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Department of Chemistry

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Characterisation and efficiency test of a decentralized water purification system (pilot phase)

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Declaration:

Herewith I declare that this thesis is the result of my independent work. All sources and auxiliary materials used by me in this thesis are cited completely.

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I. Abstract

South Africa is a country, which is currently categorised as water stressed. The International Water Management Institute (IWMI) has predicted a scenario of water scarcity by the year 2025. Studies have been done to find a way to avoid this future scenario. They have led to the conclusion that a sustainable water management is necessary. These management tools include strategies of wastewater management, among others. One example is the treatment and reuse of wastewater directly on-site, especially in rural areas and urban settlements, which are not connected to the municipal sewage system.

This can be done with decentralized water purification systems.

A system of this type has been installed at the Lilyfontein School in the Eastern Cape province of South Africa.

It is based on the principle of a submerged fixed-film bioreactor. This system consists of four parts: a balancing tank, the two bioreactors and a clarifier. The wastewater is pumped from the balancing tank, which serves as a second septic tank, into the first bioreactor. This tank is packed with a plastic material with a big surface. The sludge in the water can settle down on this material to form biofilms with many different types of bacteria. Because of external aeration oxidation reactions take place, which are carried out by these microorganisms. The same happens in the second bioreactor. Finally the water ends up in the clarifier, where it is disinfected and stored until it is pumped into a big reservoir.

In this project samples were taken from the four parts of the system over a period of approximately two months to characterise this biological wastewater treatment plant and to test its efficiency. The parameters examined were the physical-chemical parameters temperature, pH, electrical conductivity (EC), dissolved oxygen (DO) and the chemical oxygen demand (COD), as well as ammonia-nitrogen and the anions fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulphate.

The results for the effluent were compared to the Target Water Quality Range (TWQR) provided in the *South African Water Quality Guidelines, Volume 4:*

Agricultural Use: Irrigation. These guidelines were used because the final effluent is intended to be used for irrigation. This paper only covers the first phase of a bigger project. The major aim is to get a base of knowledge about this kind of wastewater treatment to convince municipalities and governments to install such systems in rural areas and urban settlements, which are not connected to the municipal sewage system.

The water purification system showed to have a COD removal rate of 73% and a nitrification, which causes an ammonia removal rate of 95%. This is an indication that the system is working properly and the water is purified successfully. The only restriction is the lack of a denitrification so that the nitrate levels in the effluent are too high. A possible solution to solve this problem is suggested in this paper.

II. List of abbreviations

cm	centimetre
COD	chemical oxygen demand
DO	dissolved oxygen
DWAF	Department of Water Affairs and Forestry
EC	electrical conductivity
EPS	extracellular polymeric substances
FAO	Food and Agriculture Organisation of the United Nations
IC	ion chromatography
IWMI	International Water Management Institute
KHP	potassium hydrogen phthalate
km ²	square kilometres
l	litre
m	metre
m ³	cubic metre
mg	milligram
ml	millilitre
mm	millimetre
mS	milliSiemens
n. d.	not detectable
nm	nanometre
PE	polyethylene
UV	ultraviolet (spectrum of light)
VIS	visible (spectrum of light)
WSU	Walter Sisulu University
WTW	Wissenschaftlich Technische Werkstätten
µS	microSiemens

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1. Introduction

1.1 South Africa and its water problems

The Republic of South Africa is the southernmost country on the African continent. Its area of 1.22 million km² is bordered by Botswana and Zimbabwe to the north, Mozambique and Swaziland to the northeast and east, the Indian Ocean to the southeast and south, the Atlantic Ocean to the southwest and west, and Namibia to the northwest. In the eastern part of the country the independent constitutional monarchy of Lesotho is surrounded by South African territory. The population of South Africa is approximately 45.4 million, estimated in 2004. 42 % of it is considered as rural. The average population density is 37 inhabitants/km². It ranges from 21 in rural to more than 100 inhabitants/km² in urbanised areas.

South Africa is a net food exporter. Nevertheless one third of the population is strongly vulnerable to food shortages because of poverty and the lack of suitable infrastructure in the deep rural areas. This problem could be solved by homegrown vegetables (FAO, 2005).

But most parts of the country are considered as arid or semi-arid land, which means that 65 % of South Africa is receiving too less rainfall for agriculture.

An annual rainfall of at least 500 mm/year is required for successful dry land farming. But South Africa's average rainfall is only 450 mm/year (the world average is 860 mm/year). That leads to the conclusion that irrigation is necessary for agriculture.

Therefore it is no surprise that 60 % of the total water requirements of South Africa are represented by agriculture. Because of that high water demand and the low annual rainfall the water resources of the country are scarced and limited (Otieno and Ochieng, 2004).

This has dramatic consequences on the population because of a decrease of the annual freshwater availability. According to Otieno and Ochieng (2004) the annual freshwater availability in South Africa is estimated by the FAO to 1154 m³ per capita/year. While the index for water stress is 1700 m³ per capita/year, the country is categorised as water stressed (Otieno and Ochieng, 2004).

The annual population growth rate is estimated at about 1.2 % (FAO, 2005). Based on that the water demand projections in South Africa indicate an annual growth rate of 1.5 % between 1990 and 2010 (Otieno and Ochieng, 2004). That leads to further problems in the future. Otieno and Ochieng presented a report in 2004 suggesting water management tools to avert these problems. They refer to an estimation of the International Water Management Institute (IWMI) that by the year 2025 South Africa will face a scenario of physical water scarcity because the annual freshwater availability will be less than 1000 m³ per capita, which is the index for water scarcity. These water management tools suggest possible solutions to avert this future scenario. Some of them are the demand management of water, identifying and developing alternative supply systems, applying techniques to improve water quality for particular uses and the water transfer from surplus areas to deficit areas (Otieno and Ochieng, 2004).

Another reason for the decreasing availability of clean drinking water is the pollution of surface waters and groundwater by the discharge of wastewater. This is especially a problem in developing countries like South Africa. On the one hand the polluted water bodies require expensive treatment techniques to clean the water to drinking water standards. And on the other hand the water is just not used efficiently so that it is simply wasted. That leads to the conclusion that sustainable wastewater management strategies have to be developed.

Nhapi and Gijzen (2005) describe a “3-step strategic approach to sustainable wastewater management”. The first step is the minimisation of wastewater generation. This can be achieved by the reduction of water consumption and waste generation. For example only two litres of the drinking water consumed in an average household per person and day are really used for drinking and cooking. The rest (150 – 350 litres per person and day) is used for other purposes like washing, hygiene, gardening and flushing of toilets where water of drinking quality is not necessary. It can be suggested that water of different qualities should be delivered for different uses. This leads to the second step. This step describes the treatment and reuse of wastewater. In a third step it is suggested that after successful employment of the first two steps the remaining wastewater can be carefully discharged into receiving water bodies so that the self-purification capacity of these waters is stimulated (Nhapi and Gijzen, 2005). The problem with the second step is that facilities for the treatment of wastewater are very expensive. In most countries, centralized wastewater treatment plants are treating the wastewater of bigger settlements like cities. But in developing countries like South Africa many rural areas with a very low population density exist. Therefore centralized wastewater treatment is nearly impossible because it would be highly uneconomic. The solution lies in decentralized wastewater treatment systems. These systems treat the wastewater on-site in single households or other building clusters which are not connected to the municipal sewage system. The purified water can then be used for irrigation or other purposes where no water of drinking quality standard is necessary, or it can be discharged into the environment. Different systems are described in the literature, most of them working with biological methods for the removal of nutrients from domestic wastewater. These are, for example, constructed wetlands (Verhoeven and Meuleman, 1999), anaerobic baffled reactors (Foxon et al., 2004) and membrane bioreactors, also called fixed-film bioreactors (Oh et al., 2001; Ho et al., 2001; Lesjean et al., 2002; Cicek, 2003). This project is focussing on the characterisation and efficiency testing of such a decentralized water purification system based on the principle of a submerged fixed-film bioreactor.

1.2 The submerged fixed-film bioreactor

A submerged fixed-film bioreactor is a system, which can purify wastewater on biological basis without the addition of chemicals, which are expensive and sometimes hazardous to the environment. A certain medium with a large specific surface is submerged in a tank, which is filled with wastewater. In most cases it is a plastic material. The sludge and other suspended matter in this water contain many different microorganisms. These microorganisms develop on their own. They settle down on the medium to form so-called biofilms. A biofilm is the agglomeration of many microorganisms on a surface. It is made of extracellular polymeric substances (EPS), which are created by these microorganisms. It can be seen as the “house” of the bacteria. They are living there and are protected against external influences, for example chemicals or antibiotics (Madigan et al., 2003).

Once these biofilms have built up properly on the surface of the material in the biofilter, the wastewater flowing over this surface is purified because the bacteria gain the energy necessary for their metabolism by oxidising the energy-rich organic compounds in the wastewater (Rüffer and Masannek, 2002). The dissolved oxygen in the wastewater is almost completely consumed for these reactions. That means that additional oxygen is needed to create aerobic conditions. This is achieved by

external aeration. In most cases normal air from the surroundings is pumped into the water by using an electrical pump.

A decentralized water purification system of this type was installed at the Lilyfontein School in the Eastern Cape province of South Africa. This system was the object of interest for this project. This school is located in a rural area and not connected to the sewage system of the Buffalo City Municipality.



Figure 1: map of the Eastern Cape province (modified)

Most of the wastewater in this school comes from the toilets, which are used by approximately 300 persons (pupils and teachers), according to the caretaker of the school.

The raw sewage is flowing into a septic tank which is installed underground. Here it is stored on the one hand and on the other hand some reactions can take place in these anaerobic to anoxic conditions. These reactions are carried out by microorganisms (e.g. bacteria) and include mostly the biodegradation of the organic compounds in the sewage. The most important products of these reactions are water (H_2O) and carbon dioxide (CO_2), but also the toxic gases hydrogen sulphide (H_2S) and ammonia (NH_3), which give the wastewater an offensive odour. Heavier solids settle down on the ground of the tank while lighter ones are floating on the water surface, forming a scum layer. The cleaner water in the middle can flow out of the tank. But up to 70% of the pollutants are still in this water, so that further treatment is essential (Johnston and Smith, 2005). For this reason the system mentioned above was installed at Lilyfontein School by the company "Clearedge". This system can purify septic tank effluent with biological methods. No hazardous chemicals and very low maintenance are needed (Clearedge, 2005).

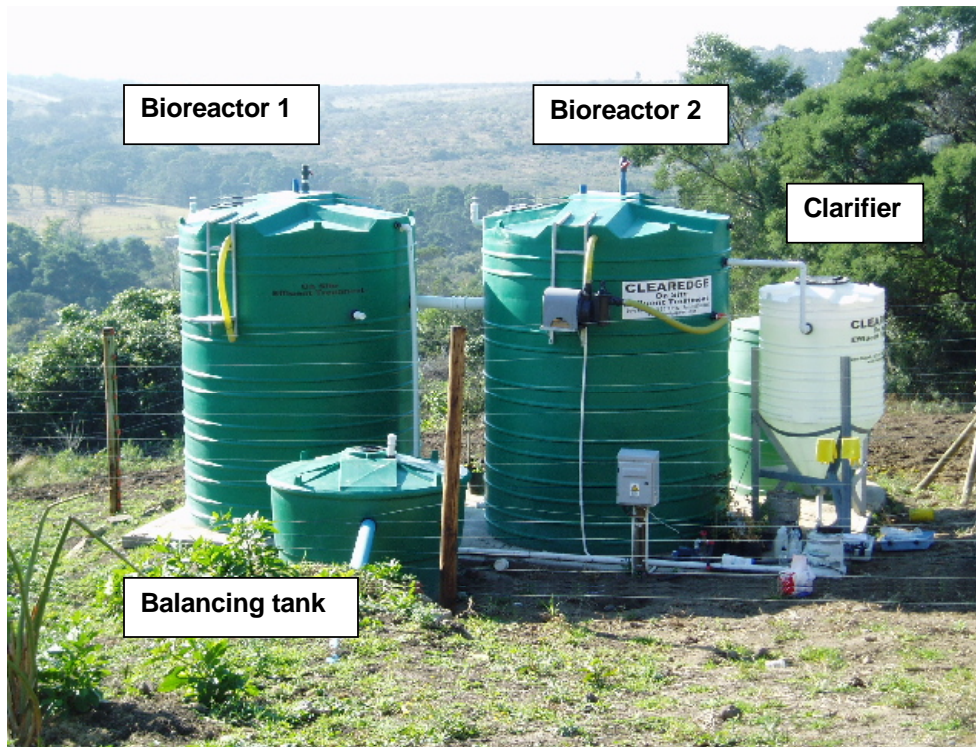


Figure 2: wastewater treatment system at Lilyfontein School

The photography above (Figure 2) shows the complete wastewater treatment system installed at Lilyfontein School. The effluent from the septic tank first flows into the balancing tank. This tank serves as a second septic tank where the same processes take place as in the original septic tank. It is also installed to store some of the wastewater so that the bioreactors are not overloaded by too much water. From this tank the water is pumped to the bottom of the first bioreactor. Numerous layers of a special plastic material with a big specific surface (see figure 3) are placed in this tank.



Figure 3: plastic material which is placed in the bioreactors

The sludge in the wastewater, which contains many different microorganisms, can settle down on this surface to form biofilms, as explained above. As the water level rises, the wastewater has contact to these biofilms, which act like a biofilter. The bacteria feed on the nutrients and decompose the organic compounds in the water. For these reactions high amounts of oxygen are needed. To create these aerobic conditions, a pump is installed on the outside wall of the tank to pump air from the surroundings into the water. When the tank is filled to the top, the water can flow through a connection pipe into the second bioreactor. It is exactly the same as the first one, with the only exception that the water enters from the top and not from the bottom. External aeration is also used. The retention time of the water is 24 hours for each bioreactor. After that the treated water flows into the clarifier. Here the remaining solids and bacteria which might have been washed off from the biofilms can settle down to form a sludge layer at the bottom of this tank. It has a conical shape so that it can be desludged by opening a valve at the bottom. The sludge flows back into the balancing tank so that the bacteria in it can be reused in the purifying process. Desludging is only necessary once in a month because there is not very much sludge in the purified water. Also once in a month a chlorine tablet, which is commercially available for the chlorination of swimming pools, is added to the water in the clarifier to kill remaining pathogenic microorganisms in the purified water. This is the only chemical needed in this system. But it is not essential. It depends on the amount of pathogens in the water. Some of these treatment plants can also run without disinfections, according to the manufacturer. This water, also called final effluent, is pumped into a big reservoir from where it can be taken for the different reuse activities, in this case irrigation of the rugby field or toilet flushing. But before the water can be reused, the quality of the final effluent has to be monitored to check if it fits the guidelines and limits set by the government.

1.3 Guidelines and parameters

There are no guidelines available for the quality of water used for toilet flushing. The only limiting factors might be aesthetic aspects like colour and smell. For that reason only the guidelines for irrigation are considered in this project. The custodian for South Africa's water resources is the Department of Water Affairs and Forestry (DWAF). This department has the mission to ensure that the quality of water resources remains fit for specific use sectors and to maintain and protect aquatic ecosystems. Therefore the *South African Water Quality Guidelines* have been developed. They serve as a source of information to achieve these goals (DWAF, 1996). Guidelines are available for several different use sectors. Because the final effluent is aimed to be used for irrigation, only the following guideline is considered for this project:

Volume 4: Agricultural Use: Irrigation

Many different parameters have to be monitored to check if their values are within the *Target Water Quality Range* (TWQR). It is defined as "the range of concentrations or levels at which the presence of a particular constituent would have no known or anticipated adverse effects on the fitness of water for a particular use" (DWAF, 1996). It has to be mentioned that this definition includes the information that water, which does not fit in the TWQR, can still be used for the desired purpose under certain circumstances.

The parameters monitored in this project have been chosen according to their importance and the availability of equipment to determine them.

1.3.1 Physical-chemical parameters

The **temperature** of water can be expressed in different units. In this project it is expressed as degrees on the Celsius temperature scale (°C). The temperature has no direct effect on the water quality. But it can influence the biological activity and the solubility of oxygen in water. The higher the temperature, the lower the concentration of dissolved oxygen. On the other hand processes and reactions taking place in the water can affect the temperature. The South African Water Quality Guidelines provide no TWQR for the temperature (DWAF, 1996)

The **pH** is defined as the negative logarithm to the base ten of the hydrogen ion activity. The pH scale ranges from 0 to 14. A pH of 7 means that the solution is neutral. If it is lower, the solution is acidic, and if it is higher, the solution is basic. Except at extremes, the pH value of water has no direct effects on the water quality. But it can cause adverse effects by solubilisation of toxic heavy metals and the protonation and deprotonation of other ions. And extreme pH values can induce corrosion of the irrigation equipment. The TWQR for irrigation is 6.5 to 8.4 (DWAF, 1996).

The **electrical conductivity** (EC) describes the amount of ions in water. These ions carry an electrical charge and therefore the water can conduct an electrical current, which is measured electrochemically. The unit of the EC is milliSiemens per meter (mS/m). The conductivity is dependent on the value of the electrical charge of the different ions, to mobility of these ions and their concentration. Water with a high EC is also called saline water. By using this for irrigation, salt is induced into the soil profile where it accumulates. This creates a saline soil. While many commercial crops are sensitive to soil salinity, they cannot be grown successfully because the crop yield is reduced. The TWQR for the EC of water for irrigation is < 40 mS/m, where most of the crops and other plants can grow. The higher the EC, the lower the crop yield and the choice of crops that can be grown successfully (DWAF, 1996).

The **dissolved oxygen** (DO) is the amount of gaseous oxygen dissolved in water. It is given in milligrams per litre (mg/l). The concentration of the dissolved oxygen depends on the biological and chemical processes and reactions, which can take place in the water where oxygen is either consumed or released. But it also depends on the temperature. The higher the temperature, the lower the solubility of oxygen, which results in a lower concentration. Water with 100% saturation of oxygen has a concentration of 9.1 mg/l at 20 °C (Grohmann and Nissing, 2002). Wastewater normally has a very low DO concentration because of the high chemical oxygen demand. A TWQR is not available.

The **chemical oxygen demand** (COD) is a measure for the sum of all organic compounds in a water sample, including the heavily degradable ones. The COD value signs the amount of oxygen used for the oxidation of the entire organic compounds in the water sample. It is given in mg O₂/l. The COD is an important parameter for the characterisation of the efficiency of a wastewater treatment plant. A high COD indicates a high organic load in the water, which is typical for wastewater. The dissolved oxygen in the water is consumed so that its concentration is very low. (Standard Methods, 1998; Rüffer and Masannek, 2002). The South African Water Quality Guidelines for irrigation do not provide a TWQR for the COD.

1.3.2 Anions

Fluoride is the anion of fluorine, which is the most electronegative member of the halogens and therefore the most reactive one. Fluorides occur in natural waters because of the leaching from fluoride containing minerals into the groundwater source. If the fluoride concentration is not excessively high, the irrigation with this water does not have adverse effects on the crop yield because most crops are relatively tolerant towards fluoride. And while fluoride normally does not accumulate in the crops, there are no health risks for animal or human consumption. Nevertheless the TWQR is set to < 2.0 mg/l (DWAf, 1996).

Chloride is the anion of chlorine. It is an essential micronutrient for plants and relatively non-toxic to them. Chlorides are highly soluble and do not tend to be absorbed by the soil in a significant degree. Therefore they are taken up by the plant roots and/or leaves, depending on the irrigation method. High chloride concentrations can cause plant injuries, which result in a decrease of crop yield. When chloride accumulates in the leaves, foliar damage like leaf burn can occur, which is especially a problem when the leaves are the marketed product. Because of the high solubility, chlorides can only be removed by expensive processes, for example reverse osmosis. Using such a technique for the treatment of water designated for irrigation would be highly uneconomic. The farmer should either accept the decreased crop yield or switch to plants, which are more tolerant towards chloride. The chloride concentrations in fresh water can vary from a few to several hundred mg/l; in seawater it is approximately 19800 mg/l. The TWQR is 100 mg/l. This is the threshold where no adverse effects occur in most plants (DWAf, 1996).

Bromide is the anion of the element bromine. No adverse or anticipated effects are known for irrigation with water containing bromide. Therefore no TWQR is available in the South African Water Quality Guidelines (DWAf, 1996).

Sulphate is a common constituent of many waters. It occurs in natural waters because of the leaching of sulphate minerals from the sediment into the water body (Grohmann et al., 2002). While it is not essential for the human body, the sulphate taken up with drinking water is excreted via the urine and faeces. Therefore sulphates also occur in wastewater. Under anaerobic or anoxic conditions they are reduced to sulphides and form the toxic gas hydrogen sulphide, which gives the wastewater an offensive odour. The bacteria responsible for these reduction processes are of the species *Desulfovibrio* and *Desulfobacter* (Brock, 2003). But the sulphides in the wastewater also come from the decomposition of organic compounds like proteins.

In biological wastewater treatment under aerobic conditions the bacteria *Thiobacillus thiooxidans* oxidise the sulphides to sulphate again.

While no adverse or anticipated effects are known for the irrigation with sulphate containing water, no TWQR is given by the South African Water Quality Guidelines.

Phosphate, in this case ortho-phosphate (PO_4^{3-}), is one of the phosphorous species occurring in wastewater. As an essential part of the human body, 1% of the body mass is phosphorous and is taken up in the form of phosphates. The organism can handle variations in the uptake of phosphorous compounds by mobilisation of parts of this big phosphorous stock. Therefore most phosphates in wastewater come from

human excrements (Grohmann et al., 2002). Phosphorous is playing an important role in the biological wastewater treatment because it is also an essential nutrient for the microorganisms. They can take up phosphorous in almost every form.

This is the same case for plants. Therefore many farmers buy fertilisers containing phosphorous. Therefore the South African Water Quality Guidelines do not provide a TWQR for phosphate in irrigation water (DWAF, 1996).

The only problem, which can occur, is eutrophication. Eutrophication describes the scenario when high loads of nutrients (mostly nitrogen and phosphorous) enter the surface water bodies. These nutrients promote excessive growth of algae and cyanobacteria, which create high amounts of organic matter when they die, as well as toxins, which are hazardous for fish and other water animals. The bacteria which decompose these organic loads consume very much of the dissolved oxygen so that the conditions switch from aerobic over anoxic to anaerobic. That leads to the death of other water organisms dependent on the oxygen dissolved in the water, mostly fish. The result of all that is the beginning of fouling processes of the water creating methane, carbon dioxide and hydrogen sulphide, so that these processes can be seen as that death of the water (Rüffer and Masannek, 2002; Brock, 2003).

Nitrogen can occur in various forms. On the one hand there are organic nitrogen compounds and on the other hand there are the inorganic compounds **ammonia**, **nitrite** and **nitrate**. The interconversion and co-existence of these different forms of nitrogen are known as the nitrogen cycle, which can be used to describe the processes in biological wastewater treatment. The organic compounds, for example amino acids, are decomposed by bacteria with ammonia as one of its products. Under aerobic conditions the organic nitrogen compounds can also be oxidised to nitrate. Ammonia is a toxic gas, which gives the wastewater, together with hydrogen sulphide, methane and other gases, a bad smell. It can be eliminated by a process called nitrification. This process requires aerobic conditions. In a first step ammonia is oxidised to nitrite. This is done by bacteria of the species *Nitrosomonas*. In a second step bacteria of the species *Nitrobacter* oxidise the nitrite to nitrate, which is the end product of the nitrification. Nitrate is, like phosphorous, a key nutrient for plants. It is also contained in fertilisers. But if the concentration is too high, it can also cause eutrophication problems, as explained above. For the nitrate removal further treatment is required. Bacteria of the species *Bacillus*, *Paracoccus* and *Pseudomonas* carry out a process called denitrification. Under anoxic conditions these bacteria use the oxygen contained in the nitrate for their respiration by reducing the nitrate to gaseous elemental nitrogen, which is released to the atmosphere (DWAF, 1996; Rüffer and Masannek, 2002; Brock, 2003).

The South African Water Quality Guidelines provide a TWQR of 5 mg/l for the sum of all inorganic nitrogen species. Ammonia, nitrite and nitrate are considered together because of their interconversion and co-existence in aquatic systems. Although nitrogen is an essential nutrient for plants, the TWQR is set relatively low because too high concentrations of nutrients can have detrimental effects on most plants and nitrate not taken up by the plants can contaminate the groundwater. Another reason is that a nutrient overload of the irrigation water can promote algal growth inside the irrigation equipment, which leads to clogging of it (DWAF, 1996).

A summary of the parameters and their TWQRs can be viewed in table 1.

Table 1: list of parameters and their TWQRs according to the South African Water Quality Guidelines, Volume 4: Agricultural Use: Irrigation

Parameter	Target Water Quality Range (TWQR)
Temperature	Not available
pH	6.5 – 8.4
Electrical conductivity (EC)	< 40 mS/m
Dissolved oxygen (DO)	Not available
Chemical oxygen demand (COD)	Not available
Fluoride (F ⁻)	Not available
Chloride (Cl ⁻)	100 mg/l
Bromide (Br ⁻)	Not available
Sulphate (SO ₄ ²⁻)	Not available
Phosphate (PO ₄ ³⁻)	Not available
Nitrogen (NH ₃ -N + NO ₂ ⁻ -N + NO ₃ ⁻ -N)	5 mg/l

2. Aims

- Characterisation and efficiency testing of a decentralised water purification system based on the principle of a submerged fixed-film bioreactor by taking samples from certain parts of the system and analysing them
- Monitoring and judging the quality of the final effluent according to the Target Water Quality Range (TWQR) given in the *South African Water Quality Guidelines, Volume 4: Agricultural Use: Irrigation*

While this project is the pilot phase of a bigger project, only a few parameters have been determined according to the available equipment for their determination. The parameter list will be expanded for the following parts of the project.

The aim of these sub-projects is to get a base of knowledge for the applicability of such decentralised water purification systems. This knowledge can serve as a source of information to improve these systems and to convince municipalities and governments to install these systems in rural areas or urban settlements not connected to the municipal sewage system. This would lead, as explained above, to a better wastewater management and could, together with other water management tools, avoid the predicted water scarcity scenario in the year 2025.

3. Material and Methods

3.1 Deionised water

The water used for rinsing the equipment (sampling bottles, glassware, pipette tips, syringes) and preparing of solutions was taken from the MilliQ-System (MilliPore) in the chemistry lab at WSU.

The tap water is first filtered through a filter with a pore diameter of 1 μm . Then it is treated with activated charcoal. After that it runs through a second filter with 0,5 μm pores. This is followed by the Milli-RO-System. Here the water is first run over an ion exchange resin and then pushed through a reverse osmosis membrane to hold back most of the ions present in the water. This treated water is stored in a reservoir tank. When water is needed, it is pumped from this tank through the Milli-Q-System, which also consists of an ion exchange resin to purify the water to a very pure grade.

3.2 Cleaning of equipment

The equipment used in this project (glassware, sampling bottles, pipette tips, syringes) had to be kept clean to avoid contaminations, which could falsify the results of the experiments. First the equipment was soaked in water containing a detergent. After that it was rinsed with tap water until it was free of detergent. Finally it was rinsed at least three times with deionised water.

3.3 Taking the samples

Samples were taken in the period from May 11th to July 8th.

The PE-bottles used for taking the samples were delivered by Amatola Water, a local water supplier. They were cleaned as explained above. Samples were taken two to three times a week. The sampling sites are indicated in figure 1. Samples were taken from the clarifier (sample "Eff") to determine the quality of the final effluent, as well as from the balancing tank (sample "In") to determine the efficiency of the treatment plant. From the third week on (27.05.05) samples were also taken from the two bioreactors (samples "Bio1" and "Bio2") to get a better understanding of the processes taking place in them.

The sampling procedure was the same for each sample. First the screw cap on the respective tank was opened. Then the sample bottle was submerged into the water to fill it. The bottle was rinsed twice with this water before filling it to the top.

After that the bottle was closed and stored in a cooler box. This was necessary to avoid alterations of the samples between the sampling and the analyses because the Lilyfontein School is approximately 50 km away from the laboratory.

Prior to the determinations done in the laboratory the samples were allowed to reach room temperature.

At July 7th one sample was also taken from the school's borehole to roughly estimate the quality of the groundwater there. This groundwater is mainly used there for flushing the toilets. This was done to help in the explanation of some of the other results.

3.4 On-site measurements

3.4.1 pH and temperature

Principle:

Today the most common method for the determination of the pH value of a water sample is the potentiometric method using a glass electrode. This glass electrode consists of a glass body filled with a buffer solution with a known pH and an inner reference electrode, in most cases a silver/silver chloride electrode. The layer of the glass electrode can be described as a glass membrane with the exception that the hydrogen ions cannot go through the membrane completely. This glass layer serves as a buffer of silicic acid and silicate where cations can be exchanged. This leads to a development of differences in the potential between the membrane and the evaluated solution on the one side, and differences in the potential between the membrane and the buffer solution on the other side of the membrane. These differences in the potential are evaluated to determine the pH. While the pH of the internal buffer solution is known, the unknown pH can be calculated by subtraction of the potential of the known solution from that of the unknown solution. But to make an absolute evaluation possible, the pH electrode has to be calibrated with a standardised buffer with a known pH. Immersing the electrode in the buffer gives the potential difference E_B and immersing in the unknown solution gives the potential difference E_X . Now the exact pH can be calculated using the following formula:

$$pH_X = pH_B - \frac{F \times (E_X - E_B)}{2.303 \times RT}$$

with

pH_X – pH of the unknown solution
 pH_B – pH of the NIST buffer solution
 F – Faraday constant (96485 C/mol)
 R – gas constant (8.314 J/K*mol)
 T – temperature in K.

The glass electrode is connected to a pH meter, which measures the potentials and does all the calculations. Most of these instruments are also equipped with a temperature sensor so that the temperature of the solutions can be calculated to a reference temperature of 25 °C (Otto, 2000; Stottmeister, 2002).

Material and chemicals:

- Portable multi parameter meter *WTW multi340i*; WTW, Germany
- pH electrode *SenTix41*; WTW, Germany
- Technical buffer, pH 4.01; WTW, Germany
- Technical buffer, pH 7.0; WTW, Germany
- Deionised water

Performance:

The measurements for pH and temperature were done on-site immediately after taking the sample. First the electrode had to be calibrated. It was rinsed with deionised water and carefully wiped with a paper towel before immersing it in the buffer solution with pH 7.0. First the “Cal” button and then the “Enter” button on the instrument was pressed to start the calibration. After that the display indicated that the second buffer was needed. After rinsing and wiping the electrode again, it was immersed in the pH 4.01 buffer and the “Enter” button was pressed. The end of the calibration was indicated by showing the result of it on the display. This calibration was done on every sampling day.

Pressing the “M” button switched the instrument back to the measuring mode. The electrode was rinsed and wiped and then immersed in the sample. To start the measuring, the button “Enter” had to be pressed. When the value was stable, the “AR” field in the display stopped blinking. The display showed the result for the pH as well as for the temperature. The results were noted in a sampling protocol. This procedure was performed for every sample.

3.4.2 Electrical conductivity

Principle:

The electrical conductivity (EC) is defined as the reciprocal value of the specific electrical resistance. The determination of the EC can be illustrated by saying that the resistance of a water sample is measured between two electrodes with a distance of 1 m and an area of 1 m² and its reciprocal value is formed. The distance and area of the electrodes are much smaller in the practical applications of this method. That means that they cannot be measured directly. The measuring cell is characterised by the quotient of distance and area, which is also called the *cell constant*. This constant is evaluated by measuring the resistances of different standard solutions with a known conductivity. The instruments for the determination of the EC are programmed with the connection between the resistance and the cell constant and the cell constant itself so that these instruments can directly display the EC instead of the resistance. The cell constant is relatively stable so that a calibration of the instrument is only seldom necessary.

The EC is very dependent at the temperature. For reasons of comparability all results are related to a reference temperature of 25 °C. Since most conductivity cells are also equipped with a temperature sensor, this calculation is also done by the instrument (Stottmeister, 2002)

Material and chemicals:

- Portable multiparameter meter *WTW multi340i*; WTW, Germany
- Conductivity electrode *TetraCon325*; WTW, Germany
- Conductivity control standard, 1413 µS/cm; WTW, Germany
- Deionised water

Performance:

The measurements of the electrical conductivity (EC) were done on-site immediately after taking the sample. A calibration was only done one time at the beginning of the project because the last calibration of the instrument was one year ago.

The electrode was rinsed with deionised water and wiped with a paper towel. After that it was immersed in the control standard. First the “Cal” button and then the “Enter” button was pressed to start the calibration. It was finished when the display showed the cell constant. A press on the “M” button switched the instrument into the measuring mode. After rinsing and wiping the electrode the samples were measured in the same way as described for the pH.

The results were given in $\mu\text{S}/\text{cm}$. For a better comparability with the guidelines they were converted into mS/m by multiplying them with 100.

3.4.3 Dissolved oxygen

Principle:

The dissolved oxygen in a water sample can be determined with an electrochemical method. Such an oxygen sensor consists of a working electrode and a counter electrode. These two electrodes are located in an electrolyte system. A gas-permeable membrane separates it from the sample. The oxygen is reduced to hydroxide ions by the working electrode. This electrochemical reaction creates an electrical current between the two electrodes. The more oxygen present in the sample, the larger the current signal. The oxygen concentration in the sample is calculated by the instrument using this signal and a solubility function stored in the instrument (WTW, 2005).

Material and chemicals:

- Portable multiparameter meter WTW multi340i; WTW, Germany
- Oxygen electrode Cellox325; WTW, Germany
- Calibration chamber OxiCal SL; WTW, Germany
- Deionised water

Performance:

The measurements of the dissolved oxygen (DO) were done on-site immediately after taking the sample. A calibration was done once in a week. For that purpose the electrode was pulled out of the storage chamber, which also serves as the calibration chamber. The sponge at the bottom of it had to be moistened with deionised water so that the air inside this chamber was saturated to 100% with water steam. The oxygen electrode was put back into the chamber. The buttons “Cal” and “Enter” were pressed on the instrument and the calibration started. After the calibration the display showed the calibration data to indicate the finished calibration. The “M” button was pressed to switch the instrument into the measuring mode. The electrode was pulled out of the calibration chamber and the samples were measured in the same way as described for the pH.

3.5 Spectrophotometer

In this project spectrophotometers were used for the colorimetric determination of the chemical oxygen demand (COD) and the ammonia-nitrogen. Therefore it seems to be necessary to explain the basic principles of a UV/VIS spectrophotometer. The light source is a tungsten lamp for the visible (VIS) and a deuterium lamp for the ultraviolet (UV) spectrum. This polychromatic light is converted into monochromatic light of a specific wavelength by the use of a monochromator. The sample is put into the beam of this light using a cuvette of a defined shape and size. The analyte in this sample weakens the intensity of the light of the chosen wavelength by absorption. To compensate losses of intensity at the surface of the cuvette by reflection and scattering, a second cuvette, containing only the solvent but not the analyte, is measured as a comparison. This compensation is also referred to as zeroing the instrument because the pure solvent should not absorb at the chosen wavelength. After the cuvette a photocell converts the outcoming light into an electric signal, which can be processed electronically. These processes can include the displaying of the absorbance of the sample or even the calculation of the concentration of the sample (Lippold et al., 2002). This calculation is done by using Beer-Lambert's Law:

$$\lg \left\{ \frac{I_0}{I} \right\} = \frac{A}{d}$$

with

I_0 – intensity of the light after the cuvette containing the pure solvent

I – intensity of the light after the cuvette containing the analyte

A – absorbance

ϵ – spectral absorption coefficient

c – concentration of the analyte

d – sample diameter.

3.6 Chemical oxygen demand

Principle:

As described above, the chemical oxygen demand (COD) indicates the amount of oxygen needed to oxidize the entire organic compounds in a water sample. The COD can be determined by using a strong chemical oxidant to oxidize the organic compounds in the water to CO_2 and H_2O . This is achieved by boiling a certain amount of the sample together with a strong acid solution containing potassium dichromate as the oxidant and silver sulphate as the catalyst. A possible interference of the COD determination is the presence of high amounts of chloride ions. To avoid this, mercuric sulphate is added to the mixture before digestion to complex them. Open reflux methods as well as closed reflux methods are described in the literature (Standard Methods, 1998). In this case a closed reflux method was used. The advantage of this method is the small amount of chemicals and sample needed compared to open reflux methods because the digestion can take place in small sealed glass ampules placed in a heating block instead of a big reflux apparatus.

This is important in terms of storage and disposal because mercury-containing compounds and potassium dichromate are very toxic and the latter can cause cancer. Potassium dichromate is used because it is a very strong oxidant and superior to other ones. It oxidizes 95-100% of the theoretical value of most organic compounds (Standard Methods, 1998). The remaining unreduced dichromate is determined either titrimetrically or colorimetrically after digestion so that the amount of the consumed oxidant can be calculated. In the titrimetric method the remaining dichromate ions are titrated with a standard ferrous ammonium sulphate titrant in the presence of a ferroin indicator. The Cr(VI) is reduced to Cr(III) by the Fe(II)-ions so that a change in the colour of the solution occurs. This change in colour is the end point of the titration.

In this project the colorimetric method was used. After digestion the colour intensity of the solution is determined with a spectrophotometer against a set of standard solutions containing a known amount of potassium hydrogen phthalate (KHP) at a wavelength of 600 nm. KHP is used as a standard because it has a known COD. The standards are also digested in the same way as the sample and the blank. A calibration curve is constructed by plotting the absorbances of the standards against their respective CODs. The absorbance of the sample is then compared to this calibration curve to calculate the COD of it.

The results of every COD determination are given in mg O₂/l.

Material and chemicals:

- COD digester, Hach, USA
- Eppendorf pipette, 500-5000 µl, Eppendorf, Germany
- Volumetric flasks, 100 ml, Brandt, Germany
- Helios spectrophotometer,
- Lovibond COD cuvettes, Tintometer GmbH, Germany
- Deionised water
- Potassium hydrogen phthalate (HOOC₆H₄COOK), (KHP)

Performance:

Due to lack of equipment at WSU the determination of the COD was done at the laboratory of Amatola Water, located at the Nahoon Dam, 20 km away from WSU. It was performed according to

Method 5220 D. Closed reflux, colorimetric method (Standard Methods, 1998).

This method was varied by using the Lovibond COD cuvettes. These cuvettes contain a mixture of sulphuric acid, potassium dichromate, silver sulphate and mercuric sulphate so that it was not necessary to prepare the reagent solutions. The advantages are the minimized waste of chemicals and the exclusion of possible mistakes that can occur while preparing the solutions.

As a first step the COD digester was preheated to 150°C for approximately 30 minutes. In the meantime the standard solutions were prepared. The preparation of the stock solution was done by dissolving 425 mg KHP in 1 l deionised water. The COD of this solution is 500 mg O₂/l because the theoretical COD of KHP is 1,176 mg O₂/mg (Standard Methods, 1998).

The following amounts were pipetted into respective 100 ml volumetric flasks to make up the standard solutions:

Table 2: preparation of COD standards

	Volume of stock solution	COD of standard
Blank	0 ml	0 mg O ₂ /l
Standard 1	2 ml	10 mg O ₂ /l
Standard 2	4 ml	20 mg O ₂ /l
Standard 3	8 ml	40 mg O ₂ /l
Standard 4	16 ml	80 mg O ₂ /l
Standard 5	30 ml	150 mg O ₂ /l

After that the flasks were filled to the mark.

Finally 2,5 ml of each standard were pipetted into the COD cuvettes. The same was done with the samples and the blank. The cuvettes were labelled accordingly, shaken well and put into the preheated digester.

After a digestion time of two hours the cuvettes were allowed to cool down to room temperature. The wavelength of the spectrophotometer was set to 600 nm. Then the blank was used to zero the instrument. After that it was switched to calibration mode. Now each of the cuvettes with the standards was inserted to read its absorbance, beginning with the lowest COD. The instrument was set so that its display showed the concentration instead of the absorbance. The concentration (here: COD) of each standard was typed in over a keypad. Based on this information the spectrophotometer was able to calculate a calibration factor.

After that the samples were measured. With the calibration factor the instrument automatically converted the absorbance of each sample into its COD value.

3.7 Anions

Principle:

All chromatographic methods are based on the principle of the separation of the analytes from each other and from their matrix. This is done by moving a so-called mobile phase over a so-called stationary phase. In the case of ion chromatography the mobile phase is called the eluent.

A typical ion chromatography system like that used in this project consists of the following parts:

- a storage container for the eluent
- a pump to transport the eluent through the system
- an injector for the sample input
- a guard column and an analytical column with a suppressor
- a conductivity detector
- a data processing system (PC).

The role of the eluent is to carry the sample containing the analyte (here: the anions) through the system. In a system with an anion exchange column with chemical suppression a hydrogen carbonate-carbonate-eluent is used. It is moved through the column, which is the stationary phase. The eluent is transported by a pump. This pump is equipped with an injector consisting of a 6-way valve. It also includes a sample loop. The sample loop is manually loaded with the sample. It is used to

ensure that always the same amount of sample (here: 25 µl) is injected into the eluent flow. This is done automatically with the 6-way injection valve.

The anion exchange column is packed with a JÁ{ Åãq ^c!Á æ[] [| [~ •Á•q Á^æ consisting of ethylvinylbenzene crosslinked with 55% divinylbenzene. The anion exchange layer of this substrate is functionalised with quarternary ammonium groups. The guard column installed prior to the analytical column consists of the same components. It is there to prevent the elution of sample contaminants onto the analytical column because it is easier to clean or replace the guard column.

The separation of the anions is based on the principle that they interact with the stationary phase. Because of their different sizes and charges they pass the column with different speeds. That means that every anion has a specific retention time, according to its size and charge. For that reason the elution of the anions occurs in the following order: fluoride, chloride, nitrite, bromide, nitrate, phosphate, and sulphate. They are detected by a conductivity detector.

The electrolytic suppressor is a can be seen as a part of the detector. A suppressor system has two major functions. The first one is to decrease the high basic conductivity of the eluent to get a better signal-to-noise-ratio. The second one is to convert the anions to be analysed into a stronger conducting form. This is achieved by cation exchange processes in the suppressor. The eluent consists of the salts of weakly dissociated acids, for example sodium hydrogen carbonate. The cation exchange processes convert it into carbonic acid, which is a weak acid and poorly dissociated so that its residual conductivity is also low. The anions to be determined, for example chloride, are also converted into the free acid form, for example hydrochloric acid, which has a higher conductivity than the salt.

By this suppression technique the sensitivity of detection is significantly increased.

The signal of the detection is plotted against the time. This results in a single peak for every anion in the sample. The peaks are assigned by the order of the elution of the anions, as explained above.

Ion chromatography is also a quantitative method. The peak area is directly proportional to the concentration of the respective ion. With a set of standard solutions of known anion concentrations one can create a calibration curve so that the concentrations of the anions in a sample can be calculated (Lippold et al., 2002; Dionex, 2005).

Material and chemicals:

- Ion chromatography system ICS-1000; Dionex, USA
- Guard column IonPac AG14, 4x50mm; Dionex, USA
- Analytical column IonPac AS14, 4x250mm; Dionex, USA
- Atlas electrolytic suppressor; Dionex, USA
- DS6 heated conductivity cell; Dionex, USA
- Software Chromeleon6; Dionex, USA
- Spatula
- Analytical balance
- Volumetric flasks, 100 ml, 1000 ml, 2000 ml; Brandt, Germany
- Eppendorf pipettes, 100 µl, 1000 µl, 5000 µl; Eppendorf, Germany
- Beakers; Schott Duran, Germany
- Syringe
- Deionised water (H₂O)
- Sodium carbonate (Na₂CO₃)
- Sodium hydrogen carbonate (NaHCO₃)
- Sodium fluoride (NaF), dried
- Sodium chloride (NaCl), dried
- Sodium bromide (NaBr), dried
- Sodium nitrate (NaNO₃), dried
- Sodium nitrite (NaNO₂), dried
- Potassium hydrogen phosphate (KH₂PO₄), dried
- Sodium phosphate (Na₂SO₄), dried

Performance:

The eluent was prepared by dissolving 21.2 g Na₂CO₃ and 2.1 g NaHCO₃ in 250 ml H₂O. This solution was the eluent concentrate with a concentration of 0.8 mol/l for Na₂CO₃ and 0.1 mol/l for NaHCO₃. From this concentrate 20 ml were pipetted into a 2000 ml volumetric flask and it was filled to the mark with H₂O. This diluted eluent was filled into the eluent storage container of the IC system.

The eluent lasted for approximately three weeks, depending on the number of samples measured.

A stock solution containing all seven anions in the concentration of 1000 mg/l was prepared by weighing the masses of their salts according to table 3 into a 1000 ml volumetric flask.

Table 3: masses of the salts

Salt	Mass of the salt in g
NaF	2.21
NaCl	1.648
NaBr	1.288
NaNO ₃	1.371
NaNO ₂	1.5
KH ₂ PO ₄	1.433
Na ₂ SO ₄	1.479

After that it was filled to the mark with H₂O. Stored in the fridge this solution was stable for approximately one to two months.

The standard solutions were made of this stock solution by diluting it to the desired concentrations. To achieve that the volumes given in table 4 were pipetted into the respective 100 ml flasks.

Table 4: volumes of the stock solution and concentrations of the standards

	Volume of stock solution	c of standard
Standard 1	0.1 ml	1 mg/l
Standard 2	1 ml	10 mg/l
Standard 3	3 ml	30 mg/l
Standard 4	7 ml	70 mg/l
Standard 5	10 ml	100 mg/l

After that the flasks were filled to the mark with deionised water.

The Chromeleon6 software on the PC was started. This program has the full control over the ion chromatography system. From there the pump, the suppressor and the column heater were started. The column heater is necessary to ensure that all measurements are done under the same temperature conditions and are not affected by variations of the air temperature in the laboratory. The temperature was set to 35 °C because it is assumed that the air temperature in the laboratory would never be higher than that.

These starting processes needed approximately 20 to 30 minutes until the instrument was ready for the measurement. In the meantime a new file was created in the software. The number of standards and samples were set, as well as other settings like the concentration of the standards and the dilution factor. This was necessary because the samples had to be diluted by the factor ten to fit in the calibration range. This dilution was done by pipetting 10 ml of each sample into the respective 100 ml flask and filling it to the mark with H₂O.

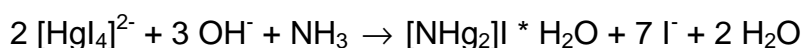
When the instrument was ready, the "Start Batch" button was clicked. Now the software asked the user for the first sample. In this case it was the first standard. A small amount of it was filled in a beaker and approximately 1 to 2 ml were sucked up with a syringe. It was important to have no air bubbles in it. The sample was injected into the sample loop of the IC system. After clicking the "OK" button 25 µl of the sample in the loop were injected into the eluent flow, as explained above. The recording of data by the software was also started automatically. After 30 seconds the injection was finished. Now it was possible to already load the sample loop with the second standard. This was done in the same way as explained for the first standard. After 13 minutes the measuring of the first standard was finished and the software asked for the next injection. While the second standard was already loaded, only the "OK" button had to be pressed to continue the measuring. These steps were repeated until all of the standards and samples were measured. When the last sample was finished, the suppressor, the column heater and the pump were switched off so that the instrument was put back into standby mode. Since all data evaluation and calculations were done by the software the user only had to assign the names of the anions to the respective peaks. After that the calibration data and the calibration curve were viewed. The calibration was accepted when the relative standard deviation was less than 5% and the correlation coefficient was better than 0.999. Otherwise the complete measurement had to be repeated. If the calibration was acceptable, the calculated concentrations of the anions were written down as results for the determination of the anions.

3.8 Ammonia-nitrogen

First it has to be mentioned that originally an electrochemical method using an ion-selective electrode was planned to be used for the determination of the ammonia-nitrogen. The required equipment had to be ordered. Unfortunately delivery problems occurred so that this equipment did not arrive during the time of this project. Finally the determinations were done at the laboratory of the Buffalo City Municipality in East London.

Principle:

The method used in this laboratory is a classical wet chemistry method, which forms a good contrast towards the other modern methods used in this project. It is called Nesslerisation or Nessler's Method. This method is named after its developer, Julius Nessler (1827 – 1905). In 1856 he showed a method for the determination of ammonia using a special reagent, which is now known as Nessler's reagent. This reagent is an alkaline solution of potassium tetraiodomercurate(II). It reacts with ammonia to form a yellowish-brown complex of polymeric nitrido-mercury(II)-iodide, which is the iodide of the so-called *Millon's Base*.



While the intensity of the colour is directly proportional to the concentration of the ammonia-nitrogen, a sample can be measured spectrophotometrically against a set of standard solutions with known amounts of ammonia-nitrogen (Wikipedia, 2005). It has to be mentioned that this method is old and has been replaced by other methods in many laboratories. This has mainly ecological reasons because mercury compounds are highly toxic so that they cause severe disposal problems. Therefore this method is not mentioned any more in the newer versions of the *Standard Methods for the examination of water and wastewater* (Standard Methods, 1998).

Materials and chemicals:

- Distillation apparatus
- Volumetric flasks, 200 ml
- Test tubes
- Volumetric pipettes
- *LKB Biochrom 4049* spectrophotometer
- Potassium hydroxide
- Nessler's reagent
- 5% sodium hydroxide solution

Performance:

The determination of ammonia-nitrogen with the Nessler method is a routine analysis in the laboratory of the Buffalo City Municipality. Therefore all needed solutions were already prepared and ready to use and the spectrophotometer was also already calibrated for the determination of ammonia-nitrogen.

First 500 ml of each sample were filled in the respective distillation apparatus and boiled together with a spatula of potassium hydroxide. The ammonia in the sample was converted into the gaseous form (NH_3) under these basic conditions. The gas escaped from the sample so that it was enriched in the distillate, where it was dissolved again. The distillate was caught in 200 ml volumetric flasks.

This distillation step was done to concentrate the ammonia-nitrogen so that also low concentrations can be determined. Considering that 500 ml were taken and concentrated to 200 ml leads to the conclusion that the ammonia-nitrogen concentration was increased by the factor 2.5.

After this step 20 ml of the concentrated sample were pipetted into a test tube. Then 1 ml of Nessler's reagent and 5 ml of the 5% sodium hydroxide solution were added. This was done with every sample. A blank was also prepared in the same way, with deionised water instead of the sample. After a reaction time of 15 minutes the spectrophotometer was zeroed with the blank and after that the absorbance of each sample was read at a wavelength of 445 nm. As mentioned above, this method is routine in this laboratory and therefore the staff members provided a factor to convert the absorbance into the concentration of ammonia-nitrogen. This factor, being 3.67, included the calibration data as well as the concentration factor mentioned above so that no further calculations were necessary.

4. Results

During this project many samples have been taken and many parameters have been determined. That leads to a large amount of results. It was decided that only average values for the different parameters and sampling sites are shown here so that the reader is not confused by big tables with hundreds of similar numerals. Only interesting results, which help to achieve the aims of this project, are shown in more detail. But nevertheless the appendix to this report provides tables with all exact results for each sample and parameter so that these data are still accessible.

4.1 Appearance and smell

The influent sample taken from the balancing tank had a high turbidity, which was visible to the human eye. This was caused by the organic matter and other colloids in the wastewater. After the treatment steps the water was visibly clear. There are two main reasons for that. The first one is that the suspended solids in the water settle down on the surface of the material in the bioreactors. That is essential for the purification process, as explained in the introduction. The second reason is that the bacteria in these biofilms decompose the organic matter.

Another significant change of the water was the smell. The influent sample had an offensive odour, mainly caused by gases like methane, hydrogen sulphide and ammonia. These were removed by oxidation reactions carried out by the bacteria. The decreasing intensity of the smell was noticeable from the first bioreactor on, and the final effluent in the clarifier had no noticeable smell.

4.2 Physical-chemical parameters

Table 5: average values of the results for the physical-chemical parameters

	T (°C)	pH	EC (mS/m)	DO (mg/l)	COD (mg O₂/l)
In	19.2	7.76	385.32	1.25	98.38
Bio1	20.82	6.87	366.92	5.23	37.46
Bio2	21.21	6.95	366.15	6.13	27.28
Eff	21.12	6.95	371.26	6.53	26.7

4.2.1 Temperature

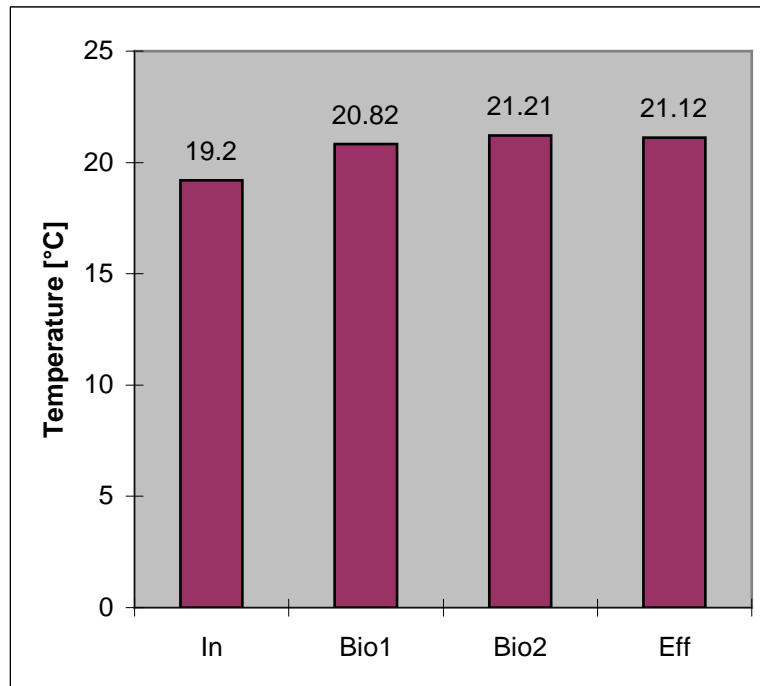


Figure 4: development of average temperatures

Figure 4 shows that the average temperatures slightly increase from the balancing tank (sample “In”) to the clarifier (sample “Eff”). This can be seen as a result of exothermic reactions that take place in the purification process. The nitrification is an example for that. The oxidation of ammonia to nitrite and the oxidation of nitrite to nitrate are both exothermic reactions. That means that energy in the form of heat is produced and released in these reactions so that the temperature of the environment (here: the water) is increased (Rüffer and Masannek, 2002). The increase is not very much in this case and the temperature of this water can be seen as normal because it is neither cold nor warm. So the temperature should have no influence on the quality of the water.

Finally it has to be mentioned that the temperatures generally decreased slightly during the time of the project. The reason for that was the upcoming winter, which led to decreasing temperatures of the environment. Figure 5 shows that development for the effluent.

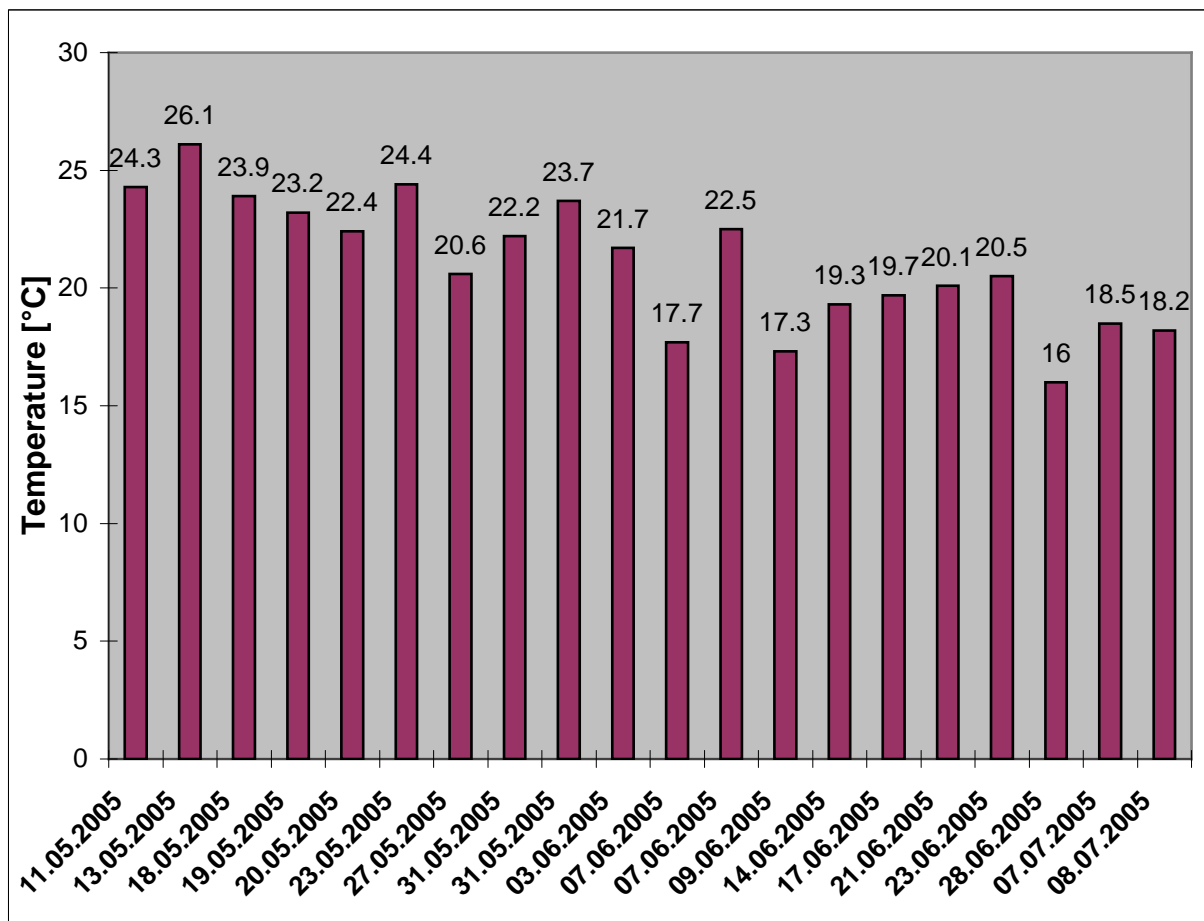


Figure 5: development of effluent temperatures during the project

4.2.2 pH

The pH of the water in the four tanks also showed a change in its value. The pH slightly decreased from the influent to the effluent. Figure 6 shows that for the average values.

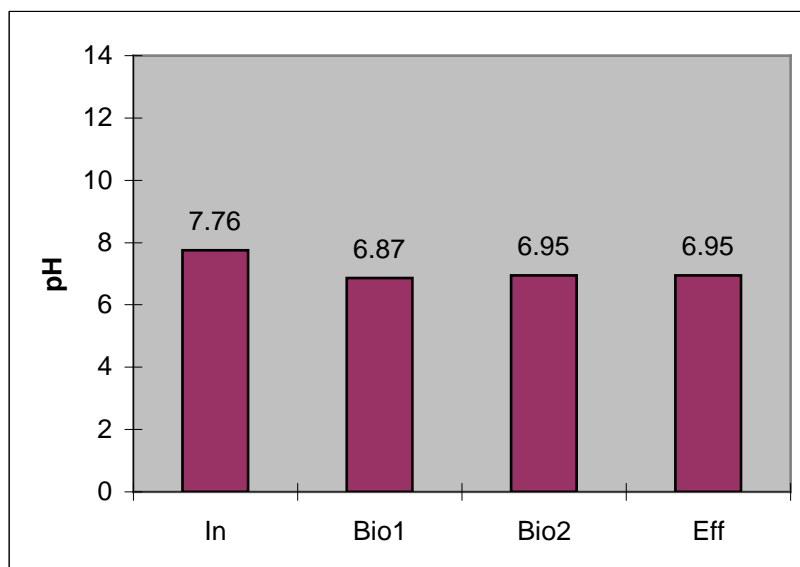


Figure 6: development of the average pH values

This decrease can be explained by the significantly increasing concentrations of sulphate and nitrate (shown later in this chapter), which are able to form sulphuric acid (H_2SO_4) and nitric acid (HNO_3). But this only happens in a small scale so that the decrease of the pH is not dramatically big.

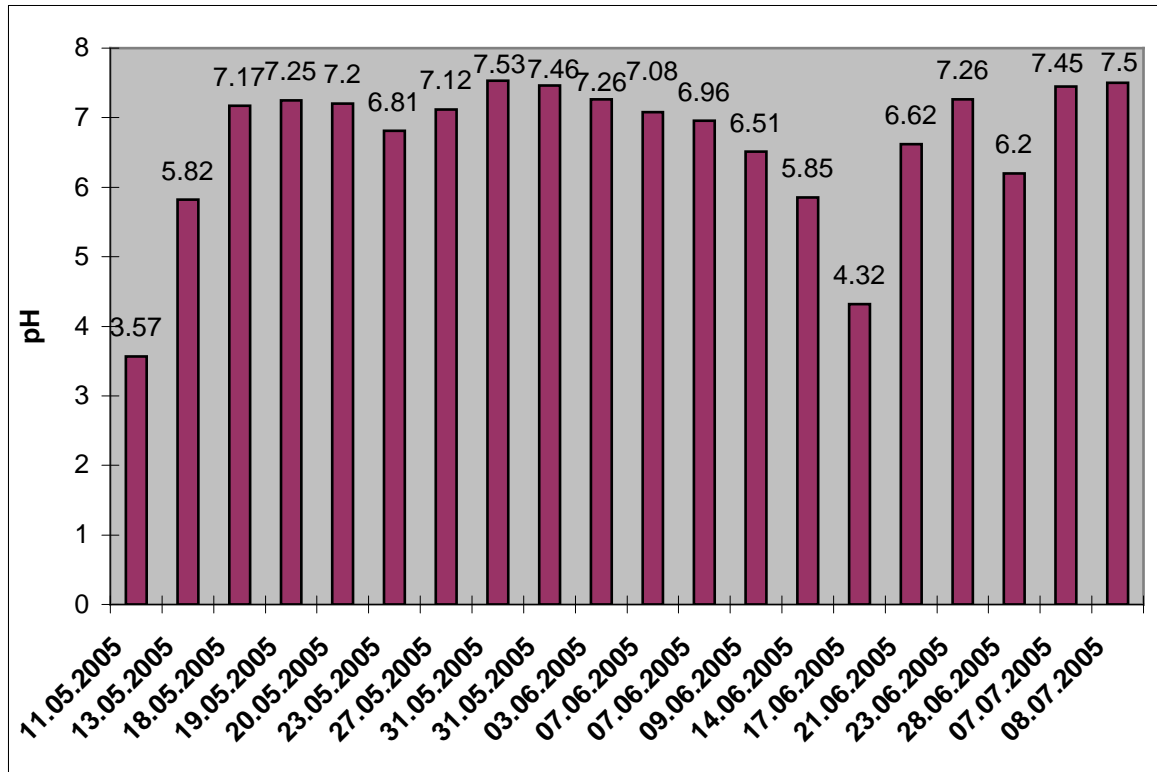


Figure 7: development of effluent pH values during the project

Figure 7 shows the development of the effluent pH values during the project. The average value was calculated under exclusion of the outliers at May 11th and June 17th. These outliers can be the result of a bad calibration, especially the first one. This is because at the beginning of the project the buffer solutions used for the calibration were too old and had to be replaced by new ones. Another reason can be a contamination of the sampling bottle or the pH electrode.

4.2.3 Electrical conductivity

The electrical conductivity (EC) showed to be very high. This was mainly caused by the very high chloride concentration (shown later). The reasons for that high EC will be explained together with the results for chloride.

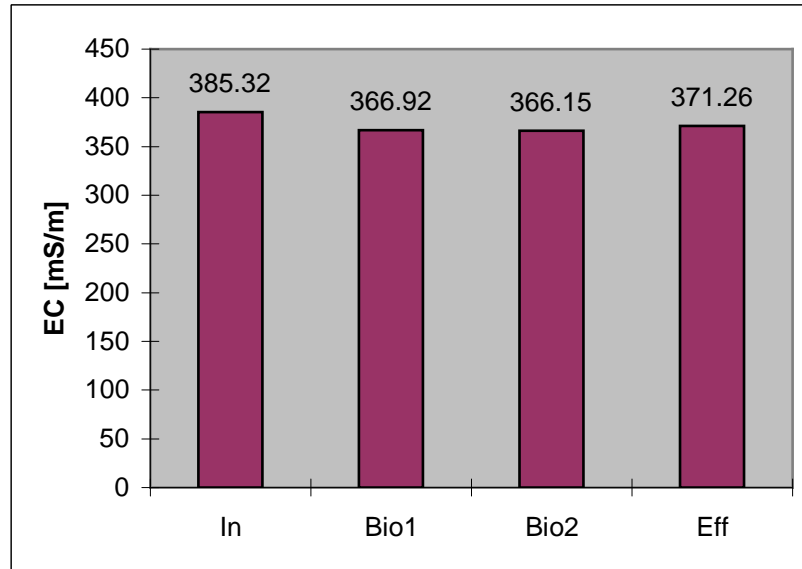


Figure 8: development of the average EC values

Figure 8 might lead to the conclusion that the EC decreased during the purification steps, but the high values are misleading in this case. The difference between the influent and the effluent is less than 4%, so that it can more likely be seen as a normal deviation caused by the method and the instrument than as a real decrease. The same can be said for all conductivity measurements in this project, which showed relatively stable results for all samples. Figure 9 will show that. But it has to be mentioned that the results for the samples of June 14th are missing because the instrument was not working so that the electrode had to be replaced by another one. That can be seen by constantly lower results in the last sampling days.

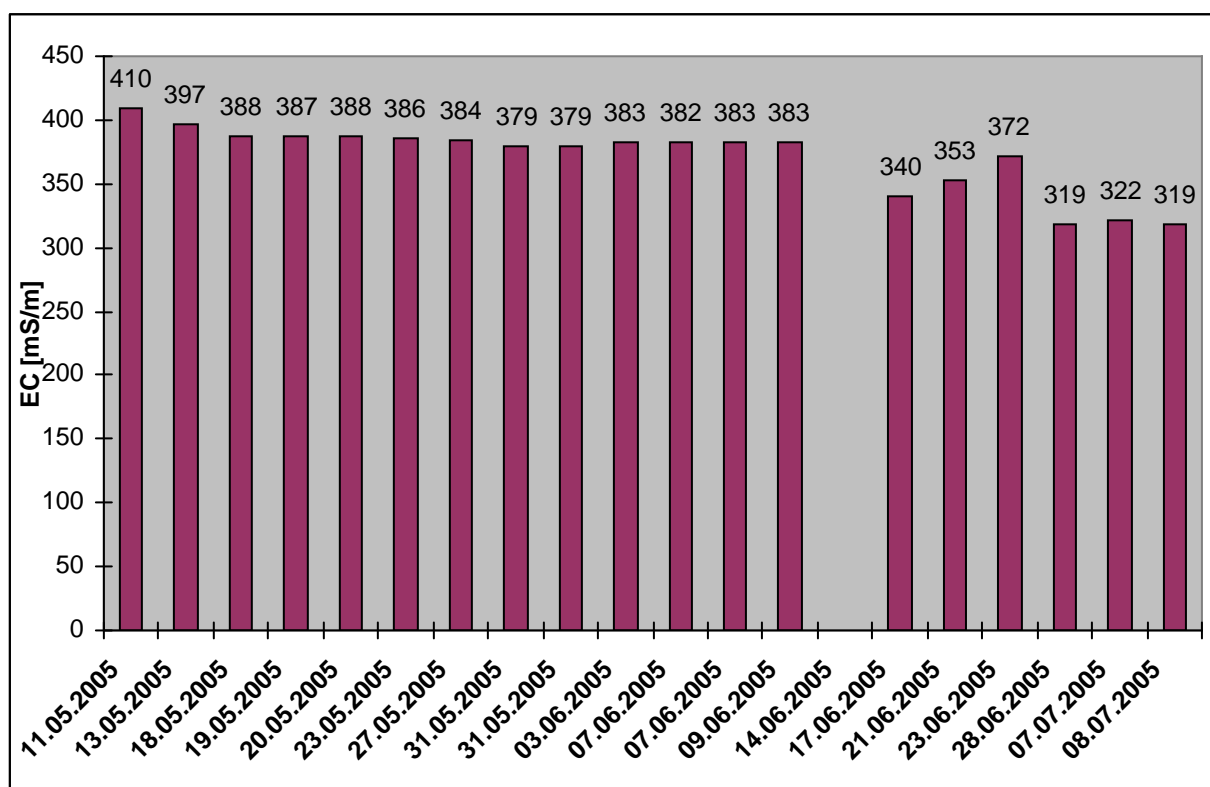


Figure 9: development of effluent EC values during the project

4.2.4 Dissolved oxygen

The dissolved oxygen (DO) was determined to examine the effects of the external aeration of the wastewater in the treatment process. Because of the degradation processes carried out by the bacteria the oxygen levels in untreated wastewater are low. The reason for that is the high oxygen demand for these processes to take place. This can also be seen in the results for the chemical oxygen demand (COD), which will be shown later.

The concentration of the DO increased significantly in the treatment process, especially in the first step, which is carried out in the first bioreactor. This is mainly caused by the external aeration. The second bioreactor showed no significant increase of the DO level because the first one worked very well. Therefore the aeration pump on the tank was switched off from time to time to see if it has an effect on the DO level. But the only effect showed to be a decrease in the concentration of the water in the second bioreactor. This had no effect on the effluent. The reason for that is that on the way from the second bioreactor to the clarifier the water has the chance to take up oxygen from the gas phase above the water surface.

Figure 10 shows the development of the average DO levels during the treatment process. Figure 11 provides a graphic that shows that the DO levels of the effluent showed to be relatively stable.

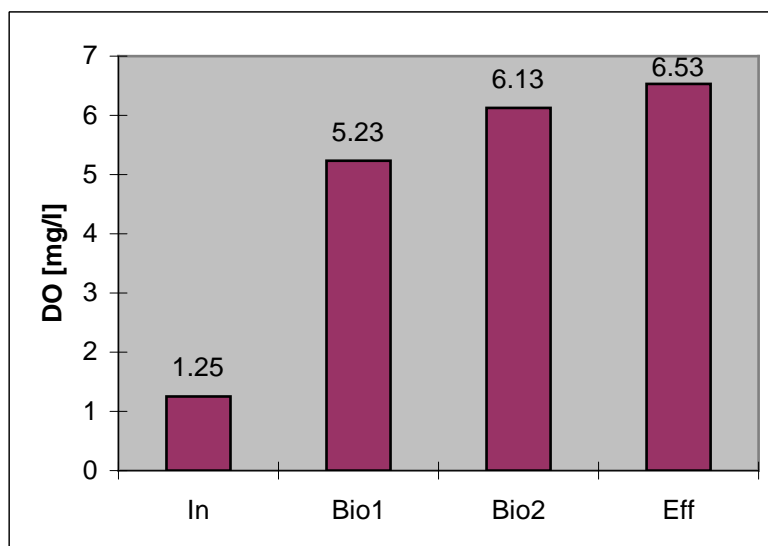


Figure 10: development of the average DO levels

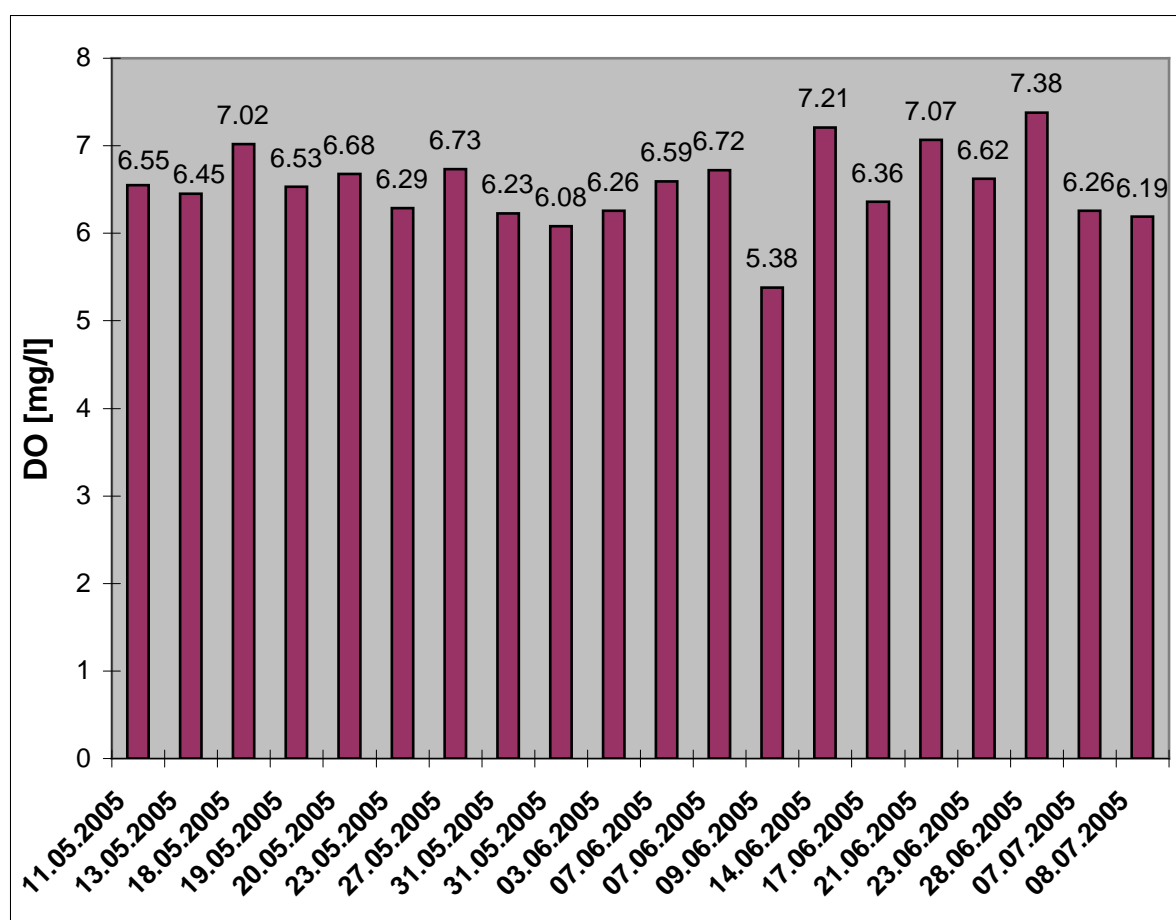


Figure 11: development of the effluent DO levels during the project

4.2.5 Chemical oxygen demand

As explained above, the chemical oxygen demand (COD) has a significant effect on the oxygen concentration. And the results show that with an increase of the DO concentration (as explained above) the COD levels decreased. This has two main reasons. The first one is the aeration itself. For the second reason one has to consider the definition of the COD, which is the amount of oxygen needed to oxidise the organic compounds in a water sample. And while the organic compounds are oxidised in this water purification system, it is quite obvious that the COD has to decrease. This development is shown in figure 12.

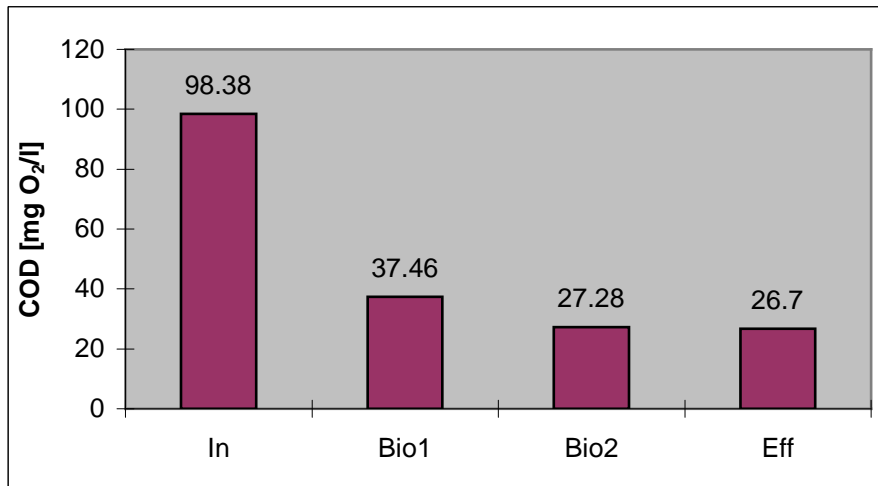


Figure 12: development of the average COD levels

From this data an average COD elimination rate of approximately 73% can be calculated. But it has to be considered that the results had a relatively high deviation from each other.

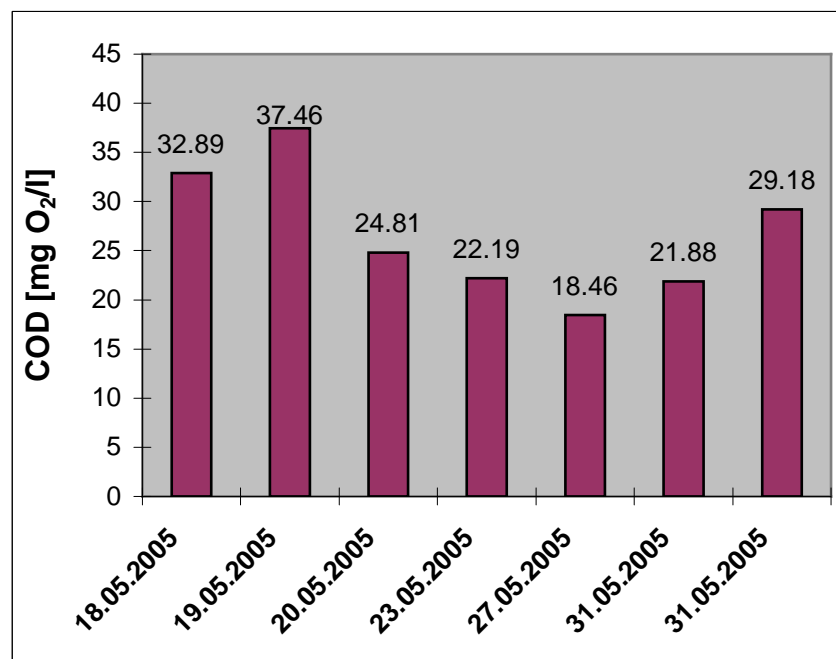


Figure 13: development of the effluent COD levels during the project

Figure 13 shows that for the effluent. In the other tanks it was similar. It is not sure if these deviations were caused by different organic loadings of the wastewater or by a possible inaccuracy of the determination method.

That means that the results for the COD have to be handled with care and that the average elimination rate is not very accurate.

But nevertheless the results show that this wastewater treatment plant has the ability to lower the COD significantly.

From the data in figure 13 one can see that the COD determinations have not been performed over the whole time of the project. As mentioned in chapter 3, the experiments had to be done in another laboratory so that it was not always possible to do the analyses.

4.3 Anions and ammonia

**Table 6: average values of the results for anions and ammonia (all given in mg/l);
n. d. = not detectable**

	F⁻	Cl⁻	NO₂⁻ (as N)	Br⁻	NO₃⁻ (as N)	PO₄³⁻	SO₄²⁻	NH₃ (as N)
In	0.49	956.83	n.d.	2.06	0.16	10.07	91.22	16.88
Bio1	0.48	935.01	8.08	2.05	50.02	10.76	114.2	0.37
Bio2	0.48	941.3	0.54	2.05	54.95	10.35	117.1	0.13
Eff	0.49	964.3	0.43	2.04	54.03	9.97	130.2	0.09

4.3.1 Fluoride

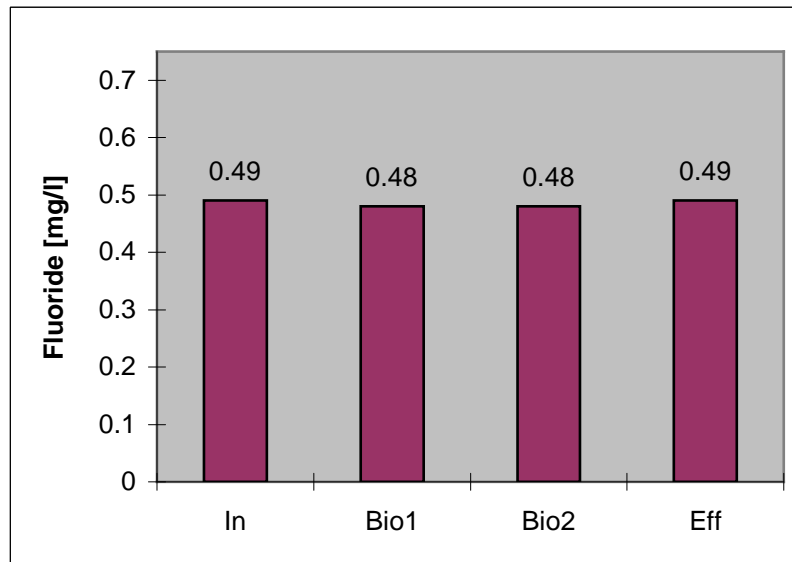


Figure 14: development of the average fluoride concentrations

From figure 14 one can see that the concentration of fluoride was not affected in the water purification step. The reason is that fluoride, like most other anions, cannot be removed from wastewater with pure biological methods. Complicated and expensive methods like reverse osmosis or electrodialysis are required for that removal. But this would be highly uneconomic in this case.

Figure 15 shows that the concentration of fluoride was also very stable over the whole time. The only exception is the first effluent sample, which is an outlier, possibly caused by a contamination of the sampling equipment.

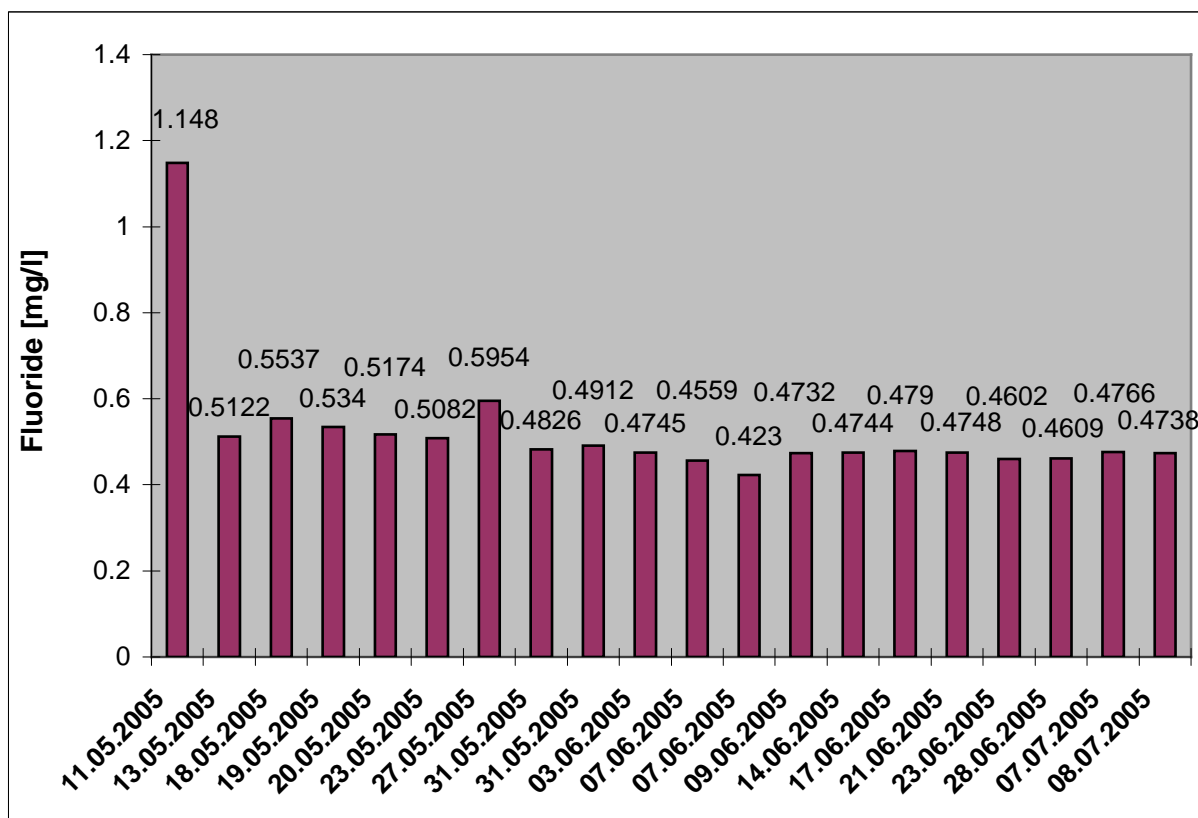


Figure 15: development of the effluent fluoride concentration during the project

The analysis of the groundwater sample showed that it has a fluoride concentration of 0.47 mg/l. This shows that the fluoride does not come from the wastewater, but from the groundwater.

4.3.2 Chloride

The chloride concentration in the effluent was excessively high. That explains the very high conductivity. In the other samples it was similarly high, which leads to the conclusion that the chloride concentration was not affected in this wastewater treatment plant (see figures 16 and 17). The reason is, as for most other anions, that expensive technologies like reverse osmosis or electrodialysis are required for the removal of chloride ions.

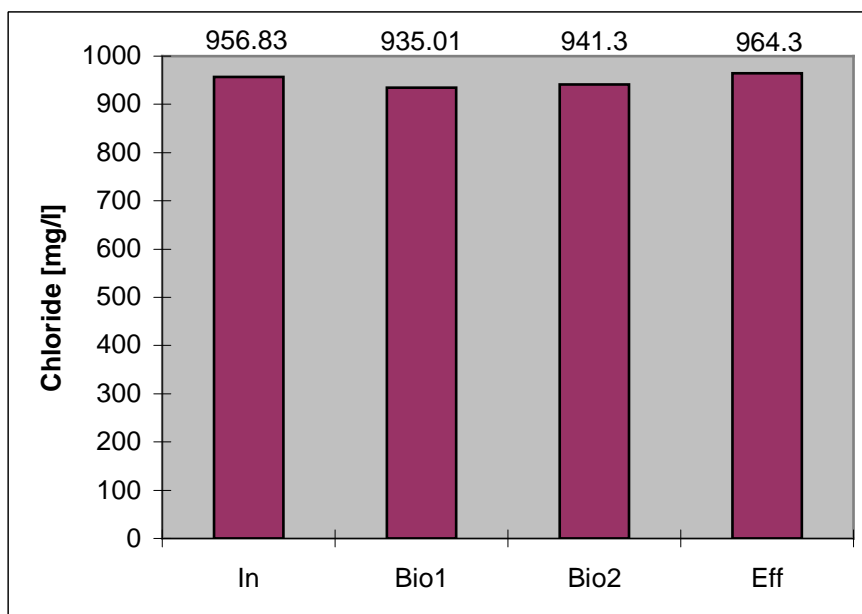


Figure 16: development of the average chloride concentrations

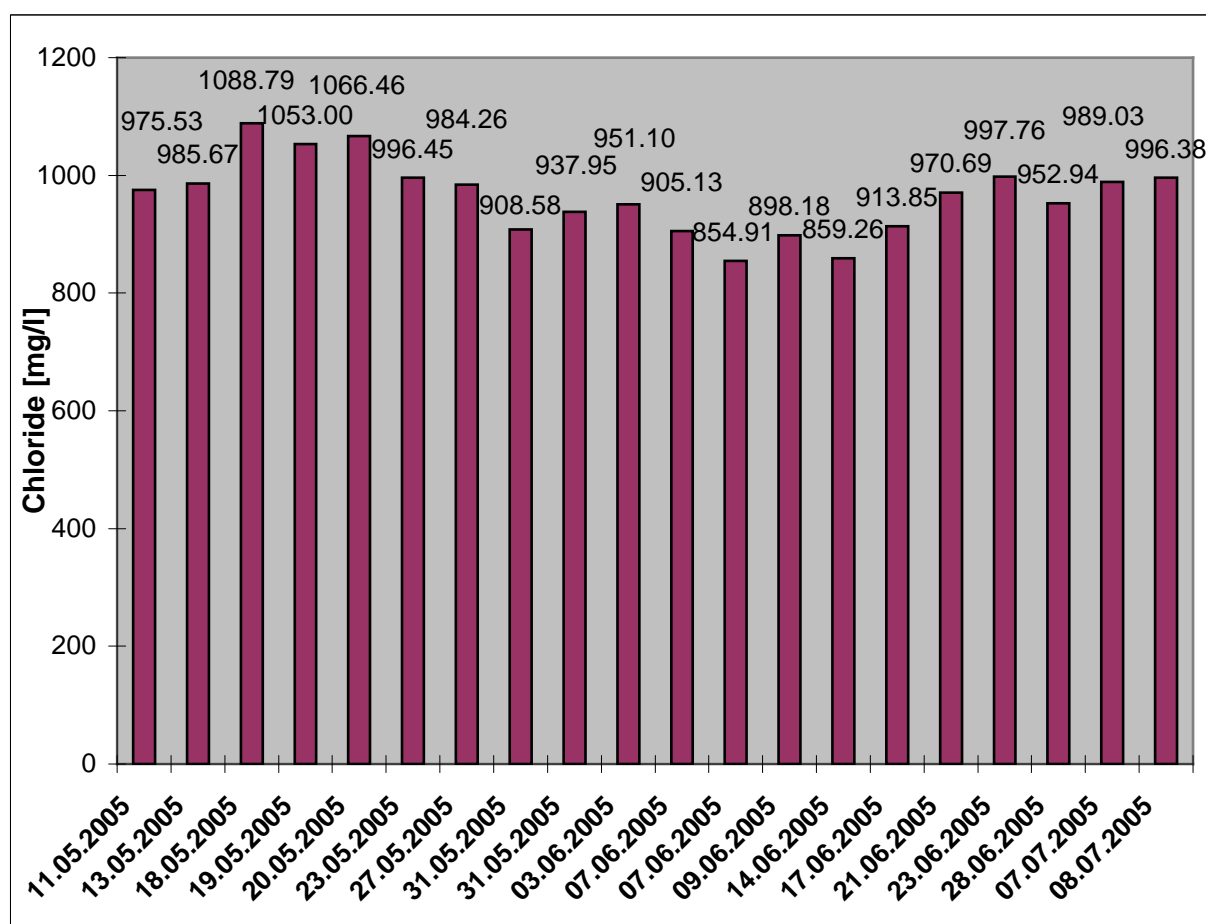


Figure 17: development of the effluent chloride concentrations during the project

In addition, it has to mentioned that the analysis of the groundwater sample also showed a very high chloride concentration (approximately 900 mg/l). That means that most of the chlorides do not come from the wastewater, but from the groundwater. The reason for this groundwater salinity is the proximity to the Indian Ocean. Seawater has a chloride concentration of approximately 19,800 mg/l (DWAF, 1996). That means that coastal regions in general might have problems with soil and groundwater salinity because of the possibility that seawater can enter the groundwater.

4.3.3 Bromide

As explained in the introduction, bromide is not very interesting for this project. Its concentration was stable over the whole time in all samples (approximately 2 mg/l), with the exception of a few outliers. Bromide cannot be removed biologically and would need treatment with reverse osmosis or similar techniques, which would be highly uneconomic because of the high costs. The bromide concentration was also caused by the groundwater, where it was also approximately 2 mg/l. All results can be seen in the tables in the appendix.

4.3.4 Phosphate

As explained in the introduction, phosphates are an essential nutrient for the bacteria in the wastewater. It is used for energy storage, as building material for cell walls and other important metabolic functions. That means that phosphates are constantly taken up and released by the microorganisms (Rüffer and Masannek, 2002). This can be seen in the results shown in figure 18: there is no significant increase or decrease in the phosphate concentrations between the different parts of the system. Figure 19 also proves that by showing significant deviations between the single samples.

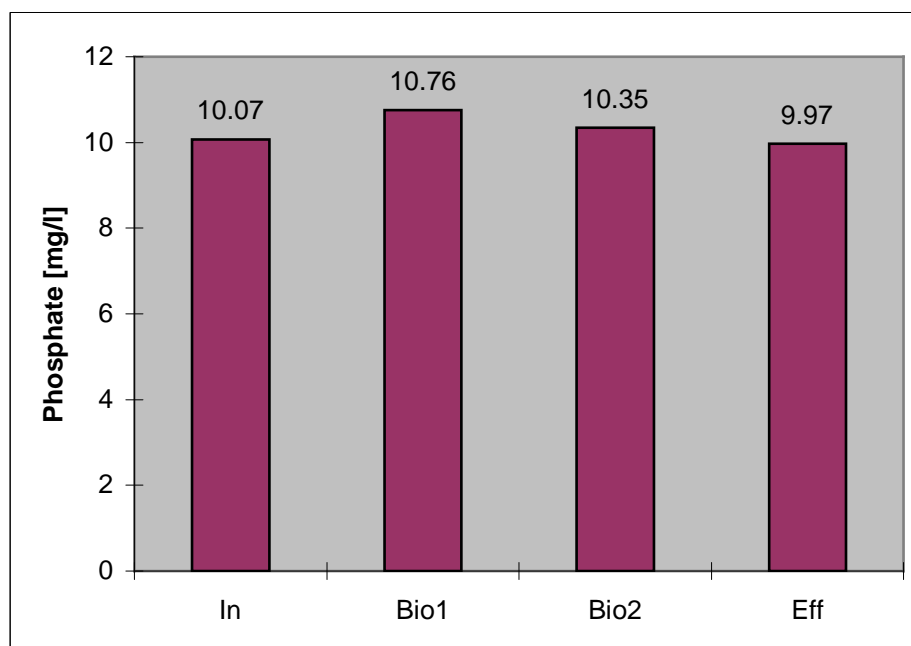


Figure 18: development of the average phosphate concentrations

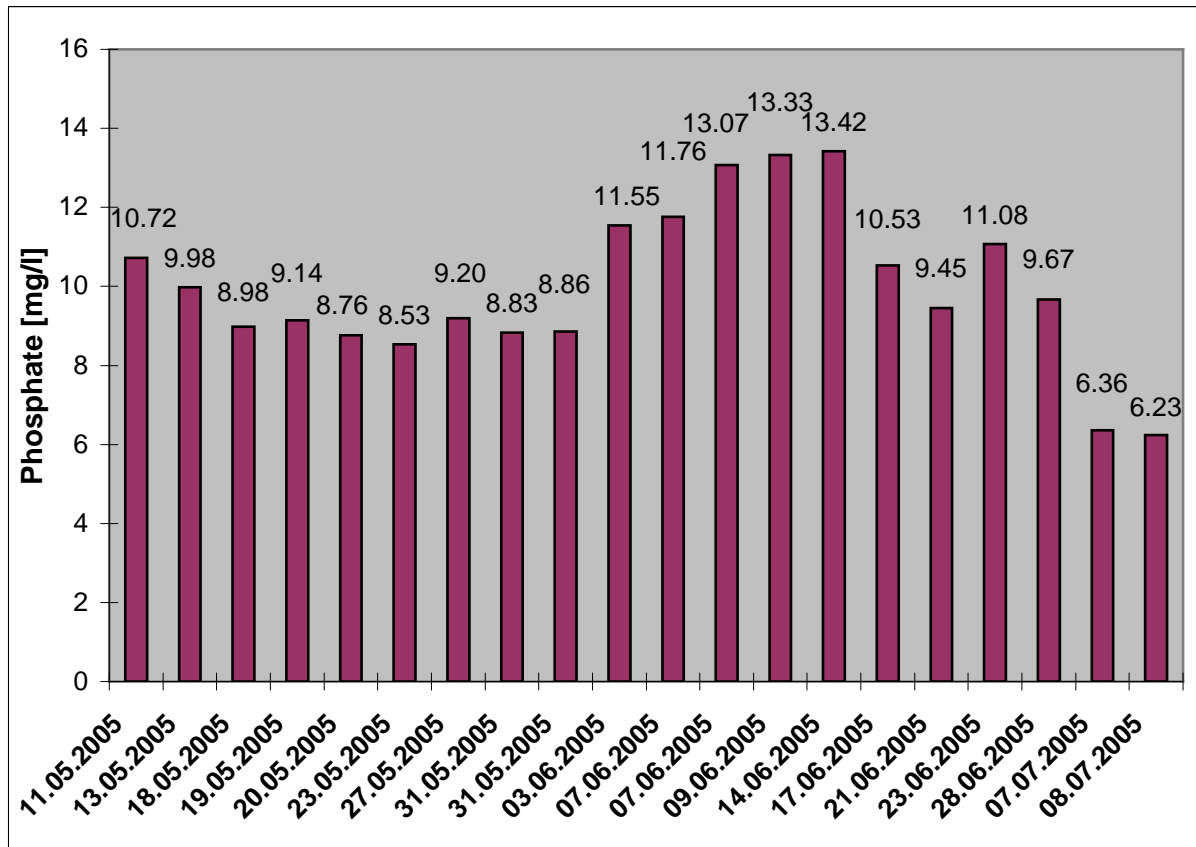


Figure 19: development of the effluent phosphate concentrations during the project

4.3.5 Sulphate

As explained in the introduction, sulphates can enter the wastewater via human excrements and via the groundwater. The analysis of the groundwater showed a concentration of approximately 118 mg/l. These sulphates, together with the sulphates of the human excrements, are reduced to hydrogen sulphide under the anaerobic conditions in the septic tank and the balancing tank. Therefore the concentration of sulphate is lower in the samples from the balancing tank. It increases again in the purification process because of the aerobic conditions in the other parts of the system, which induce the oxidation of the sulphides to sulphates. This can be seen in figure 20. Another indication of these oxidations was the elimination of the unpleasant smell of the water, which was caused by the hydrogen sulphide.

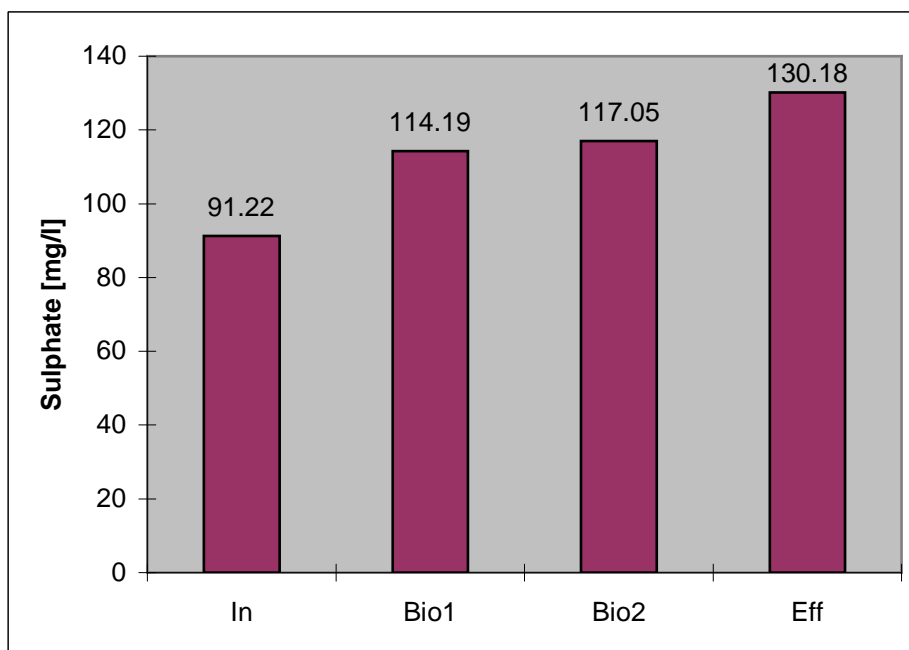


Figure 20: development of the average sulphate concentrations

4.3.6 Nitrogen

First it has to be mentioned that the results for nitrite and nitrate given by the software of the ion chromatography software are the concentrations for the respective ions. But for a better comparability they were converted to the concentration of nitrogen. This was done by multiplying the result with a certain factor. This factor is the quotient of the specific mass of nitrogen and the specific mass of the respective ion. For nitrite it is 0.3045, and for nitrate it is 0.2259.

As explained in the introduction, the nitrogen species ammonia, nitrite and nitrate have to be considered together because of their interconversions in aquatic systems. The results for nitrite showed to be very unstable. There were high deviations between the samples, and often it was not detectable. The reason for that is that nitrite is only the intermediate product of the nitrification process, where ammonia is oxidised to nitrate. Therefore the results for nitrite are not shown here, but they can be viewed in the appendix.

Looking at the results for nitrate and ammonia, one can observe a nitrification process taking place in the bioreactors. The nitrate levels increase while the ammonia levels decrease. The average ammonia removal rate can be calculated to approximately 95%.

Figure 21 shows the nitrification process graphically.

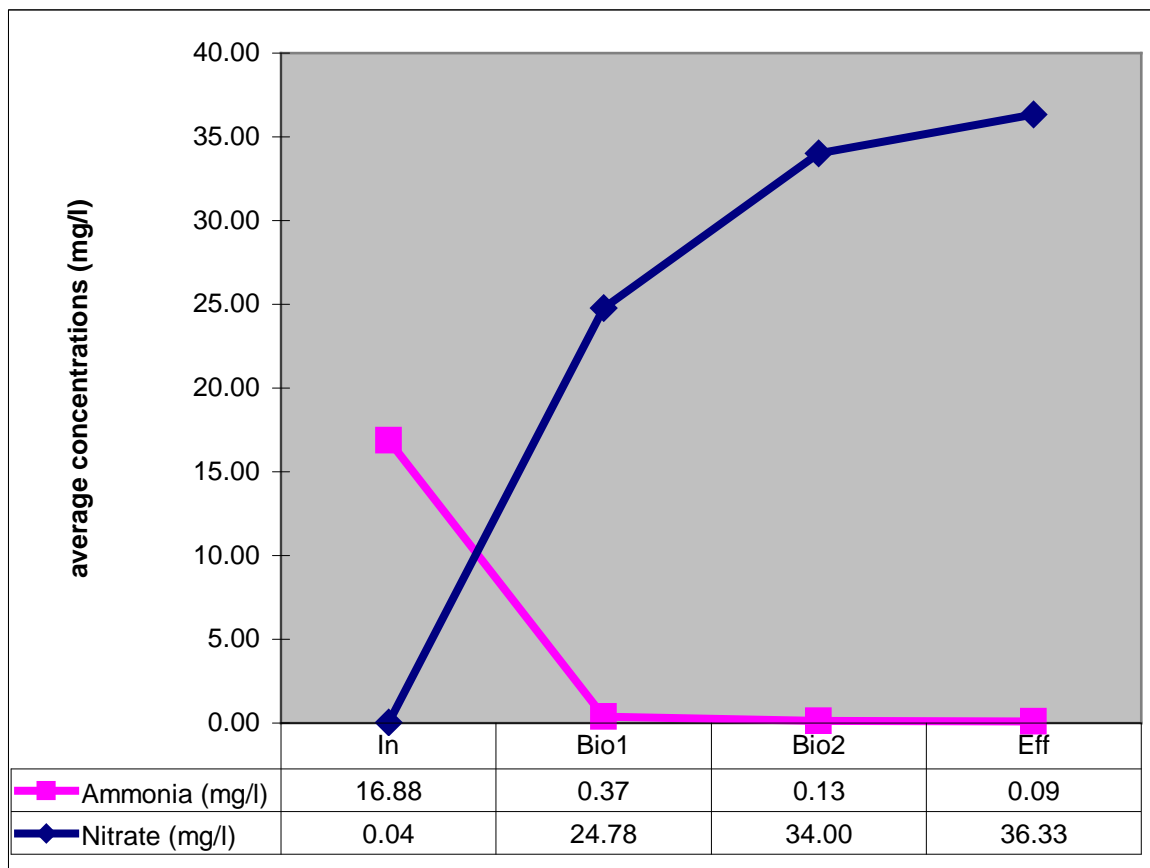


Figure 21: diagram of the nitrification process

Looking at the diagram leads to the conclusion that more nitrate nitrogen was formed than ammonia nitrogen was eliminated. The reason is that not only ammonia, but also organic nitrogen compounds can be oxidised to nitrate.

But these nitrification data have to be handled with care. The results for nitrate showed some relatively high deviations during the time of the project. These can have been caused by standard deviations of the determination method. But it is more likely that there have to be other reasons. One reason might be the different usage of the toilets in the school, which leads to different organic loadings on different days. This is definitely sure for the low nitrate concentrations of the last effluent samples because these samples were taken during the winter holidays where the toilets of the school are only very rarely used.

Another unfortunate circumstance is the fact that due to the problems with the ammonia equipment mentioned earlier in this text these determinations of ammonia were only done in this period. That means that the ammonia results are much lower than usual because of the smaller organic load in the wastewater.

The conclusion is that the calculated ammonia elimination rate (95%) cannot be seen as a safe result because the water purification system was not running under normal conditions in this time.

But nevertheless the results are good enough to show that a nitrification process is taking place in this treatment plant.

5. Discussion

Table 7: comparison of average effluent values with TWQRs

Parameter	Target Water Quality Range (TWQR)	Average value of final effluent
Temperature	Not available	21.12 °C
pH	6.5 – 8.4	6.95
Electrical conductivity (EC)	< 40 mS/m	371.26 mS/m
Dissolved oxygen (DO)	Not available	6.53 mg/l
Chemical oxygen demand (COD)	Not available	26.7 mg O ₂ /l
Fluoride (F ⁻)	< 2.0 mg/l	0.49 mg/l
Chloride (Cl ⁻)	< 100 mg/l	964.3 mg/l
Bromide (Br ⁻)	Not available	2.04 mg/l
Sulphate (SO ₄ ²⁻)	Not available	130.2 mg/l
Phosphate (PO ₄ ³⁻)	Not available	9.97 mg/l
Nitrogen (NH ₃ -N + NO ₂ ⁻ -N + NO ₃ ⁻ -N)	5 mg/l	54.55 mg/l

Table 7 shows a comparison of the average values of the final effluent and the TWQR for each parameter. A first look on the results might lead to the conclusion that this water purification system has failed according to the South African Water Quality Guidelines. But before making such a judgement, the results and observations of this project need to be analysed carefully.

First it has to be said that some of the parameters are lying well within the TWQR. These are the pH and the fluoride concentration. The parameters with no specific TWQR seem to be in an acceptable range. Sulphate, for example, occurs in natural waters in similarly high concentrations as a result of leaching of sulphate minerals from the sediment into the water body. Therefore it is no problem that the sulphate concentration increases during the purification process. This increase is a result of the oxidation of hydrogen sulphide, which is toxic and gives the water an unpleasant smell. With this oxidation from sulphide to sulphate the smell was also eliminated, which can be seen as a beneficial effect of the examined wastewater treatment plant. The next positive point is the COD removal. Its elimination rate has been calculated to 73%, but it has already been mentioned that this value is not very accurate

because of the high deviations between the single results of the COD determinations. Nevertheless it can be seen as good, compared to other treatment plants working with the same principle. Some of them are working better and show COD elimination rates of 92% (Sotirakou et al., 1999), but there are also treatment plants, which remove only 60% of the COD (Garrido et al., 1998). Another South African project with an anaerobic baffled reactor showed a COD elimination rate between 58% and 72% (Foxon et al., 2004). From this point of view the treatment plant at the Lilyfontein School is successful, although the rate could be higher. It is suggested that further analyses have to be performed to get more accurate results.

Another very significant effect of this submerged fixed-film bioreactor system is the nitrification. The ammonia is almost completely eliminated in the purification process (95%), which can be seen as a very good rate. Similar ammonia removal rates other biological water purification systems are described in the literature (Verhoeven and Meuleman, 1999; Oh et al., 2001; Ho et al., 2001; Lesjean et al., 2002; Cicek, 2003; Foxon et al., 2004).

The biggest problem in the final effluent of this water purification system is the excessively high chloride concentration, which also causes the very high electrical conductivity (EC). It is caused by the groundwater, where these values are similarly high because of the proximity to the ocean. The system cannot be held responsible for that. Chloride, as well as most other ions, can only be removed with reverse osmosis or similar techniques, which are characterised by the high costs. Therefore it would be highly uneconomic to apply such techniques for the treatment of water, which is intended to be used for irrigation. A farmer with saline irrigation water has only two chances: he can either accept the reduced crop yield which might be caused by that, or he has to switch to other plants and crops which are more tolerant towards high chloride concentrations (DWAF, 1996).

In the case of the Lilyfontein School this problem does not occur because it is no farm. The school has two big rugby fields, which are intended to be irrigated with the treated wastewater. Only grass is growing on a normal sports field, and most grass species are very tolerant towards high chloride concentrations (DWAF, 1996).

That means that the final effluent can still be used here as long as only the grass of the rugby fields is irrigated with it.

But another problem of the final effluent is its high nitrate concentration, which also exceeds the TWQR significantly. Nitrate is a key nutrient for plants and commercially available fertilisers also contain nitrates. But if the concentration exceeds the requirements of the plants, they cannot take up this excess of nitrate so that it can contaminate the groundwater.

This problem can be solved by a process called denitrification where nitrate is reduced to gaseous elemental nitrogen, which can escape to the atmosphere. This is currently not happening in this fixed-film bioreactor. But with some technical modifications according to conventional wastewater treatment plants in Germany this denitrification step could be realised.

Denitrification requires anoxic conditions. The first idea would be to shut down the aeration of the second bioreactor to create these conditions so that denitrification can take place after the nitrification in the first bioreactor. But this is not practicable because the bacteria responsible for that process also require organic compounds as an energy source. But these have already been decomposed in the aerobic step of the first bioreactor. It would be possible to add organic compounds, for example methanol, to the water in the second tank, but this would be highly uneconomic. To solve this problem, the system has to be modified. The first bioreactor has to become the anoxic step and the second bioreactor has to become the aerobic step. Further a

pipe has to be installed so that a part of the water in the second reactor can flow back to the first one. After doing that, the following should happen:

First the water flows through the anoxic part of the system where no significant reactions occur so that the water is still rich in organic compounds. In the second (aerated) reactor all the described reactions occur, which are sulphide oxidation, COD removal and nitrification. Now a part of the nitrate-rich water is recirculated into the first reactor where anoxic conditions and organic compounds can be found so that the denitrification can take place. The water should have a low nitrate concentration after that step. Then this water will travel through the second tank again and can finally flow into the clarifier (Rüffer and Masannek, 2002).

This suggestion is only theoretical. But it should be tested in the following parts of this project because a denitrification step is essential for the success of this water purification system to produce water, which can be used for different purposes. If these modifications would be successful, the nitrate levels would be lowered so that the final effluent fits the TWQR set by the DWAF.

That leads to the next point. As described in chapter 2, the whole project has got the aim to convince municipalities and governments of the applicability of these decentralized water purification systems. This could lead to installations of such systems on a bigger scale in rural areas and urban settlements, which are not connected to the municipal sewage system. The result would be a better water management so that the predicted water scarcity mentioned in the introduction might be avoided.

But after this first part of the project it is hard to say if the system tested here can be judged to be good or bad because there are good and bad results. The high chloride concentration and the high conductivity are a local problem of this coastal region so that this cannot be seen as a disadvantage of the treatment process.

But an advantage is the relatively good COD removal rate and the elimination of unpleasant smells.

The only thing that has to be improved is the mentioned denitrification step. And it is quite obvious that more parameters have to be determined in future projects. The parameters tested here were quite important, but other parameters, for example the biochemical oxygen demand (BOD), total suspended solids (TSS), turbidity, total nitrogen, total phosphorous and biological parameters like *E. coli* and coliforms, have to be added to the list. This is important because the only final judgement of the effluent quality can be made on the base of a complete parameter list.

But, as mentioned above, this project was only a part of a bigger project. The results can lead to the final conclusion that this decentralized water purification system installed at the Lilyfontein School in the Eastern Cape of South Africa is working well and that this technology, after the suggested modifications, has the ability to assist in solving South Africa's water problems to avoid the predicted water scarcity in 2025.

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7. Appendix

Table 8: results for the samples taken from the balancing tank (Influent)

Influent	T (°C)	pH	EC (mS/m)	DO	F ⁻	Cl ⁻	NO ₂ ⁻ (as N)	Br ⁻	NO ₃ ⁻ (as N)	PO ₄ ³⁻	SO ₄ ²⁻	NH ₃ (as N)	COD
11.05.2005	24.3	7.15	421	3.03	0.906	953.31	n.d.	2.0419	6.7121	10.0172	152.8638		
13.05.2005	26.1	7.7	421	1.73	0.5429	975.66	n.d.	2.0903	0.0792	10.3704	136.3035		
18.05.2005	23.9	7.79	406	0.85	0.5661	1087.10	n.d.	2.0936	0.0663	8.176	147.6455		65.78
19.05.2005	23.2	7.74	398	1.56	0.544	1057.74	n.d.	2.0735	0.0455	8.8031	124.1061		71.17
20.05.2005	22.4	7.71	406	1.07	0.5129	1068.86	n.d.	2.0996	0.0886	8.0906	95.6326		80.65
23.05.2005	24.4	7.35	400	0.34	0.4837	981.26	n.d.	2.0811	0.0218	9.127	87.3422		135.1
27.05.2005	20.6	7.42	384	1.75	0.5642	957.65	n.d.	2.0784	0.0549	5.6266	99.3798		53.34
31.05.2005	22.2	7.96	411	1.49	0.4533	892.71	n.d.	2.0697	0.3715	9.7215	58.3652		155
31.05.2005	23.7	8.11	421	0.95	0.4819	940.89	n.d.	2.0662	0.0265	13.1017	92.7973		127.6
03.06.2005	21.7	8.09	427	1.21	0.4606	914.57	n.d.	2.0301	0.0394	14.6105	29.8734		
07.06.2005	17.7	7.73	398	2.85	0.4777	861.11	n.d.	1.5938	21.4155	11.8316	73.1329		
07.06.2005	22.5	7.94	408	1.71	0.425	876.51	n.d.	2.026	1.5982	12.5045	96.4268		
09.06.2005	17.3	8.19	408	1.26	0.4785	877.98	n.d.	2.0582	0.1621	13.5948	40.9866		
14.06.2005	19.3	8.04		0.86	0.4738	959.27	n.d.	2.0599	0.03	14.652	31.0201		
17.06.2005	19.7	8.09	362	1.13	0.4715	874.49	n.d.	2.0465	0.0474	10.1518	27.6133		
21.06.2005	20.1	7.98	344	1	0.4742	958.84	n.d.	2.0428	0.0286	9.4244	95.9916		
23.06.2005	20.5	8.33	379	0.8	0.4683	991.65	n.d.	2.0669	0.0283	11.4457	89.3002		
28.06.2005	16	7.45	307	0.9	0.4629	931.39	n.d.	2.0367	0.0347	9.2481	99.2564	25.9836	
07.07.2005	18.5	7.22	308	1.07	0.4735	980.04	n.d.	2.0185	0.0594	5.3551	120.9365	11.025	
08.07.2005	18.2	7.26	312	1.29	0.4756	995.59	n.d.	2.069	0.0347	5.5573	125.5247	13.623	
Average	19.20	7.76	385.32	1.25	0.49	956.83		2.06	0.16	10.07	91.22	16.88	98.38

- n.d. = not detectable
- outliers are indicated in red and were not included in the average values
- the blue dates indicate the days when the clarifier was desludged

Table 9: results for the samples taken from the first bioreactor (Bioreactor1)

Bioreactor1	T (°C)	pH	EC (mS/m)	DO	F ⁻	Cl ⁻	NO ₂ ⁻ (as N)	Br ⁻	NO ₃ ⁻ (as N)	PO ₄ ³⁻	SO ₄ ²⁻	NH ₃ (as N)	COD
27.05.2005	20.1	6.83	383	4.69	0.6005	988.41	30.5571	2.0887	27.841	8.1575	131.5094		43.09
31.05.2005	21.6	6.74	381	4.17	0.4872	920.78	11.8731	2.0369	35.3259	9.6696	111.6063		32.82
31.05.2005	23.3	6.82	386	4.13	0.4705	946.98	19.8324	2.0592	30.4847	11.7414	114.5578		36.47
03.06.2005	21.9	6.63	391	4.19	0.482	957.25	22.1857	2.0494	45.4644	14.2904	109.7085		
07.06.2005	20.6	6.51	382	4.44	0.4738	904.91	2.4442	1.681	57.1256	11.7867	102.6809		
07.06.2005	21.6	6.61	382	4.43	0.426	889.06	5.1675	2.0407	51.3926	13.6493	103.3158		
09.06.2005	20.8	6.5	381	5.1	0.4798	885.73	2.0104	2.0535	61.6505	13.7286	109.4987		
14.06.2005	19.8	6.78		5.09	0.4727	897.03	4.2638	2.064	65.6901	14.3444	100.8363		
17.06.2005	20	6.17	341	4.8	0.4722	894.05	1.2392	2.046	70.8784	10.0374	107.0188		
21.06.2005	20.1	7.15	350	5.71	0.4737	943.84	0.5769	2.0471	46.0836	9.4805	113.0244		
23.06.2005	20.7	6.48	377	4.93	0.463	987.53	1.4762	2.0615	61.1962	11.9756	124.3469		
28.06.2005	20.3	7.51	350	6.5	0.4647	902.37	n.d.	2.0357	47.0665	9.7672	112.1076	0.0367	
07.07.2005	20.1	7.65	332	7.45	0.4788	976.08	0.2856	2.0346	14.1215	6.0526	129.8766	0.378	
08.07.2005	20.6	7.74	334	7.53	0.4762	996.09	3.1653	2.0508	13.1503	5.9675	128.5892	0.708	
Average	20.82	6.87	366.92	5.23	0.48	935.01	8.08	2.05	50.02	10.76	114.19	0.37	37.46

- n.d. = not detectable
- outliers are indicated in red and were not included in the average values
- the blue dates indicate the days when the clarifier was desludged

Table 10: results for the samples taken from the second bioreactor (Bioreactor2)

Bioreactor2	T (°C)	pH	EC (mS/m)	DO	F ⁻	Cl ⁻	NO ₂ ⁻ (as N)	Br ⁻	NO ₃ ⁻ (as N)	PO ₄ ³⁻	SO ₄ ²⁻	NH ₃ (as N)	COD
27.05.2005	21.5	7.16	386	6.93	0.5619	982.78	1.5954	2.0134	41.5225	8.5567	138.9523		30.77
31.05.2005	22.6	7.46	379	6.23	0.4943	900.24	0.1789	2.0379	36.4963	8.6598	114.8992		21.88
31.05.2005	24.3	7.34	379	5.99	0.4868	943.72	0.7884	2.0439	35.903	9.2387	117.2359		29.18
03.06.2005	23.1	7.17	383	6.69	0.4777	956.04	0.5071	2.0473	48.4197	12.0749	120.3181		
07.06.2005	21.1	7.07	383	6.7	0.469	911.76	n.d.	1.683	57.1597	11.5127	110.4794		
07.06.2005	22.6	6.8	382	5.75	0.4297	916.29	0.2745	2.0447	54.9	13.7395	105.347		
09.06.2005	19	6.51	382	2.14	0.4761	888.20	0.2794	2.0605	59.701	13.936	110.2222		
14.06.2005	20.6	6.06		6.84	0.4762	908.37	0.1661	2.0593	66.8887	14.4076	102.6836		
17.06.2005	20.3	5.11	340	6.56	0.4699	916.48	n.d.	2.0432	74.412	10.5261	107.2885		
21.06.2005	21.6	6.86	366	6.77	0.4745	963.04	n.d.	2.0412	61.1711	9.646	112.1444		
23.06.2005	21.7	7.17	376	6.53	0.4655	990.98	n.d.	2.0689	64.4192	11.1479	126.2018		
28.06.2005	20.6	7.35	356	6.42	0.4626	920.58	n.d.	2.0372	58.3619	9.2701	114.6897	0.1101	
07.07.2005	19.1	7.59	327	4.29	0.4709	987.74	n.d.	2.0566	23.702	6.2935	129.0333	0.202	
08.07.2005	18.9	7.69	321	4.05	0.472	992.03	n.d.	2.0561	19.9427	5.8813	129.2247	0.08	
Average	21.21	6.95	366.15	6.13	0.48	941.30	0.54	2.05	54.95	10.35	117.05	0.13	27.28

- n.d. = not detectable
- outliers are indicated in red and were not included in the average values
- the blue dates indicate the days when the clarifier was desludged

Table 11: results for the samples taken from the clarifier (Effluent)

Effluent	T (°C)	pH	EC (mS/m)	DO	F ⁻	Cl ⁻	NO ₂ ⁻ (as N)	Br ⁻	NO ₃ ⁻ (as N)	PO ₄ ³⁻	SO ₄ ²⁻	NH ₃ (as N)	COD
11.05.2005	24.3	3.57	410	6.55	1.148	975.53	1.0897	2.045	59.2764	10.7173	180.43		
13.05.2005	26.1	5.82	397	6.45	0.5122	985.67	0.8956	1.9992	57.5801	9.9761	178.67		
18.05.2005	23.9	7.17	388	7.02	0.5537	1088.79	0.3214	2.0917	53.9591	8.978	161.07		32.89
19.05.2005	23.2	7.25	387	6.53	0.534	1053.00	0.3032	2.0568	50.2351	9.1426	149.25		37.46
20.05.2005	22.4	7.2	388	6.68	0.5174	1066.46	0.3515	2.0954	49.6066	8.7592	152.12		24.81
23.05.2005	24.4	6.81	386	6.29	0.5082	996.45	0.3684	0.4891	45.1576	8.5302	137.36		22.19
27.05.2005	20.6	7.12	384	6.73	0.5954	984.26	1.5022	2.0532	40.334	9.1957	135.49		18.46
31.05.2005	22.2	7.53	379	6.23	0.4826	908.58	0.0525	2.0184	35.1727	8.8339	117.33		21.88
31.05.2005	23.7	7.46	379	6.08	0.4912	937.95	0.3711	2.0436	35.9855	8.8574	117.33		29.18
03.06.2005	21.7	7.26	383	6.26	0.4745	951.10	0.1467	2.0543	46.6491	11.5495	119.89		
07.06.2005	17.7	7.08	382	6.59	0.4559	905.13	n.d.	1.5531	54.1301	11.7585	110.50		
07.06.2005	22.5	6.96	383	6.72	0.423	854.91	0.0314	2.01	53.3786	13.0739	105.67		
09.06.2005	17.3	6.51	383	5.38	0.4732	898.18	0.0312	2.0472	59.1451	13.3251	110.94		
14.06.2005	19.3	5.85		7.21	0.4744	859.26	0.0882	2.0619	67.0178	13.4193	103.14		
17.06.2005	19.7	4.32	340	6.36	0.479	913.85	n.d.	2.044	73.6971	10.5267	107.87		
21.06.2005	20.1	6.62	353	7.07	0.4748	970.69	n.d.	2.0469	64.9916	9.4474	113.75		
23.06.2005	20.5	7.26	372	6.62	0.4602	997.76	n.d.	2.0607	64.6529	11.0779	125.43		
28.06.2005	16	6.2	319	7.38	0.4609	952.94	n.d.	0.8131	61.5354	9.6661	116.19	0.06973	
07.07.2005	18.5	7.45	322	6.26	0.4766	989.03	n.d.	2.0151	24.6782	6.3587	130.25	0.165	
08.07.2005	18.2	7.5	319	6.19	0.4738	996.38	n.d.	2.0034	22.7777	6.2333	130.97	0.044	
Average	21.12	6.65	371.26	6.53	0.49	964.30	0.43	2.04	54.03	9.97	130.18	0.09	26.70

- n.d. = not detectable
- outliers are indicated in red and were not included in the average values
- the blue dates indicate the days when the clarifier was desludged