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CHALMERS UNIVERSITY OF TECHNOLOGY
Department of Sanitary Engineering
Applied Environmental Measurement Techniques

MASTER THESIS

Evaluation of a Technique for Measuring Biodegradable Dissolved Organic Carbon (BDOC) in a Continuous Bioreactor

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Master Thesis 1996:1

ABSTRACT

The biodegradability of glucose under different conditions has been chosen to evaluate and, based on the results, develop a continuous plug flow bioreactor for biodegradable dissolved organic carbon (BDOC) on-line measurements, as well as to find out what the continuous plug flow bioreactor really measures in terms of BDOC.

Plug flow biofilm reactors were colonised by microorganisms indigenous to streamwater and lakewater. Seven different kinds of experiments have been performed, namely experiments with sand-filtered raw water to test the columns, long-term experiments with glucose solution, concentration experiments with glucose solution, hydrodynamic experiments with methylene blue and three different kinds of recirculation experiments with glucose solution.

The hydrodynamic experiments demonstrated a retention time of 50 hours or longer for organic molecules in the size range of 200-300 Å. This fact proves that the continuous plug flow bioreactor in the case of BDOC on-line measurements only measures an average effect and provides doubtful values for BDOC.

Optimisation of retention time by optimising the pore size considering the surface area has been proposed to develop the method. A semi-batch and a trickling bioreactor have been suggested as alternative kinds of reactors for BDOC on-line measurements.

Other measurement results have been influenced by the error caused by the wrong retention time or by another error which occurred due to the leakage of organic carbon from connection tubes (Viton).

Table of contents

List of Figures

1 INTRODUCTION

Interest in, as well as the relative importance of, biodegradable organic matter (BOM) has increased over the past two decades. Reducing bacterial regrowth in drinking water distribution systems while limiting disinfection by-products is a common aim of all research into the determination of biodegradable dissolved organic carbon (BDOC). Today numerous proposed methods exist to measure BDOC or the regrowth potential of different kinds of waters. Each method has certain advantages and disadvantages with regards to the complexity of analyses, time required and personal choice. To be able to create a standard method measuring the bacterial regrowth potential in drinking water, more details about the degradation of BOM function have to be known. Which part of the dissolved organic matter (DOC) is going to be degraded is one of the most interesting questions but also the question about a required contact time between the sample and the bacteria used is very important. Another interesting point is the colonisation of the bacteria, does it matter if river water or lake water is used ? Are there any differences in the structure of the bacteria which might be important for the biodegradability? Test substances with known biodegradability as well as known similarity for BOM in drinking water have to be chosen for a standard method to be able to guarantee reproducibility. The aim of this thesis was to evaluate how a continuous plug flow bioreactor (Kaplan and Newbold, 1995) works in detail. To find out what the columns in this reactor are really measuring, or more generally, what does the BDOC measured in these columns really mean and is it BDOC? The biodegradability of glucose under different conditions has been chosen to reach this aim. The second aim was to consider the future development of the methods considering the results measured.

2 DEFINITIONS

Biodegradable dissolved organic carbon (BDOC) is the portion of the organic carbon in the water that can be mineralised by heterotrophic microorganisms (Huck, 1990).

Bacterial regrowth describes the phenomena of bacterial growth in treated water, typically in drinking water distribution systems.

3 THEORY

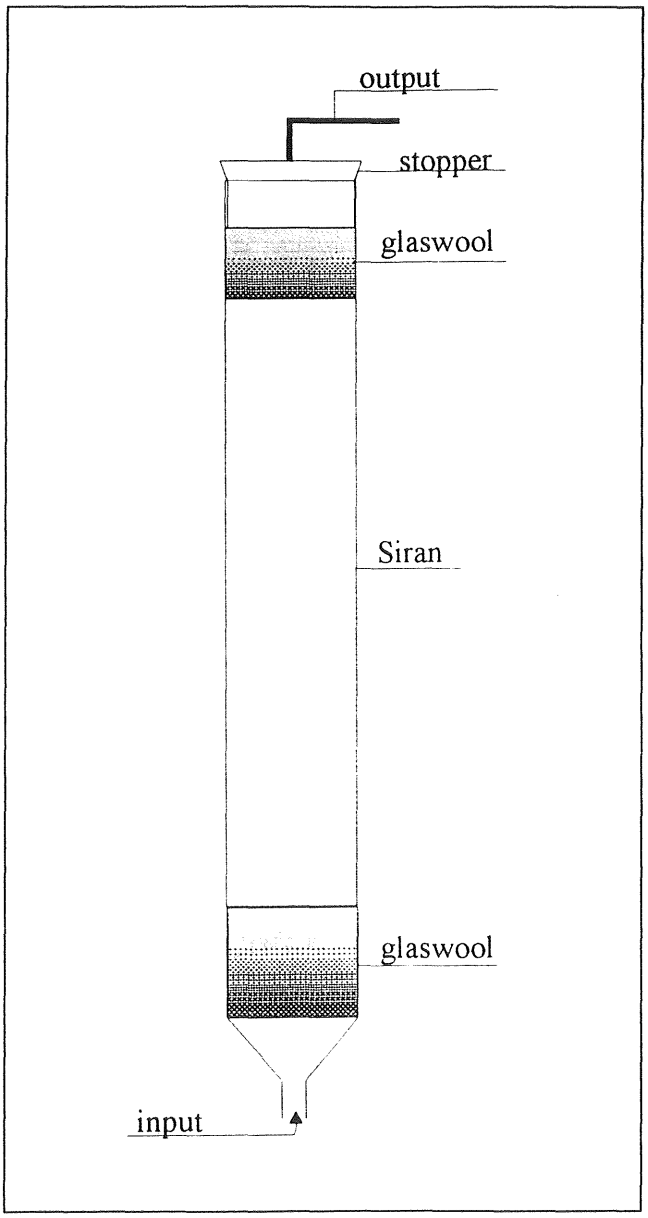
Dissolved organic matter (DOM) provides energy and nutrients for heterotrophic bacteria in aquatic ecosystems, but not all DOM can be metabolised. The biodegradable dissolved organic fraction of the DOM is mainly responsible for the growth of micro-organisms in water distribution systems. BDOC cannot be characterised chemically because of the heterogeneous mixture of molecules that range from the very labile to near refractory, their low concentrations and their irregular presence. The only BDOC measurement techniques available are of bioassay type. They are subject to bacterial and carbon contamination. Several experimental methods have been proposed. Two different kinds of methods can be distinguished. One approach is to measure the assimilable organic carbon (AOC) by the use of pure strains of standardised bacteria, or mixed inocula of indigenous bacteria. The measured parameter is biomass (as heterotrophic plate count, ATP levels, etc.) formed as a consequence of biodegradable carbon assimilation (Jago and Stanfield, 1985; Kemmy *et al.*, 1989; Van der Kooij *et al.*, 1982). In contrast, BDOC is measured through the decrease of dissolved organic carbon (DOC) in samples after a defined period of time (Frias *et al.*, 1992; Kaplan and Newbold, 1995). For the BDOC approach the mechanisms of biodegradation are not really understood.

For this thesis work a plug-flow bioreactor after Kaplan and Newbold (1995), has been chosen to examine what kind of organic substances are biodegraded, in which range and under which conditions. The bacteria used have been colonised from river and lake water used for drinking water production. These two kinds of water have been chosen to get similar conditions as in drinking water distribution systems and to check if bacteria from different sources show differences in biodegradation patterns. Glucose has been chosen as a test substance due to the fact that it is a nutrient and very easily biodegraded. The general aim of understanding the mechanisms in these kind of bioreactors is to create a method to analyse the bacterial regrowth potential in different kinds of water.

4 METHODOLOGY AND MATERIAL

The study was conducted in two different drinking water treatment plants, Lackarebäck and Alelyckan in Göteborg, Sweden. These two treatment plants have been chosen due to the fact that Lackarebäck uses lake water for drinking water production and Alelyckan water from the river Göta älv. The aim of choosing two different kinds of water for colonisation of the bacteria was to find out if any differences in the degradation of BOM could be found due to different kinds of bacteria. The experiments at Alelyckan had to be reduced to BDOC measurements in sand-filtered raw water due to problems with the equipment.

4.1 DESCRIPTION OF THE EQUIPMENT



For the study a continuous flow biofilm reactor (CFBR) has been used. Six reactors were constructed (three for each sampling site) after the description of Kaplan and Newbold (1995) from 63 cm sections of 2.5 cm diameter glass tubes (see figure 1) with a volume of 310 cm^3.

The columns were filled with borosilicate glass beads (Siran, Schott). Siran is an open-pored sintered glass. Spheres of 1-2 mm diameter with 60-300 µm pore diameters that provide a 90,000 : 1 surface to volume ratio were used. The glasswool at the bottom and the top of the columns was used to retain the glass beads in the column. The columns were closed with a plastic stopper and made tight with silicone at the top, the stopper contained a tube for the outlet. The reactors were kept in the dark at a temperature between 19 °C and 22 °C and supplied continuously with water in an upflow mode. The water was pumped through the columns at 7 ml/min using a peristaltic pump and silicon tubes. All the other tubes were Viton and plastic.

Figure 1 Continuous flow biofilm reactor after Kaplan and Newbold (1995)

Figure 2 shows the set-up of the testing plant which has been used for all experiments except for the recirculation experiments.

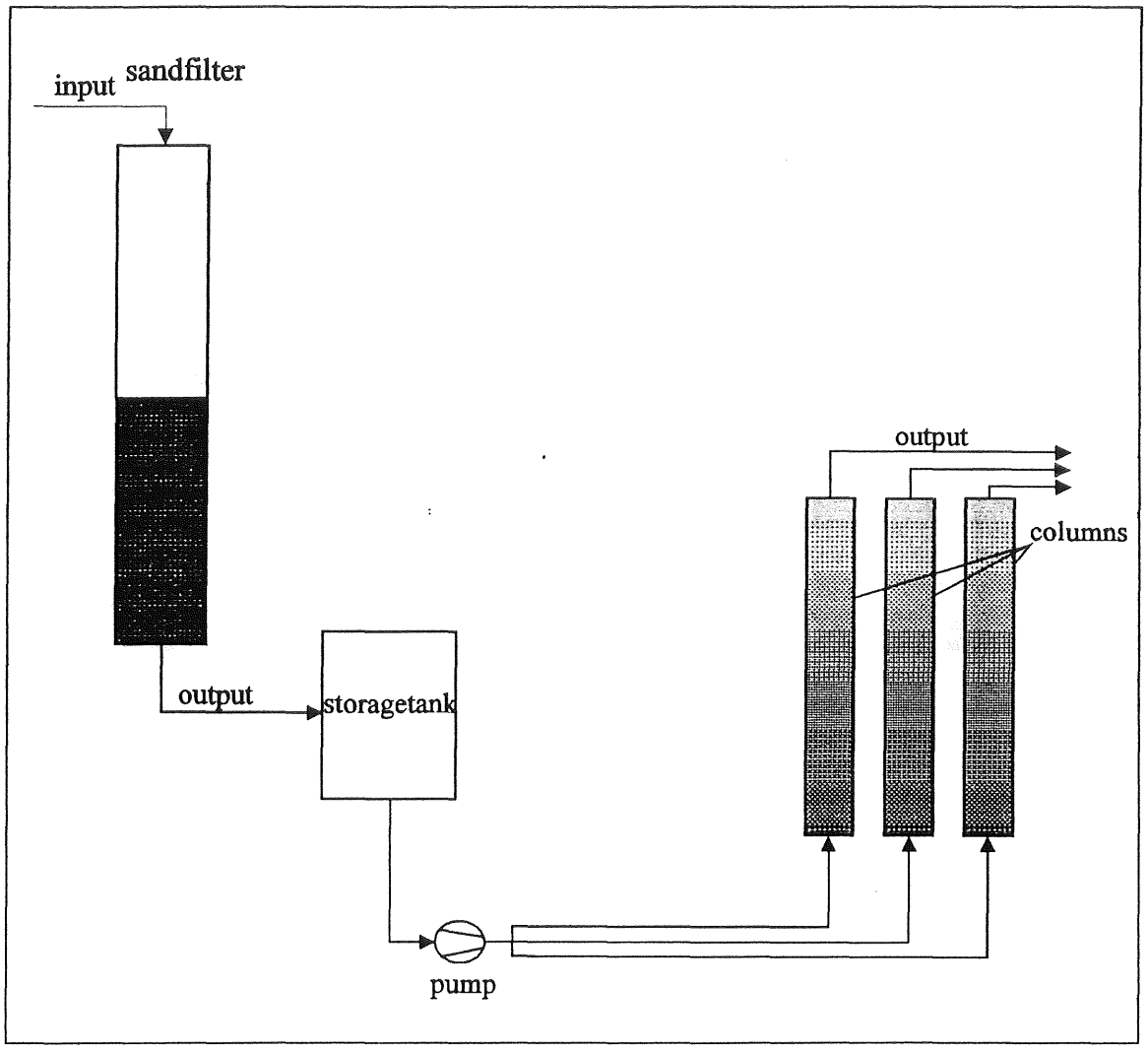


Figure 2 Set-up of the testing plant

For the recirculation experiments the output of each column has been connected with the input of the pump to provide a closed circle (see figure 3). The small storage tanks (polyethylene bottles 100 ml, filled half with either glucose solution or sand-filtered raw water) between the output of the columns and the input of the pump have been used to avoid air in the recirculation system and to be able to take samples.

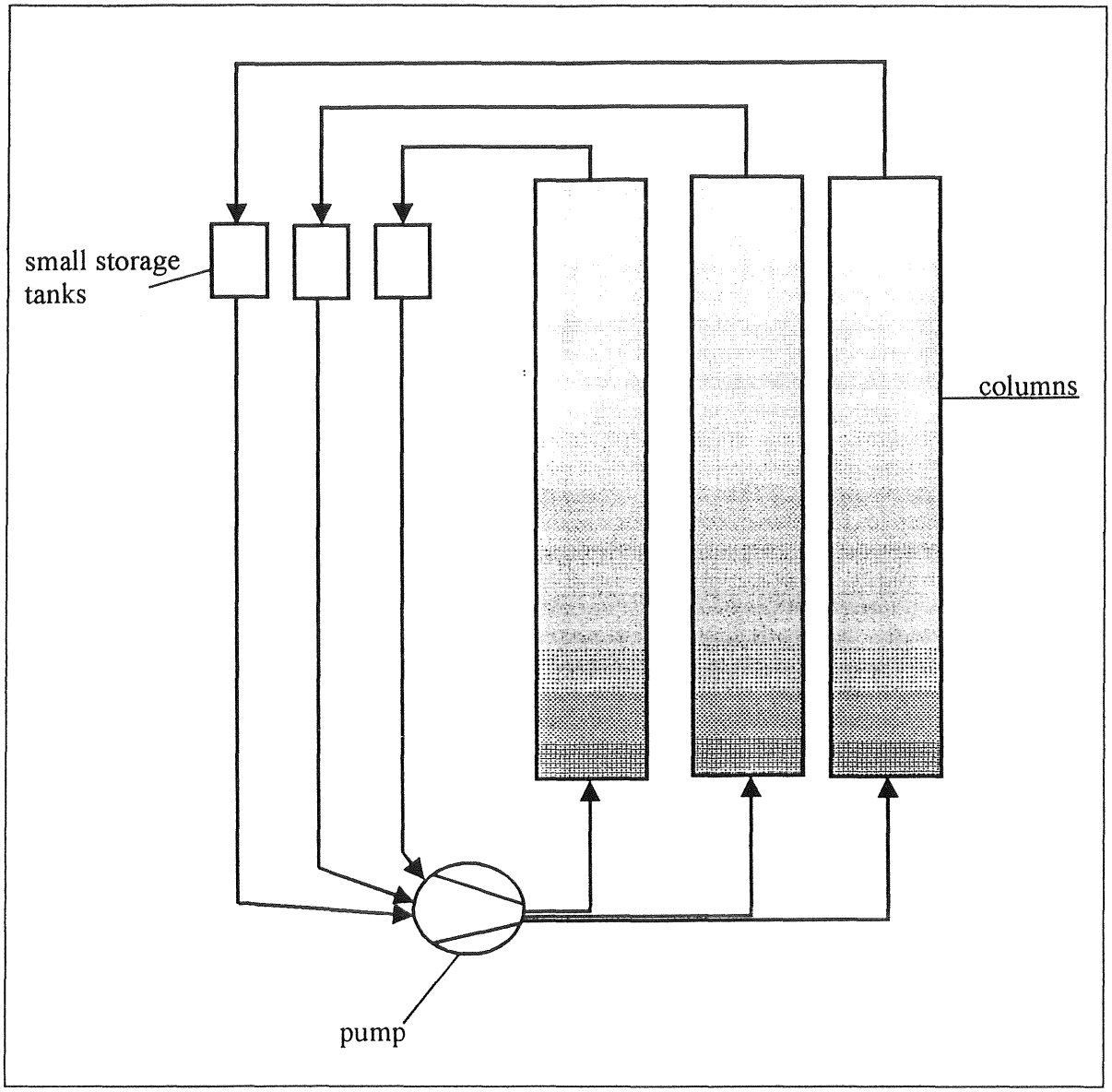


Figure 3 Set-up of the testing plant for the recirculation experiments

The set-up of the testing plant for the recirculation experiments containing a filter system is comparable to the set-up for the recirculation experiments without the filter system. Figure 4 shows the set-up for the recirculation experiments including a filter system. GF/C filters were used in small syringe filter holders.

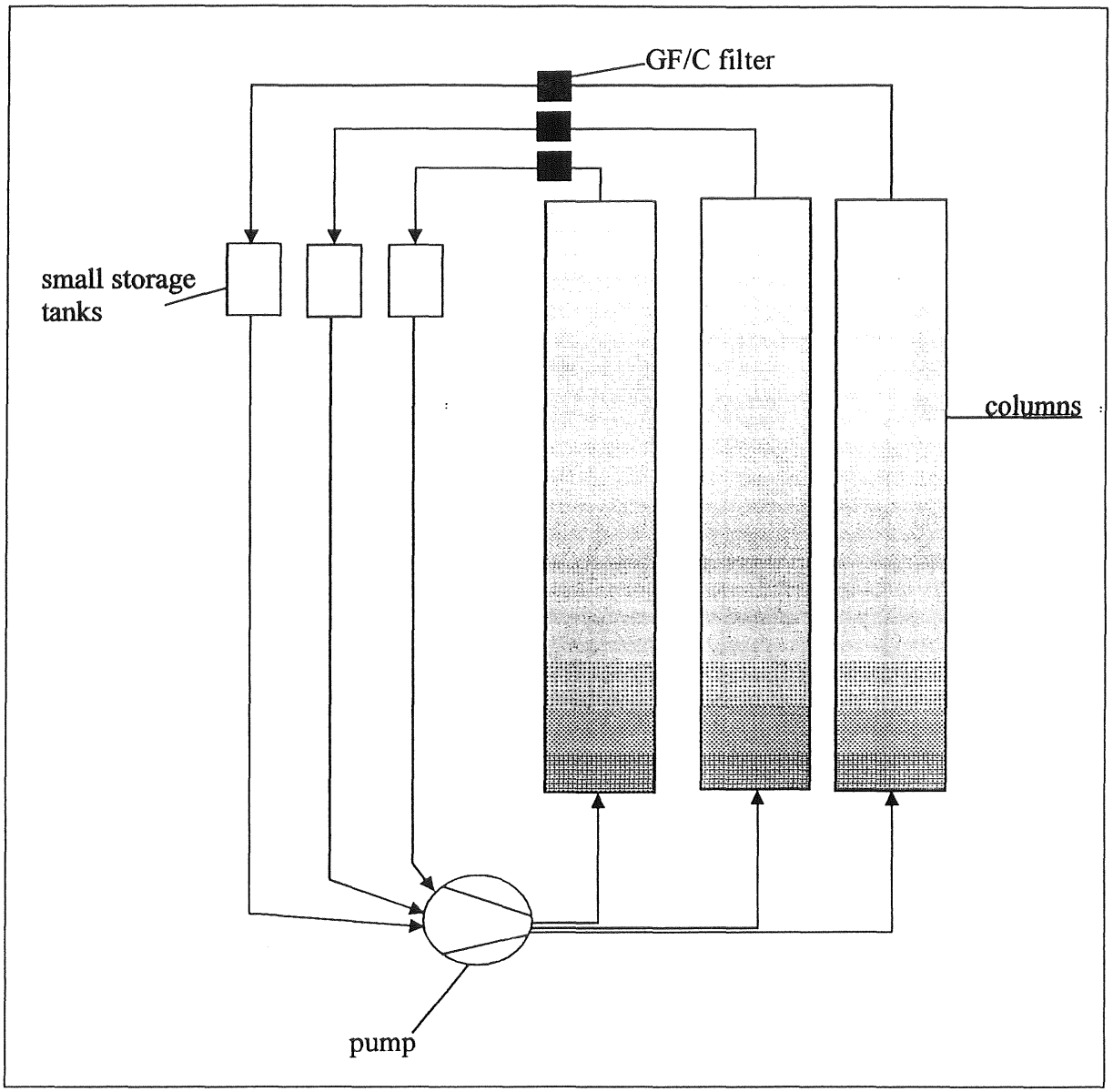


Figure 4 Set-up of the testing plant for the recirculation experiments including a filter system

4.2 COLONISATION

The reactors were installed at Lackarebäck on 18th April and at Alelyckan on 29th May.

Feed water for the columns in Lackarebäck was sand-filtered raw water from Delsjön, a lake close to Göteborg. For the columns in Alelyckan sand-filtered raw water from the river Göta älv has been used.

The measurements were started on 1st July 1996.

4.3 SAMPLING

Samples were taken in 100 ml polyethylene-bottles which were cleaned in a laboratory washing machine and rinsed at least three times with nanopure water. Some of the samples have been filtered through nanopure water rinsed glass fibre filters (GF/C) before measuring to study if dead bacteria affect the BDOC level in the samples. The samples were stored in a freezer until analysis and allowed to defrost in a refrigerator. The storage of the samples in the freezer was for two reasons. First, the biological activity in the samples should be minimised until analysis and second, the TOC bottles may leak organic carbon during storage in the refrigerator, while freezing minimises this effect (Skoog, 1995). The plastic bottles were filled totally to minimise the effect of dissolved carbon dioxide. For statistical reasons a minimum of 3 and a maximum of 5 samples have were for each measurement.

4.4 MEASUREMENT METHODS

4.4.1 TOC measurements

Total organic carbon (TOC) was analysed on a Shimazdu 5000 TOC-analyser together with an autosampler ASI 5000. This instrument measures the Non Purgable Organic Carbon content (NPOC) or the Total Carbon content (TC) and the Inorganic Carbon content (IC) of a sample. TOC can be calculated as the difference between TC and IC.

For the analysis of TC, the sample is combusted totally in the TC-reactor at 680 °C. The TC-reactor is an aluminium catalyst waded with 0.5 % platinum, which guarantees a total combustion to CO and CO_2. Synthetic air is used as a carrier gas to get a continuous flow through the instrument. The products CO and CO_2 are carried to the IC-reactor, where all CO reacts to CO_2. For oxidising all CO to CO_2 in the IC-reactor, the sample is acidified to $pH < 2$. At this pH, CO reacts to CO_2 because of the carbon-carbonate equilibrium. The amount of CO_2 in the sample is than detected by an Infrared-detector (IR-detector).

For the analysis of IC, the sample goes directly into the IC-reactor and the inorganic carbon reacts to CO_2. The amount of CO_2 is than detected by the IR-detector. The IR-detector is made of two tubes separated by a flexible membrane. The CO_2 containing carrier gas in one tube absorbs more Infra-Red light than the pure carrier gas in the other and warms up. Due to the higher temperature the gas expands to a larger volume and a difference in pressure between the two tubes can be measured at the membrane.

Standard curves have to be used to calibrate the instrument. In this case three-point calibration has been used with TC concentrations of 10, 5, 1 ppm and IC concentrations of 5, 2, and 1 ppm. The standards have been chosen due to the fact that TC concentrations around 8 ppm and IC concentrations around 4 ppm are common for sand-filtered raw waters. The glucose solutions had TC concentrations of 1 ppm and less, although TC standards with less than 1 ppm are very unstable.

The standard solutions and the samples should always be at room temperature (20 °C) while analysing them, due to the fact that the density of water changes with temperature. Due to this fact the results vary with temperature. To control the stability of the instrument TC standards should be analysed after at most every 10 samples.

4.4.2 UV measurements

For the UV-measurements at 254 nm wavelength a UV/Vis-spectrophotometer (UNICAM UV/Vis-spectrophotometer UV2) has been used. At wavelength 254 nm especially carbon containing molecules with higher molecular weight like aromatics absorb the energy.

This instrument works with a double beam system. For this kind of measurement the sample is measured against a reference sample. In this case nanopure water has been used as a reference sample. The sample and the reference have to be filled in quarz cuvettes. As a light source a deuterium arc lamp with an inline connector has been used. After leaving the monochromator the beam is directed onto a beamsplitter to produce the sample and the reference beams. The beamsplitter sends most of the available energy down to the sample beam. Just beyond the beamsplitter the beams pass through a modulator. This is under software control and permits the detector to see either the sample beam, the reference beam or dark. After passing through the sample compartment the beams are recombined and directed onto the detector.

The detector is a photodiode detector. A photodiode detector is a solid state detector, made of doped crystalline silicon. A voltage is generated (by the photovoltaic effect) when light falls onto the P-N-junction of a semiconductor. The type of photodiode used in this case is the PNN+ variety, which has a high sensity in the UV region, and a low dark current. Figure 5 show a PNN+ photodiode detector.

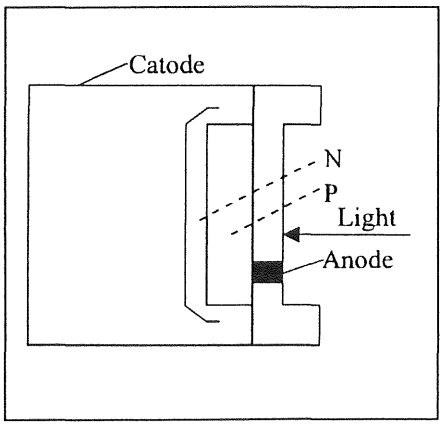


Figure 5 PNN+ photodiode detector

To calibrate the instrument both cuvettes were filled with nanopure water and measured against each other. Then the instrument was zeroed and the cuvettes were checked against each other.

It is very important that the cuvettes are totally clean and dry at the sides the light goes through to avoid measuring errors. To be sure about the stability of the instrument nanopure water should be measured between the samples. To avoid the drift of the deuterium arc lamp the instrument should be switched on at least one hour before the measurements.

4.5 DESCRIPTION OF THE EXPERIMENTS AND HYPOTHESIS

4.5.1 Experiments with sand-filtered raw water to test the columns

For colonisation and testing, the columns were supplied with sand-filtered raw water in an upflow stream. Samples were taken at least once a week. Sand-filtered raw water was chosen because of the known range of BDOC values. The experiments with glucose solution were started as soon as the BDOC values for sand-filtered raw water were stable in the known range for BDOC in natural waters (0.2 - 0.6 mg l^{-1} (Kaplan and Newbold, 1995)). The sandfilters needed extra care. They had to be backwashed at least once a week. This is due to the fact that algal growth in the filters was very high during the summer months. It was expected to find an

increasing value for BDOC until it reaches a more or less stable level at a value around 0.2 - 0.6 mg l^{-1} (Kaplan and Newbold, 1995).

4.5.2 Long-term experiments with glucose solution

For the long-term experiment one column was supplied with a glucose solution containing 1 mg C/l in an upflow for five days. Samples were taken every 24 hours. The aim of this experiment was to find out if the bacteria in the columns would adapt to the test substance. If this would be the case a dependence of the BDOC values on the time the column is supplied with the test substance could be measured. It was expected that an increasing value for BDOC would occur which should reach a stable level.

4.5.3 Concentration experiments with glucose solution

Glucose solutions with different concentrations have been used to find out if the BDOC values of the test substance depend on the concentration of the available organic material. The glucose solutions were pumped in an upflow stream through one column (always the same to guarantee reproducibility). Care was taken that the column should not adapt to the glucose solutions so there was always one day between the experiments. It was expected that a maximum value for BDOC would show up for one special concentration or for a concentration range.

4.5.4 Recirculation experiments with glucose solution and sand-filtered raw water

For the recirculation experiments a glucose solution containing 1 mg C/l was recirculated in one column for 1, 5, 10, 50 and 100 circulations (one circulation was equivalent to 45 min. which is the hydrodynamic retention time[1]). The same was done with sand-filtered raw water in the other two columns. The aim of this experiment was to find out if the BDOC values for the test substance depend on the contact time between the sample and the bacteria. It was expected to find an increasing BDOC value with increasing number of recirculations.

4.5.5 Recirculation experiments with glucose solution and sand-filtered raw water including a filter system

These recirculation experiments were carried out in the same way as the recirculation experiments before. The only exception was the GF/C filters which were installed in the recirculation circle (see figure 4). The aim of this experiment was to find out if parts of the biofilm or dead bacteria were released from the columns during the recirculation experiments. It was expected to find lower values for TOC in the samples because the parts of the biofilm would not have had the possibility to enrich in the solution during the recirculations.

4.5.6 Recirculation experiments with glucose solution and sand-filtered raw water where the samples were filtered during the sampling procedure

These recirculation experiments were also carried out as in 4.5.4 and 4.5.5 before but the samples were filtered through GF/C filters during the sampling procedure. The aim of this experiment was to find out if parts of the biofilm or dead bacteria were released from the columns during the recirculation experiments and if any difference could be found compared to the recirculation experiments with glucose solution and sand-filtered raw water including a

[1] Hydrodynamic retention time is the retention time which has been calculated based on the empty bed volume and the pumping rate (45 min.).

filter system. It was expected to find no differences compared to the experiments with glucose solution and sand-filtered raw water including a filter system.

4.5.7 Hydrodynamic experiments

To find out the hydrodynamic situation in the columns methylene blue with a concentration of 1 mg/l was injected as a plug into a column while nanopure water was pumped through. The outcoming methylene blue was measured with a UV spectrophotometer. In a second step, methylene blue with a concentration of 10 mg/l has been injected into a column as a plug while nanopure water was pumped through. The movement of the colour was photographed. Two different columns were used, a new column containing fresh Siran and a column containing an established biofilm. The aim of this experiment was to find out if the columns really work as plug flow reactors. It was expected to be able to see a plug-flow in both columns during the retention time of 45 min.

5 DISCUSSION OF POSSIBLE ERRORS

Several possible errors during sampling, storage and measurements have to be considered:

5.1.1 The TOC instrument is only reliable to two decimals

The BDOC value of raw water appears to be around 0.2 - 0.6 mg l^{-1} (Kaplan and Newbold, 1995). Due to the fact that the TOC instrument is, in the normal sense mode, only reliable to two decimals for mg l^{-1} some of the calculated BDOC values might not be sufficiently precise, since BDOC is a calculated difference between two TOC values.

5.1.2 TOC bottles not rinsed enough with nanopure water

The sampling bottles have been washed in an laboratory dishing machine and rinsed at least three times with nanopure water. But sometimes some contamination might have been left and influenced the measurements.

5.1.3 Leakage of the storage tanks for the glucose solution

The glucose solution was stored in 2 l polyethylene bottles which were rinsed with nanopure water several times. Due to the fact that the bottles were new and not washed before use it might be possible that they leaked some organic carbon. This might have influenced the results of the glucose experiments at the beginning.

5.1.4 Glucose age

The glucose used was more than 10 years old. Due to this fact the structure of the molecules might have changed or humidity might have come into the storage bottle. This could be the reason for some weighing and concentration problems.

5.1.5 High temperature in the TOC room

During some measurements the temperature in the room where the TOC instrument is located was around 30 °C this could have influenced the instrument and the conditions of the samples in the auto sampler. The high temperature may also be responsible for dissolution of carbon dioxide from the samples. So the TOC content of the samples might have been influenced by the high temperatures. The density of water is influenced by temperature too and this could also cause an error.

5.1.6 Change of the carbon dioxide content in the samples

The TOC instrument was mostly run over night. Due to this fact the samples stood in open tubes for 10 to 12 hours during the analyses. The IC content of the samples, and due to the calculation also the TOC content might have been influenced by the solution or dissolution of carbon dioxide in the samples during this time.

5.1.7 Contamination of the sample during the filter action process because of contaminated filters

The GF/C filters have been rinsed carefully with nanopure water and sample and glassfibre filter should not release any organic carbon. But contamination of the filters might have contaminated the samples during the filtering procedure. This might be an explanation for some of the results for the filtered samples.

5.1.8 Bacterial growth in storage tank

Bacterial growth in the storage tank for the sand-filtered raw water may have influenced the BDOC content before the input into the column. This decrease of BDOC might be responsible for some low BDOC values especially at Alelyckan. The raw water in Alelyckan seemed to be much more biologically active than in Lackarebäck.

5.1.9 Algal growth in the tubes and filters

The tubes and the sandfilter in Alelyckan were covered with algal. This might have caused errors because of less flow. Organic material from the algal might have entered the test columns and caused a change of BDOC.

5.1.10 Losses of part of the biofilm

Due to natural reproduction or strange conditions, like high glucose concentrations, parts of the biofilm might die and flow out with the sample. These parts of the biofilm influence the TOC values a lot and may be responsible for errors especially during the recirculation experiments.

5.1.11 Leakage of the tubes

Some of the tubes used leaked carbon in the range of 30 ppm for 100 circulations, this has definitely influenced the TOC results, especially for the recirculation experiments (see discussion part).

5.1.12 Retention time

The chemical retention time of the columns proved to be much longer than the hydrodynamic retention time. The BDOC values have been calculated as the difference between input and output of the columns based on the hydrodynamic retention time. Since the chemical or real retention time was shown to be much longer (ca. 50 h for molecules of the size of 200-300 Å instead of 45 min) input and output measured have not been the same water. This has influenced especially the glucose measurements but also the sand filtered raw water measurements.

6 RESULTS

6.1 EXPERIMENTS WITH SAND-FILTERED RAW WATER TO TEST THE COLUMNS

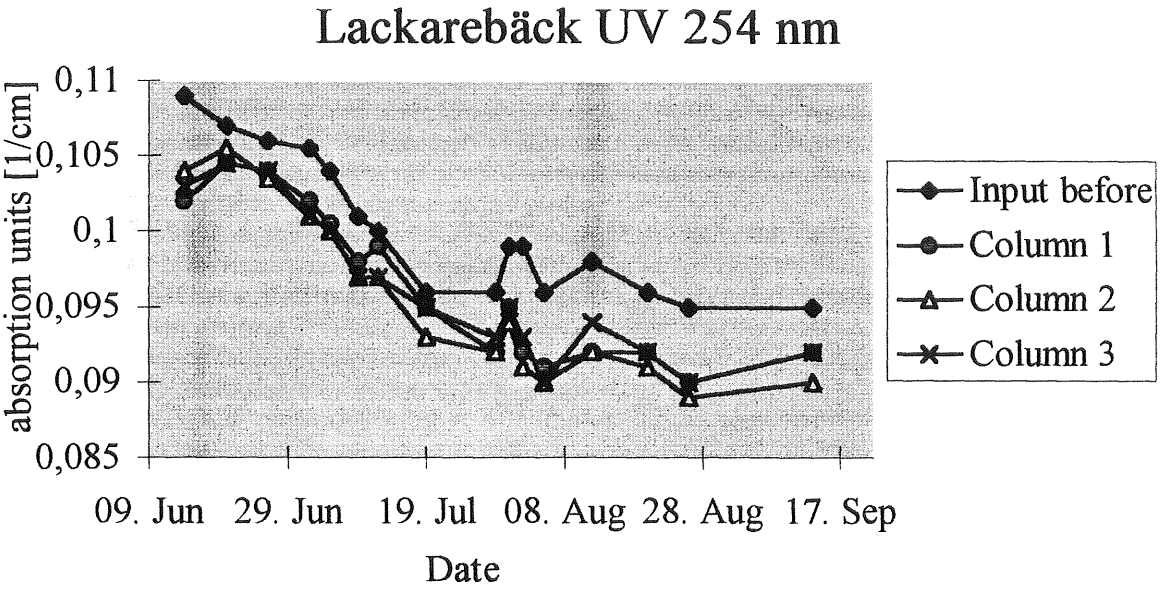


Figure 6 Results of the experiments with sand-filtered raw water in Lackarebäck (UV 254 nm measurements), June-September 1996.
Note that the y-axis does not start from 0.

From this diagram it can be seen first that the input of the columns always got higher absorption values, which is equivalent with a higher amount of carbon, compared to the output of the columns. The values decreased during the first two month and stabilised at a value between 0.09 and 0.095 absorption units.

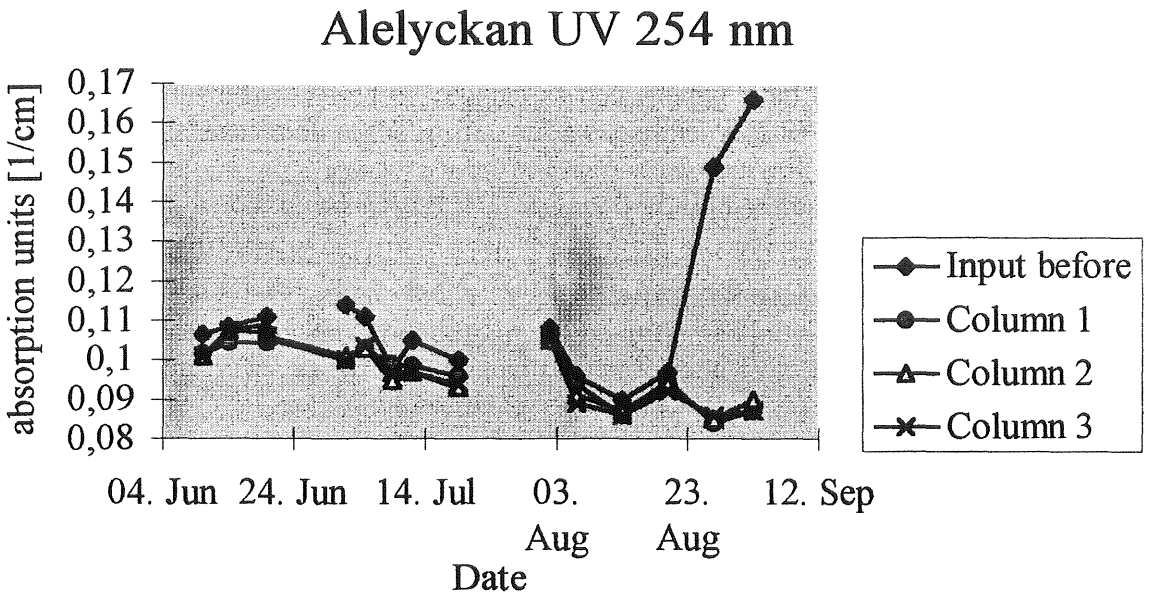


Figure 7 Results of the experiments with sand-filtered raw water in Alelyckan (UV 254 nm measurements), June-September 1996
Note that the y-axis does not start from 0.

This diagram shows that the columns at Alelyckan did not work as well as those at Lackarebäck. The values did not stabilise and the input values were not always higher than the output values.

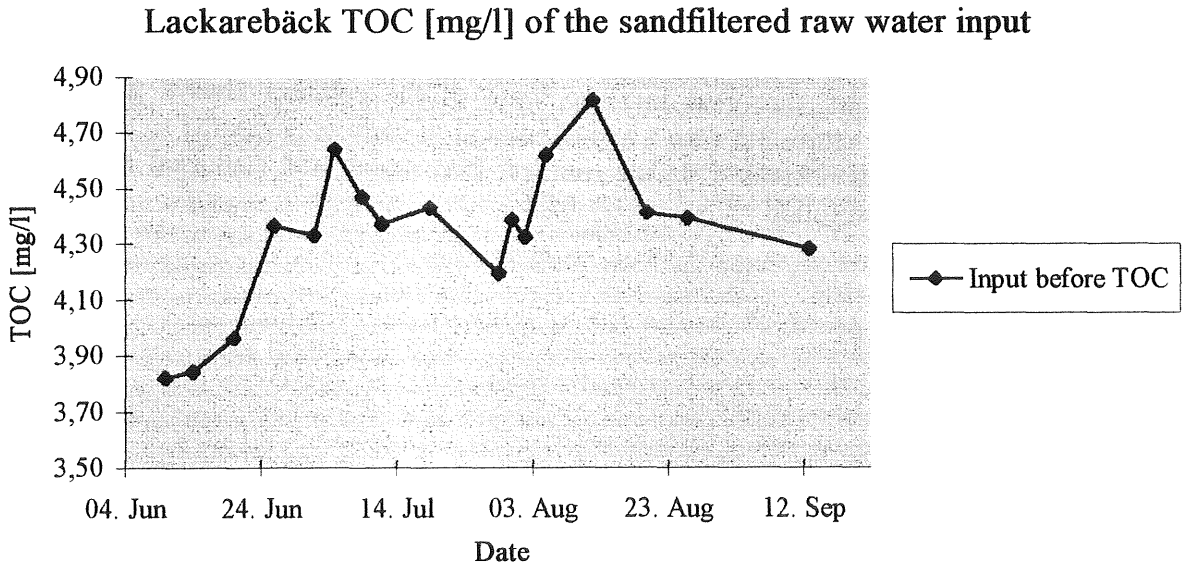


Figure 8 TOC results for the sand-filtered raw water input in the columns at Lackarebäck, June-September 1996
Note that the y-axis does not start from 0.

It can be seen from this diagram that the input values of TOC for the columns at Lackarebäck did not vary much during the evaluated time period.

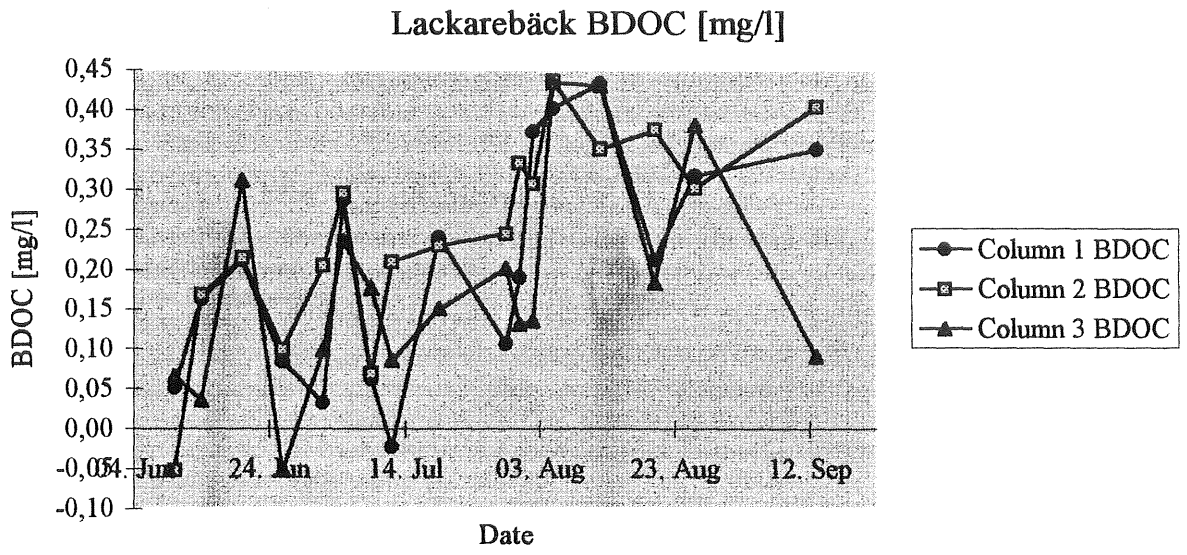


Figure 9 BDOC results for the experiments with sand-filtered raw water in Lackarebäck, June-September 1996

A gradual increase and stabilisation of the BDOC values at approximately 0.4 mg l^{-1} can be seen from this diagram.

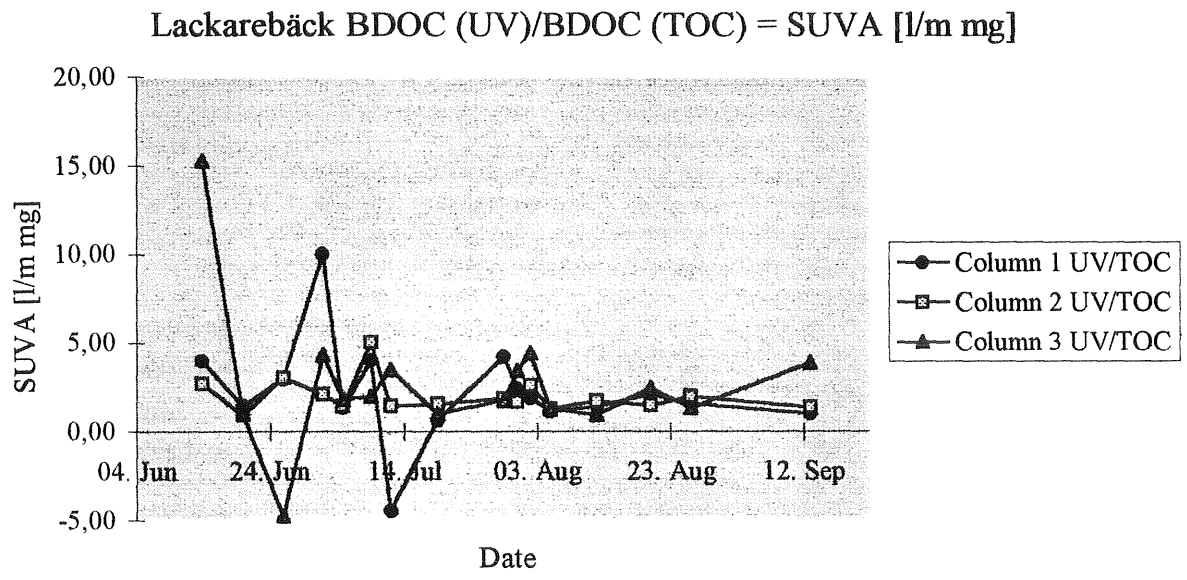


Figure 10 SUVA results for sand-filtered raw water in Lackarebäck, June-September 1996

SUVA is the relation of BDOC values from UV measurements to BDOC values from TOC measurements. Since UV 254 nm reflects absorption by larger organic molecules, this diagram shows the relation of degration of the larger molecules to the degration of all molecules. The stabilisation of the values can be seen very clearly in this diagram.

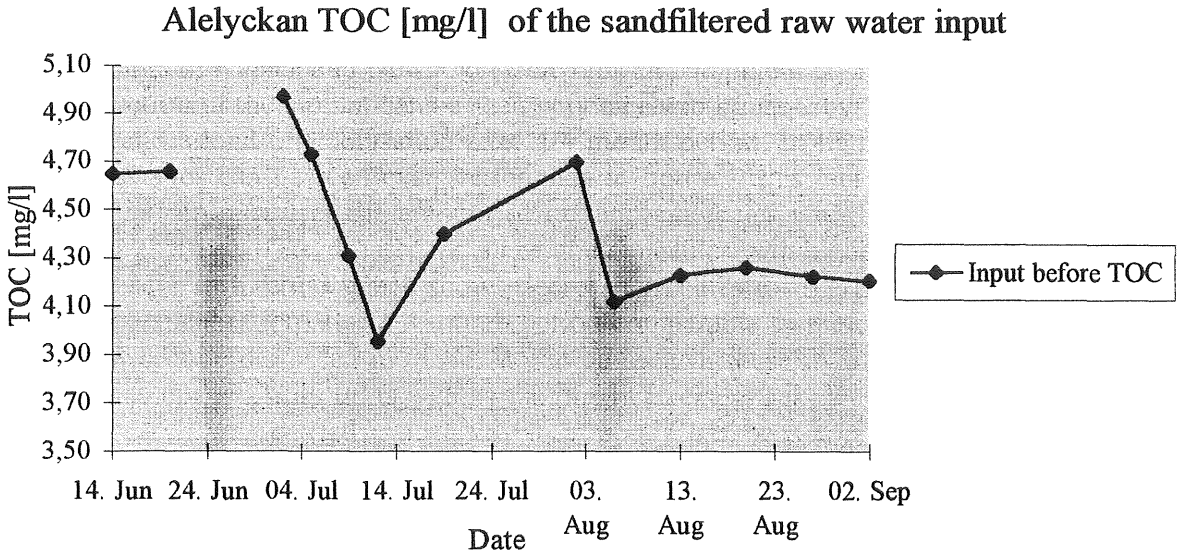


Figure 11 TOC results for the sand-filtered raw water input in the columns in Alelyckan, June-September 1996
Note that the y-axis does not start from 0.

This diagram shows that the input values for Alelyckan vary much more than those for Lackerebäck but they can still be considered fairly constant.

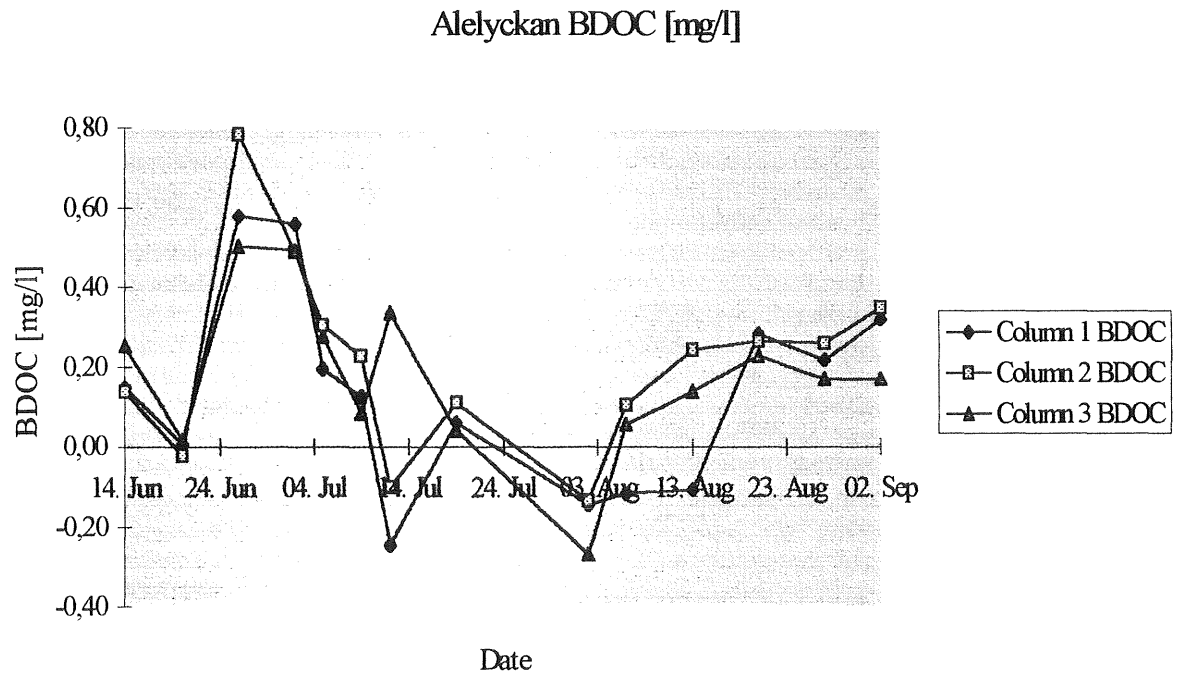


Figure 12 BDOC results for the experiments with sand-filtered raw water in Alelyckan, June-September 1996

It can be seen from this diagram that the BDOC values at Alelyckan did not stabilise during the evaluated period.

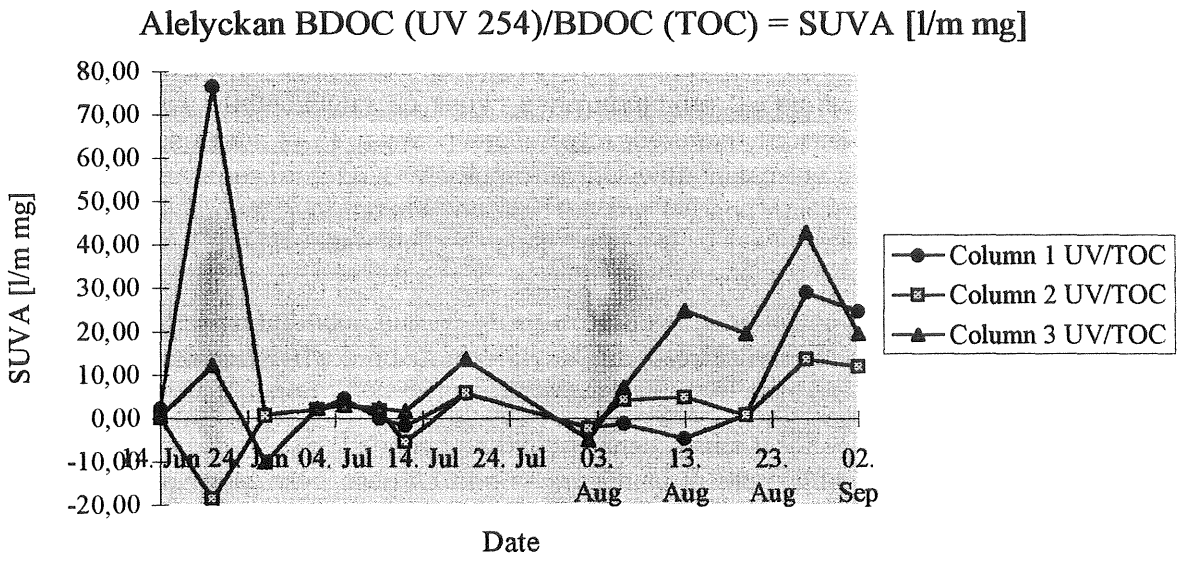


Figure 13 SUVA results for sand-filtered raw water in Alelyckan, June-September 1996

This diagram shows as well as diagram 12 that the BDOC values did not stabilise during the evaluated time period.

6.2 LONG-TERM EXPERIMENTS WITH GLUCOSE SOLUTION

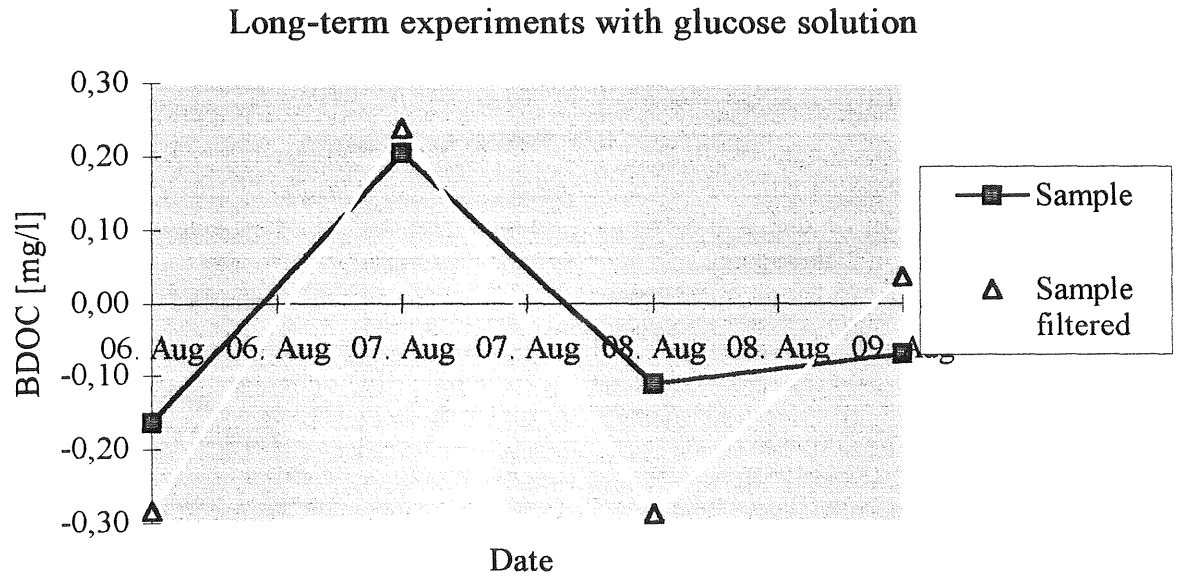


Figure 14 BDOC results for the long-term experiments, 1996

Increasing BDOC values were expected caused by an adaptation of the bacteria to the glucose solution. Unfortunately this was not the case as can be seen in figure 14.

6.3 CONCENTRATION EXPERIMENTS WITH GLUCOSE SOLUTION

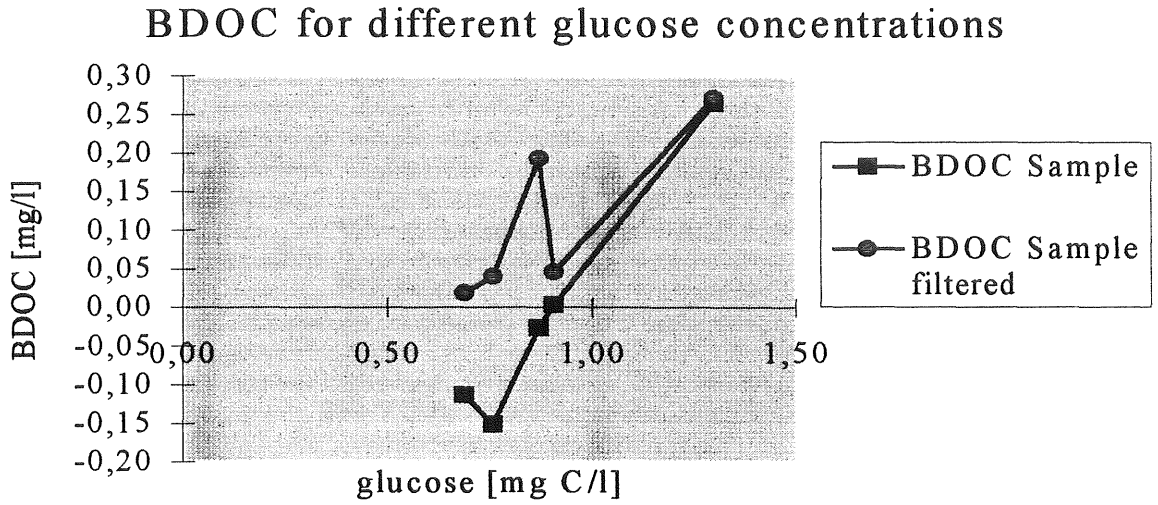


Figure 15 BDOC results for the experiments with different glucose concentrations, 1996

The diagram shows higher BDOC values for the filtered samples than for the unfiltered samples. The BDOC values increase with increasing glucose concentration. Unfortunately no concentration or concentration range with maximum BDOC, as was expected, can be seen.

6.4 RECIRCULATION EXPERIMENTS WITH GLUCOSE SOLUTION AND SAND-FILTERED RAW WATER

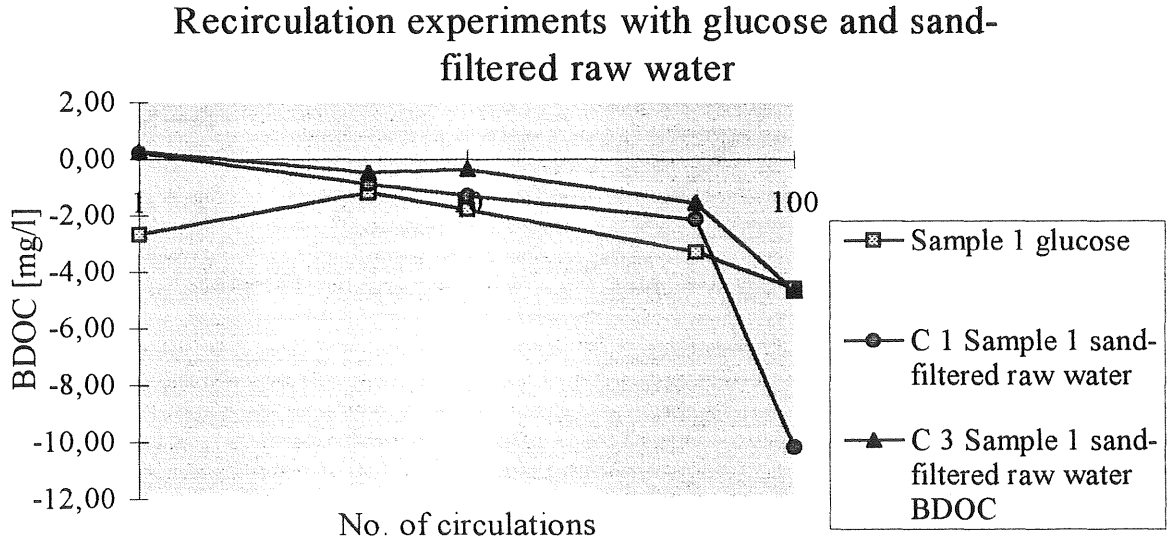


Figure 16 BDOC results for the first samples taken after the recirculation process for glucose solution (1 mg/l C) and sand-filtered raw water, 1996

C 1 and C 3 are short for column 1 and column 2. The columns were numbered to be able to distinguish them.

Increasing BDOC values were expected for an increasing number of circulations, but unfortunately the diagram shows exactly the opposite. BDOC values decreased with increasing number of circulations. Negative BDOC values occur when the TOC values at the output of the columns are higher than the TOC values of the input.

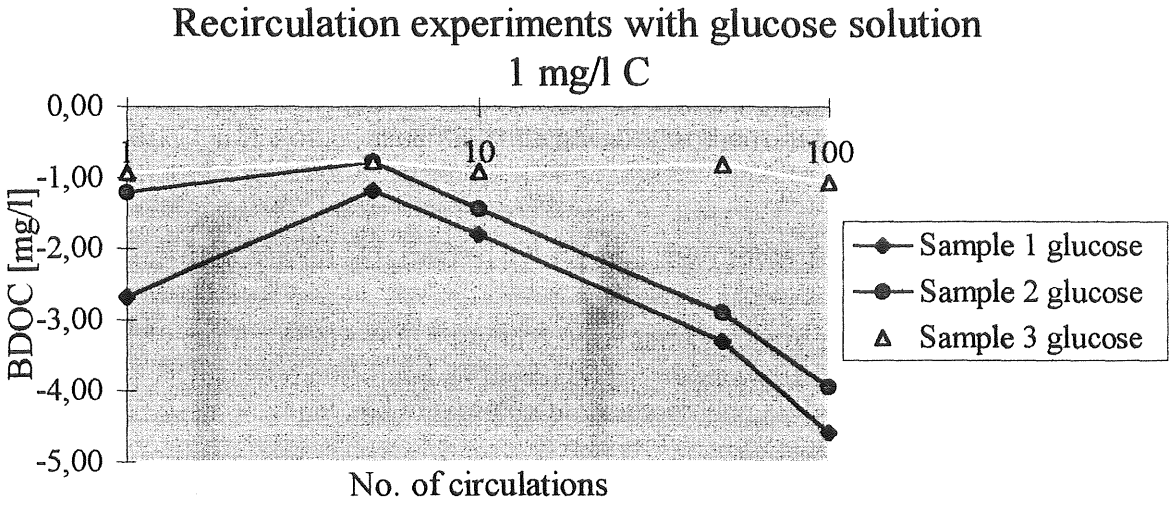


Figure 17 BDOC results for the three samples taken after the recirculation process with glucose solution, 1996
Three samples were taken successively and numbered in the order they were taken.

An increase of BDOC with the number of samples can be seen from this diagram. The BDOC values for the third sample were much higher than the ones for the first. But for all the samples the BDOC values decreased with increasing number of circulations.

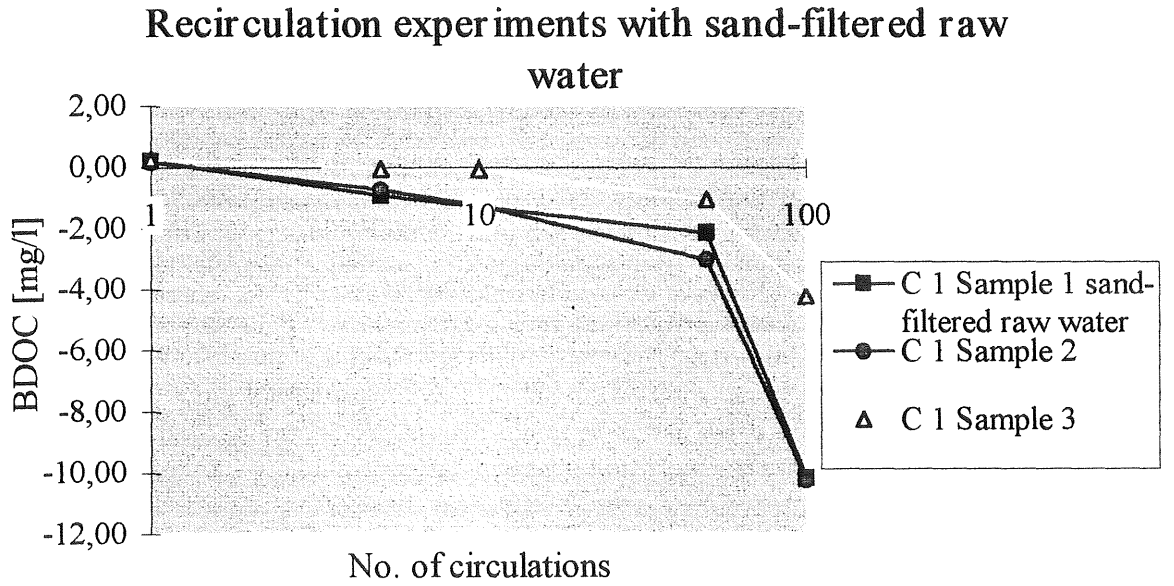


Figure 18 BDOC results for the three samples taken after the recirculation process with sand-filtered raw water, 1996
C 1 is short for column 1.

The same phenomena as in figure 17 can be seen here too. The BDOC values increase with the number of samples taken, but they decrease for all samples with increasing number of circulations.

6.5 RECIRCULATION EXPERIMENTS WITH GLUCOSE SOLUTION AND SAND-FILTERED RAW WATER CONTAINING A FILTER SYSTEM

The results of these experiments are not going to be presented in this thesis work . This fact is due to an enormous error caused by organic carbon leaking from the Viton tubes. For more information see the discussion of the recirculation experiments (7.5).

6.6 RECIRCULATION EXPERIMENTS WITH GLUCOSE SOLUTION AND SAND-FILTERED RAW WATER WHERE THE SAMPLES WERE FILTERED DURING THE SAMPLING PROCEDURE

The results of these experiments are not going to be presented in this thesis work . This fact is due to an enormous error caused by organic carbon leaking from the Viton tubes. For more information see the discussion of the recirculation experiments (7.5).

6.7 HYDRODYNAMIC EXPERIMENTS

These experiments showed that the real retention time for molecules of the size of methylene blue (200-300 Å) is around 50 hours in the new column and even longer in the column containing a biofilm. In fact the real retention time in the column containing a biofilm was impossible to measure because methylene blue was biodegraded before reaching the top of the column. The calculated hydrodynamic retention time based on the empty bed volume[2] and the flow rate was 45 min.

[2] The empty bed volume is the volume of the column without filling material.

7 DISCUSSION OF THE RESULTS

In this part of the thesis all results presented in chapter 6 are going to be discussed and explained as precisely as possible.

7.1 HYDRODYNAMIC EXPERIMENTS

The results of these experiments show that the retention time for small organic molecules is very long in the columns. The size spectrum of organic molecules in natural waters which is presented in figure 19 shows that natural water includes an enormous spectra of molecules.

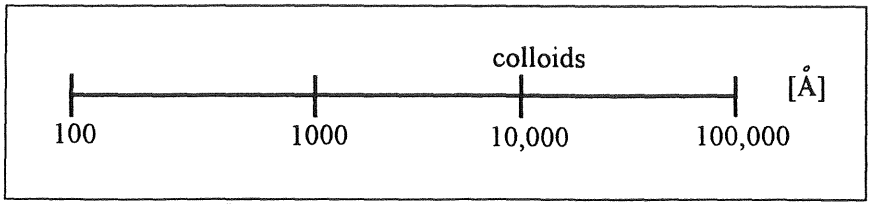


Figure 19 Size spectrum of organic material in natural waters (Förstner, 1990)

Two different transport mechanisms occur in the columns and the sintered glass beads, convection[3] and diffusion[4]. The larger molecules are transported by convection through the column as shown in figure 20. The smaller molecules are also transported by convection, but their transport through the column is dominated by diffusion into the pores of the sintered glass beads and into the biofilm. Which means that a kind of gel filtration occurs in the columns and the molecules are separated on the basis of size. The bigger molecules reach the top of the column first while the part of the smaller molecules which has not been biodegraded by the bacteria in the biofilm, come much later.

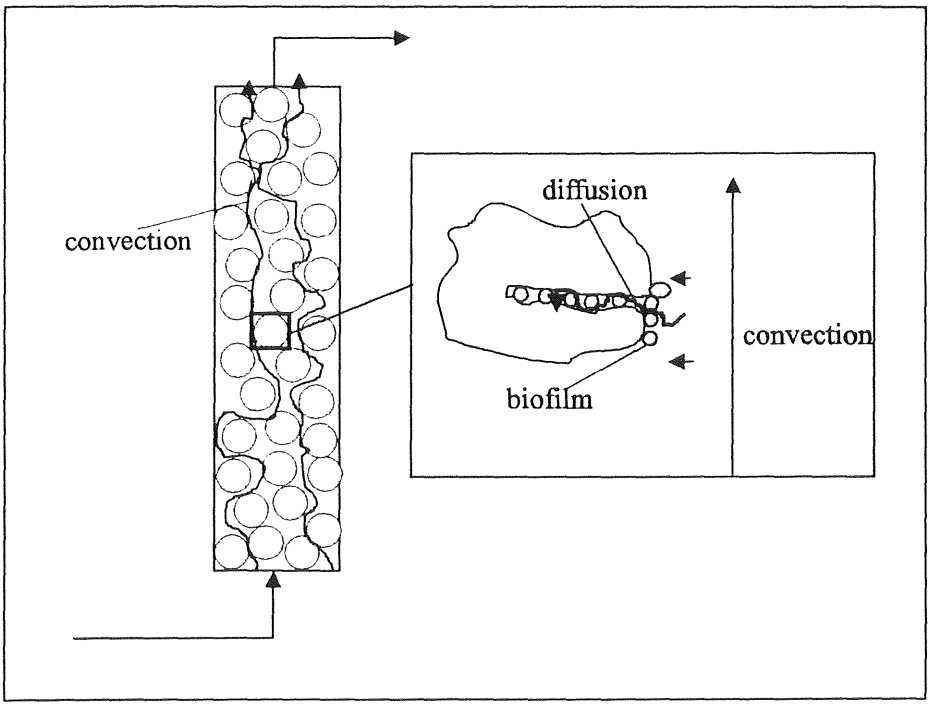


Figure 20 Convective and diffusive transport mechanisms in the columns

[3] Convection is the enforced transport of a particle by the flow.
[4] Diffusion is the transport of a particle due to the concentration gradient.

7.2 EXPERIMENTS WITH SAND-FILTERED RAW WATER TO TEST THE COLUMNS

The results of the experiments with sand-filtered raw water to test the columns harmonise well with the results of Kaplan and Newbold (1995) for an equipment constructed in the same way. The construction of the biofilm can be seen very nicely in figure 9 by the increase of the values for BDOC and a kind of stabilisation after a 4 month period. In figure 10 the stabilisation of the BDOC values can be seen even better than in figure 9 this fact had not been suspected since UV 254 nm measures the amount of organic molecules with higher molecular weight. But it seems that BDOC is also dependent on the molecules with higher molecular weight. This can also be seen in figure 6 which shows decreasing values for the construction phase of the biofilm and a stabilisation after a 4 month period comparable to the one in figure 9. Figure 7, 11 and 12 won't be discussed in detail. It can be seen in these figures that the equipment at Alelyckan has not worked out as well as the one in Lackarebäck. Due to this reason no more detailed research was carried out at this location. It has been found during hydrodynamic experiments that the real retention time is much higher than the hydrodynamic retention time based on the empty bed volume and the flow rate. The effect of the gel filtration and the longer retention time, discussed above, has to be considered for the discussion of the results. Due to the longer retention time the basis of the calculations for the BDOC values (the input has always been measured 45 min before the output) of these experiments was wrong. But since the input values of the columns have not varied significantly (see figure 8) it can be assumed that the error which has occurred due to the mistake with the retention time, is negligible. Due to the fact that the sand-filtered raw water has been pumped through for a very long time the effect of the gel filtration should not affect the measurements.

7.3 LONG-TERM EXPERIMENTS WITH GLUCOSE SOLUTION

The results of these experiments show clearly the influence of the long retention time. The glucose molecule (ca. 100 Å) is even smaller then the methylene blue molecule (ca. 200-300 Å) this leads to an even longer retention time. Figure 21 shows, in general, the connection between the retention time and the size of the molecule. Unfortunately these experiments were only carried out for one week. Figure 14 Points out that at the end of the measurements the BDOC values seem to stabilise even if the values are still negative. The fact that the BDOC values are still negative even after one week shows that the retention time for molecules with the size of glucose molecules must be longer than one week. Another possibility considering the values for the filtered samples might be the contamination of the samples by losses of the biofilm or extracellular polymers released by the bacteria.

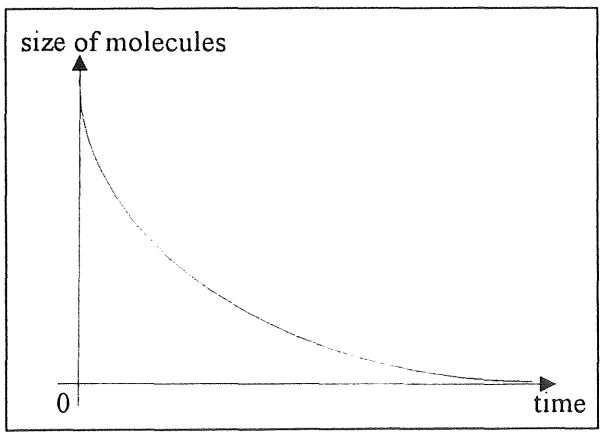


Figure 21 Connection between molecular size and retention time in general

The last value for the filtered sample (figure 14) might be a single point but it could also be the beginning of the stabilisation of positive BDOC values. More experiments are necessary to be able to know which of these hypothesis is correct.

7.4 CONCENTRATION EXPERIMENTS WITH GLUCOSE SOLUTION

For these experiments a maximum of degradation has been expected for one concentration or a range of concentrations. Figure 15 shows a maximum, for the unfiltered sample, for the highest glucose concentration (1.28 mg C/l) used. From these experiments it cannot be known if the increase of the values for BDOC would go further with increasing glucose concentrations. The filtered sample shows two maxima, one for 0.8 mg C/l and one for 1.28 mg C/l. It might be possible that the samples were contaminated with parts of the biofilm so that the first maximum can only be seen in filtered samples. The second maximum is the same one as for the unfiltered samples with the same uncertainties. More experiments would be necessary to be able to be sure if two maxima for the biodegradability of glucose really exist or if these values occurred only due to contamination.

The explanation above would be a possibility to discuss the results which were measured if the retention time would have been 45 min as presumed in the beginning. For these experiments the glucose solutions were pumped through the columns for 90 min before sampling. Considering the size of the glucose molecules the probability that any glucose has been measured in the output of the columns is very low. What has been measured instead are probably organic molecules from the sand-filtered raw water. The positive BDOC values for the highest glucose concentration might be due to longer rinsing of the columns with the glucose solution so that no larger molecules were left in the columns. The higher BDOC values for the filtered samples might be really due to contamination of the samples by parts of the biofilm which can be removed by filtering the samples. It would be very interesting to measure the dependence of biodegradation from the concentration, but the retention time has to be taken into consideration to make sure that glucose will really be measured.

7.5 RECIRCULATION EXPERIMENTS

The results of the recirculation experiments cannot be discussed in this thesis work. The testing of the Viton tube material in the equipment with nanopure water for 72 h, which is equal to the experiments with 100 circulations, showed values around 30 mg l^{-1} TOC. So the contamination of the samples has been much higher than the expected TOC values from the sand-filtered raw water and the glucose solution. This contamination makes it impossible to discuss the measured results. The enrichment of TOC, coming from the Viton tubes, during the recirculation process can be seen very nicely in figures 16, 17, and 18.

8 CONCLUSIONS

Considering the results of the measurements, the method which has been used (continuous flow biofilm reactor after Kaplan and Newbold (1995)), should be reflected on in this part of the thesis work. On the other hand the consequences of the results on the term BDOC should be discussed.

8.1 CONSEQUENCES OF THE RESULTS ON THE TERM BDOC FOR CONTINUOUS MEASUREMENTS

Considering the results of this study it would seem appropriate to think about the term BDOC[5] once again. BDOC is a defined part of the BOM[6] in water which is possible to measure as the difference between the input and output of a bioreactor.

The results of the hydrodynamic experiments make it necessary to think over the term BDOC in continuous methods again. Which part of the BOM is biodegradable, the larger or the smaller molecules? This question is the most important one. If the larger organic molecules in the water are the biodegradable part of the BOM, the method will give us the right results by measuring the input and output of the column based on the hydrodynamic retention time[7]. But if the small organic molecules, small in this case can be defined as small enough to be able to diffuse into the pores of the sintered glass beads, in the water are the biodegradable part of the BOM then it is only possible to have a look at the average effect. This is due to the fact that the retention time for decreasing molecular size increases significantly (see figure 21) which makes it impossible to measure exact values.

So the size of the biodegradable part of BOM seems to play a significant role when choosing a method to measure BDOC in water.

8.2 EVALUATION AND IDEAS FOR THE DEVELOPMENT OF A CONTINUOUS PLUG FLOW BIOFILM REACTOR AS A METHOD FOR BDOC MEASUREMENTS

The problems of the continuous plug flow biofilm reactor after Kaplan and Newbold (1995) as a method for BDOC measurements, which were pointed out in this study, are related to the retention time of the organic molecules in the column. The very long retention time especially for small organic molecules makes it impossible to measure exact BDOC values continuously.

The idea of continuous methods for BDOC measurements was to be able to get on-line results. To reach this aim the pore size of the filling material has to be optimised to reach a suggested retention time while the surface area also has to be considered to get enough bacteria. To be able to optimise the pore size of the filling material, to optimise the retention time, it is important to find out which molecular size range of BOM is responsible for BDOC.

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[5] Biodegradable dissolved organic carbon (BDOC) is that portion of the organic carbon in the water that can be mineralised by heterotrophic micro-organisms (Huck, 1990).

[6] BOM = biological organic matter

[7] Hydrodynamic retention time is the retention time which has been calculated based on the empty bed volume and the pumping rate (45 min.).

A lot of different filling materials in all sizes and forms are already available from chemical reaction technology and could be tested. Care should be taken not to used materials which may leak organic carbon in any form. The material should neither be biodegradable, nor toxic for bacteria.

The temperature effect has not been evaluated in this study but might be an important parameter to control the degradation of organic material. To find out the ideal temperature for the bacteria in the biofilm might increase the degradation, so it would be possible to speed up the whole method.

Some other kinds of reactors could also be used considering the aim of on-line measurements. Two different ones should be discussed here in some more detail.

A semi-batch reactor might be one possibility to get results with only a short delay while the contact between bacterial matter and water could be increased without using porous material (Keil, 1994). A possible semi-batch reactor is presented in figure 22.

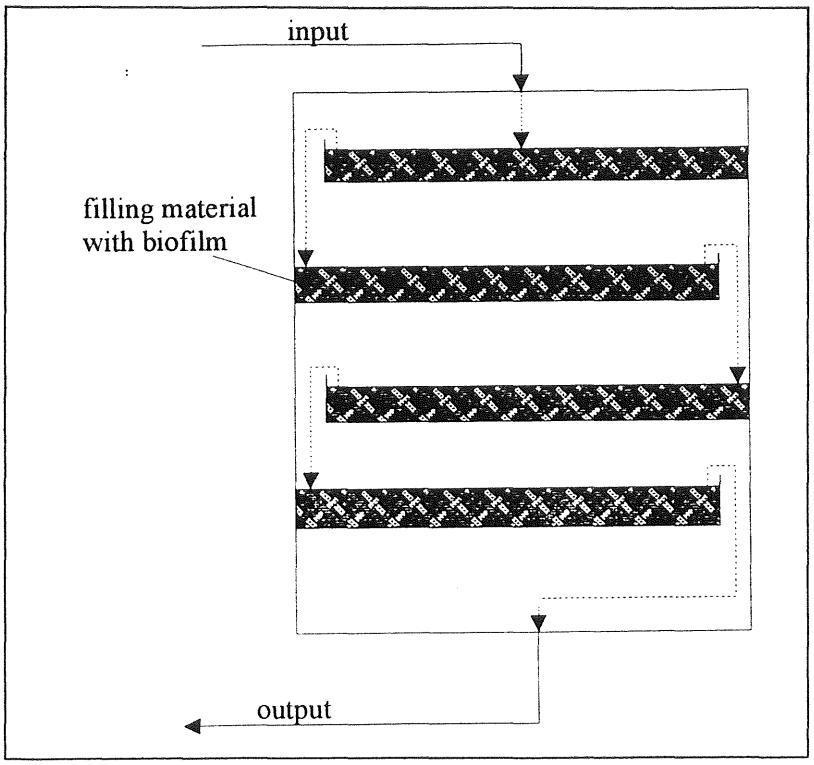

Figure 22 Semi-batch bioreactor

The retention time in this reactor can be controlled either by the number of steps or by the flow rate. Care has to be taken to construct the reactor in a way that makes it impossible for the filling material to move away with the water through the overflow. These kind of semi-batch reactors are used in chemical reaction technology for extraction processes.

The second possibility might be a trickling-reactor comparable to the ones used for sewage water treatment (Förstner, 1990). In this case the retention time could be regulated by the flow while very cheap sand could be used as basement for bacteria growth. This method would be much slower than the method of Kaplan and Newbold (1995) but still much faster than the batch method used by e.g. van der Kooij (1982). Figure 23 presents a possibility for a trickling bioreactor. The disadvantage of this method is the fact that very slow pumps have to be used to produce really only drops of water.

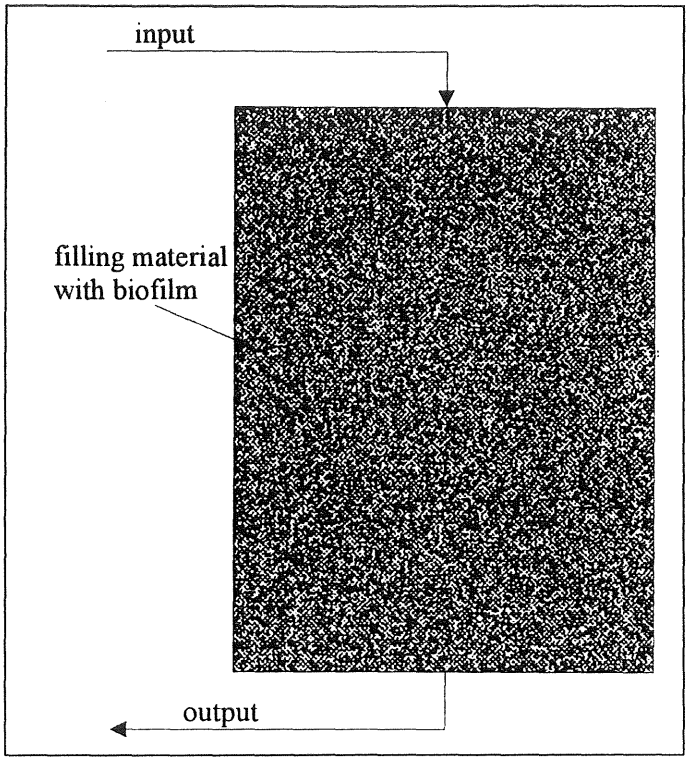

Figure 23 Trickling bioreactor

This water slowly drain through the reactor while the BDOC is degraded by the bacteria of the biofilm.

A general problem for all continuous methods for measuring BDOC will be that a larger pore size always means less surface area and less surface area requires a longer retention time.

So the optimisation of both pore size and retention time requires the identification of the meeting point of two contrary curves.

9 FURTHER INVESTIGATIONS

A lot of open questions are still left about the method used in these study and some of them even are due to the results carried out. In this part of the report some ideas for further studies are mentioned. The idea is not to write a complete description of further studies but to give some ideas.

First of all it would be very interesting to figure out if the carbon leaking Viton tubes really affected the measurements as much as considered in this thesis. Tubes which definitely do not leak any organic carbon (i.e. Teflon) would be worth a try. This would especially be interesting for the recirculation experiments.

The diameter of the pores for the borosilicate glass beads was supposed to be 60-300 µm but has never been tested. To test the real range of the diameter in the glass beads and as well the amount of closed pores would be very interesting. Existing methods like the Wicke-Kallenbach method could be used. This would be interesting for both, new glass beads and some with biofilm to know how the pores change after the biofilm has grown up. It might be, that there are not any pores left and the problems with the long retention time for small molecules are due to biodegradation or absorption.

The reproducibility of the columns has never been tested. It would be very interesting to run exactly the same water once a week over a longer period to look for the reproducibility of the samples taken.

To figure out if bacteria from different sources like lakes and rivers influence the BDOC measurements would be also very interesting.

It would also be interesting to know the real size range of the organic molecules which exist in the sand-filtered raw water used. Gel filtration could be used to analyse this.

In this thesis a flow rate of 7 ml/min instead of 4 ml/min, as proposed in the original paper from Kaplan and Newbold (1995), has been used. It would be interesting to run the columns with a flow rate of 4 ml/min to see if any differences could be found.

As already mentioned in the discussion part of these document, methylene blue is a very small molecule. To figure out the retention time and the hydrodynamic situation for natural water in the columns with grown biofilm on the glass beads other tracers should be used. Care should be taken about the size of the tracer molecules and the absorption tendency of the biofilm. Different molecule sizes should be considered which could be compared with water molecules and different organic molecules.

Since it is not known until now which part of the BOM in natural water is really responsible for BDOC it would be very interesting to investigate in research about the size range of organic molecules which are the biodegradable part of BOM. With the results of these experiments filling materials for the columns could be chosen to optimise the retention time and the surface area.

The same kind of upflow bioreactor should be tried out, filled with different filling materials, considering the results above. Different materials should be tried to find out if any differences can be found.

One other problem of the measurements for this thesis might have been the release of extracellular polymers from the bacteria. To be able to include this value into the calculations of BDOC some investigation on these release of extracellular polymers from the bacteria would be necessary.

The effect of different temperatures on the column would also be very interesting to investigate. It might be possible to optimise the method by choosing the ideal temperature for difuusion and bacteria growth.

10 ACKNOWLEDGEMENTS

I want to thank Greg Morisson and Lena Björklund-Persson for a lot of interesting discussions and constructive criticism about my thesis work and for a very good supervision during all the time. You have done a really great job. Thank you also for reading and correcting the thesis this belongs especially to Greg who corrected a lot of German-English sentences.

Thank you also Lena for all the nice talks in "between" about Sweden and everything else they have always been fun.

I want to thank Evy Axén who has helped me with all the analyses in the lab and with everything which belonged to this. Thank you also Evy for a lot of nice talks during this time it was really nice to work together with you all the time.

Thanks also to Clas Aykborn who was responsible for setting up the equipment. It was up to him that all the equipment was working so very well all the time. Thank you also for taking care of the equipment when I have not been available.

Thank you Åsa Edell for a lot of very valuable discussions about possible sources for contamination and other things.

Thanks also to Lars-Ove Söderman who was also responsible for setting up the equipment and who gave me very valuable hints about the nicest Volvo 245 DL all over the world.

And last but not least thanks to whole department of sanitary engineering for a lot of nice coffee breaks and lunch times.

Thanks also to Ingibjörg Björnsdottir and Mehboob Hassani for being my opponents for the presentation of this thesis.

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12 APPENDIX

Appendix I

Results of the experiments with sand-filtered raw water to test the columns

UV 254 nm results (Lackarebäck)

Date	Input before	Column 1	Column 2	Column 3	Input after
14. Jun	0,109	0,102	0,104	0,103	0,108
20. Jun	0,107	0,1045	0,1055	0,1045	0,108
26. Jun	0,106	0,104	0,1035	0,104	0,107
02. Jul	0,1055	0,102	0,101	0,101	0,105
05. Jul	0,104	0,1005	0,1	0,1	0,1045
09. Jul	0,101	0,098	0,097	0,097	0,1
12. Jul	0,1	0,099	0,097	0,097	0,1
19. Jul	0,096	0,095	0,093	0,095	0,097
29. Jul	0,096	0,092	0,092	0,093	0,097
31. Jul	0,099	0,095	0,094	0,095	0,1
02. Aug	0,099	0,092	0,091	0,093	0,099
05. Aug	0,096	0,091	0,09	0,09	0,095
12. Aug	0,098	0,092	0,092	0,094	0,098
20. Aug	0,096	0,092	0,091	0,092	0,097
26. Aug	0,095	0,09	0,089	0,09	0,095
13. Sep	0,095	0,092	0,09	0,092	0,096

Appendix I

Results of the experiments with sand-filtered raw water to test the columns

UV 254 nm results (Alelyckan)

Date	Input before	Column 1	Column 2	Column 3	Input after
10. Jun	0,1065	0,1015	0,101	0,101	
14. Jun	0,1085	0,1045	0,1075	0,1075	0,1075
20. Jun	0,111	0,1045	0,107	0,109	0,111
20. Jun		0,1055	0,106	0,106	0,111
02. Jul	0,114	0,1	0,101	0,1	0,1085
05. Jul	0,111	0,103	0,103	0,1035	0,113
09. Jul	0,098	0,099	0,095	0,097	0,1
12. Jul	0,105	0,0985	0,097	0,097	0,1
19. Jul	0,1	0,096	0,093	0,094	0,099
29. Jul					
31. Jul					
02. Aug	0,108	0,105	0,105	0,105	0,108
06. Aug	0,096	0,094	0,091	0,089	0,095
13. Aug	0,09	0,086	0,087	0,086	0,092
20. Aug	0,097	0,095	0,094	0,092	0,098
27. Aug	0,149	0,084	0,085	0,086	0,146
02. Sep	0,166	0,087	0,09	0,087	0,167

Appendix I

Results of the experiments with sand-filtered raw water to test the columns

TOC results (Lackarebäck)

Date	Input before		Input before	Column 1		Column 1	Column 1	Column 2	
	TC	IC	TOC	TC	IC	TOC	BDOC	TC	IC
10.06.1996	6,65	2,83	3,82	6,61	2,84	3,77	0,05	6,76	2,88
14.06.1996	6,66	2,82	3,84	6,53	2,85	3,68	0,16	6,45	2,77
20.06.1996	6,80	2,83	3,96	6,72	2,88	3,84	0,21	6,66	2,83
26.06.1996	7,30	2,90	4,36	7,23	2,89	4,34	0,08	7,18	2,86
02.07.1996	7,20	2,87	4,33	7,19	2,91	4,28	0,03	7,02	2,90
05.07.1996	7,53	2,89	4,64	7,28	2,97	4,31	0,29	7,27	2,97
09.07.1996	7,43	2,96	4,47	7,29	2,95	4,34	0,06	7,32	2,99
12.07.1996	7,34	2,96	4,37	7,39	3,00	4,38	-0,02	7,13	2,98
19.07.1996	7,34	2,91	4,43	7,25	3,04	4,21	0,24	7,18	2,95
29.07.1996	7,22	3,02	4,20	7,21	3,11	4,09	0,11	7,08	3,13
31.07.1996	7,31	2,98	4,39	7,12	2,95	4,17	0,19	7,10	3,08
02.08.1996	7,32	3,00	4,32	7,27	3,07	4,20	0,37	7,31	3,04
05.08.1996	7,65	3,03	4,62	7,31	3,00	4,32	0,40	7,39	3,01
12.08.1996	7,93	3,11	4,82	7,52	3,14	4,38	0,43	7,65	3,19
20.08.1996	7,47	3,06	4,41	7,33	3,13	4,20	0,21	7,13	3,10
26.08.1996	7,41	3,02	4,39	7,17	3,10	4,07	0,32	7,17	3,09
13.09.1996	7,57	3,28	4,28	7,53	3,35	4,18	0,35	7,47	3,34

Appendix I

Results of the experiments with sand-filtered raw water to test the columns

TOC results (Lackarebäck)

Date		Column 2	Column 3			Column 3	Input after		
	TOC	BDOC	TC	IC	TOC	BDOC	TC	IC	TOC
10.06.1996	3,87	-0,05	6,61	2,86	3,76	0,07			
14.06.1996	3,67	0,17	6,57	2,77	3,81	0,04	6,58	2,74	3,84
20.06.1996	3,83	0,21	6,72	2,99	3,74	0,31	7,02	2,89	4,13
26.06.1996	4,32	0,10	7,38	2,90	4,48	-0,05	7,28	2,80	4,48
02.07.1996	4,11	0,20	7,06	2,84	4,22	0,10	7,16	2,86	4,30
05.07.1996	4,30	0,30	7,18	2,82	4,36	0,23	7,30	2,75	4,55
09.07.1996	4,33	0,07	7,23	3,01	4,22	0,18	7,29	2,96	4,33
12.07.1996	4,15	0,21	7,23	2,96	4,27	0,09	7,26	2,92	4,34
19.07.1996	4,22	0,23	7,29	2,99	4,30	0,15	7,41	2,94	4,47
29.07.1996	3,95	0,24	7,09	3,09	4,00	0,20	7,09	2,89	4,20
31.07.1996	4,03	0,33	7,28	3,05	4,23	0,13	7,37	3,04	4,34
02.08.1996	4,27	0,31	7,46	3,02	4,44	0,14	7,87	3,05	4,82
05.08.1996	4,28	0,44	7,30	3,02	4,29	0,43	7,71	2,89	4,82
12.08.1996	4,46	0,35	7,52	3,13	4,38	0,43	8,04	3,23	4,81
20.08.1996	4,04	0,38	7,36	3,13	4,23	0,18	6,61	2,75	3,87
26.08.1996	4,08	0,30	7,12	3,12	4,00	0,38	7,47	3,09	4,37
13.09.1996	4,13	0,40	7,66	3,22	4,44	0,09	7,98	3,20	4,77

Appendix I

Results of the experiments with sand-filtered raw water to test the columns

TOC results (Alelyckan)

Date	Input before		Input before	Column 1			Column 1	Column 2	
	TC	IC	TOC	TC	IC	TOC	BDOC	TC	IC
14. Jun	7,89	3,24	4,65	7,55	3,29	4,26	0,15	7,45	3,18
20. Jun	7,85	3,20	4,66	8,10	3,44	4,65	0,01	8,03	3,35
26. Jun				8,52	4,00	4,51	0,58	8,88	4,54
02. Jul	9,10	4,13	4,97	8,77	4,50	4,27	0,56	8,68	4,34
05. Jul	7,81	3,09	4,73	7,58	3,13	4,45	0,19	7,39	3,05
09. Jul	7,79	3,48	4,31	7,94	3,67	4,28	0,13	7,76	3,58
12. Jul	6,92	2,97	3,96	7,70	3,27	4,43	-0,25	7,63	3,34
19. Jul	7,71	3,31	4,40	8,05	3,73	4,32	0,06	8,03	3,76
02. Aug	8,05	3,35	4,70	8,05	3,38	4,67	-0,15	8,24	3,58
06. Aug	7,34	3,23	4,12	7,51	3,27	4,24	-0,12	7,36	3,34
13. Aug	7,90	3,67	4,23	7,47	3,22	4,25	-0,11	7,07	3,17
20. Aug	7,38	3,12	4,26	7,41	3,43	3,98	0,28	7,47	3,47
27. Aug	7,96	3,74	4,22	7,88	3,91	3,97	0,22	7,94	4,01
02. Sep	7,47	3,21	4,21	8,49	4,50	4,00	0,32	8,43	4,46

Appendix I

Results of the experiments with sand-filtered raw water to test the columns

TOC results (Alelyckan)

Date	Input before		Input before	Column 1			Column 1	Column 2	
	TC	IC	TOC	TC	IC	TOC	BDOC	TC	IC
14. Jun	7,89	3,24	4,65	7,55	3,29	4,26	0,15	7,45	3,18
20. Jun	7,85	3,20	4,66	8,10	3,44	4,65	0,01	8,03	3,35
26. Jun				8,52	4,00	4,51	0,58	8,88	4,54
02. Jul	9,10	4,13	4,97	8,77	4,50	4,27	0,56	8,68	4,34
05. Jul	7,81	3,09	4,73	7,58	3,13	4,45	0,19	7,39	3,05
09. Jul	7,79	3,48	4,31	7,94	3,67	4,28	0,13	7,76	3,58
12. Jul	6,92	2,97	3,96	7,70	3,27	4,43	-0,25	7,63	3,34
19. Jul	7,71	3,31	4,40	8,05	3,73	4,32	0,06	8,03	3,76
02. Aug	8,05	3,35	4,70	8,05	3,38	4,67	-0,15	8,24	3,58
06. Aug	7,34	3,23	4,12	7,51	3,27	4,24	-0,12	7,36	3,34
13. Aug	7,90	3,67	4,23	7,47	3,22	4,25	-0,11	7,07	3,17
20. Aug	7,38	3,12	4,26	7,41	3,43	3,98	0,28	7,47	3,47
27. Aug	7,96	3,74	4,22	7,88	3,91	3,97	0,22	7,94	4,01
02. Sep	7,47	3,21	4,21	8,49	4,50	4,00	0,32	8,43	4,46

Appendix II

Results of the long-term experiments with glucose solution

Date	glucose		glucose	Sample 1			Sample 1	Sample 1 filtered		
	TC	IC	TOC	TC	IC	TOC	BDOC	TC	IC	TOC
06.08.1996	1,25	0,00	1,25	1,47	0,06	1,41	-0,16	1,60	0,07	1,53
07.08.1996	1,25	-0,01	1,26	1,10	0,04	1,05	0,20	1,07	0,05	1,02
08.08.1996	0,81	0,03	0,76	0,89	0,03	0,87	-0,11	1,16	0,12	1,04
09.08.1996	0,64	0,00	0,64	0,71	0,00	0,71	-0,07	0,72	0,11	0,61

Date	Sample 1 filte	Sample 2			Sample 2	Sample 2 filtered			Sample 2 filte	Sample 3
	BDOC	TC	IC	TOC	BDOC	TC	IC	TOC	BDOC	TC
06.08.1996	-0,28	1,31	0,02	1,29	-0,05	1,35	0,09	1,05	0,20	1,43
07.08.1996	0,24	1,31	0,05	1,27	-0,01	1,14	0,09	1,05	0,21	1,15
08.08.1996	-0,29	0,77	0,04	0,73	0,03	1,02	0,06	0,97	-0,21	0,77
09.08.1996	0,04	0,70	0,01	0,69	-0,04	0,91	0,10	0,81	-0,17	0,70

Date	Sample 3		Sample 3	Sample 3 filtered			Sample 3 filte	Sample 4		
	IC	TOC	BDOC	TC	IC	TOC	BDOC	TC	IC	TOC
06.08.1996	0,08	1,36	-0,11	1,37	0,08	1,29	-0,04			
07.08.1996	0,00	1,15	0,11	0,99	0,05	0,94	0,32	1,19	0,02	1,16
08.08.1996	0,04	0,73	0,03	0,78	0,10	0,67	0,08			
09.08.1996	0,05	0,65	-0,01	0,85	0,07	0,78	-0,14			

Date	Sample 4	Sample 4 filtered				Sample 5			
	BDOC	TC	IC	TOC	BDOC	TC	IC	TOC	BDOC
06.08.1996									
07.08.1996	0,09	1,08	0,08	1,00	0,26	1,21	0,05	1,16	0,10
08.08.1996									
09.08.1996									

Date	Sample 5 filtered								
	TC	IC	TOC	BDOC					
06.08.1996									
07.08.1996	1,14	0,07	1,07	0,19					

Appendix III

Results for the concentration experiments with glucose solution

Date	glucose		glucose	Sample 1			Sample 1	Sample 2		
	TC	IC	TOC	TC	IC	TOC	BDOC	TC	IC	TOC
12.08.1996	0,69	0,00	0,69	1,21	0,34	0,87	-0,18	1,15	0,31	0,85
07.08.1996	0,80	0,04	0,76	1,31	0,29	1,02	-0,26	1,24	0,27	0,98
05.08.1996	0,87	-0,04	0,87	1,28	0,22	1,06	-0,19	1,28	0,17	1,12
31.07.1996	0,84	-0,07	0,91	1,11	0,14	0,97	-0,06	0,98	0,15	0,83
02.08.1996	1,28	-0,02	1,30	1,37	0,20	1,17	0,13	1,29	0,17	1,12
Date	Sample 2	Sample 3			Sample 3	Sample 4			Sample 4	Sample5
	BDOC	TC	IC	TOC	BDOC	TC	IC	TOC	BDOC	TC
12.08.1996	-0,16	1,04	0,31	0,73	-0,05	1,06	0,24	0,82	-0,14	1,03
07.08.1996	-0,22	0,99	0,24	0,75	0,01	1,27	0,22	0,99	-0,23	1,06
05.08.1996	-0,25	1,20	0,19	1,01	-0,14	0,94	0,19	0,75	0,12	1,12
31.07.1996	0,08	1,11	0,13	0,98	-0,08	0,92	0,10	0,82	0,09	0,97
02.08.1996	0,18	1,21	0,17	1,04	0,26	1,10	0,19	0,91	0,39	1,08
Date			Sample5							
	IC	TOC	BDOC							
12.08.1996	0,30	0,73	-0,05							
07.08.1996	0,24	0,82	-0,06							
05.08.1996	0,18	0,94	-0,07							
31.07.1996	0,06	0,91	-0,01							
02.08.1996	0,16	0,92	0,38							

Appendix III

Results for the concentration experiments with glucose solution

Date	Sample 1 filtered			Sample 1 filte	Sample 2 filtered			Sample 2 filte	Sample 3 filtered	
	TC	IC	TOC	BDOC	TC	IC	TOC	BDOC	TC	IC
12.08.1996	1,11	0,42	0,70	-0,01	1,05	0,32	0,73	-0,04	0,93	0,33
07.08.1996	1,09	0,36	0,73	0,03	0,93	0,30	0,64	0,12	1,02	0,28
05.08.1996	0,91	0,24	0,66	0,21	1,21	0,25	0,96	-0,09	0,72	0,23
31.07.1996	1,13	0,14	1,00	-0,09	0,98	0,13	0,85	0,06	0,88	0,13
02.08.1996	1,16	0,20	0,96	0,34	1,25	0,24	1,01	0,29	1,27	0,18

Date		Sample 3 filte	Sample 4 filterd			Sample 4 filte	Sample5 filered			Sample5 filere
	TOC	BDOC	TC	IC	TOC	BDOC	TC	IC	TOC	BDOC
12.08.1996	0,60	0,09	0,91	0,28	0,62	0,06	1,01	0,31	0,70	-0,01
07.08.1996	0,74	0,02	1,00	0,23	0,77	-0,01	0,98	0,27	0,71	0,05
05.08.1996	0,50	0,37	0,74	0,20	0,54	0,33	0,80	0,25	0,56	0,31
31.07.1996	0,75	0,15	0,95	0,15	0,80	0,11	1,01	0,11	0,90	0,00
02.08.1996	1,10	0,20	1,25	0,20	1,05	0,25	1,23	0,21	1,02	0,28

Appendix IV

Results of the recirculation experiments with glucose solution and sand-filtered raw water

	glucose 1mg/l C									
No. of circul	Input		Glucose 1 m	Sample 1			Sample 1 glu	Sample 2		
	TC	IC	TOC	TC	IC	TOC		TC	IC	TOC
1	1,03	0,00	1,03	3,95	0,24	3,71	-2,68	2,35	0,12	2,24
5	0,94	0,00	0,94	2,58	0,46	2,13	-1,18	2,15	0,42	1,72
10	0,87	0,00	0,87	3,99	1,31	2,68	-1,80	3,46	1,15	2,31
50	0,79	0,00	0,79	6,22	2,12	4,10	-3,30	5,60	1,91	3,69
100	0,69	0,00	0,69	7,16	1,89	5,28	-4,59	6,29	1,66	4,63
No. of circul	Sample 2 glu	Sample 3			Sample 3 glucose					
		TC	IC	TOC	BDOC					
1	-1,21	2,01	0,05	1,96	-0,93					
5	-0,78	1,72	0,01	1,71	-0,76					
10	-1,44	1,98	0,23	1,79	-0,91					
50	-2,90	2,02	0,41	1,61	-0,82					
100	-3,94	2,24	0,49	1,75	-1,06					
	Sand-filtered raw water									
No. of circul	Input		Sand-filtered	C 1 Sample 1			C 1 Sample 1	C 1 Sample 2		
	TC	IC	TOC	TC	IC	TOC		TC	IC	TOC
1	7,47	3,02	4,45	7,37	3,13	4,24	0,21	7,43	3,14	4,29
5	7,54	3,16	4,38	8,86	3,38	5,28	-0,90	8,49	3,39	5,10
10	7,56	3,14	4,43	9,75	4,02	5,74	-1,31	9,49	3,80	5,69
50	7,74	3,09	4,65	11,75	4,95	6,80	-2,15	12,37	4,69	7,68
100	7,68	3,21	4,47	19,42	4,77	14,65	-10,19	20,94	6,23	14,71

Appendix IV

Results of the recirculation experiments with glucose solution and sand-filtered raw water

No. of circul	C 1 Sample 2	C 1 Sample 3			C 1 Sample 3	C 3 Sample 1			C 3 Sample 1	C 3 Sample 2
		TC	IC	TOC		TC	IC	TOC	BDOC	TC
1	0,16	7,27	3,08	4,19	0,26	7,36	3,16	4,20	0,25	7,32
5	-0,71	7,50	3,06	4,44	-0,06	8,43	3,55	4,88	-0,50	8,77
10	-1,27	7,66	3,17	4,50	-0,07	8,67	3,86	4,81	-0,38	8,58
50	-3,03	9,03	3,31	5,72	-1,07	10,52	4,30	6,22	-1,57	11,19
100	-10,25	12,45	3,76	8,69	-4,23	14,68	5,55	9,13	-4,66	16,29

No. of circulations			C 3 Sample 2	C 3 Sample 3			C 3 Sample 3			
	IC	TOC	BDOC	TC	IC	TOC	BDOC			
1	3,10	4,21	0,24	7,33	3,10	4,23	0,22			
5	3,44	5,33	-0,95	7,46	3,04	4,42	-0,04			
10	3,65	4,93	-0,50	7,70	3,10	4,60	-0,17			
50	4,11	7,08	-2,43	8,49	3,19	5,30	-0,65			
100	5,28	11,01	-6,55	10,69	3,48	7,21	-2,75			