56.0	180.6
	20.6	28.7	3.2	12.8	61.7	133.4
	15.0	28.7	2.6	5.4	50.3	227.8
1800	22.1	24.9	2.7	9.8	73.8	166.5
	24.9	26.9	3.0	13.5	79.4	214.0
	19.3	22.9	2.4	6.5	68.1	719.3
2000	23.4	23.4	2.4	4.4	67.1	174.9
	26.2	21.4	2.7	8.1	72.8	222.1
	20.6	23.4	2.1	0.7	66.5	127.7
2200	23.1	23.1	2.8	3.7	61.6	182.9
	25.9	25.1	3.1	7.4	67.3	135.7
	20.3	21.1	2.5	0.9	55.3	230.1
2400	22.4	22.4	2.8	4.6	62.0	192.0
	25.2	24.4	3.1	8.3	67.7	239.2
	19.6	20.4	2.5	1.0	56.3	144.8
0200	22.3	22.3	2.7	2.7	61.0	192.0
	19.5	20.3	3.0	6.4	66.7	144.8
	25.1	24.3	2.4	0.9	55.3	239.2
0400	21.5	21.5	2.8	2.8	60.4	177.8
	18.7	23.5	2.5	6.5	54.7	225.0
	24.3	19.5	3.1	0.9	66.1	130.6

Table 2. The variation in the original measurements (n = 3) for assessing the diurnal cycle below the outfall measured in the Runde River in 2006.

Time (h)	Above outfall T(°C)	Below outfall T(°C)	Above outfall DO (mg/l)	Below outfall DO (mg/l)	Above outfall Cond (mg/l)	Below outfall Cond (mg/l)
0600	16.1	16.0	1.1	0.7	58.4	184.4
	18.5	17.4	4.9	1.1	64.1	200.1
	13.3	14.6	2.7	0.3	52.7	168.7
0800	16.5	16.5	0.9	0.6	66.9	198.0
	13.7	17.9	4.7	1.0	61.2	213.7
	19.3	15.1	2.9	0.2	72.6	182.3
1000	17.4	18.1	8.7	1.0	61.7	143.0
	20.2	16.7	4.9	0.6	67.4	127.3
	14.6	19.5	12.5	1.4	56.0	158.7
1200	18.2	16.4	9.9	1.3	58.4	156.8
	15.4	17.8	6.1	1.7	64.1	172.5
	21.0	15.0	13.7	0.9	52.7	141.1
1400	17.8	19.8	10.6	1.2	50.7	165.8
	20.6	18.4	14.4	1.6	45.0	150.1
	15.0	21.2	6.8	0.8	56.4	181.5
1600	22.1	19.8	9.1	1.0	56.0	180.6
	24.9	21.2	5.3	1.4	61.7	196.3
	24.9	18.4	12.9	0.5	50.3	164.9
1800	21.6	19.3	9.8	1.0	73.8	166.5
	24.4	17.9	13.6	0.6	79.5	182.2
	18.8	20.7	6.0	1.4	68.1	150.8
2000	21.6	18.7	4.4	1.3	67.1	174.9
	18.8	17.3	8.2	1.7	72.8	190.6
	24.4	20.1	0.6	0.9	61.4	159.2
2200	21.5	18.7	3.7	1.4	61.6	182.9
	24.3	20.1	1.2	1.8	55.9	198.6
	18.7	17.3	7.5	1.0	67.3	167.2
2400	21.3	18.0	4.6	2.0	62.0	192.0
	24.1	19.4	8.4	2.4	67.7	176.3
	18.5	16.6	1.1	1.6	62.0	207.7
0200	21.1	17.4	2.6	0.9	61.0	192.0
	23.9	16.0	6.4	1.3	55.3	207.7
	18.3	18.8	1.2	0.5	66.7	176.3
0400	16.1	16.5	1.1	0.7	60.4	177.8
	13.7	15.1	4.9	0.3	54.7	193.5
	18.6	17.9	2.7	1.1	66.1	162.1

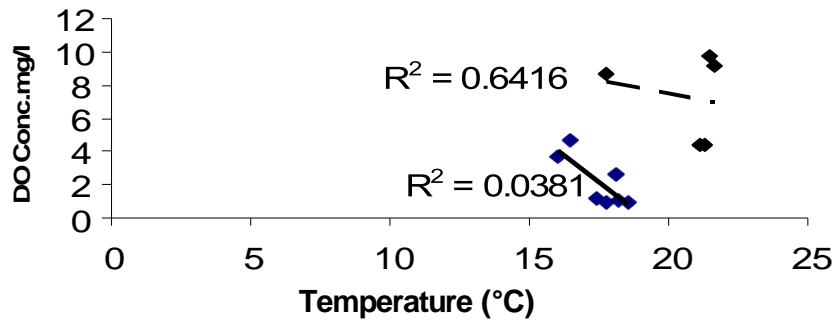


Figure 8. Correlations between daytime above outfall dissolved oxygen concentration (mg/l) and temperature (°C) ($R^2 = 0.64$, $P = 0.03$) and nighttime dissolved oxygen concentration (mg/l) and temperature (°C) ($R^2 = 0.04$, $P = 0.75$), in two sites. Regression lines show levels during the daytime (dashed line) and nighttime (solid line). $P = 0.058$ for a comparison between regression lines.

cycles of pH, conductivity and total dissolved solids in the upstream of effluent outfalls and downstream of effluent outfalls suggest that diurnal patterns are rarely a simple function of light intensity but of complex factors. Figure 6d shows that the increases in DO may be related to solar radiation and its decline to consumption by aquatic organisms. Bonachela et al. (2007) found that DO dynamics was mainly depended on photosynthetic activity and the environmental factors and management practices controlling it, presence/absence of aquatic vegetation and trophic status.

The Runde River waters exhibit wide variations in relative acidity and alkalinity, not only in actual pH values but also in the amount of dissolved material producing the acidity or alkalinity. Since lethal effects of most acids begin to appear near pH 4.5 and of most alkalis near pH 9.5 (Stumm and Morgan, 1996), buffering can be of major importance in the maintenance of life. pH has a direct affect on organisms and an indirect effect on the toxicity of certain other pollutants in the water (Environmental Protection Agency, 1972). A high pH of water in a stream or pond may indicate that it has drained from a limestone area, or associated with liming agricultural lands and be associated with a large mollusk population. The animals, which require calcium to form their shells, are often absent from acid water. The pH of water is important because many biological activities can occur only within a narrow range (Environmental Protection Agency, 2000), so any variation from the range could be fatal to a particular organism. The Runde River site below the outfall shows substantial increases in pH, DO concentration and DO saturation concentration during the day and decreases at night, in response to changes in relative rates of aquatic photosynthesis and respiration. Environmental Protection Agency (1972) suggests that the buffering capacity of natural water is also important because it determines the effect of acid precipitation. Environmental Protection Agency (1972) also suggests that fish and many other organisms are unable to survive large

drops in pH. Trout are especially sensitive to decreases in pH, sudden acid inputs to pH below 4.5 - 5.0 can kill fish (such as spring runoff from melting snow) (Environmental Protection Agency, 1972). The pH recorded in this study ranged between 8.2 - 11.9 and these pH figures are above the Environmental Protection Agency guidelines suggesting alkaline conditions.

Conductivity maxima of 200 μScm^{-1} at a station below the outfall occur at 0600 and 0200 h and a minimum of 150 μScm occurs at 0900 h. Daily fluctuations at a station above the outfall occur around 50 μScm . Diurnal cycles of conductivity in the water column give an indication of the amount of ionisable substances dissolved in it, such as phosphates, nitrates and nitrites which are washed into streams after fertilizer is applied to surrounding fields or are present in sewage treatment installations. Most organic substances present in sewage are not ionisable and so do not affect conductivity because many are present as solid or suspended particles (Ottoway, 1980). Wetzel (2001) suggests that once decay begins, they start to break down to inorganic, ionisable substances (nitrate, nitrite, phosphate).

The fluctuations represented by elevated total dissolved solids occur near sunrise, followed by an increase throughout the day, with lowest values occurring near midnight. Diurnal changes monitored at both the control and tests stations on the Runde River show the inherent fluctuations of the characteristics over 24 h in temperature, dissolved oxygen concentration, pH, conductivity and total dissolved solids.

Simultaneously measured DO concentration and temperature values were closely correlated with temperature during the daytime above the outfall (Figure 8). Insignificant and almost identical regression lines between DO concentration and temperature were noted during the nighttime below the outfall. Below the outfall oxygen demanding wastes may reduce oxygen levels in the water column to a low level. Morse (1981) observed that diurnal patterns are rarely a simple function of light

intensity but of complex factors and that the observed cases of diurnal variations in this study do not belong to a rare category.

The diurnal variation may be explained partly by mechanisms related to stream processes, and partly by the diurnal variations in solar radiation (Morse, 1981). This study indicates that fluvial conditions characterized by fluctuations in diurnal changes may be a strong signature to catchment activities and need to be looked at in conjunction with other fluvial measures such as flow rate, depth and channel discharge that may also be naturally challenging to aquatic organisms.

Conclusion

Both the reference sites and test sites show diurnal variations but do not tend to show wide shifts in magnitude of diurnal variations between the years. Diurnal variations of river water may reflect complex biogeochemical signatures of catchments and these can be used with caution to elucidate the dominant pathways of impacts of agricultural development on river water quality. However, the diurnal variation of water quality variables may play a role in the oxygen and carbon dioxide dynamics essential in the maintenance of ecosystem processes. Diurnal cycles in the composition are in-situ measured and compared to assess the impact of human interferences. The diurnal dimension of the composition may be of large relevance for the aquatic ecosystem. Such measurements are sparse for similar conditions and mostly focus on dams. The measuring conditions and the sample size however, are very limited due to scarce resources, hampering clear conclusions. The data presented strengthens the relevance of testing of the significance of e.g. rejecting the hypothesis of constant concentrations in streams.

The key questions in the paper focus on linking measured composition to the agricultural development in the areas discharging to the measurement station. These questions make sense, particularly when aiming at relevance for water management. Catchment land use includes commercial sugarcane production under irrigation. Agricultural runoff is channelised to the Runde River. Some overland flow finds its way to the Runde River through non-point sources. The major sources of runoff carried by the Runde River are domestic effluent, agricultural waste and sewage which transport the critical elements in the chemical composition constraining locations in being a suited habitat for key species.

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