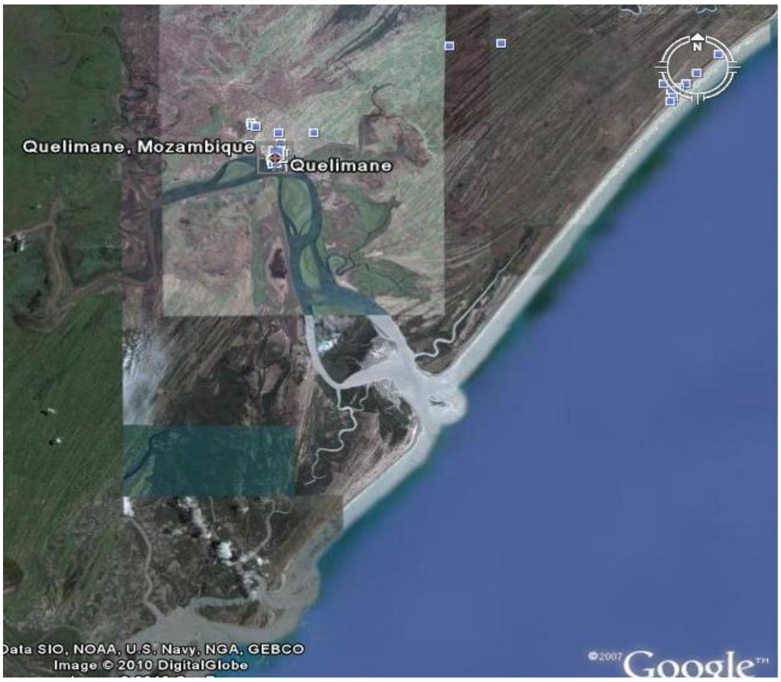
Dissolved Oxygen and Biochemical Oxygen Demand in the waters close to the Quelimane sewage discharge.



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Abstract

The River dos Bons Sinais Estuary is one of the most important estuaries in the central region of the Mozambican coast. It is situated between the confluence of Cuácua and Licuári rivers and the Mozambican Channel in the Indian Ocean. The climate is subtropical with the rain season generally from November to April. The domestic wastes from the city of Quelimane are discharged directly into the Bons Sinais Estuary and across from the city there is industrial aquaculture activity. The estuary is also the way of entrance to the port of Quelimane, 20 km away from the ocean.

The aim of this study was to analyze the dissolved oxygen and the biochemical oxygen demand in the port of Quelimane, where the discharge of municipal sewage is entering the estuary. BOD indicates the amount of organic matter present in the water. Therefore, a low BOD is an indicator of good quality water, while a high BOD indicates polluted water.

The results found during the measuring period indicate that during August dissolved oxygen values were more than critical the value of 2 mg L^{-1} whereas during September and October dissolved oxygen had values lower than this critical value. The values of biochemical oxygen demand obtained are characteristic of unpolluted waters which suggest that the municipal effluents discharged into the estuary are negligible or are flushed away by the tides.

Contents

Chapter 1

Introduction

The city of Quelimane is situated at the margin of the River dos Bons Sinais Estuary (17° 52′ 35″ S, 36° 53′ 14″ E). River dos Bons Sinais Estuary is one of the most important estuaries in the central region of the Mozambican coast. It is situated between the confluence of Cuácua and Licuári rivers and the Mozambican Channel in the Indian Ocean (Figure 1. 1). The climate is subtropical with the rain season generally from November to April. The mean annual precipitation is around 1400 mm. The annual temperature average is around 25ºC with the lowest monthly temperature average (16ºC) in June. The margins of the Bons Sinais Estuary have large areas of mangrove forests and the estuary is a great source of marine resources, such as fish, crabs, and shrimps. It has several branches at both margins; in the southern margins some of the branches are interconnected forming small islands.

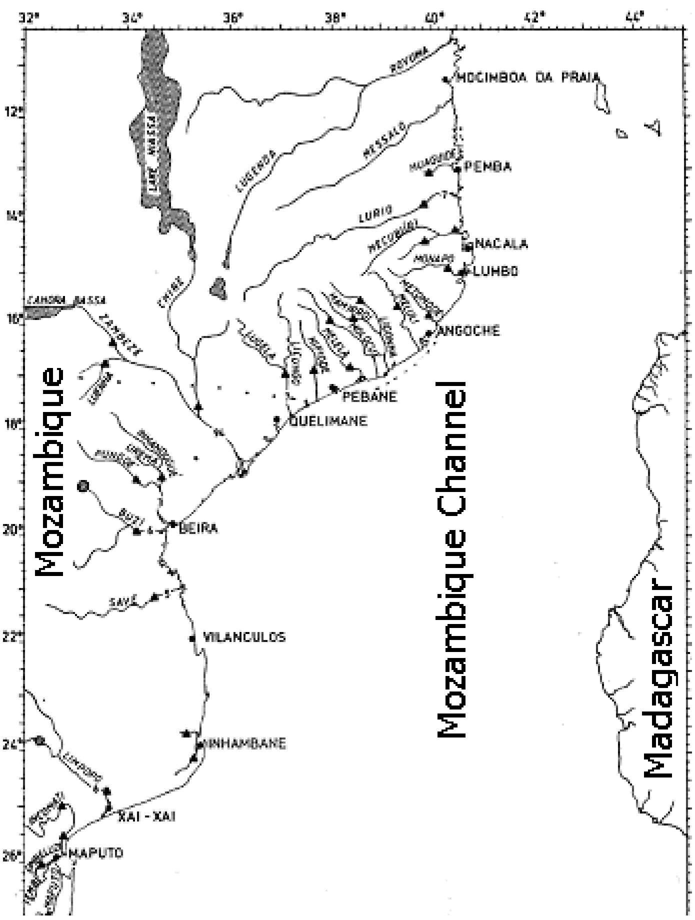


Figure 1.1. Map of the coast of Mozambique showing the main rivers and the location of Quelimane (with some modifications from Sete *et al.*, 2002)

Mozambique has 104 identified river basins, considering only catchments of rivers that flow into the Indian Ocean. The largest and most important is the Zambezi River in central Mozambique, the fourth longest river in Africa. North of the Zambezi River, important sources of water are the Rovuma (650 km), Ligonha, Lúrio (605 km), and Lugenda Rivers. South of the Zambezi River, the Pungue, Buzi (320 km), Limpopo, Save, and Komati Rivers are important resources (Figure 1.1). These rivers are associated with estuaries rich in natural resources directly exploited by local communities such as mangrove trees and many aquatic species.

The economic importance of estuaries translates into providing food for humans and animals, besides serving as a place of navigation, trade, rest, and leisure. Estuaries are preferential areas for occupation and urbanization due to its localization and socio-economic importance. From the ecological point of view, the importance of estuaries is translated by high diversity, being nurseries for many species of fish, crustaceans, molluscs, and birds. Estuaries provide food and habitat for a large range of organisms and for some migratory species the estuaries are mandatory crossing points between the marine and fluvial ecosystems. Estuaries are the main source of nutrients to the coastal region, as they receive and concentrate the material originated from their drainage basin and can receive significant contributions from human action. All this nutrient input makes estuaries among the most productive systems in the world with high rates of primary production and levels of autotrophic and heterotrophic biomass. This environment is vulnerable to the introduction of organic and inorganic compounds through domestic and industrial effluents.

The aim of this study was to analyze the dissolved oxygen and the biochemical oxygen demand (BOD) in the port of Quelimane, where the discharge of municipal sewage is entering the estuary. BOD is one of the most common measures of pollutant organic material in water. BOD indicates the amount of organic matter present in water. Therefore, a low BOD is an indicator of good quality water, while a high BOD indicates polluted water. The estuaries are susceptible to receive organic matter mainly from agriculture, domestic, and industrial wastes.

There are many studies in tropical estuaries in which the BOD has been used to evaluate the water quality (e.g. Jonas, 1997 in Chesapeake Bay; Tripathy *et al.*, 2005 in Andhra Pradesh, India). There are few published studies about Mozambican estuaries, examples are Graas and Savenije (2008) that studied the salt intrusion in the Pungue Estuary and Hoguane *et al.* (1999) who analysed the variation of temperature and salinity in the Ponta Rasa in Maputo Bay, but non on BOD measurements.

The domestic wastes from the city of Quelimane (Figure 1.2) are discharged directly into the Bons Sinais Estuary and across from the city there is industrial aquaculture activity. The estuary is also the way of entrance to the port of Quelimane, 20 km away from the ocean.

These things may affect the water quality of the estuary. The bathymetry of the Bons Sinais Estuary and the rivers are shown in Figure 1.2. The tidal range varies between less than 35 centimetres and about 500 centimetres during extreme spring tides. Tidal amplitudes vary over the year between 100 centimetres during neap tides and about 380 centimetres during spring tides.

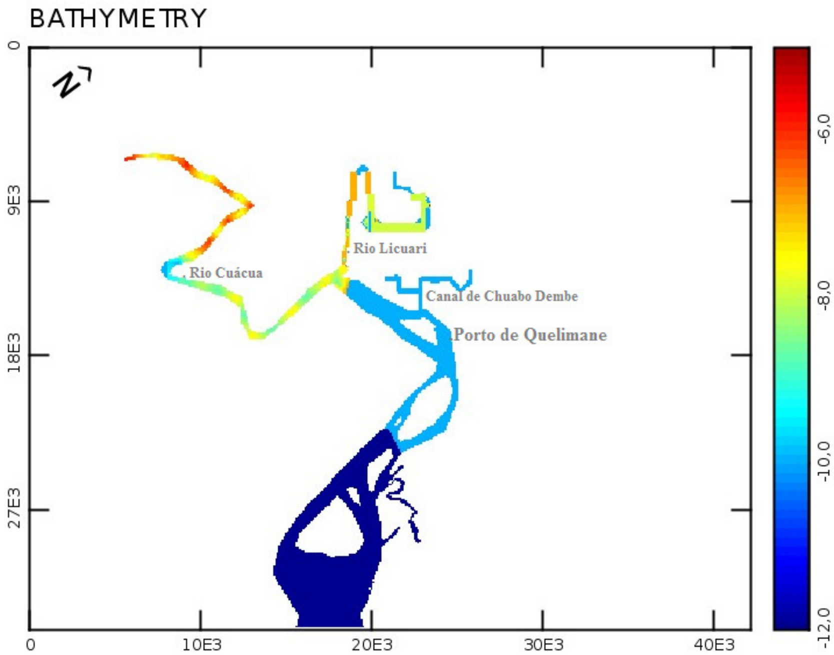


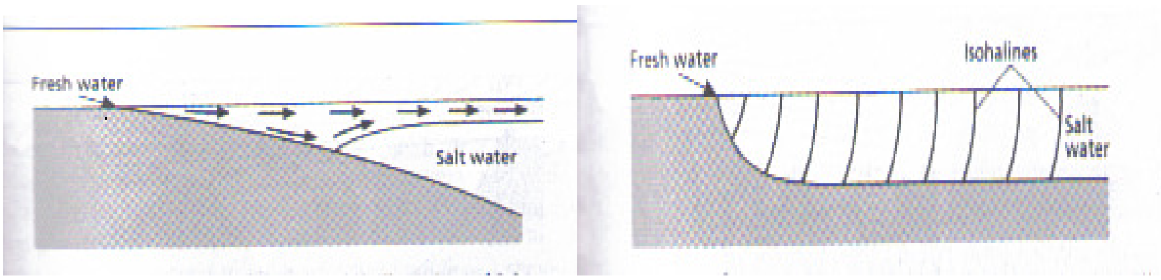
Figure 1.2. Esquematic representation of localization and bathymetry of the Bons Sinais Estuary.

Chapter 2. Oxygen in estuaries

2.1. Classification of estuaries

There are many definitions of an estuary, possibly the most satisfactory consider that an estuary is a semi-enclosed coastal body of water which has free connection to the open sea, extending into the river as far as the limit of tidal influence, and within which sea water is measurably diluted with fresh water derived from drainage (e.g. Dyer, 1997; Lazier and Mann, 2006). The estuary can be divided into five sectors: (1) Head, where the river flow dominates and the salinity is generally < 5, and the river currents are strong; (2) Upper reaches, which is the main area of mixing of fresh and saline water, the salinity is highly variable (5-18) and the currents can be negligible; (3) Middle reaches, where the flows are more dominated by tidal currents, the salinity varies between 18 and 25; (4) Lower reaches, here the tidal currents are faster, and the salinity is from 25 to 34; and (5) Mouth, where the estuary meets the sea, the tidal currents are strong and generally oceanic saline conditions (Kaiser *et al.*, 2005).

The influence of tides in estuaries causes high variability in physico-chemical parameters, resulting in extremely stressful conditions (Kaiser *et al.*, 2005). There is spatial variability of salinity and, in tropical estuaries, the salinity can exceed the oceanic value due to high evaporation. In the mid-estuary area the salinity varies considerable between low and high tide. The salinity also varies seasonally due to changes in fresh water flow. Temperature does not vary greatly over a tidal cycle and spatial changes in temperature are quite minimal (Kaiser *et al.*, 2005).



a) b)

Figure 2. 1. Classification of estuaries. a) The salt-wedge and b) the tidally mixed estuary, where isohalines are nearly vertical, with highest values near the sea and lowest values near the river (from Lazier and Mann, 2006).

The flow of fresh water causes a circulation pattern in which less saline and lighter water flows out of the estuary in the surface layer and a deeper flow brings more saline water from the open ocean into the estuary. When the river inflow dominates the tides, the estuary is a river-dominated system, and its water column is highly stratified; in this case it is called a salt-wedge estuary (Figure 2.1a). The sea water intrudes upstream as a wedge and the freshwater overlying the wedge tends to entrain salt water as it moves seaward, thereby becoming more brackish as it approaches the estuary of the mouth. Currents in the surface layer are vigorous and turbulent, while flow in the bottom salty layer is much calmer because of the weak tidal currents (Pinet, 2006). In the partially mixed estuary, friction between the bottom and the tidal currents produces enough turbulence to weaken the vertical stratification. The salinity varies continuously through the depth of the water column with no evidence of a marked interface between the upper and lower layers. Well mixed estuaries occur when tidal mixing dominates the river input of freshwater. The water column is unstratified (Figure 2.1b) and the salinity distribution is almost uniform with depth. In this estuary system the surface and bottom waters are completely mixed by the strong turbulence due to the vigorous tidal flows (Dyer, 1997; Pinet, 2006).

2.2 Estuarine circulation

The estuarine salinity structure is a result of the interplay between the buoyancy flux from riverine inflow, advection by tides and the estuarine circulation, and mixing. The driving force of the circulation is the horizontal pressure gradient that is created down the estuary by the fresh water in the surface layer and the resident salt water. The force lies in the surface layer and is directed down the estuary, a way from the source of fresh water. The movement of the water may be regarded as composed of three parts: displacement due to the flow from the land, tidal oscillation, and dispersal by mixing.

The water mixing is influenced by area of cross section, turbulence, wind, waves, shipping, obstacles, and the nature of the bottom. The turbulence motions are generated by breaking waves at surface, rough flow over the bottom and sides of the estuary, breaking of internal waves on the interface between the two layers. The internal waves are created by wind waves at the surface, pressure variations in the atmosphere, and flow over irregularities in the bottom bathymetry, etc. In an estuary the inflow of fresh water tends to carry sea water seawards by entrainment. The sea water is carried toward the head of the estuary by mixing brought by tidal action. These two processes determine the salinity in the estuary at any point.

Salt wedge estuaries are characterized by a net landward-directed bottom current and a net seaward-directed surface current. Breaking internal waves along the halocline produce an upward flow of water. Partially mixed estuaries have strong currents, with net landward flowing bottom currents and net seaward flowing surface currents. Well mixed estuaries have net currents that are landward directed at all depths on one side of the estuary and seaward directed flow at all depths on the other side (Pinet, 2006).

In an estuary if the area of cross section is large, water which travels farthest up the estuary in the fastest currents may not mix completely at slack water, and the amount which is returned to the original neighbourhood will depend on the difference in position of the fastest currents of the ebb and flood tides. Globally, estuaries demonstrate a wider range of tidal amplitude than other marine system, ranging from less than a metre in many tropical systems to over 16 m.

The speed of tidal waves depend upon the depth and there is asymmetry in the tidal cycle, with a relatively long time interval between high water and the succeeding low water, and a shorter interval between low water and next high tide (Brown *et al.*, 2006); the highest velocities thereby occur on the flood tide (Dyer, 1997). At the estuary mouth the tide will coincide with high water; whereas further up-river, the high tide will be of slack water. Therefore, the ebb current will be longer than the flood as result of the asymmetry of the estuarine tidal cycle, bottom friction that produce greater friction in shallower water (Dyer, 1997), and fresh water discharge into the river which result in net seaward discharge of water (Brown *et al.*, 2006).

2.3. Dissolved oxygen

Oxygen enters the water by photosynthesis of aquatic biota and by the transfer of oxygen across the air–water interface. Dissolved oxygen (DO) refers to the volume of oxygen that is contained in the water. Oxygen in the aquatic environment is produced by photosynthesis of algae and plants and is removed by respiration of plants, animals, and bacteria, BOD degradation process, sediment oxygen demand, and oxidation (Radwan *et al.*, 2003; Lin *et al.*, 2006). Variations in DO can occur seasonally, or even over 24 hour periods, in relation to temperature and biological activity (i.e. photosynthesis and respiration).

There is a release of oxygen into the water as a result of photosynthesis during the day by the plants and algae, and there is an uptake from the water as a result of respiration by aquatic organisms. The simplified photosynthesis process is represented by the equation:

$$6H_2O + 6CO_2 + \text{light energy} \rightarrow 6O_2 + C_6H_{12}O_6. \quad (1)$$

which shows that water (H_2O) together with carbon dioxide (CO_2) and energy from the sun is transformed into oxygen (O_2) and organic matter ($C_6H_{12}O_6$). The respiration is the inverse of photosynthesis; it is the process during which organic matter is decomposed to obtain chemical energy contained in it. The respiration occurs in all living organisms and the energy is obtained by combining the organic matter with oxygen:

$$C_6H_{12}O_6\ (aq) + 6\ O_2\ (g) \rightarrow 6\ CO_2\ (g) + 6\ H_2O + \text{chemical energy} \quad (2)$$

The water at noon have high levels of dissolved oxygen due to oxygen generated from photosynthesis; once night falls, photosynthesis stops and plants consume oxygen as they respire, decreasing the dissolved oxygen levels (Gao and Song, 2008).

In addition to biological factors the distributions of dissolved oxygen in estuaries are affected by different physical parameters like turbulence, atmospheric pressure, surface re-aeration, river flow, and estuarine circulation. The overall partitioning of oxygen between the atmosphere and the water is sensitive to mixing and biological production, as well as temperature and salinity. The solubility of oxygen decreases as temperature and salinity increase and is more dependent on temperature variation (Figure 2.2.) than on salinity variation (Pinet, 2006; Sarmiento and Gruber, 2006).

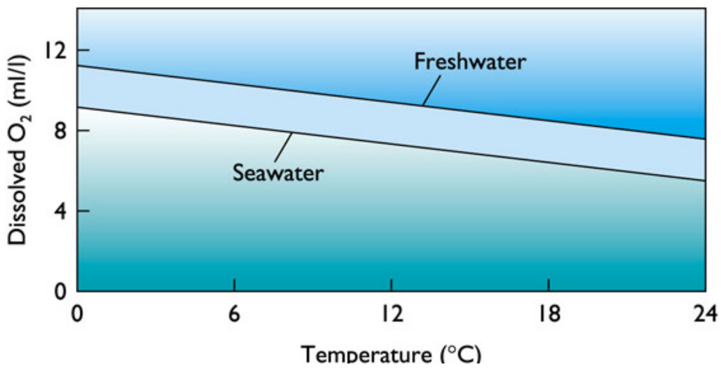


Figure 2.2. Solubility of oxygen (ml L^{-1}) in equilibration with air in fresh water and sea water (Pinet, 2006).

The oxygen transfer velocity between the atmosphere and the water is a function of a number of parameters and processes such as wind speed, turbulence at the interface, air bubbles, etc. Bubbles increase the effective ocean surface area available for gas transfer and thus increase air–sea gas fluxes (Falck and Gade, 1999; Gao and Song, 2008). The oxygen cycle is intimately linked to the organic matter cycle, the exchange fluxes between the atmosphere and the water surface, and the input fluxes from the rivers and resuspension from the deeper layers of the water column.

Hypoxia refers to conditions where the dissolved oxygen concentration decreases to the point where organisms are adversely affected. Various investigators have chosen different oxygen concentrations, usually either < 2 mg L^{-1} (Wei *et al*., 2007; Bianchi and Allison, 2009) or < 3 mg L^{-1} (Miller *et al*., 2002), as the criterion for hypoxia. Recent work has shown that the number of hypoxic zones globally in the coastal margin is doubling every decade (Bianchi and Allison, 2009). Strong correlation between hypoxia and human activity has been found in many areas such as the Gulf of Mexico, Texas–Louisiana; the Northern Adriatic Sea, Italy–Croatia; Kattegat, and Sweden–Denmark (Diaz, 2001).

Both estuarine waters and sediments can have extremely high levels of organic material and consequently very high levels of bacterial activity. Aerobic bacteria dominate the decomposition of organic matter in estuarine waters, and consequently use up dissolved oxygen in the process, resulting in reduced oxygen levels in mid-estuary water. Oxygen levels tend to be high at the head and mouth of an estuary, so an along-estuary profile of oxygen concentration would show a notable decrease in the mid-estuary.

2.4 Relation between hypoxia, organic matter, and eutrophication

Many studies have demonstrated a correlation through time between population, increased nutrients discharges, increased primary production in coastal areas, and increased occurrence of hypoxia and anoxia (Diaz, 2001). One of the different sources of organic matter in estuaries are macrophytes tissues (dead leaves, seagrasses, macroalgae, mangroves and terrestrial plant material), but according to Gray *et al*. (2002) this is not thought to be a significant source compared with the planktonic components.

According to a review presented by Gray *et al*. (2002), the major external sources of nutrients to coastal waters are domestic sewage and agricultural fertilizers input, largely via rivers. Aquaculture systems are another source of nutrients, provided as feed or fertilizer and by the biological transformations occurring in these high biomass systems (Anderson *et al*., 2002). Estuarine and coastal ecosystems are also influenced by seasonal and multi-annual hydrologic variability such as droughts, wet periods, and El Ninõ vs La Ninã years and short-term episodic perturbations such as floods, tropical storms, and hurricanes (Paerl *et al*., 2006).

The eutrophication process can be divided into three key elements: (1) increased nutrient levels leading to (2) production of particulate and dissolved organic matter and (3) degradation of the organic matter leading to lowered oxygen concentration (Gray *et al*., 2002). Key nutrients of concern are nitrogen (N) and phosphorus (P) because the supply rates of these nutrients most often control aquatic autotrophic production and biomass formation.

Downstream estuarine and coastal waters are physically, chemically, and biologically distinct from freshwater ecosystems and, as a result, their responses to nutrient inputs and over-enrichment can contrast those observed in freshwater ecosystems (Paerl, 2009). At upstream freshwater locations, P is often the growth-limiting macronutrient. At the freshwater–saltwater transition zone, P and N may both be colimiting, while the downstream zone is usually N limited (Paerl *et al.*, 2006).

In most aquatic ecosystems nutrient enrichment promotes an increase in phytoplankton biomass and decrease in water clarity. Phytoplankton generally have fast growth rates which can accumulate as partially or ungrazed organic matter (Paerl *et al.*, 2006). The material derived from dead phytoplankton that has sunk into deep waters provide labile carbon substrates for benthic respiration (Pinckney *et al.*, 2001), leading to a large oxygen demand that can exceed supply if there is inefficient vertical exchange (Jickells, 1998).

When bottom-waters become hypoxic, it can drive motile organisms out of these areas creating dead zones where demersal, epi-benthic and benthic communities had previously established, but those incapable to swim can experience stress or die as dissolved oxygen decrease to zero. For most organisms values of dissolved oxygen below 6 mg L^{-1} are suitable to create stress. According to Gray *et al.*, 2002 growth is affected at dissolved oxygen between 6.0 and 4.5 mg L^{-1} and aspects of metabolism are affected at between 4 and 2 mg L^{-1}.

Estuarine eutrophication often results in the formation of hypoxic bottom-waters which result from the decomposition of phytoplankton that have accumulated in stratified bottom-water. The degree of accumulation is generally associated with phytoplankton density in the overlying waters, with high phytoplankton densities occurring when nutrients are sufficiently high to maintain the phytoplankton's biomass (Lowery, 1998). Under conditions of limited oxygen at the bottom, rates of nitrogen and phosphorous remineralization and sulfate reduction increase. The resulting production of sulfide in combination with low oxygen can prove lethal to benthic organisms. The consequence is that sustained hypoxia can have significant trophic implications (Lin *et al.*, 2006).

The accumulation of organic matter and nutrients in the system can be viewed conceptually as the difference between inputs and outputs (export) (Figure 2.3). Thus, ecosystem responses depend on several critical physical–chemical characteristics and processes. Estuary size, depth, volume, flushing rate, water residence time, tidal exchange, vertical mixing, and stratification are all factors that affect the transport, transformation, retention, and export of nutrients (Pinckney *et al.*, 2001).

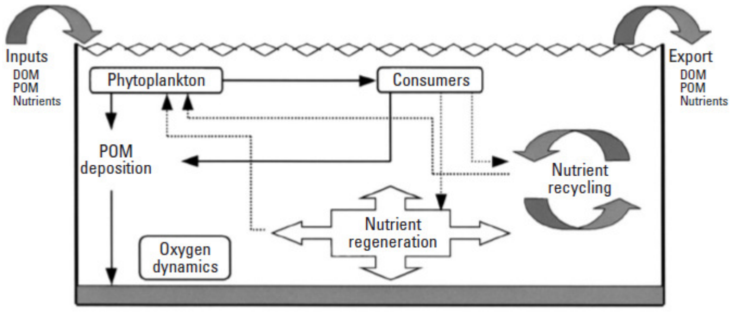


Figure 2.3. Major estuarine processes related to estuarine eutrophication. DOM and POM refer to dissolved and particulate organic matter, respectively (Pinckney *et al*., 2001).

Flowing water is more likely to have high dissolved oxygen levels than is stagnant water because of the water movement at the air–water interface. In flowing water, oxygen–rich water at the surface is constantly being replaced by water containing less oxygen from below as a result of turbulence, creating a greater potential for exchange of oxygen across the air–water interface. The introduction of excess organic matter may result in a depletion of oxygen from an aquatic system, mainly during warm, stagnant conditions that prevent river water mixing (Radwan *et al*., 2003). The cascading effects resulting from excesss of nutrients inputs on estuarine surface waters are conceptualized and summarized in Figure 2.4. Hypoxia in estuaries has been linked with: seasonal temperature increases which cause high oxygen demand, neap-spring tidal cycles, salinity and/or temperature stratification which limits vertical mixing, and eutrophication (Engle, 1999).

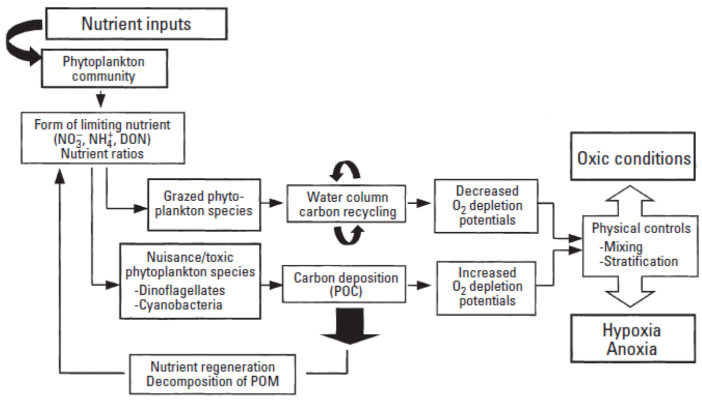


Figure 2.4. Relationships among nutrient inputs, phytoplankton responses, and oxygen dynamics (Pinckney *et al*., 2001)

Nutrients and organic matter can be exported from the estuary also through microbial processes that convert the combined form into an elemental form (regeneration). Ammonium, a primary decomposition product from organic matter (OM), is first transformed by microbes to nitrite (NO_2^-) and then to nitrate (NO_3^-) under oxic conditions (nitrification). Under anoxic conditions, NO_3^- and NO_2^- can be used as oxidants in bacterial respiration processes, termed denitrification, leading to its stepwise reduction to N_2 (Pinckney *et al.*, 2001; Gruber, 2008).

2.5. Influence of Wastewater in water quality

The effluents are an important source of organic matter with a heavy input of nitrogen and phosphorus, as well as a source of heterotrophic bacteria whose activity causes significant oxygen depletion immediately downstream of the effluent discharge point. The wastewater comprises a mixture of the liquid water-carried wastes removed from residence, institutions, commercial and industrial establishments, ground water, surface water and storm water (Table 2.1).

Table 2. 1. Major classes of municipal wastewater contaminants and their significance and origin.

Contaminant	Significance	Origin
Settleable solids (sand, grit)	Settleable solids may create sludge deposits and anaerobic conditions in sewers, treatment facilities or open water	Domestic, runoff
Organic matter (BOD); Kjeldahlnitrogen	Biological degradation consumes oxygen and may disturb the oxygen balance of surface water; if the oxygen in the water is exhausted anaerobic conditions, odour formation, fish kills and ecological imbalance will occur	Domestic, industrial
Pathogenic microorganisms	Severe public health risks through transmission of communicable water borne diseases such as cholera	Domestic
Nutrients (N and P)	High levels of nitrogen and phosphorus in surface water will create excessive algal growth (eutrophication). Dying algae contribute to organic matter (see above)	Domestic, rural run-off, industrial
Micro-pollutants (heavy metals, organic compounds)	Non-biodegradable compounds may be toxic, carcinogenic or mutagenic at very low concentrations (to plants, animals, humans). Some may bioaccumulate in food chains, e.g. chromium (VI), cadmium, lead, most pesticides and herbicides, and polychlorinated biphenyl	Industrial, rural run-off (pesticides)
Total dissolved solids (salts)	High levels may restrict wastewater use for agricultural irrigation or aquaculture	Industrial, (salt water intrusion)

Source: Helmer and Hespanhol (1997).

Industrial wastewater commonly originates in designated development zones or, as in many developing countries, from numerous small-scale industries within residential areas. Industrial water demand and wastewater production are sector-specific, depending on the industrial process, the concentration and composition of the waste flows can vary significantly. Domestic wastewater generation is commonly expressed in litres per capita per day ($L\ cap^{-1}\ d^{-1}$) or as a percentage of the specific water consumption rate. Domestic water consumption, and hence wastewater production, typically depends on water supply service level, climate, and water availability.

Van Drecht *et al*. (2009) predict a rapid increase in global sewage emissions. In the developing countries, sewage N and P discharge will likely increase by a factor of 2.5 to 5.5 between 2000 and 2050. Projected patterns occur because of a combined effect of increasing population, urbanization, and development of sewage systems, leading to increased concentrations of N and P in sewage water. In Africa, because of the fast population growth, the N discharge to surface water will increase by up to 425% (from 428 to 2247 Gg N y^{-1}), and P discharge grows by 408% (from 91 to 460 Gg P y^{-1}) between 2000 and 2050 (Van Drecht *et al*., 2009).

2.6 Influence of aquaculture in water quality

The most common fertilizers used in ponds are nitrogen and phosphorus compounds. Nitrogen, usually in the form of ammonia, is very important for aquatic microorganisms and is major sources of natural food for shrimps. Adding nitrogen to culturing water increases the population of these microorganisms and hence increases the growth of shrimps (Troell *et al*., 2003). In addition urea has been used widely as fertilizer in aquaculture. Urea not only provides ammonia as a nitrogen source but also the carbon dioxide which microorganisms directly use for their growth. A significant proportion of such nutrients that are introduced in ponds are subsequently discharged to local waters with pond effluents, as only a small fraction of the added nutrients ultimately winds up in the marketable product (Glibert *et al*., 2006).

Urea is a significant contributor to the total nitrogen used by phytoplankton in estuarine and coastal waters. Kudela and Cochlan (2000), in reviewing the range of literature values for urea uptake as a percentage of total nitrogen uptake by phytoplankton, found that urea can contribute up to 56% of the total nitrogen taken up in ocean regions and that it commonly constitutes more than 50% of the total nitrogen taken up in coastal and estuarine regions. Dissolved nutrients in shrimp effluents are predominantly ammonia, whereas sewage effluents are proportionally higher in nitrate and Phosphate (Jones *et al.,* 2001)

2.7. Biochemical oxygen demand

When organic matter decomposes, it is fed upon by aerobic bacteria. In this process, organic matter is broken down and oxidized (combined with oxygen). Biochemical Oxygen Demand (BOD) is the amount of oxygen required by aerobic microorganisms to stabilize the organic material of wastewater, wastewater treatment plant effluent, polluted water, or industrial waste. Figure 2.6 gives a schematic overview of the most dominant processes related to the analysis of BOD.

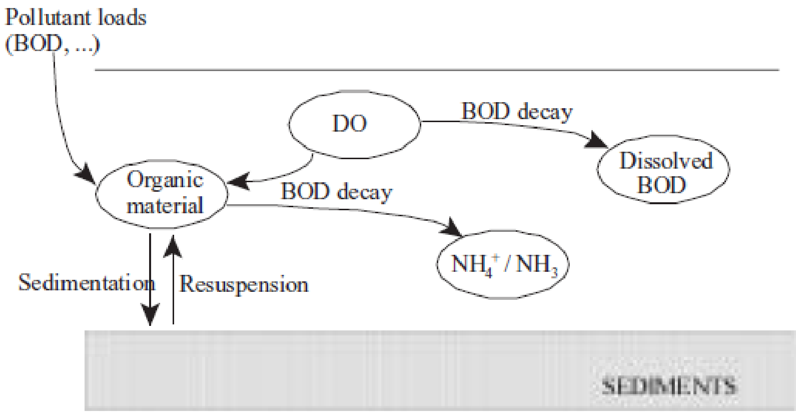


Figure 2.6. Processes related to the analysis of BOD (Radwan *et al.*, 2003).

The BOD is usually proportional to the amount of organic matter present and, therefore, is a measure of the strength of the waste (Marske and Polkowski, 1972). Because organic matter needs varying time spans to be oxidized, and in order to standardize BOD as indicator, the BOD measurement has been defined to be the oxygen consumption, in a sample, after 5 days of incubation at 20ºC. The BOD value is the difference between the dissolved oxygen values before and after incubation. In practice, results obtained after incubation for five days are used but the values only represent a portion of the total BOD, complete biochemical oxidation by oxygen may require 20 -25 days (Pisarevsky *et al.*, 2005)

BOD is widely used to indicate the organic strength of the water. It indicates the concentration of biodegradable organic matter in the water. Usually BOD is measured for wastewaters and heavily polluted watercourses, because these types of water usually contain high concentrations of organic matter. Unpolluted waters typically have BOD values of 2 mg L^{-1} or less, whereas water bodies receiving wastewater may have BOD values up to 10 mg L^{-1} or more (Prandi-Rosa and Farache Filho, 2002), particularly near points of discharge.

One of the major disadvantages of the BOD test is the time lag between the collection of samples and the final calculation of results. Since the BOD test is dependent on biological activity, the major interferences will be those substances which inhibit the growth of the microorganisms. These will include chlorine, caustic alkalinity or acidity, mineral acids, and heavy metals. In addition procedures are diverse and results are not consistent.

Chapter 3

Data and methods

Measurements of oxygen, temperature, and salinity were taken in the port of Quelimane, in the area where the main outlet of the waste water from Quelimane city discharges into the Bons Sinais Estuary. This outlet can be seen to the left of the biggest pier in the lower middle part of Figure 3.1.

Figure 3.1. Quelimane port, situated along the Bons Sinais estuary.

The measurements were taken at 21 locations in a small rectangular area, divided into grids, outside the outlet, as shown in Figure 3.2. The measurements were done upstream and downstream from the outlet, location 10 is just outside the outlet and location 12 at the altitude of the pier.

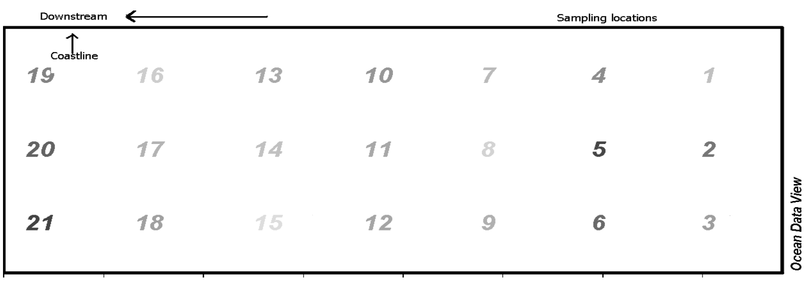


Figure 3.2. Sampling positions. The numbers indicate the locations where the samples were taken. The coordinates of the points 1, 3, 19 and 21 are: point 1 (17º 53' 00.08" S, 036º 53' 09.5" E); point 3 (17º 53' 01.5" S, 036º 53' 08.9" E); point 19 (17º 53' 03.6" S, 036º 53' 15.1" E); and point 21 (17º 53' 04.3" S, 036º 53' 14.7"). Point number 10 is the location where the effluents are discharged (see also Figure 3.1) and the upper row is parallel to the coast.

Repeated measurements were taken the 12. and 21. of August, 5. of September, and 4. and 11. of October 2009 in low tide situations during the dry season. The salinity was only measured on the last two days. On all occasions the sampling started upstream of the town area (location 1) toward the mouth of the estuary (location 19). The distance between location 1 and 3 is 8 m and between 1 and 19 is 150 m. The depths of the sampling locations were measured once during neap tide and are shown in Table 4.2.

Using a small rowing boat, water samples were collected at each position. A plastic bucket was used to collect water from about half a meter below the surface. First, a handheld digital meter, the YSI Model 85, measured the dissolved oxygen, temperature, and salinity of the water sample. The YSI Model 85 is a handheld digital meter, micro-processor based, designed for use in the field and in the lab too, and its typical performance is shown in Table 3.1. Immediately after that a BOD bottle was filled with water from the bottom of the bucket. The BOD bottle was closed before it was taken out of the bucket. The BOD samples were placed in a box, covered with a black plastic and brought back to the laboratory. After five days of incubation at room temperature the dissolved oxygen level in the BOD bottles were measured using the same digital meter. The value of BOD was determined by subtracting this DO level from the DO level found five days previously:

$$\text{BOD} = \text{mg L}^{-1}\text{ DO (measured in the field)} - \text{mg L}^{-1}\text{ DO (measured after incubation)} \qquad (3)$$

The BOD determined is the amount of oxygen consumed by organic matter and associated microorganisms in the water over a five-day period.

Table 3.1. Performance of the YSI Model 85

Sensor type	**Range**	**Resolution**	**Accuracy**
Conductivity	0 to 499,9 µS/cm	0,1µ/cm	±0,5% FS
	0 to 499,9 µS/cm	1,0µS/cm	±0,5% FS
	0 to 49,99 mS/cm	0,01mS/cm	±0,5% FS
	0 to 200,0 mS/cm	0,1mS/cm	±0,5% FS
Salinity	0 to 80 ppt	0,1ppt	±2% or ±0,1
Temperature	-5 to +95ºC	0,1ºC	±0,1ºC
Dissolved oxygen	0-200% 0-20mg/l	0.1% 0,01mg/l	±2% ±0.3mg/l

For more information on the digital meter the reader should go to www.ysi.com

Oxygen saturation was calculated as the proportion between the values of dissolved oxygen measured and the theoretical calculated saturation concentration. The theoretical values were obtained using the equation by Weiss (1970):

$$LnC = -173.4292 + 249.6339 * \left[\frac{100}{(273.15+t)}\right] + 143.3483 * LN\left[\frac{(273.15)}{100}\right] - 21.8492 * \left[\frac{(273.15)}{100}\right] + S * \left\{-0.03396 + 0.014259 * \left[\frac{(273.15+t)}{100}\right] - 0.0017 * \left[\frac{(273.15+t)}{100}\right]^2\right\} \quad (4)$$

Where C is concentration, t is temperature, and S is salinity.

Chapter 4: Results

The dissolved oxygen, temperature, and salinity values measured at the 21 locations during the sampling period are shown in Table 4.1 together with the calculated BOD values.

Table 4.1. Dissolved oxygen, temperature, biochemical oxygen demand and salinity measurements.

Location	Dissolved oxygen (mg L^{-1})					Temperature (ºC)					BOD					Salinity	
	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	4	5
1			2.30	1.64				25.40	27.80				0.94	0.77		31.1	
2			2.33	1.76				25.40	27.30				0.65	0.68		32.0	
3			2.41	1.93				25.60	27.30				0.71	0.90		31.7	
4	3.63	2.84	2.38	1.66	1.37	24.8	25	25.5	27.10	29.10	1.73	1.08	1.45	0.59	0.72	30.4	31.7
5	3.83	3.15	2.55	1.73	1.51	24.70	24.80	25.30	27.30	28.70	1.66	1.14	0.75	0.67	0.91	31.0	32.0
6	4.37	3.13	3.31	1.81	1.52	24.70	24.70	25.40	27.30	28.70			1.35	0.81	0.97	31.0	31.7
7	3.62	3.64	2.34	1.53	1.58	24.90	24.70	25.30	26.60	29.30		1.74	1.17	0.67	0.93	31.6	32.0
8	3.86	3.88	2.40	1.40	1.41	24.80	24.80	25.20	26.70	28.80	2.00	2.16	1.15	0.13	0.76	30.6	32.0
9	4.24	3.54	2.58	1.59	1.41	24.7	24.7	25.2	26.90	28.70	1.71	1.68	1.19	0.61	0.77	30.6	31.9
10	2.70	3.28	2.52	1.97	1.01	25.70	24.70	25.20	26.70	29.60	2.28	2.81	1.17	1.84	0.83	26.3	24.0
11	3.66	3.79	2.72	1.99	1.28	25.50	24.40	25.00	26.50	29.00	2.06	2.12	1.14	0.95	0.52	31.4	31.8
12	3.85	4.05	2.82	1.80	1.35	25.10	24.50	25.00	26.50	28.70		2.35	1.20	0.86	0.57	31.5	31.9
13	3.22	3.66	2.47	1.94	1.66	25.20	24.50	25.20	26.60	29.30	1.42	2.18	1.10	1.07	1.06	31.5	32.0
14	4.13	3.70	2.42	1.60	1.73	25.30	24.40	25.20	26.60	29.00	2.69	1.88	1.00	0.76	1.16	31.7	32.0
15	3.70	3.87	2.65	1.50	1.54	25.10	24.50	25.20	26.30	28.70		1.77	1.15	0.59	0.82	31.5	32.0
16	3.85	4.30	2.52	1.54	1.59	25.10	24.30	25.20	26.50	29.60		2.27	1.26		1.10		32.0
17	4.15	3.80	2.23	1.70	1.64	24.90	24.40	25.20	26.70	29.10	1.91	1.74	1.13	0.78	0.82	31.7	32.0
18	4.42	3.64	2.40	1.65	1.76	24.80	24.50	25.10	26.60	28.80	1.95	1.88	0.82	0.75	1.10	31.4	32.0
19		3.11	2.60		1.99		24.40	25.10		29.20		1.21	1.48		1.63		32.1
20		3.92	2.81		2.32		24.40	25.00		28.80		2.17	1.44		1.78		32.1
21		3.94	2.98		1.83		24.50	25.00		28.80		2.14	1.44		1.03		32.0

The numbers at the top of the columns (1 to 5) indicate sampling dates as follow 12. August, 21. August, 5. September, 4. October, and 11. October, respectively. Salinity measurements were only taken on the 4^{th} and 11^{th} of October. Empty columns: no data. BOD: Biochemical Oxygen Demand

Individual measurements showed that the highest temperatures occurred in October for all sampling locations and the lowest occurred in August. In August the maximum temperatures were 25.70 ºC (on 12th) and 25 ºC (on 21st); in September 25.6 ºC (on 5th) and in October the maximum were 27.80 ºC (4th) and 29.6 on (11th). The discharge point showed the highest values of temperature on August (on the 12th) and October (on the 11th). Two measurements of salinity were done in October (on the 4th and the 11th) and it was found that lowest salinity values occurred at the location where the discharge of municipal effluent occurs. The discharge point had 26.3 (on 4th) and 24 (on 11th) of salinity whereas in other locations the salinity ranged from 30.4 to 32.1 (Table 4. 1).

4.1. Changes in dissolved oxygen

The individual measurements showed a decrease in the concentration of DO during the sampling period. The highest value of dissolved oxygen (4.42 mg L^{-1}) was found at location 18 in August and the lowest value (1.01 mg L^{-1}) was found at location 10 (discharge point) in October. The discharge point had the lowest values of dissolved oxygen on day 1 (in August) and day 5 (in October) (Table 4. 1). Table 4.2 and Figure 4.1 show that, in general, close to the riverside the waters had lower dissolved oxygen concentration than toward the riverbed.

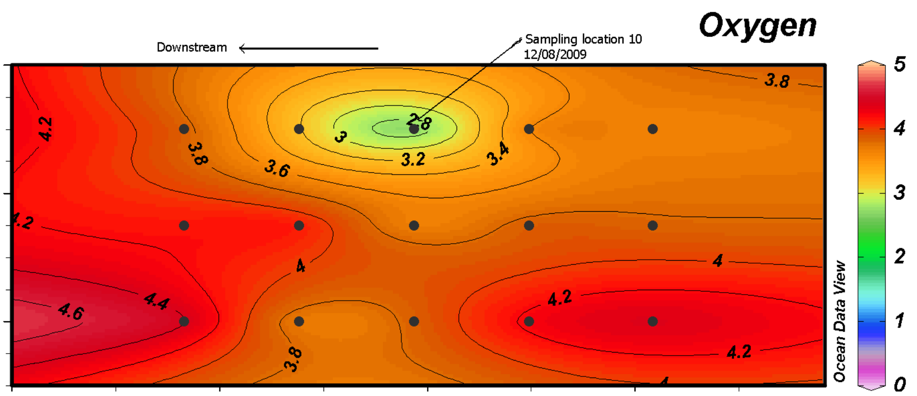


Figure 4.1 Distribution of dissolved oxygen on the 12. of August. Dots indicate the sampling locations.

Figure 4.1 shows the dissolved oxygen distribution in the study area on the 12th of August. The dissolved oxygen ranged from 2.7 mg L^{-1} (location 10) to 4.42 mg L^{-1} (location 18). Except for location 10 all values were higher than 3 mg L^{-1} (see also Table 1). The value of 4.6 mg L^{-1} in the lower left corner was generated by the Ocean Data View program (Schlitzer, 2010) and is not real.

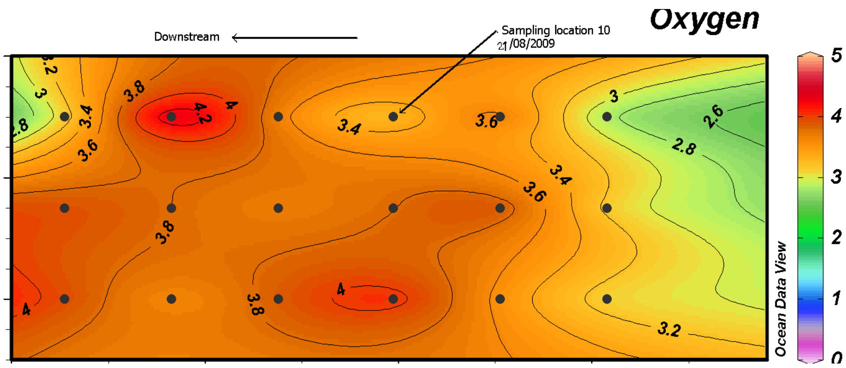


Figure 4.2 Distribution of dissolved oxygen on the 21st. of August. Dots indicate the sampling locations.

Figure 4.2 shows the values of dissolved oxygen obtained on the 21. of August. The dissolved oxygen ranged from 2.84 mg L^{-1} (location 4) to 4.30 mg L^{-1} (location 16). Most of the sampling locations had values higher than 3 mg L^{-1}; the discharge point had 3.28 mg L^{-1}. The DO distribution shows higher values occurring toward downstream.

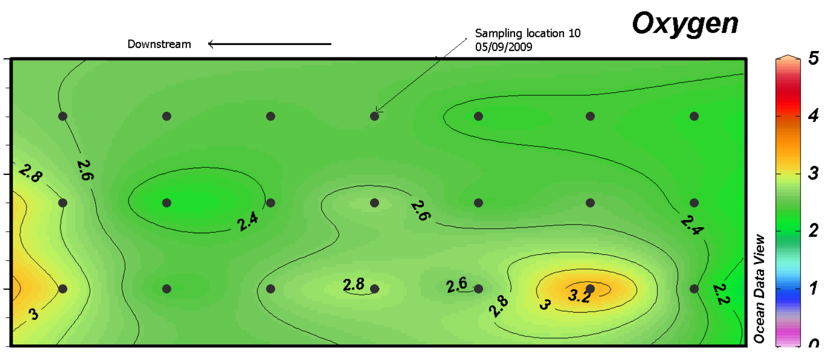


Figure 4.3 Distribution of dissolved oxygen on the 5th. of September. Dots indicate the sampling locations.

In September the lowest value of dissolved oxygen was 2.23 mg L^{-1} (location 16) and the highest was 3.31 mg L^{-1} (location 6). Except the in location 6 all values were lower than 3 mg L^{-1} and the discharge point had 2.52 mg L^{-1} (Figure 4.3).

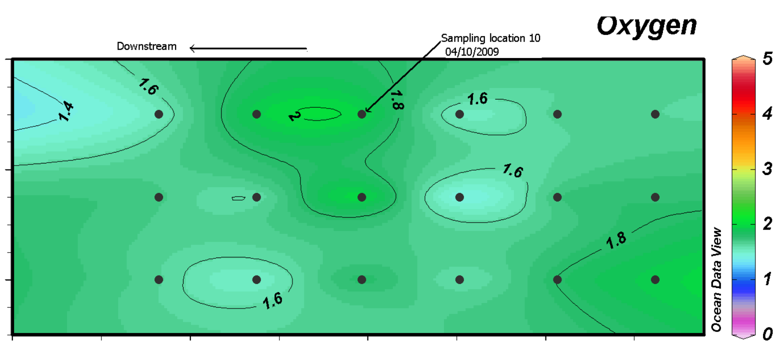


Figure 4.4. Distribution of dissolved oxygen on the 4th. of October. Dots indicate the sampling locations.

Most of the values of dissolved oxygen obtained in October were less than 2 mg L^{-1}. On the 4^{th} the lowest value was 1.40 mg L^{-1} (location 8), the highest was 1.99 mg L^{-1} (location 11), and the discharge point had 1.97 mg L^{-1} (Figure 4.4). On 11. of October the range was from 1.01 mg L^{-1} (location 10) to 2.32 mg L^{-1} (location 20) (Figure 4.5).

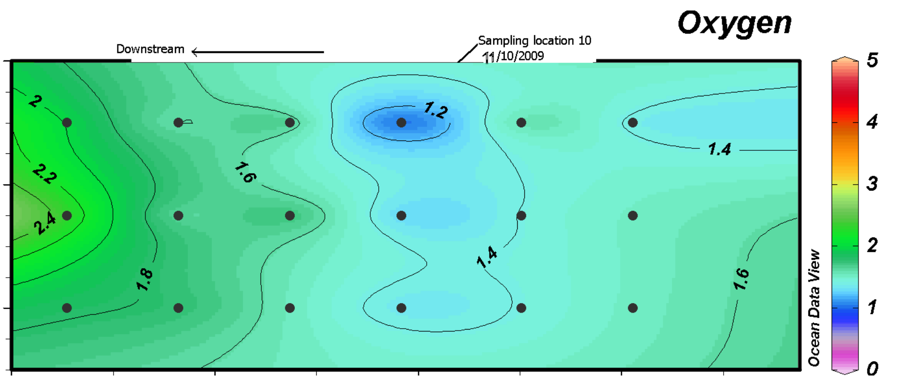


Figure 4.5. Distribution of dissolved oxygen on the 11th. of October. Dots indicate the sampling locations.

4.2 Biochemical oxygen demand

There was a decrease in BOD during the sampling period at all the locations. In terms of individual measurements the highest value of BOD (2.81 mg L^{-1}) was found at location 10 in August whereas the lowest (0.13 mg L^{-1}) value occurred in October at location 8.

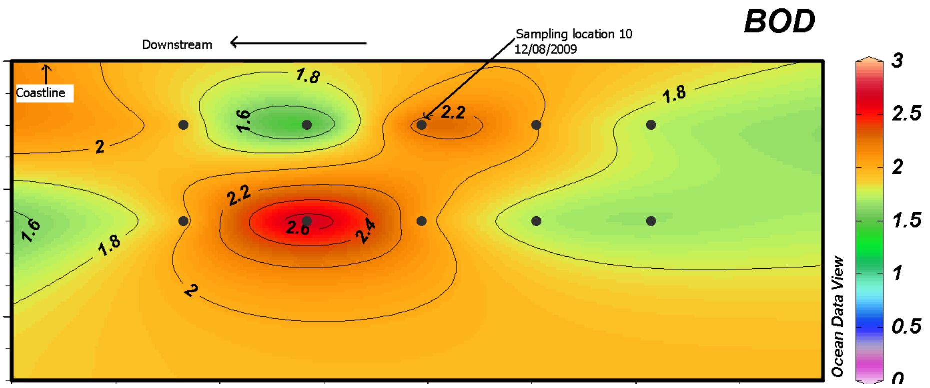


Figure 4.6. Distribution of BOD obtained from sampling on the 12. of August. Dots indicate the sampling locations.

Figure 4.6 shows BOD obtained from water samples after 5 days of incubation, taken on the 12^{th} of August. The values showed in this figure are from only 10 locations (black dots) and ranged from 1.42 mg L^{-1} (location 13) to 2.69 mg L^{-1} (location 14). At the discharge point (location 10) the value was 2.28 mg L^{-1}, and together with locations 8, 11, and 14 the BOD vales were above 2 mg L^{-1}.

Figure 4.7 shows values of BOD obtained from water samples collected on the 21st August. The BOD values varied from 1.08 mg L^{-1} (location 4) to 2.81 mg L^{-1} in the discharge point (location 10). Some of the locations with BOD above 2 mg L^{-1} occurred surrounding the discharge point and it can be seen that there is a continuum of theses values toward the riverbed.

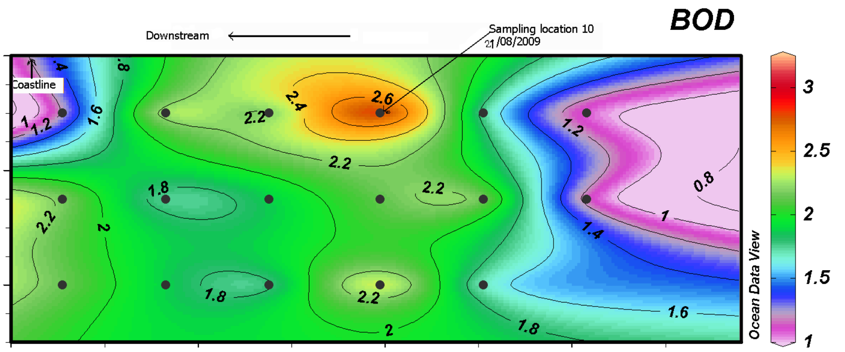


Figure 4.7. Distribution of BOD obtained from sampling on the 21. of August. Dots indicate the sampling locations.

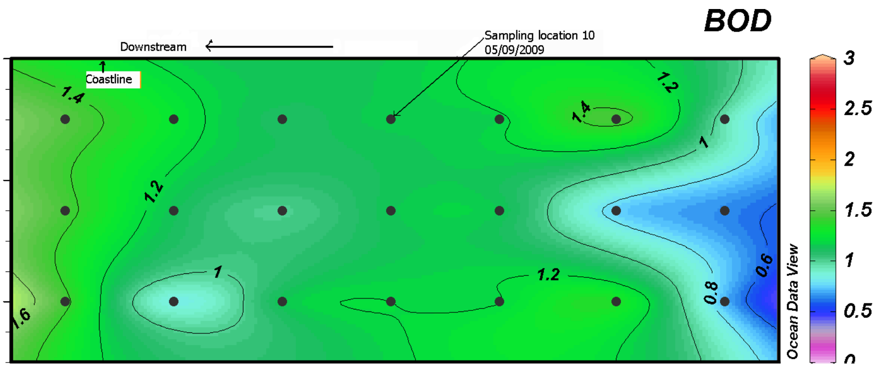


Figure 4.8. Distribution of BOD obtained from sampling on the 5. of September. Dots indicate the sampling locations

In September the BOD values ranged from 0.65 mg L^{-1} (location 2) to 1.48 mg L^{-1} (location 19) and the discharge point had 1.17 mg L^{-1}. Some locations had BOD values lower than 1 mg L^{-1} (Figure 4. 8).

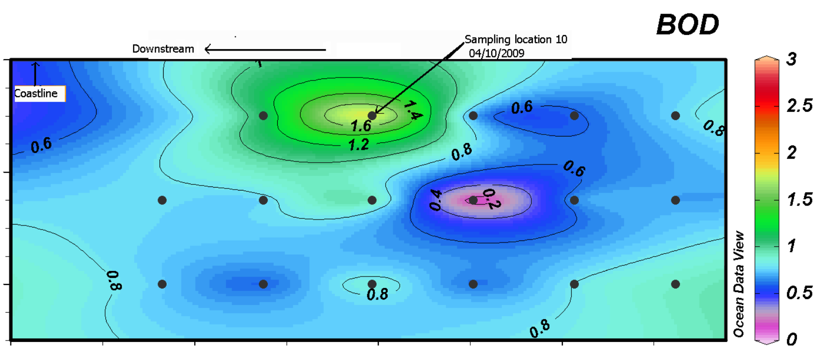


Figure 4.9. Distribution of BOD obtained from sampling on the 4. of October. Dots indicate the sampling locations.

Most of the water samples collected in October had values of BOD lower than 1 mg L^{-1}. On the 4th (Figure 4.9) the BOD varied from 0.13 mg L^{-1} (location 8) to a maximum of 1.84 mg L^{-1} (location 10). On the 11th of October (Figure 4.10) the variation was from 0.52 mg L^{-1} (location 11) to 1.63 mg L^{-1} (location 19).

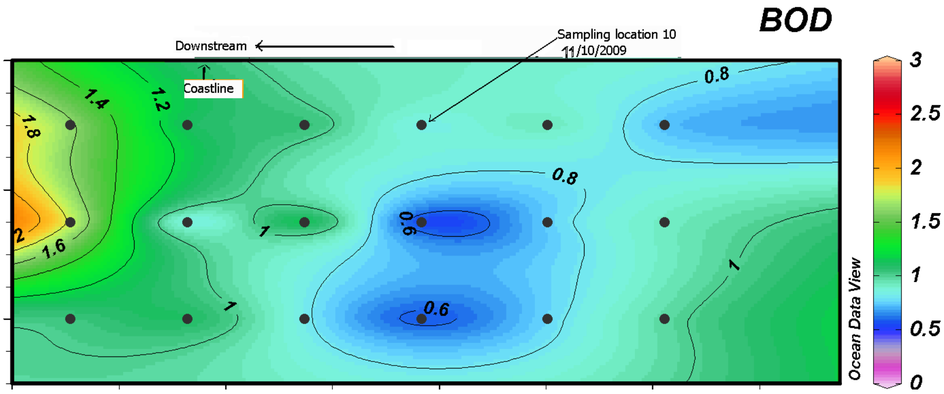
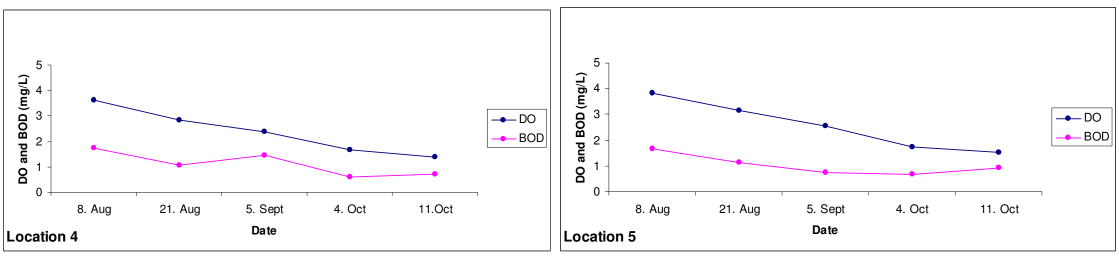
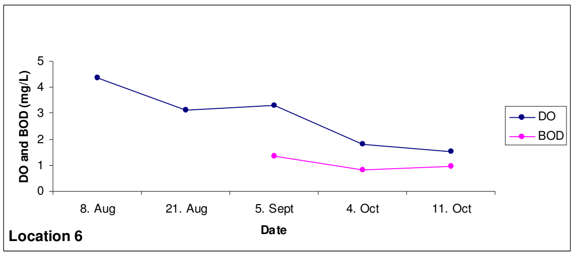


Figure 4.10. Distribution of BOD obtained from sampling on the 11. of October. Dots indicate the sampling locations

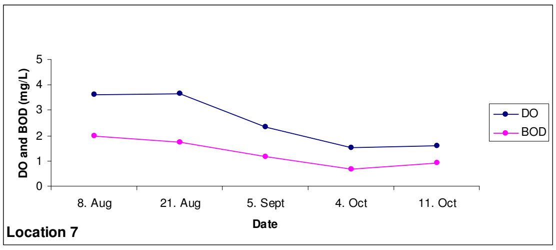
During the sampling period there were locations in which the BOD had values above 2 mg L^{-1}. This situation was found in August and occurred in the locations close to the margin, including the discharge point (Table 1 and Figures 4.6 and 4.7). It was in August that the highest value of BOD was found, 2.81 mg L^{-1}, in location 10. All the BOD values obtained in the three last experiments were lower than 2 mg L^{-1}. Moreover, in October most of the BOD values found were lower than 1mg L^{-1}. From individual values it appears that the lowest values of BOD occurred toward upstream of the discharge point. Figures 4.6 and 4.7 show that values of BDO close to 2 mg L^{-1} or more starting at the discharging point and the nearest locations go toward the riverbed of the estuary.

Figure 4.12 show the variation of both DO and BOD for each location during the sampling period. The figure shows that the DO and the BOD had the same pattern of variation in most cases; with a general decrease during the measuring period. There was high consumption of oxygen relative to the initial values of dissolved oxygen during August and October in the discharge point (location 10) and during August for location 14.

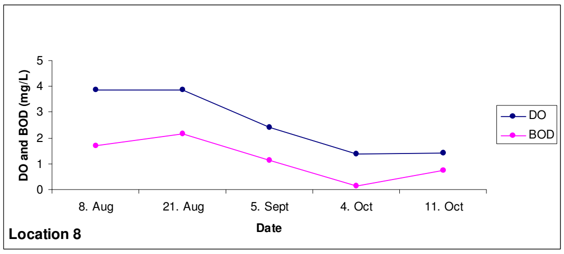




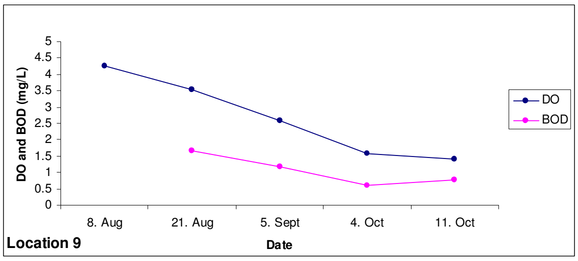
Location 6



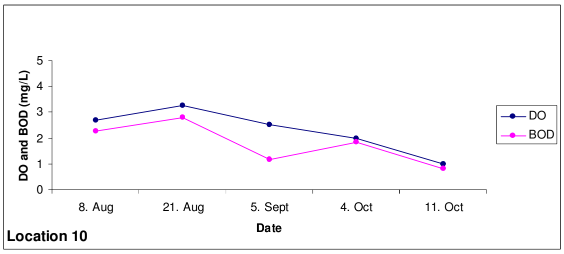
Location 7



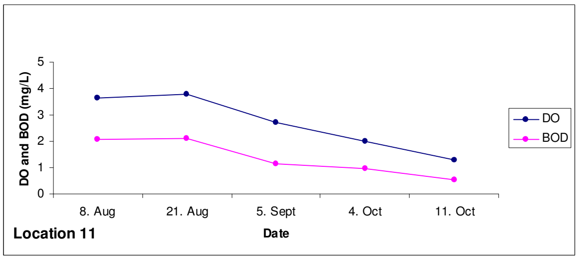
Location 8



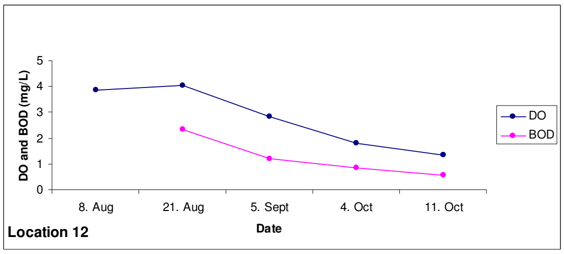
Location 9



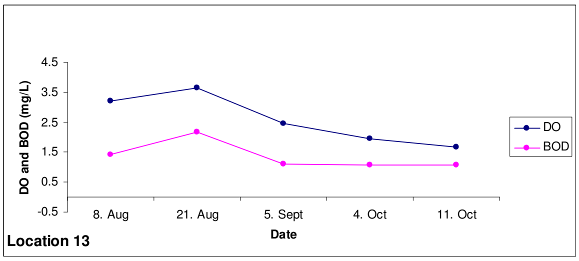
Location 10



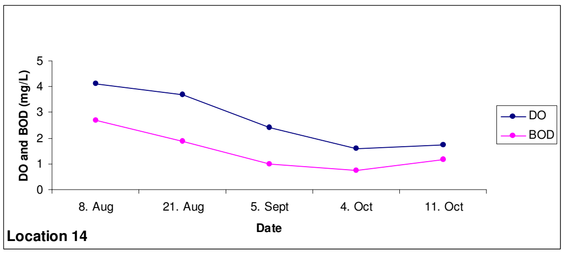
Location 11



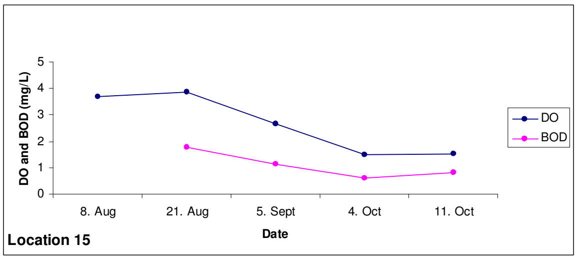
Location 12



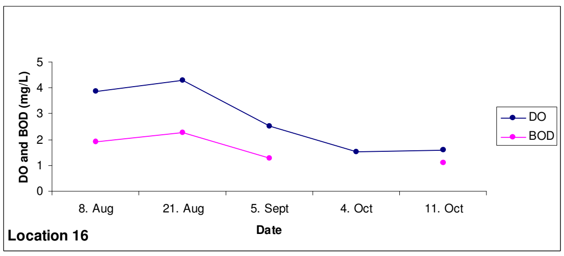
Location 13



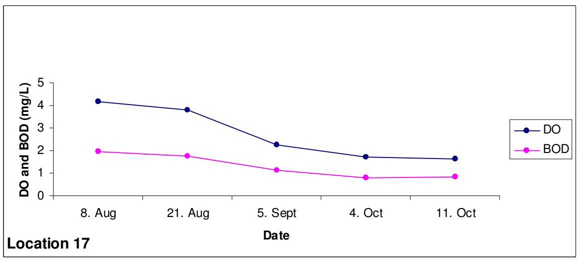
Location 14



Location 15



Location 16



Location 17

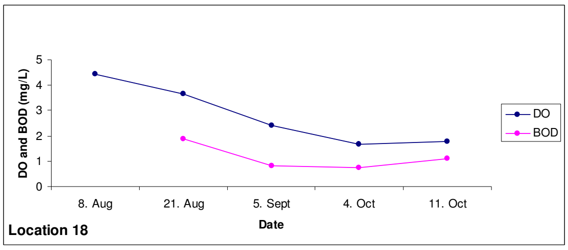
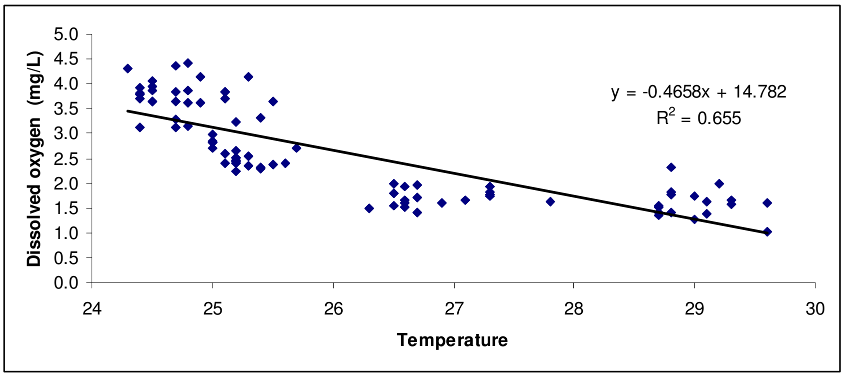


Figure 4.12 Variation of dissolved oxygen (DO) and biochemical oxygen demand (BOD) for each point during the sampling period. Missing points means no data.

Individual values of dissolved oxygen for each sampling location for whole period where plotted against individual values of temperature and there was a significant correlation (R^2 = 0.655), indicating that the variation on dissolved oxygen can be influenced by the variation of temperature.



Figures 4.13 Correlation between the temperature and dissolved oxygen.

4.3 Mean conditions during the sampling period

Table 4.2 shows the depth for each sampling location and mean values of dissolved oxygen, temperature, and BOD calculated from the five measurements. The salinity mean was calculated using data obtained on days 4 and 5; also the saturation mean was calculate using values of dissolved oxygen, salinity, and temperature obtained on days 4 and 5.

The locations situated closest to the margin have depths less half a meter including the discharge point (location 10) with depth of 0.3 m. The maximum depth (5.5 m) was found at locations 18 and 21 and the minimum was 0.2 m, found in location 7.

The mean values of temperature obtained for each day were 25.04, 24.56, 25.18, 26.73, and 28.99ºC respectively for the first, second, third, fourth, and fifth sampling days. The highest mean temperature (26.6 ºC) was found at location (1) and the lowest (25.96 ºC) was found at locations 12, 15, and 18 (Table 4. 2).

Table 4.2. Depth and the mean values of temperature, salinity, dissolved oxygen, percentage oxygen saturation, and biological oxygen demand for each sampling location.

Location	Depth (m)	Temp (ºC)	Salinity	DO (mg L^{-1})	Oxyg. Sat.	BOD
1	0.34	26.6	31.1	1.97	24.9	0.86
2	3.1	26.4	32	2.05	26.6	0.67
3	3.9	26.5	31.7	2.17	29.2	0.81
4	0.4	26.3	31.05	2.38	23.1	1.11
5	3.1	26.16	31.5	2.55	24.7	1.03
6	3.9	26.16	31.35	2.83	25.4	1.04
7	0.2	26.16	31.8	2.54	23.8	1.13
8	3	26.06	31.3	3.38	21.3	1.24
9	3.9	26.04	31.25	2.67	22.8	1.19
10	0.3	26.38	25.15	2.30	21.9	1.66
11	3.4	26.08	31.6	2.69	24.8	1.40
12	5.1	25.96	31.7	2.77	23.8	1.40
13	0.3	26.16	31.75	2.59	27.4	1.35
14	3.4	26.1	31.85	2.72	25.4	1.24
15	5.1	25.96	31.75	2.65	23.1	1.40
16	0.4	26.14	32	2.76	22.1	1.54
17	3.8	26.06	31.8	2.70	25.5	1.28
18	5.5	25.96	31.7	2.77	25.9	1.30
19	0.3	26.23	31.1	2.86	31.1	1.44
20	3.8	26.06	31.1	3.67	36.0	1.78
21	5.5	26.10	32	3.46	28.4	1.54

Mean values of salinity ranged from 25.15 (location 10) to 32 (locations 2, 17, and 21). But except for location 10 all mean values of salinity were more than 31. Oxygen saturation had values under 50% at all sampling locations and it ranged from 21.3% (location 8) to 36% (location 20), and at the discharging it was 21.9%.

Figure 4.14 shows the pattern of dissolved oxygen distribution using the mean values obtained from individual measurements for each sampling location. It can be seen that in general the lowest mean dissolved oxygen occurred close the margin and in the locations upstream of the discharge point. It can also be seen that there was an increase in the mean dissolved oxygen from the coastline toward the riverbed. The discharge point (location 10) together with locations 1 had the lowest of means dissolved oxygen among the locations situated close to the margin (Table 4.2 and Figure 4.14). But the measurement of dissolved oxygen at location 1 was done in two days when the dissolved oxygen decreased.

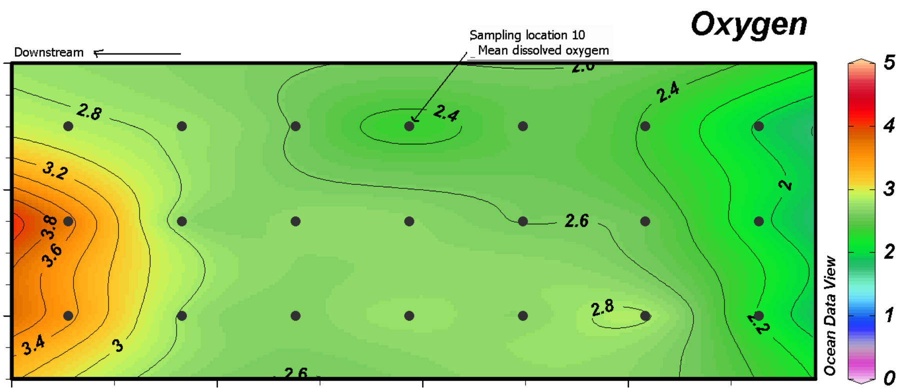


Figure 4.14. Distribution of mean values of DO (mg L^{-1}) for the measurement period.

The mean values of dissolved oxygen obtained for each day were 3.82, 3.62, 2.56, 1.71, and 1.58 mg L^{-1} respectively for the first, second, third, fourth, and fifth sampling days. Except for location 1, in all sampling locations mean values of DO for the sampling period were more than 2 mg L^{-1} and in the discharge point it was 2.30 mg L^{-1}. The lowest mean value of DO (Table 4.2) was found in location 1 (1.97 mg L^{-1}) and maximum was found in location 20 (3.67 mg L^{-1}). In locations 1, 2, and 3 the mean values were determined using the individual measurements obtained in the two days (Table 4. 1). The mean value of 3.8 mg L^{-1} in the left was generated by the Ocean Data View program (Schlitzer, 2010) and is not real.

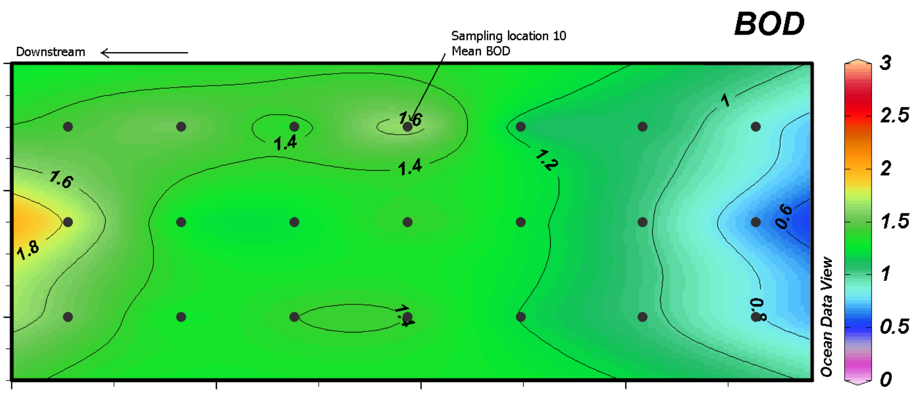
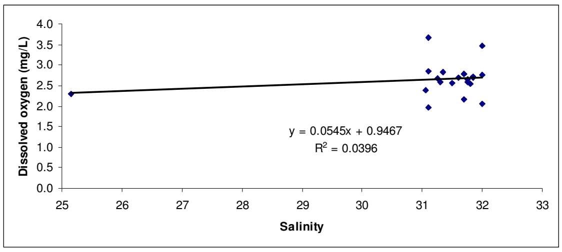
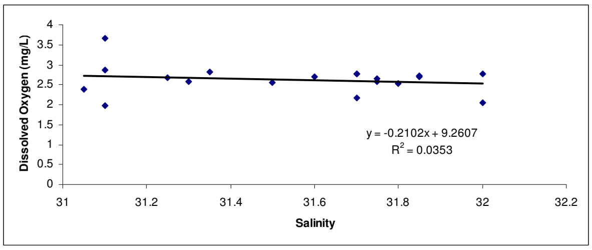


Figure 4.15. Distribution of Mean values of BOD during the sampling period. Dots indicate the sampling locations.

All mean values of BOD calculated from individual measurements were less than 2 mg L^{-1}. The mean values of BOD obtained for each day were 1.94, 1.90, 1.19, 0.79, and 0.97 mg L^{-1} respectively for the first, second, third, fourth, and fifth sampling days. The highest mean value of BOD (1.78 mg L^{-1}) was found at location 20 and the discharge point had mean value of BOD 1.66 mg L^{-1}. The lowest mean value was found in location 2 (0.67 mg L^{-1}).

Mean values of salinity was plotted against the mean values of DO and the correlation coefficient obtained between them was not significant (Figure 4. 16).





a) b)

Figure 4.16. Correlation between mean values of dissolved oxygen and mean values of salinity. Figure "a" was obtained using data from all measurement points and "b" after removing values from point 10.

Chapter 5

Discussion

The values of dissolved oxygen (mg L^{-1}) obtained for each sampling day did not show great differences in most of the different sampling locations. The discharge point showed the lowest values of dissolved oxygen in August and October. The distribution of dissolved oxygen in the study area was almost homogenous mainly in measurements done in September. The values of dissolved oxygen quite different from others where found in restricted locations.

The dissolved oxygen distribution pattern in the study area can be explained by the local hydrographical features and physic-chemical properties of the water. The measurements were done in shallower waters of very small area and it can be assumed that there are no significant variations of the external factors influencing the dissolved oxygen such as atmospheric pressure, air temperature, wind speed, circulation, and tides.

There were no situations of hypoxia in the first three measurements because all dissolved oxygen values obtained ranged from 2.23 to 4.42 mg L^{-1}. Hypoxia is the situation in which the dissolved oxygen fall to values less than 2 mg L^{-1}(Gao and Song, 2008; Diaz, 2001). There where a decrease in dissolved oxygen during the sampling period and values obtained in the last two sampling days were all below the critical value of 2 mg L^{-1}. According to Nezlin *et al*.(2009) hypoxia is difficult to detect because dissolved oxygen vary over short time scales, i.e., less than a day, due to variable rates of oxygen production and consumption, which fluctuate in response to different environmental factors. The two principal factors that lead to the establishment of hypoxia are water column stratification, which isolates the bottom water from exchange with oxygen-rich surface water, and decomposition of organic matter in the bottom water, which reduces oxygen levels (Diaz, 2001).

Theoretically, well-mixed estuaries with short bottom water residence time are assumed to be free from extended hypoxia (Nezlin *et al*., 2009). Hypoxia can be a seasonal phenomenon, in general occurring during summer and lasting for a few days in estuaries and fjords (Gau and Song, 2008); the hypoxia occurrences will persist as long as oxygen consumption rates exceed those of replenishment. Gray *et al*. (2002) gave only two examples of periodic, but non-seasonal hypoxia, both from rivers entering Chesapeak Bay, lasting from days to weeks.

Based on the fact that the measurements of the dissolved oxygen were done close to the water surface the dissolved oxygen deeper down could have values higher than the critical value. Values of dissolved oxygen at the surface are generally higher because of photosynthesis occurring in this layer that releases oxygen into and the oxygen entering the water from the atmosphere. Hypoxic waters are present more typically between 5 and 30 m. Hypoxia occurs mostly in the lower water column but encompasses as much as the lower half to two-thirds of the column (Rabalais *et al*., 1999).

The oxygen solubility is very dependent on water temperature; the dissolved oxygen content reduces sharply with increase in temperature. There was a negative significant correlation (R^2 = 0.655) between dissolved oxygen and temperature (Figure 4.13). Thus, the decrease in dissolved oxygen during the period can be explained by the increase in temperature (Table 4.1). The temperature affects the dissolved oxygen not only by reducing the solubility but also increasing the speed of breakdown of organic matter and consequently influencing the dissolved oxygen concentration in the water (Kaiser *et al*., 2006).

The discharge point (location 10) had the lowest values of dissolved oxygen among all locations in day 1 (in August) and day 5 (in October) (Table 4. 1). The discharge point is in a shallower location that is always flushed by tides. These lower values of DO measured have been determined by temperature or other physical parameters. In shallow estuaries, low oxygen events are more difficult to observe because periods of hypoxia and anoxia are shorter and spatially limited as a result of mixing events (D'Avanzo and Kremer, 1994).

Despite that there was not found any significant differences in the daily measurements, the downstream or seaward positive longitudinal dissolved oxygen gradient found from mean values is expected because the estuarine circulation can replenish estuarine waters with marine waters rich in oxygen. One disadvantage for using mean values is that it can mask events of low dissolved oxygen occurred in some periods (Summers *et al*., 1997) as was found in this study.

The oxygen saturation determined from means of salinity and temperature showed that most of the sampling locations were undersatureted. Similar results were observed in the Rappahannock and York Rivers in Virginia (Lin *et al*., 2006) where low oxygen concentrations (<50% saturation) was found in the majority (>50%) of the surveys when water temperature exceeded 20 ºC.

There was a decrease in the biological oxygen demand during the sampling period; the observed values varied from 0.13 to 2.81 mg L^{-1}. Waters with BOD lower than 4 mg L^{-1} (Prandi-Rosa and Farache Filho, 2002) or 5 mg L^{-1} (Sadhuram *et al*., 2005) are considered reasonable clean, and seriously polluted waters have BOD greater than 10 mg L^{-1} and it is an indicative of high concentration in degradable organic matter (Wahid et al., 2007; Prandi-Rosa and Farache Filho, 2002).

The biological oxygen demand test is used to evaluate the level of bio-chemically degradable organic matter in the wastewater. The results found can be explained in term of quantity and composition of the wastewater discharged and the processes related to its decomposition and dispersion in the estuary. Aerobic bacteria are the principal agent responsible in the decomposition of the organic matter and they use oxygen in this process. Thus, values of biological oxygen demand will depend on the amount and nature of organic matter and the activity of the bacteria species present in the wastewater. Some substances such as chlorine, caustic alkalinity or acidity, mineral acids, and heavy metals inhibit the bacteria action.

The mean values of dissolved oxygen and biochemical oxygen demand can suggest that the influence of the sewage is restricted to the discharge point despite that the values of both parameters don't reach the critical values above what the water quality is concern. Low salinity level also was confined to the discharge point confirming this limited influence of sewage in the Quelimane harbor.

Dispersion and mixing of wastewater in estuaries is influenced by numerous factors such as flushing by tides, topography, curvature of the estuary in the longitudinal direction, and winds (Allen, 1982; Dilorenzo *et al.*, 2004). The water sampling in this study was done in neap tides in order to minimize the effect of tides in the wastewater dispersion. Because of shallow depths and intense tidal mixing, Quelimane harbor is a well-mixed location and the wastewater discharged is flushed and mixed with the estuary water mass resulting in values of biological oxygen demand considered to be lower than the threshold limit (< 4 mg L^{-1}).

The horizontal distribution of BOD shown in Figures 4.6 and 4.7 can be use to explain the dispersion pattern of the wastewater from the outlet. It is likely that from the outlet the wastewater is conducted from the margin toward the river bed. This pattern of dispersion could be influenced by local estuarine circulation and the infrastructures found in the local (Figure 3.1). It's important to recall that there is mangrove forest in the margin close to the discharge point, so the organic matter resulting from mangrove decomposition can contribute on the waters BOD values.

This study gave an idea of the magnitude of the wastewater influence in water quality at Quelimane harbor. Future studies will need the inclusion of other parameters such as coliform bacteria counts, phosphates, nitrates, and turbidity. One important tool is the use of mathematical models in river basin management for the estimation of effluent impacts on water quality in the receiving stream.

Chapter 6

Summary and conclusions

In this study dissolved oxygen and biochemical oxygen demand in the waters close to the Quelimane sewage discharge were analyzed from August to October 2009. The results found during the measuring period indicate that during August the dissolved oxygen values were above the critical value of 2 mg L^{-1} whereas during September and October the dissolved oxygen had values lower than this critical value. It is not clear if the lower values found correspond to the reality because in shallower waters is expected high concentration of oxygen.

The values of Biochemical oxygen demand obtained are characteristic of unpolluted waters which can be used to suggest that the municipal effluents discharged into the estuary are negligible or are flushed away by tides. To access the trophic status of the area studied it will be necessary to analyse other ecological parameters such as nutrients and chlorophyll concentration, and turbidity.

Chapter 7

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