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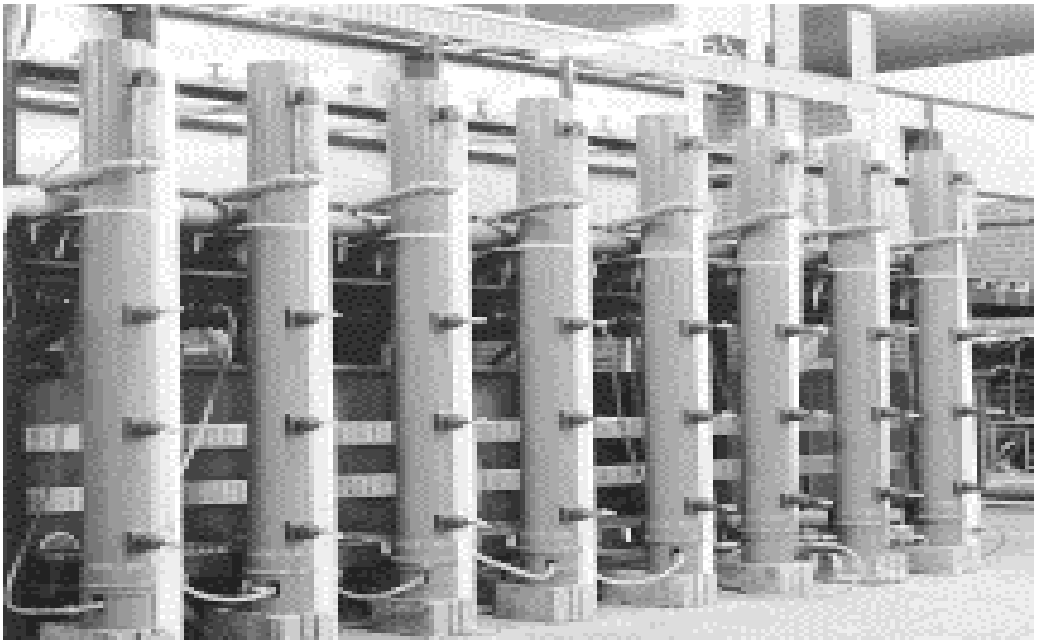

Biodegradable Dissolved Organic Carbon (BDOC) in raw and biologically treated water from the pilot plant at Lackarebäck waterworks

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Master's thesis 2001:13

Abstract

Most water intended to be potable needs some degree of disinfection, in most of the cases chlorination. The dose added depends on the content of the biodegradable fraction of organic matter that can lead to bacterial regrowth in the distribution system. However, the use of chlorine compounds becomes a matter of concern since it forms harmful by-products. It is necessary to reduce the use of chlorine compounds.

Biofiltration is one way to accomplish this. That consists on removal of the biodegradable fraction of organic matter by utilizing the degrading capacity of the microorganisms attached a filter material. This process can reduce the amount of Biodegradable Dissolved Organic Carbon (BDOC), which is one method to measure the biodegradable fraction of organic matter.
The author studied the role of the specific surface area of the filter material in which the microorganisms can growth in a pilot-scale filter containing biologically filter media. The difference in specific surface area among four different filter media seems to control the removal of Biodegradable Dissolved Organic Carbon

1. Introduction

Drinking water safety is a worldwide concern. Contaminated drinking water has the greatest impact on human health for more than one-half of the world population. Drinking untreated or improperly treated water is a major cause of illness in developing countries
Communities obtain their potable water from surface or underground sources. However, biological and chemical pollutants can contaminate both types of water. Surface waters include lakes, rivers and streams and their quality rapidly changes as a response to changes in the surrounding watershed. For example, relatively high concentrations of nutrients (N, P) results in eutrophication of surface waters with an excessive growth of algae, leading to excessive levels of microorganisms and turbidity in the source water (Bitton, 1999).
Water contains several chemical and biological contaminants that must be removed efficiently in order to produce drinking water that is safe and aesthetically pleasing to the consumer. The first approach should be the protection of water sources and the second is to get rid of chemical contaminants such as nitrate, heavy metals, pesticides and others xenobiotics which put at risk in a more directly way to humans as an acute effect (poisoning). The next step is that the finished product must also be free of microbial pathogens and parasites that are known as disease causing organisms. Finally, further parameters such as turbidity, color, taste and odor are important in order to achieve a good and pleasing taste for the consumers. Water must be also suitable for distribution. This means that it must have the right chemistry for corrosion control of different piping materials.
To reach this goal, raw water (surface water or groundwater) is subjected to a series of physicochemical processes described in chapter 4.2. Even though the raw water is properly

treated, there are several problems to be considered. Thus, drinking water as the final product can deteriorate during storage and transport through water distribution pipes (Bitton, 1999). This deterioration is due to several causes:

1. - Improperly built and operated storage reservoirs that should be covered to prevent airborne contamination and to exclude animals.
2. - Growth of microorganisms in storage reservoirs. This is a result of a long residence time of the water and enough amount of nutrients that support the development of microorganisms.
3. - Taste and odor problems due to the growth of algae and fungi.
4. - Bacterial colonization of water distribution pipes. This is a consequence of enough quantity of nutrients supporting bacterial growth along with low dose of disinfection, e.g. chlorination, prior to distribution.
5. –Decreasing water demand and old, oversized networks cause a long residence time in the pipes. This allows the development of microorganisms as biofilms in the pipe surface.

The content of biodegradable organic matter is a critical factor in the treatment of drinking water. Since the produced drinking water will be transported a considerable distance (and time) in pipes before it reaches the consumers, microorganisms flourish in the pipes as biofilms. Hence, the objective is to produce a biologically stable drinking water, which means that it does not support the growth of microorganisms in the supply-system (Heinicke, 1999). Even though, there are additional factors discussed in chapter (3.2) that determine this biofilm growth as well.

Heterogeneous microorganisms compose biofilms and it has to be pointed out that they are part of the problem attaching to pipes surfaces consequently decreasing the quality of the drinking water and to a greater extent putting on a risk the consumers health. However, they are also part of the solution by using them attached to different materials within the bioreactors. They are expected to degrade a significant amount of the biodegradable fraction of the organic matter dissolved in the raw water taken directly from Delsjöarna Lake. This paper describes the development of a testing method in order to figure out which method is more suitable to carry out further biodegradable dissolved organic carbon measurements of raw and biologically treated water from the bioreactors located at Lackarebäck drinking water treatment plant. Finally, these measurements will provide an idea of the performance of the different biofilm carrier material in removing the biodegradable fraction mentioned.

2. Objective

The aim of this work is to analyze the content of biodegradable dissolved organic matter (BDOC) in the raw water from Delsjöarna and after biological treatment in bioreactors with different biofilm carriers materials named biofiltration. Materials comprise Granular Activated Carbon (GAC), KMT plastic carriers (Kaldness MiljØteknologi AS) and Light Expanded Clay Aggregates (LECA). For this purpose, it has been carried out several

testing experiments in order to find out which carrier material (sand or leca) is the most suitable to perform the BDOC measurements in the samples of raw and biologically treated water from the Lackarebäck pilot plant. Additionally, in order to increase the sensibility of the TOC machine, several adjustments were done.
Moreover, the use of coarse versus fine filter material was tested in these kinds of bioreactors regarding operational cost since the use of fine material appears to have clogging problems preventing the water flow and disturbing biological work..

This study is part of a project, which has been set up in the basement of Lackarebäck waterworks, east of Gothenburg consisting on eight bioreactors filled with 30 liters of biofilm carrier media Its main objective is to minimize the use of chemicals for treatment and if it is possible, produce drinking water of such a quality that disinfection is unnecessary. Moreover, there also health concerns about the use of chlorination, since trihalomethanes (THMs) and chlorination by-products form during chlorination have carcinogenic properties (Hsu *et al*., 2001).

3. Scientific Background

3.1 Biofilms

Biofilms are relatively thin layers (up to a few hundred microns thick) of microorganisms that form microbial aggregates and also attach and grow on surfaces. They are ubiquitous developing at solid-water interfaces and are commonly found in e.g. trickling filters, rotating biological contactors, activated carbon beds, pipe surfaces, groundwater aquifers, aquatic weeds, tooth surfaces and medical prostheses. They also comprise corrosion by-products, organic detritus and inorganic particles such as silt and clay minerals. They contain heterogeneous assemblages of microorganisms, depending on the chemical composition of the pipe surface, the chemistry of finished water, and redox potential in the biofilm. They take days to weeks to develop, depending on nutrient availability and environmental condition. Biofilm growth proceeds up to a critical thickness when nutrient diffusion across the biofilm becomes limiting.

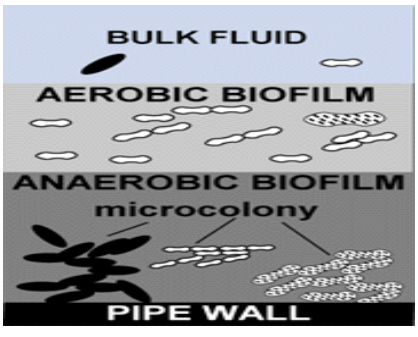

Fig. 1. Different layers of a mature biofilm (web.ref.1).

The decreased diffusion of oxygen is conductive to the development of facultative and anaerobic microorganisms in the deeper layers of the biofilm (Flemming, 1999) (fig.1). In this study, it is important to highlight the key role played by the biofilm as a part of the problem to solve due to development in distribution network, which causes corrosion and possible releasing of pathogens microorganisms from them. But it is also a part of the solution suggested by using them as a tool to remove organic matter and to a greater extent to minimize the use of chemicals added to the drinking water.

3.2 Processes contributing to biofilm development in distribution systems

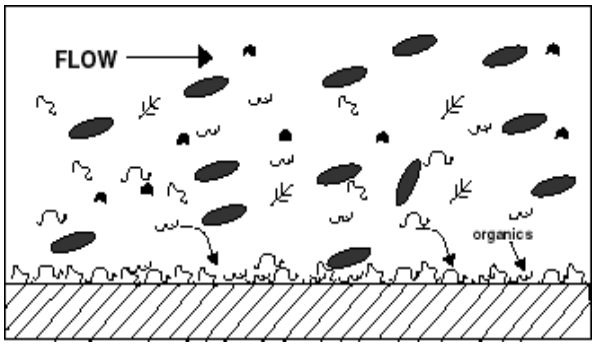

Fig. 2. Adsorption of organic molecules on a clean surface (web. ref. 1)

Surface conditioning is the first step in biofilm formation. Minutes after exposure of inorganic surfaces to water flow, a surface-conditioning layer, made of organic molecules, initially adsorb to the surfaces. These organics are said to form a "conditioning layer" which neutralizes excessive surface charge, which may prevent a bacteria cell from approaching near enough to initiate attachment (fig. 2).

In addition, the adsorbed organic molecules often serve as a nutrient source for bacteria (Keevil C., el al.,1999). And the chemotaxis process that is the movement of organisms in response to a chemical (nutrient) gradient may also enhance the rate of bacterial adsorption to surfaces under more inactive flow.

- Adsorption of bacterial to surfaces is a two-step. The first step is reversible sorption mainly controlled by electrostatic interactions between the adsorbent and the cell. The second step consists of irreversible adsorption of cells, resulting from the production of extracellular exopolymers at the surface (fig. 3)

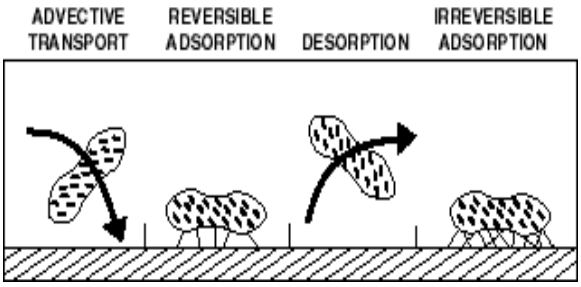

Fig 3. Transport of bacteria cells to the conditioned surface (web. ref. 1)

The ability of bacteria to attach to surfaces is controlled by nutrient availability (Keevil *et al*.,1999).

Biofilm bacteria excrete *extracellular polymeric substances* (EPS) or glicocalix, which hold the biofilm together and cement it to the pipe wall. This polymeric material, or *glycocalyx*, consists of charged and neutral polysaccharides groups that not only facilitate attachment but also act as an ion-exchange system for trapping and concentrating trace nutrients from the overlying water (fig. 4).

In addition, these polymer filaments trap limited nutrients and also act as a protective outside layer for the attached cells that mitigates the effects of protozoa predation, biocides and others toxic substances (Wingender *et al*, 1999).

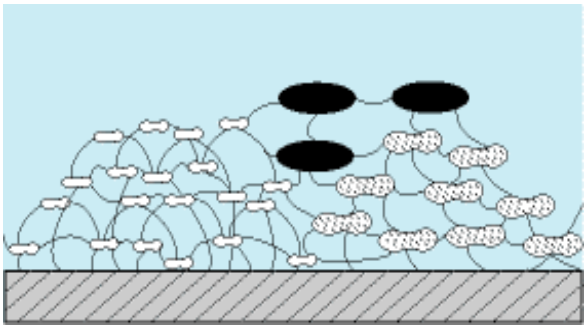

Fig 4. Biofilm formed by microorganisms and extracellular polymers (web. ref. 1)

A biofilm can spread at its own rate by ordinary cell division and it will also periodically release new 'pioneer' cells to colonize downstream sections of piping.

As the film grows to a thickness that allows it to extend through the boundary layer into zones of greater velocity and more turbulent flow, some cells will be sloughed off.

This detachment of cells from biofilms also occurs under low nutrient or low oxygen levels and it increases with chlorine treatment. Conversely, the detachment decreases by surface roughness (Keevil *et al*.,1999).

To maintain the safe of quality of the drinking water there are two approaches; disinfection e.g. chlorination applied in United States at high dose before the water is distributed. The other one is to reduce the content of TOC (total organic carbon) prior to chlorination, which is applied in Europe. However, the dose of disinfectant will not maintain its effect throughout the pipe system. Furthermore, not all the microorganisms are killed off by chlorination.

3.3 Natural organic matter in water

Natural organic matter (NOM) present in water is a complex mixture of different organic species found in all potable water sources. Within NOM humic substances usually comprise a significant portion. Humic substances are divided into humic acids, fulvic acids and humus. All of these groups consist of relatively high molecular weight organic substances and an infinite variety of molecular structures. The mayor structural elements include substituted benzene rings, carboxylic acid and phenolic functionalities.

The structure and functionalities present and to some extent the biodegradability are influenced by the source of organic matter from which the humic substances are derived. Due to there is no single structure, the total humic content of water must be measured using a group parameter such as total organic carbon (TOC) (Huck, 1999).

Within NOM it is a biodegradable fraction of organic matter, the biodegradable organic matter (BOM) the substrate that allows bacterial development in the drinking water (Block *et al*., 1993). This work is focused in one of the suitable method to measure the BOM fraction, which is the measure of Biodegradable Dissolved Organic Carbon (BDOC) that uses dissolved organic carbon (DOC) as a group parameter.

However, it has to be pointed out that to carry out BOM measurements carbon must be the limiting factor and it is usually that way (SØndergaard, 2001). But there are some cases regarding natural waters in which phosphate can limit the growth, not BOM. These are clean and clear waters in which the content of phosphate is rather low.

3.4 Importance of BDOC in drinking water

On average, BDOC represents 20 to 30% of the total dissolved organic carbon in the water. The growth of bacteria in distribution systems in the form of a biofilm on pipes surfaces can lead to the deterioration of water quality, including high bacterial concentrations, bad tastes, odour and colour, pipe corrosion and constitutes a food source for macroinvertebrates. The concentration of biodegradable organic matter is important for bacterial regrowth because organic carbon is utilized by the heterotrophic flora for a production of new cellular material and as a source of energy (Volk *et al.*,1994).

Despite treatment, the water produced contains enough biodegradable matter to support undesired microbial growth in the distribution network in many cases, and pathogenic bacteria have been observed to survive and proliferate in biofilms under drinking water conditions (Keevil *et al*.,1999).

Moreover, disinfecting the treated water previous to distribution is by chlorine gas Cl_2, or NaOCl. But, it is known that free chlorine not only kill bacteria but also reacts with Natural Organic Matter (NOM) forming halogenated organic substances such as trihalomethanes (THMs). A number of them are suspected to be carcinogenic such as chloroform, which has the higher cancer risk (Hsu *et al*., 2001). But also, all the oxidants added to the water such as ozone (ozonation), UV-radiation and chlorination are suspected to oxidize NOM and produce BOM, which allows bacteria growth in the network system if added previous distribution.

4. Site Background

4.1. Raw water storage in the Delsjö lakes

Raw water flows into both the Alelyckan and Lackarebäck plants via a tunnel system connecting the river Göta to the Delsjö lakes. From the intake at Lärjeholm, water runs to the raw water pumping station at the Alelyckan plant and to a pumping station 90 metres below ground near the lake Härlanda Tjärn. The water is then pumped up into the lake Lilla Delsjön, which is connected via a channel to the lake Stora Delsjön, from where it runs through a tunnel to the Lackarebäck plant.

Raw water supply is therefore secured even in the occurrence of a temporary interruption in the pumping of water from the river (web. ref. 2).

4.2. Chemical precipitation and disinfection at Lackarebäck

Commonly, several processes are used to treat water and there are two philosophies regarding the use of chlorine before distribution (disinfection). In United States the use of high doses of chlorine is a spread method while in Europe the water is often distributed without disinfection or in a small amount. Disinfection may be combined with coagulation, flocculation and filtration (fig. 5).

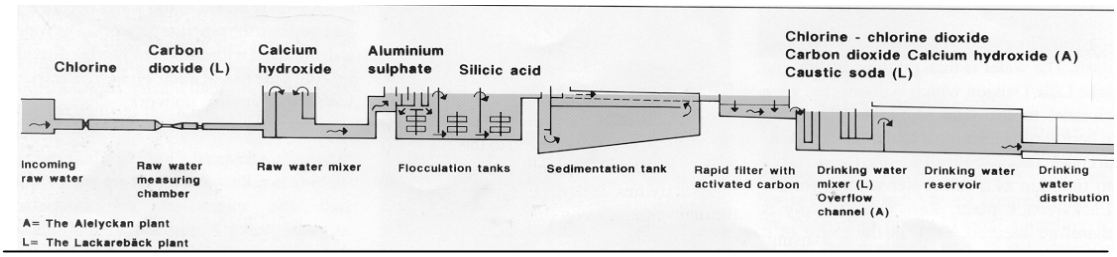

Fig. 5. Flow chart of the purification plant.

Additional treatments to remove specific compounds include pre-aeration and activated carbon treatment (Bitton, 1999). In water treatment plants, microbial pathogens and parasites can be physically removed by processes such as coagulation, precipitation, filtration and adsorption or they can be inactivated by disinfection or by the high pH resulting from water softening.

The purification method used at Lackarebäck consists on chemical precipitation, sedimentation, filtering and adsorption using activated carbon. The precipitation process starts by adding aluminium sulphate to the untreated water. Then, flocculation takes place, attracting and trapping the substances that give the water its cloudiness and colour. The process of adding sodium silicate can promote the process. The flocculated particles are heavier than water and therefore sink to the bottom when the water passes through the sedimentation tanks (fig. 5) (web. ref. 2).

To achieve a pH value of about 8, calcium hydroxide is added to the water before it is pumped into the pipeline network. The water is disinfected with chlorine/chlorine dioxide to reduce the risk of microbiological activity within the pipeline network but a very low dose.

4.3 The Pilot Plant and the Biofilms Carriers Materials

Biological treatment is becoming increasingly important for the removal of the biodegradable fraction of dissolved organic carbon (DOC) in water. This kind of treatment in drinking water in the pilot plant at Lackarebäck occurs as a biofilm process in which microbial growth takes place on different biofilms carriers materials.

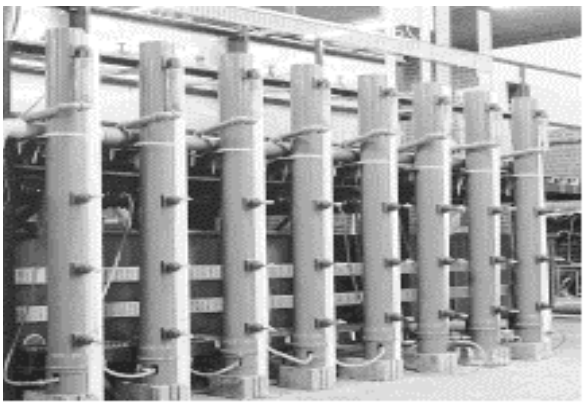

Fig.6. The pilot plant at Lackarebäck, Göteborg.

Even though, ozonation is considered to increase biodegradability of NOM by reducing size and altering functionalities (Gilbert, 1998), biofilms will grow in any drinking water filter that is not continuously exposed to an oxidant in the influent such as ozone.

Thus, a pilot plant at Lackarebäck with eight parallel bioreactors (fig. 6) receives raw water directly from Lake Delsjöarna and flows through the plant by gravity.

They currently operate with four different carriers materials: Granular Active Carbon (GAC), KMT plastic carriers (Kaldness MiljØteknologi AS) and Light Expanded Clay Aggregates (LECA) in two different grain size classes.

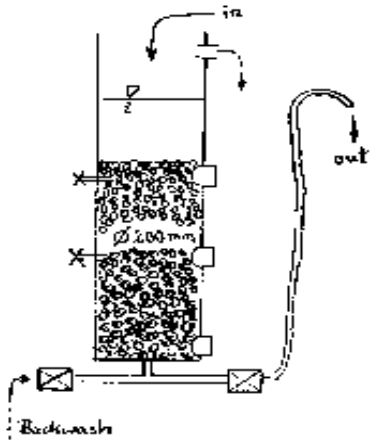

Fig 7. Scheme of bioreactors

Each of the eight bioreactors contains 30 liters of filter material. They have openings for taking water and biofilm samples at different levels. In this way it is possible to follow the microbiological processes and the removal of substances such as BDOC throughout the bioreactors (fig.7).

These submerged biofilm carriers that perform as biofilters, are backwashed regularly to prevent clogging and to remove excess biomass. That can disturb the biological work and prevent water flow.

The bioreactors have been running since January 2001 in order to establish indigenous microorganisms as biofilm on the carrier material.

The reason of using different biofilm carriers is that bioreactors with different biofilm carriers offer different specific surface area (biofilm surface area per unit volume of bioreactor, m^2/m^3). And it has been found that these differences affect the removal of substances from the water since the more specific surface area the more area is available for microorganisms to develop. As a result of that, a major number of microorganisms may be involved in the degradation of a mayor number of biodegradable organic matter compounds.

Table 1. Specific surface area of the biofilms carrier materials.

Bioreactor	d_{10} [b]	α [a] (1/m)
KTM plastic		500
Leca (coarse)	2.5-4 mm	>1240
Leca (fine)	0.9 mm	>4000
GAC	0.9 mm	>4000

[a] Specific surface area (m^2/m^3)
[b] Effective size

The equation 1 is used to calculate the specific surface area of the biofilm carrier materials. The term d_{10} is the effective size and it is calculated for perfect smooth and rounded spheres. It is expected therefore a higher specific surface area due to this biofilms carrier materials are not smooth but they have irregularities and a large quantity of pores that increase to a greater extent the theoretical specific surface area.

$$\alpha = \frac{6}{d_{10}} (1- Є) \qquad \text{Equation 1}$$

Additionally, Є is the porosity of the filter media in the bioreactor and it is fixed to 40%. This percent is closely the porosity created in a filter media in a bioreactor making the assumption that the filter media consist on perfectly rounded material, which is not the case in reality.
Moreover, Zhang and Huck (1996) developed a formula (equation 2) that defined the depth of column required to achieve a given BOM removal. In that formula, the removal of BOM is proportional to the specific surface area (α).

$$X^* = \Theta \frac{\alpha Df}{\tau} \qquad \text{Equation 2}$$

They defined X^* as the dimensionless contact time and they showed that BOM removal increased with increasing X^*. In this formula, Df (diffusion constant) is the speed in which the substrate is transported into the biofilm by diffusion. This term is related to a particular biofilm and it is constant. The diffusion constant (Df) along with τ is function of the biofilm and both of them are unknown in this study. The time in which the water is in contact with the biofilter media is included in the term Θ and it is the same in all the bioreactors (30 min). So, the term that varies along the different biofilm carriers is the

specific surface area (table 1). In the case of GAC, it is well known that it has several advantages as a biofilm carrier material. Under drinking water conditions, bacteria are concentrated in areas which are protected from washed away and GAC has a high amount of pores and others surface irregularities (large specific surface area) in which bacteria can grow. Additionally, GAC adsorbs nutrients/substrate and oxygen supplying the bacteria. This also means that the effective contact time between bacteria and nutrients/substrate is incremented so the biodegradation process is therefore facilitated (Dusset., 1996). The biology in the GAC reaches steady state conditions pretty soon. This is quite important since this initial adsorption to the surface may affect the measurements of BDOC removed by biofilm.
The disadvantages are that GAC is a very expensive material, it has to be heated periodically in order to reactivate it and backwashed in order to get rid of all the organic matter which is trapped in the surface

In this work, the use of expanded clay aggregates as biofilter material is tested as well. Expanded clay aggregates are manufactured by burning clay to form inert ceramic particles with a dense shell surrounding a porous core. Escaping expansion gases form labyrinth like structures of micropores during the process. By crushing the expanded clay beds, the surface area is extended and along with its high porosity provides a large surface for microbial growth (Melin, 1999). This material has been used as filter material in drinking and wastewater treatment as well as biofilm support media. Here, two types of expanded clay aggregate materials that are coarse (2.5-4 mm particle diameter) and fine (0.9 mm particle diameter) were used to study the removal of BOM.

Finally, the KMT plastic biofilm media developed in Norway for wastewater treatment. The carrier elements are shaped like small cylinders (about 10 mm in diameter and 8mm in height) with a cross inside the cylinder and longitudinal fins on the outside (Ødegaard, 1996). They are usually made of polyethylene but in this study a version with higher density is used (density 1.45 g/cm^3). The reason for that is the media was not supposed to move during the development of the biofilm in the plastic device and for further BOM removal. Disadvantages of this material are that it has a small specific surface area comparing with the other materials (table 1) and it is a relatively open material. The water goes through easily so the contact time between substrate and the biofilm attached to the surface of the material is low. Therefore, it is suspected a lower BOM biodegradation due to that together with a small specific area.

All these materials have been successfully tested in biofiltration plants. Furthermore, leca material is a very cheap material being a suitable option to test along with the plastic material. The purpose of this work is to test the efficiency in performing BOM removal of these different materials based on their differences in the specific surface area since the time in which the water is in contact with the biofilm media is fixed in all the bioreactors (30 min).

5. Background method

5.1 Measurements of Bioavailable Organic Matter

Natural organic matter (NOM) in water can be divided into two fractions: biodegradable, and refractory. There are mainly two different methods that have been developed to quantify the biodegradable fraction of organic matter in water. The first method, the AOC (assimilable organic carbon) bioassay, is one in which the growth of a test organism is correlated with the concentration of BOM. This is done by using the growth yield of the bacteria derived from calibration curves obtained using standard concentrations of organic compounds (e. g. acetate or oxalate). The second method, the BDOC (biodegradable dissolved organic carbon) assay, consists of measuring the consumption of DOC (dissolved organic carbon) through the ability of a mixed microflora to catabolize organic carbon to carbon dioxide and/or new biomass (Huck, 1990).

In assessing and contrasting methods, it is important to define the purpose for which the measurement is being made. If the concern is with bacterial growth in the distribution network, the parameter that should be measured is bacterial biomass. An appropriate term for the organic matter producing this growth is AOC. On the other hand, if the concern is the reduction in chlorine demand or disinfection by-products formation potential through a biological process, then a more closely related parameter is DOC. In the case of biologically chlorine demand, the most appropriate term would be BDOC (Huck, 1990).

Since the objective of the project is to reduce the content of chemicals added such as chlorine as well as to reduce the amount of disinfection by-products such as trihalomethanes, the use of BDOC method seems to be more suitable.

However, it has been pointed out that BDOC bioassay has been used for measuring growth potential as well but not to a greater extent as AOC bioassay. This is probably due to the detection limit of 0.1-0.2 mg/L of the TOC analyzer for the BDOC bioassay. The higher detection limit means significant AOC changes on the order of up to 100 µg/L as acetate-carbon are usually undetectable by BDOC analysis. Thus, while BDOC value is lower than the detection limit, AOC levels of the same sample can be significant (Escobar, 2001). The reasons for measuring BDOC are:

- It was reported that AOC values in drinking water represent 15-22% of the BDOC concentrations. This may be mainly due to the fact that, in the BDOC method, several drinking water microorganisms are involved of the wide range of compounds found in drinking water whereas AOC methods use two specific strains of bacteria. (Volk *et al*, 2000).

- The equipment for BDOC calculation (TOC analyzer) is available at Chalmers.

Additionally, concerning AOC estimation, the yield factor of the organisms is less than 1 so not all the carbon degraded is converted into biomass but also in carbon dioxide being the results unreliable.

The BDOC assays are based on the measurement of dissolved organic carbon before and after incubation of the sample in the presence of an indigenous bacterial inoculum (river water or sand filter bacteria). In this study we use bacteria attached to two different material carriers, sand and crushed leca. It is argued that indigenous bacterial populations are more suitable than pure cultures for testing the biodegradation of natural organic compounds (Bitton, 1999). The biodegradable dissolved organic carbon, BDOC, is given by the following formula:

BDOC (mg/L) = initial DOC – final DOC

The general approach is as follows:
A water sample is sterilized by filtration through a 0.2 μm pore size filter, inoculated with indigenous microorganisms and incubated in the dark at 20 C for 10-30 days, until DOC reaches a constant level. BDOC is the difference between the initial and final DOC values (Bitton, 1999). This is named BDOC determination using suspended microorganisms.

A novel proposed method consists of passing water continuously through one or two glass columns filled with sand or sintered porous glass and conditioned to obtain the development of a biofilm on the supports provided. BDOC is the difference between the inlet of the first column and the outlet of the second column (Bitton, 1999).

Another approach consists of seeding the water sample (300 ml) with prewashed biologically active sand with mixed populations of attached indigenous bacteria. BDOC is estimated by monitoring the decrease in dissolved organic carbon. The incubation period at 20^{o}C is 3-5 days. One advantage of this method is the use of biofilm microorganisms as inoculum, simulating situations occurring in water distributions systems. Substrate availability, as measured by this technique, appears to correlate well with the regrowth potential (Bitton, 1999). This is the method used in this study and it is also named batch incubation.

6. Materials and Methods

6.1. Method development and testing sand and leca

It has been developed a method to carry out the BDOC measurements for several months in order to come up with the best approach. It was necessary to reduce the number of 500 ml-flask to facilitate the aeration system in such a way that allows an approximately equal flow in all of them. At the end of the testing period peristaltic pumps were fixed to the set-up

with the purpose to assure an equal flow. Several measurements (data not shown) and adjustments were carried out to improve the sensitivity of the TOC analyzer.

Using bacteria fixed on a biofilm carrier was chosen since intercalibration experiments between 2 laboratories Université Libre de Bruxelles and Frias J., *et al* (1995) one, showed that BDOC concentrations determined using fixed bacteria were two times higher than those measured with suspended bacteria. Furthermore, the degradation kinetics with fixed bacteria was 2-4 times faster than with suspended bacteria (Frias *et al*.,1995). The set-up is as follows (Fig. 8)

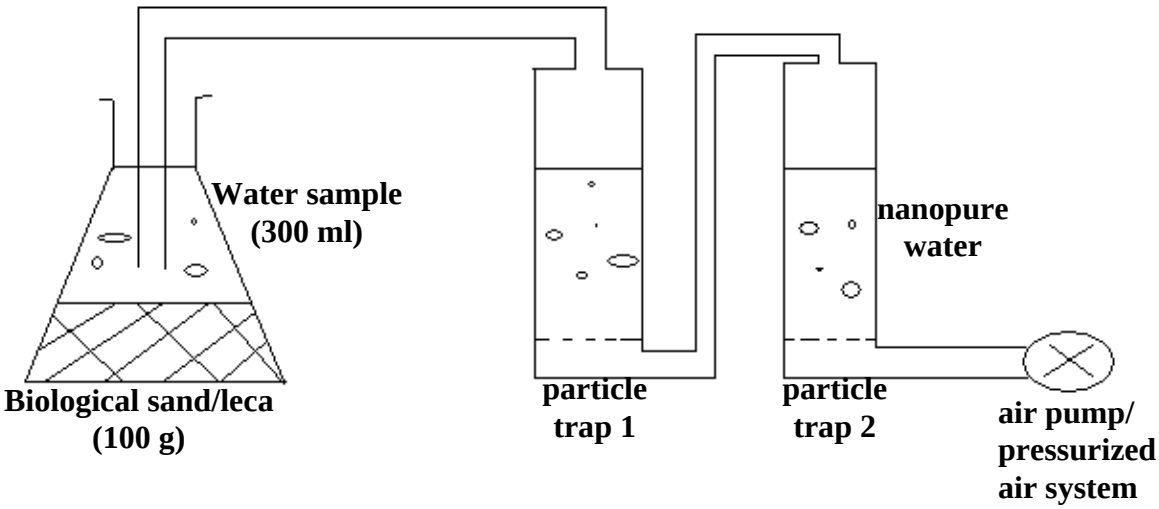

Fig. 8. . Schematic illustration of the equipment used to measure BDOC concentrations with bacteria attached to sand/leca..

Indeed, one of the objectives of this study was to compare sand and leca suitability as biofilms carriers to perform further BDOC measurements of raw and biologically treated water from Lackarebäck. However, those experiments started using leca because no bio-sand (sand colonized with bacteria) was available at the beginning.

From top to bottom of the bioreactor, BOM concentration is expected to decrease, so it is expected to find less bacteria deep in the filter media. At the same time, both contamination and bacterial colonisation are expected to be highest close to the surface. Therefore, the leca was taken from the middle of the filter media column where the leca is colonized enough but it is not so contaminated as the leca close to the surface.

On the other hand, the sand colonized with bacteria (biological sand) was sampled from the slow sand filters of a water treatment plant located in Jönköping without a prechlorination stage. The different biocarriers were prewashed 100 times with nanopure water before use. The DOC content of the last washing water measured and compared with the DOC content of nanopure water. The biological carriers were considered ready for use as inoculum when

the biofilm carriers released no detectable DOC. If released DOC is detected, additional washings should be performed (Volk, 1994).

The set-up consisted on 9 flasks. Three flasks were run with leca, three with sand in order to have enough replicates to perform statistical analysis such as mean value and standard deviation. This seems to be important to verify the results considering that biological parameters and processes naturally show considerable variation over time and between duplicate measurements.

Furthermore, two more flasks were run with nanopure water and sand, leca to check organic matter release from the biofilm carriers after washing them. One of the flasks was run with no biofilm carrier to check organic matter release from the flask or the aeration. No significant amount of organic matter was observed from the flasks incubated with nanopure water (data no shown).

6.2. Methodology of the bioassay

Frias, *et al*., (1995) tested different inoculums size for BDOC determination using attached bacteria, and they found out that a sand: water ratio of 100 g: 300 ml allowed a rapid decrease in DOC concentration and an optimal biodegradation of the organic matter. Thus, the initial DOC of the water sample (raw water) to be analyzed was checked. 100g of the biological sand were weighed in a 500 ml-flask. Then 300 ml of water sample were poured gently into the flask containing sand.

The experiments were carried out at room temperature (18°C). It is well known by studies with slow sand filtration that its optimal efficiency is achieved for temperatures higher than 8°C (Welté, 1999). The DOC of the water sample (in the presence of the sand) was checked again (T_O). Frias, *et al* (1995) tested that measurements performed without or with 4 l h^{-1} aeration showed evidence that aeration facilitates the DOC removal. Thus, aerating the water sample by the air-pressurized system installed in the lab began the testing experiments even though the flow was not verified. Furthermore, three of the 15 flasks incubated in order to perform BDOC calculation from raw and biologically treated water were aerated by the air-pressurized system as well. A peristaltic pump aerated the rest of the flasks.

The initial DOC value was defined as the mean of the initial DOC of the water sample (water before incubation) and the first sample (T_O) value after a comparative study of different statistical methodologies carried out in chapter 7.1

6.3. DOC measurements and BDOC calculation

It is important to take into consideration that dissolved organic carbon implies that the sample has been run through a filter with 0.45 μm pore size previous to analysis to keep out

particles. The term *dissolved* is operationally defined in this context. The limit of 0.45 μm does not have any chemical meaning except that the filter medium is supposed to retain bacteria (Drever, 1997). It should be noted that some colloidal material could pass the 0.45 μm filters and therefore may be included in the parameters termed as dissolved.

Measurements of the net DOC removal in the batch cultures were done by daily collection of water sample incubated with biological sand for seven days. This is done with a clean glass syringe mounted with a 25 mm filter holder. 20 ml of water sample were filtered with muffled glass-fibre filters (Whatman® GF/F) with a porous membrane (pore size = 0.7μm).

The glassware was muffled for 4 hours at 550°C .The pipettes, glass syringe and glass water bottles for storage were muffled at 300°C for 4 hours as well in order to prevent the release of organic matter from these material. The samples were preserved and stored frozen until analysis in triplicate in a Shimadzu® TOC-5000 standardized with a 4-point calibration curve.

BDOC was calculated from the difference between the average of DOC water before incubation and the average (flask A, B and C) of the first sample (T_O) minus the minimum value of DOC reached during the incubation period.

6.4. TOC analyzer

The measuring principle is based on a TC (Total Carbon) combustion tube filled with oxidation catalyst and heated to 680°C. For reference, TC is composed of TOC (total organic carbon) and IC (inorganic carbon). When sample has been introduced by a sample injector into the TC combustion tube, TC component in the sample combusted or decomposed to become CO_2. The carrier gas, which contains combustion product from the TC combustion tube flows through an IC reaction container and cooled and dried by a dehumidifier. It is sent then through a halogen scrubber into a sample cell set in a non-dispersive infrared gas analyzer (NDIR) where CO_2 is detected. The NDIR outputs a detection signal, which generates a peak whose area is proportional to the TC concentration of the sample (Shimadzu®, 1997).

All the samples were analyzed using a four-point calibration curve with TC = 10, 5, 2 and 0 ppm and 0,1, 2, 5 ppm for IC.

All along this study, in order to increase the sensibility of the TOC machine, several adjustments were done. That include for example, change in the syringe plunger (the little white plastic tip inside of the syringe) due to old plungers can give erratic injection volumes due to wear, residues and by forming bubbles as film on the plunger surface. This latter problem appeared later and it was supposed to be solved by changing the syringe that injects the sample into the analyzer but it persisted until the last run of the study.

7. Results and Discussion

7.1. Testing experiments

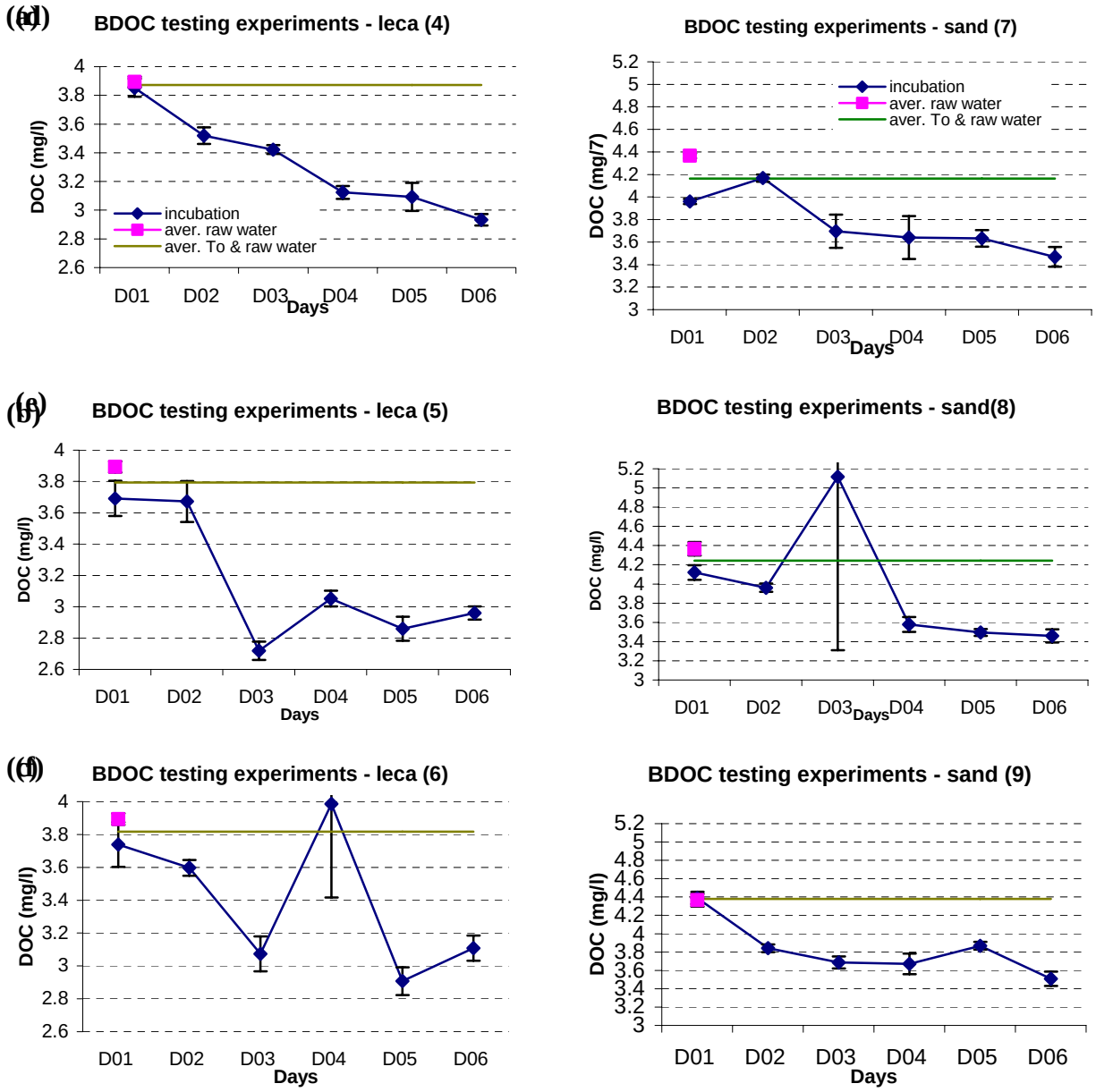

Fig. 9. Results from testing experiments. Results from nanopure water incubation are not shown(flasks 1, 2 and 3). Sampling date 10/9

This testing experiment was designed in order to assess which biofilm carrier material (sand or fine leca) is more suitable to carry out further BDOC measurements of raw and biologically treated water from the pilot plant at Lackarebäck. The removal of DOC over time from the flasks incubated with leca (number 4,5,6) and the ones with sand (number 7,8,9) is presented in Figure 9.

Observing all the graphs it seems to exist a general downwards pattern in the concentration of DOC that is expected both in sand and leca (fig. 9). Microorganisms attached at those biofilm carrier materials use this DOC present in the water phase as a carbon source converting it either in biomass and carbon dioxide.

It can also be noticed in some graphs that after reaching minimum DOC concentration, DOC showed again an increase (fig. 9 b,c,f). Bacterial lysis or DOC desorption could explain it. Additionally, in most of the graphs there is a large difference between the DOC concentration of water before incubation and the DOC of the first sample (T_O), which should be the same (fig. 9 e,b,c). This is can be explained by a dilution effect due to washing those biofilm carrier materials with nanopure water. So it is suspected that a portion of nanopure water remains in the material interstitials and dilutes the water sample resulting in a low T_O value.

It is also observed in general a similar precision of the TOC analyzer resulting in stable standard deviations. However, there are some exceptions such as the flask 7 (fig. 9d), in which there is a high fluctuation in the standard deviations along the incubation period. This is due mainly to a variation in the precision of the TOC analyzer but there are some others explanations such as errors in sample handling, contamination. As explained in *Method development* chapter (6.1) no significant amount of organic matter was observed releasing from the flasks incubated with nanopure water so no mayor errors in sample handling were made.

Furthermore, it can be notice contamination in single days and in single flasks (fig. 9 d,e,c) since most of them show DOC values above the DOC in the raw water. As a result of that are elevated standard deviations, which means that some of the triplicates of the sample got contamination.

Additionally, different statistical methodologies were carried out in order to assess how the way of calculating BDOC affects the results (Table 2). One approach is that the initial DOC is calculated as the DOC average of water before incubation (flaks 4,5,6 in the case of leca and flasks 7,8,9 in the case of sand) and the first sample (T_O) from the flask. Leca BDOC value is higher than sand, while standard deviations are small and similar in some cases (table 2).

Table 2. Different methods of calculating BDOC from testing experiments as mg/l. Triplicates samples (4,5,6 corresponding to leca and 7,8,9 corresponding to sand).

LECA	**4**	**5**	**6**	**Average**	**Standard deviation**
Average of raw water and the first sample (T_O)	0.94	1.07	0.90	0.97	0.08
Raw water	0.96	1.17	0.98	0.88	0.02
First sample (T_O)	0.92	0.97	0.83	0.90	0.07
SAND	**7**	**8**	**9**	**Average**	**Standard deviation**
Average of raw water and the first sample (T_O)	0.69	0.78	0.86	0.78	0.08
Raw water	0.89	0.90	0.85	0.88	0.02
First sample (T_O)	0.49	0.66	0.88	0.67	0.19

Even if the calculations are carried out only regarding water before incubation or first sampling (T_O) leca incubation always results in a higher BDOC concentration than sand one (table 2).

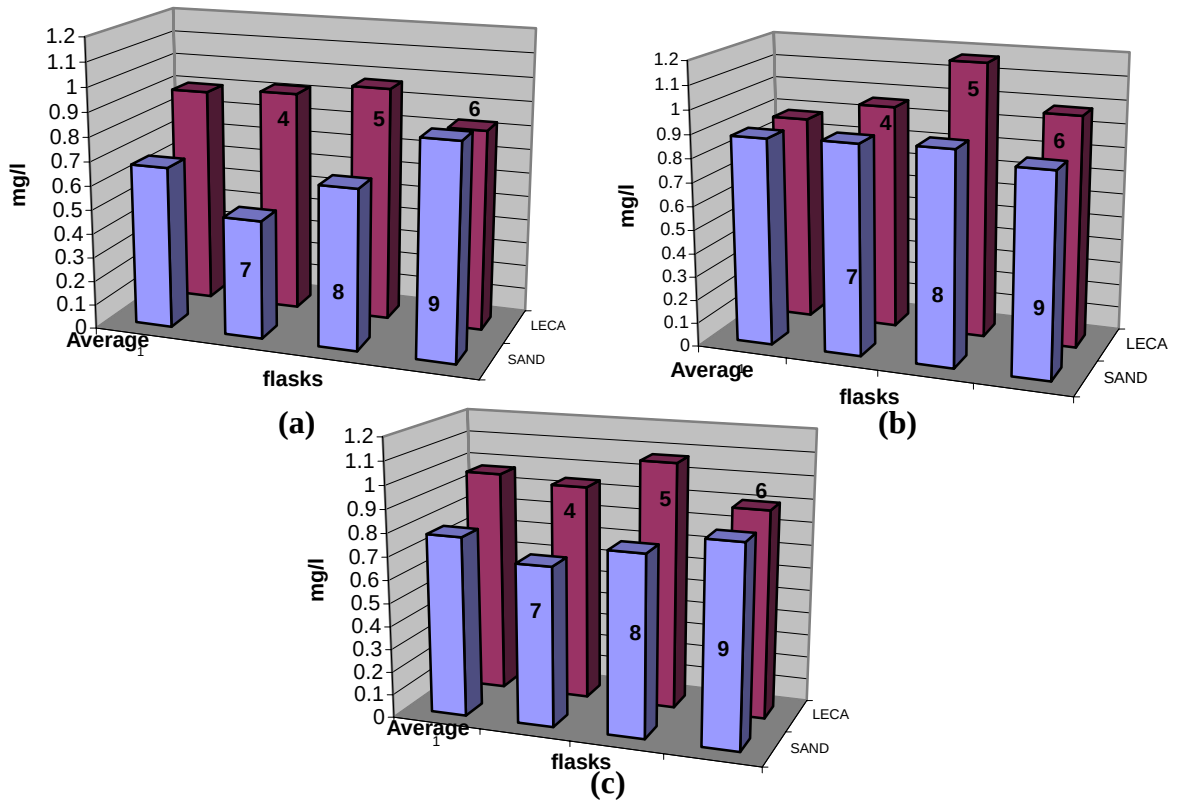

Fig. 10. Variation in BDOC calculation using (a) average of T_O as initial DOC, (b) average of water before incubation as initial DOC and (c) average of T_O and water before incubation average as initial DOC.

These statistical methodologies pointed out the advantages of using average in this study. The approach of using averages of DOC of the first sample (T_O) and the averages of DOC from water before incubation resulting in less variation the comparison between leca and sand (fig.10 c).

On the opposite, the other approaches, both using DOC values from water before incubation (fig. 10 b) and DOC values from first sample (T_O) (fig. 10 a), show a high variation due to the fact that there are outlier values that shift the average and therefore resulting in elevated standard deviation. Thus, the DOC of the first sample (T_O) in flask 7 (fig. 9 d) is fairly lower than the average of DOC of the water before incubation resulting in a smaller BDOC concentration and a further higher standard deviation than leca one when it is compared with flask 8 and 9 (table 2, fig. 10 a). In addition, a rather low value in flask 5 (fig. 9 b) results in a high BDOC value giving a higher standard deviation than sand one when it is compared with flask 4 and 6 (table 2, fig. 10 c).

According to the approach of using DOC averages of the first sample (T_O) and the averages from the water before incubation, which is the most common way of analyzing BDOC (Volk, 1994), leca seems to be the a viable option to choose. However, there are some possible explanations to leca and sand behavior along the incubation period:

1. - Adsorption of more DOC to the leca surface than to the sand (Fig. 9 a.b,c) although leca is not considered an adsorptive material (Ødegaard, *pers comm*.). Even though these experiments do not allow an assessment of DOC adsorption, it was assumed that a sand/water ratio of 100 g: 300 ml used in this study seems to be the most appropriate to obtain a rapid response for BDOC determination while minimizing the biosorption effect (Volk, 1994).

2. - Biodegradation on sand may be incomplete after 5 days. On sand, all the lowest values occur after 5 days whereas with leca it was after 3,4 and 5 days in the different flasks (Fig. 9).

3. - The biomass of leca is adapted to Lackarebäck´s natural organic matter and not the bio-sand, which comes from a waterworks located in Jönköping. This may explain a high degradation speed in the case of the leca.

In addition, analyzing the slope of the graphs gives the idea that the biodegradation could keep going in the case of the sand. A further reason to choose sand is that results from sand studies are comparable to others studies but not leca ones. Therefore, it was decided to use bio-sand for the measurements of raw and biologically treated water from Lackarebäck incrementing the incubation period until 7 days due to an expected ongoing degradability. Samples were not taken during the weekend (first days of incubation). Before starting the incubation the sand was set for a week as a slow sand filter at Lackarebäck in order to adapt the biomass attached to a new kind of water.

7.2 Measurements of raw water and biologically treated water

Samples of raw water and biologically treated water from four bioreactors (plastic, active carbon coarse and fine leca) were taken. Each biologically treated water and the raw water sample was incubated in triplicate (flasks A, B and C), which are 15 flasks in total. Each flask water sample (15) was taken daily and after a sealed period in the freezer, it was run in triplicate in the TOC analyzer.
Furthermore, water samples after biological treatment were taken from the same bioreactors (plastic, active carbon coarse and fine leca) at Lackarebäck to have them as water before incubation value to do further average with DOC from the first sample (T_O).

Results from the incubated raw water sample taken in October the 12th show an almost systematic contamination reaching values from approximately T_O = 4.5 to 10 mg/l in the last day in the flask (C) so no BDOC concentration could be measured (see appendix IV). This can be explained by contamination due to the fact that these raw water flasks were aerated by using the lab pressurized air system and not by peristaltic pump as the rest of the incubation flasks. In fact, the pressurized air comes from a central compressor at Chalmers. They have a filter even though it does not guarantee purity so it is recommended to have an extra filter for this kind of sensitive analysis. The contamination is suspected because construction work took place in the same building as the lab and some dust particles may contaminate the air system. Moreover, there were some disturbances when the filter was changed (Dellming, *pers comm.*).

Therefore, the results from the biologically treated water were compared with BDOC results from sand incubation in testing experiments despite the fact that they are results from another incubation. Hence, it has to be taken into consideration the seasonability of organic matter in lakes being the organic matter inputs into the lake different along the year (Sondergaard, 2001). However, results from a study carried out in the lake Aurevann (Norway) showed a rather stable water quality regarding NOM (natural organic matter). That was a result of analyzing the TOC (total organic carbon) content along with the average of retention time for NOM in the lake (Hem, 1998). So, it is suspected that there is not so much difference in BDOC concentration within a month.

Analyzing the results, all the first sample values (T_O) from the Lackarebäck experiments show less DOC concentration than the water samples from the bioreactor after biological treatment. As mentioned above, that may be explained as the result of a dilution process that takes place when water sample is poured into the flask, which contains sand and an amount of nanopure water as well. The nanopure water is suspected to dilute the water sample resulting in further low T_O DOC values. For that reason, the BDOC values from the raw and biologically treated water experiments are corrected by a dilution factor calculated as the ratio of the average of the T_O DOC values of the three flasks (A, B and C) in which

each water sample is spread out, divided by the average of the water sample (run in triplicates) taken from the bioreactors after biological treatment (data not shown).

Table 3. BDOC values from Lackarebäck experiments as mg/l. Sampling date 12/10

BDOC	Raw water(*)	KTM plastic	Granulated Active Carbon	Fine leca
Number of flasks	3	3	2	2
Average	0.78	0.65	0.11	0.26
Stdv	0.08	0.17	0.001	0.09
%BDOC removal		15	85	66

(*) Raw water BDOC values from testing experiments (table 1)
Note: BDOC values of coarse leca were not included due to bubble problems inside the syringe that inject the sample into the analyzer. This gave erratic injection volumes.

As could be expected from the different characteristics among the different biofilm carriers tested, such as specific surface area (m^2/m^3), there are differences in the performance of removal of BDOC.

Thus, no significant amount of removed BDOC performed by KTM plastic is noticed resulting in BDOC concentration from the bioreactor filled with KTM plastic nearly similar to BDOC concentration from raw water (table 3). This is a result of a low specific surface area (table 3) and a relatively open material, which is a feature of this plastic device. The water flows through the material easily and therefore there are no favorable conditions for adhesion of organic matter to the biofilm and further biodegradation.

On the contrary, granulated active carbon (GAC) is the material that removes higher amount of BDOC of the ones tested. A reasonable explanation is that GAC has much higher specific surface area characterized by a high number of pores and others surface irregularities. GAC has also an absorption capacity trapping nutrients and substrate. This enlarges the effective contact time with the biomass; encouraging more rapid colonization.

The adsorption of NOM to the surface also allows biodegradation even when there is low concentration of growth-promoting substances (Dussert, 1996). These characteristics enhance the biodegradation process.

In addition; measurements of UV_{254} absorption at Lackarebäck indicate that the carbon material still has some of its absorption capacity left (table 4). UV_{254} reflects the content of humic matter with a high proportion of aromatic groups, which is refractory to degradation as long as the water is not ozonated. Adsorption may therefore contribute to the high BDOC removal.

Table 4. Percentage removal of UV absorbance at 254 from the biofilms carriers. Date: 23/11

Material	% Removal of UV absorption
KTM	0
GAC	23
LECA (fine)	7
LECA (coarse)	1

The removal of DOC in GAC incubation shows however a rather high standard deviation and a high variation in that along the incubation period due probably to a less TOC analyzer accuracy in that run (see appendix III). Additionally, a difference between T_O and raw water of approximately 0.3 mg/l in all the graphs (see appendix III) seems to be a result of a dilution process discussed above.

Furthermore, they show contamination in the fourth day (D04) in flask C and second day (D02) in flask A as well (see appendix III). The graph of the flask C was not taken into account in calculating BDOC concentration due to the value differs significantly from the flasks A and B (see appendix III). The reason for this is that the first sample (T_O) value from the flask C is higher than the average between T_O and water before incubation. It does not develop therefore dilution process as the rest of the 14 flasks incubated. A feasible reason for that may be that contamination took place for that specific sample.

Additionally, the flask B shows an increase in DOC in the latest days of the incubation (see appendix III). That may be due to a release of carbon from the GAC surface and also to bacteria lysis as discussed in chapter 7.1 (*Results from testing experiments*)

In the case of fine leca, even though it cannot be compared with coarse one due to technical problems during analysis, it seems to perform quite well the removal of BDOC since the figures show a BDOC value near to GAC one (table 3). Analyzing all the plots shows a quite stable curve with stable TOC analyzer standard deviation as well along the incubation period (see appendix II).

The latter was a result of an improvement in the TOC analyzer reliability since the syringe in which the sample is injected into the TOC analyzer was changed due to the existence of bubbles inside the syringe. That caused that the volume injected to the analyzer was wrong and therefore the concentration calculated was wrong as well.

However, it can be noticed some exceptions such as possible contamination in the second day (D02) of the flask C and a too low T_O value in the flask B resulting in a negative BDOC concentration, which is not reliable at all (see appendix II). Thus, flask B was excluded in calculating BDOC concentration.

Finally, comparing the removal of BDOC among the different biofilm carriers showed that the larger available specific area and the larger contact time are viable explanations for the better performance of the GAC bioreactor and to a lesser extent the leca one. On the contrary, no significant amount of BDOC were removed by KTM plastic device

8. Conclusion

The pilot plant studies described in this paper show that biological pre-treatment could be implemented as a first step in drinking water treatment. The choice of biofilm carrier medium affected the BDOC removal as expected. The bioreactor with carrier medium of leca, offering high specific surface area, performed better in removing BDOC than KTM with relatively open plastic material.
Thus, monitoring of the elimination of BDOC in the three different bioreactors at Lackarebäck has shown that KTM plastic bioreactor permits a minimum decrease in BDOC of 15%.

The efficiency of the crushed fine leca biofilm carrier seems much less than that of the GAC biofilm carrier resulting in a BDOC removal of 66%. Finally, GAC shows a much higher BDOC removal of 85% due mainly to a much higher specific surface area and favorable conditions in which microorganisms can grow.

According with fine leca performance regarding testing experiments, leca seems to be a viable option to test in order to carry out BDOC measurements. Leca is not considered as an adsorptive material so it seems to achieve a significant removal by biodegradation.

The result of this experiment has also revealed the balance of using coarse versus fine materials as biofilm carriers as a general operational dilemma in this kind of bioreactors. Regarding efficiency in BDOC removal, the fine material appears to perform better due to higher specific surface area than the coarse one.

But the use of fine material in bioreactors has operational drawbacks since the fine material along with the organic matter present in water tend to clog the filter media preventing the water flow. As a result of this it is a high time consuming regarding operational maintenance. On the contrary, the use of coarse material does not have this drawback.

One challenge in this project is to find which material is more suitable to perform removal along with reasonable operational maintenance cost. The fine material seems to perform well with no clogging problems noticed.

9. Uncertainties

● There are few values to perform test statistics. It is needed to have a higher number of BDOC values to rely in further calculation of removal percentages. This is a requisite to verify the results considering that biological parameters and processes naturally show considerable variation over time and between duplicate measurements. Therefore, these removal values should be seen as indications that need to be verified by further experiments, Thus, in the project, the BDOC measurements are accompanied by measurements of biofilm growth on glass cassettes. And now, the BDOC measurements are complemented by AOC estimations.

In addition, since it has been noticed a possible instrument drift from one TOC analyzer run to another all the samples should have been spread in all the run. Furthermore, the triplicates of each sample should have been spread in the 78 vials available in the TOC analyzer due to a possible drift of the instrument during the run.

● In lakes the concentration of BDOC can vary seasonally over medium time-scales. The calculation of BDOC concentration by using raw water sample as T_O from the testing experiments and the minimal DOC value from the measurements of water from Lackarebäck could bias the results.

10. Acknowledgements

I would like to thank to my supervisor Gerald Heinicke for reading the drafts, giving ideas and discussions about BDOC measurements.
Frank Persson for ideas about BDOC measurements and experimental set-up support together with Gerald.
Jesper Knutsson for his help in the lab. Thank you for innumerable adjustments in the TOC analyzer.
And Sharon for her help in statistics.

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12. Appendix A. Evolution of DOC during incubation of raw and biologically treated water from the Lackarebäck pilot plant.

Appendix A. Evolution of DOC during incubation of raw and biologically treated water from the pilot plant.

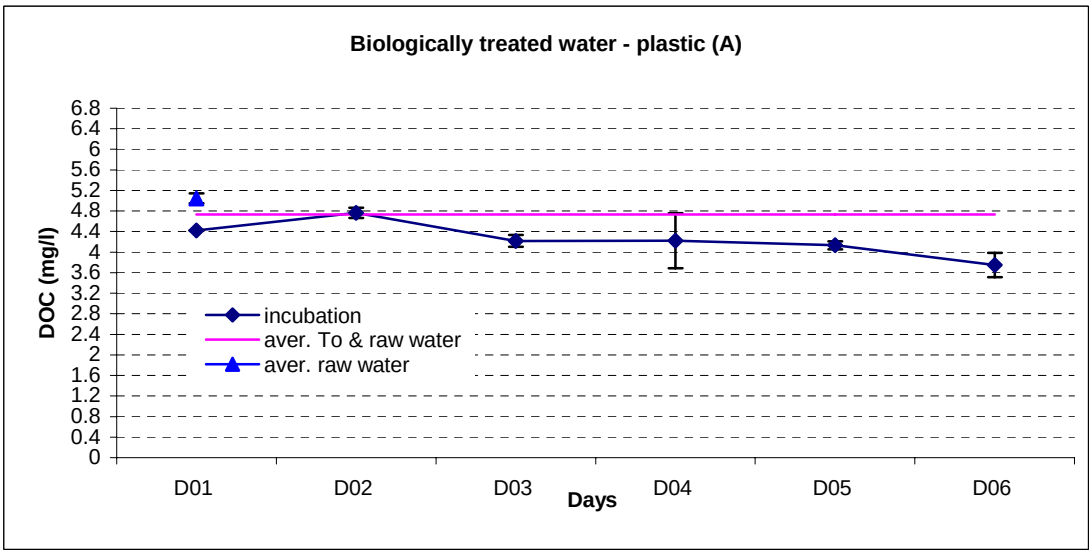

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Figure: Flask A. DOC removal over time in biologically treated water with KTM plastic material.

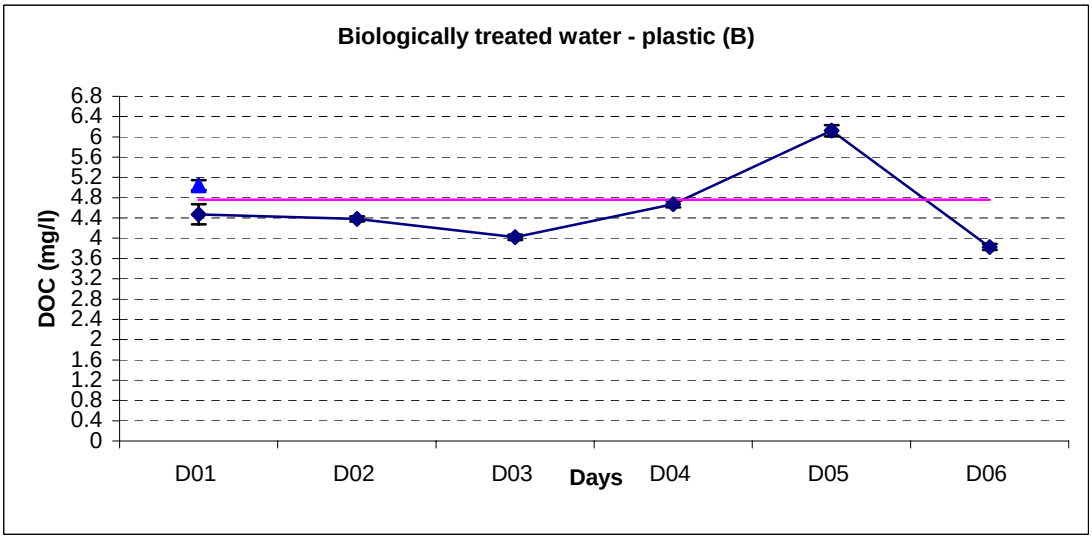

Figure: Flask B. DOC removal over time in biologically treated water with KTM plastic material.

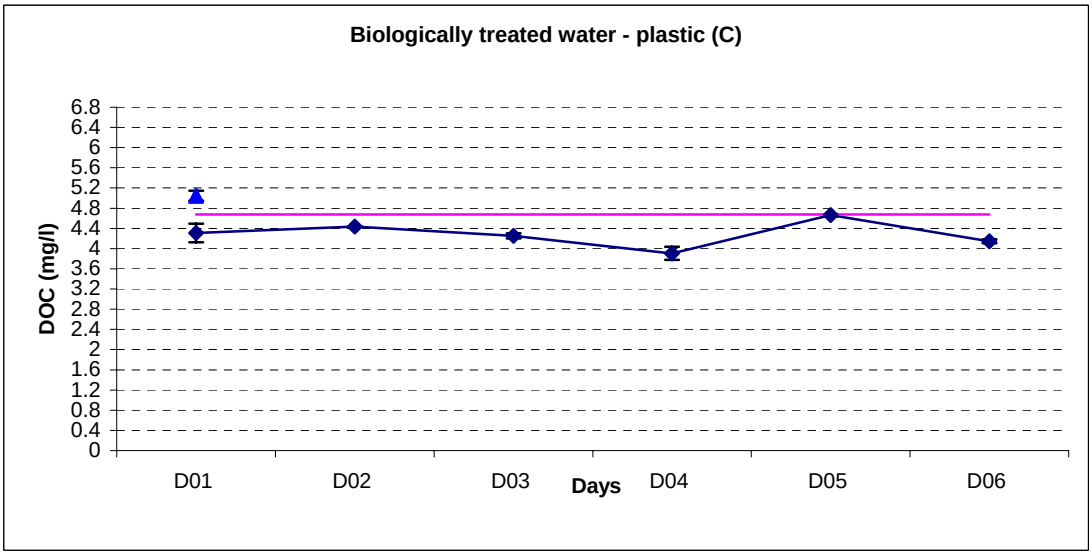

Figure: Flask C. DOC removal over time in biologically treated water with KTM plastic material.

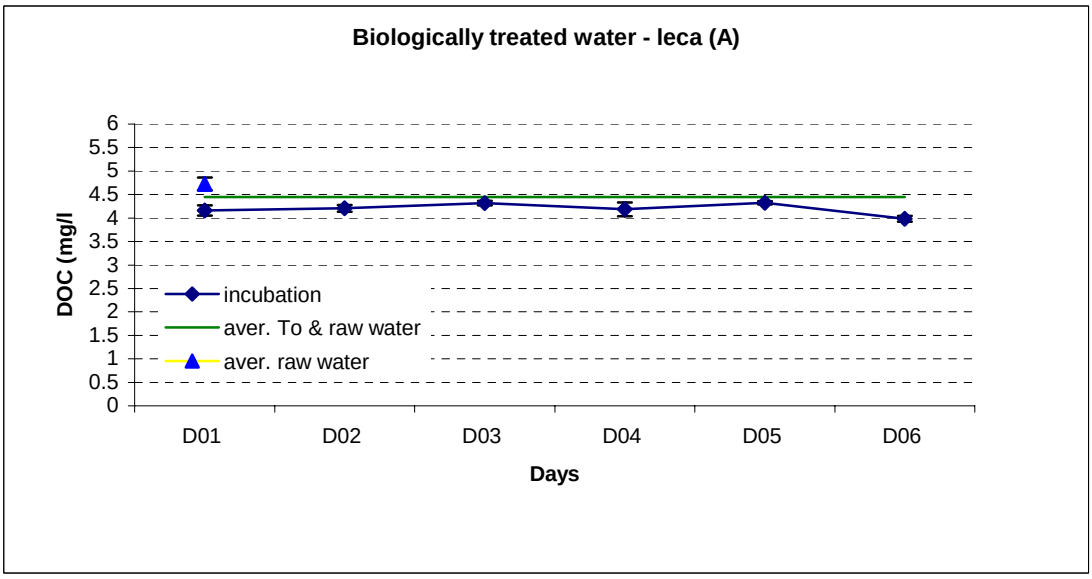

Figure: Flask A. DOC removal over time in biologically treated water with fine leca material.

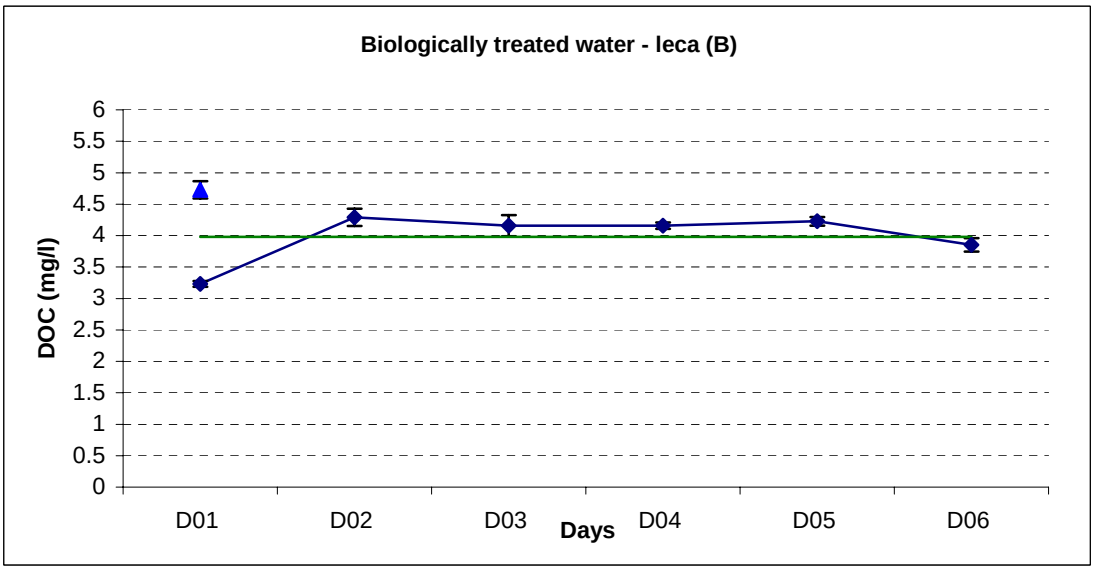

Figure: Flask B. DOC removal over time in biologically treated water with fine leca material

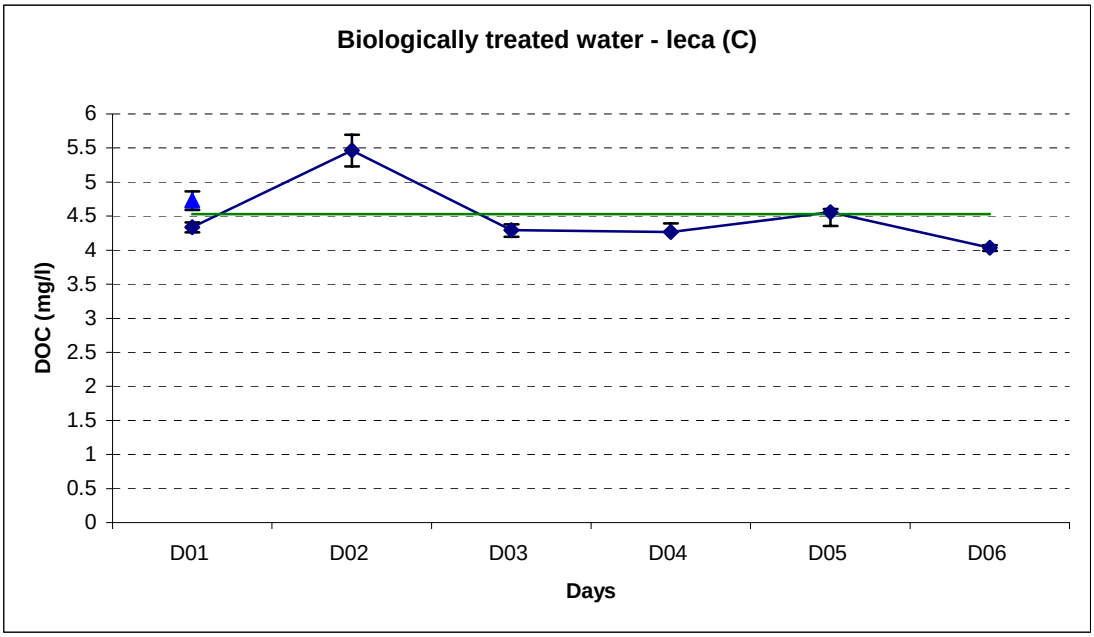

Figure: Flask C. DOC removal over time in biologically treated water with fine leca material

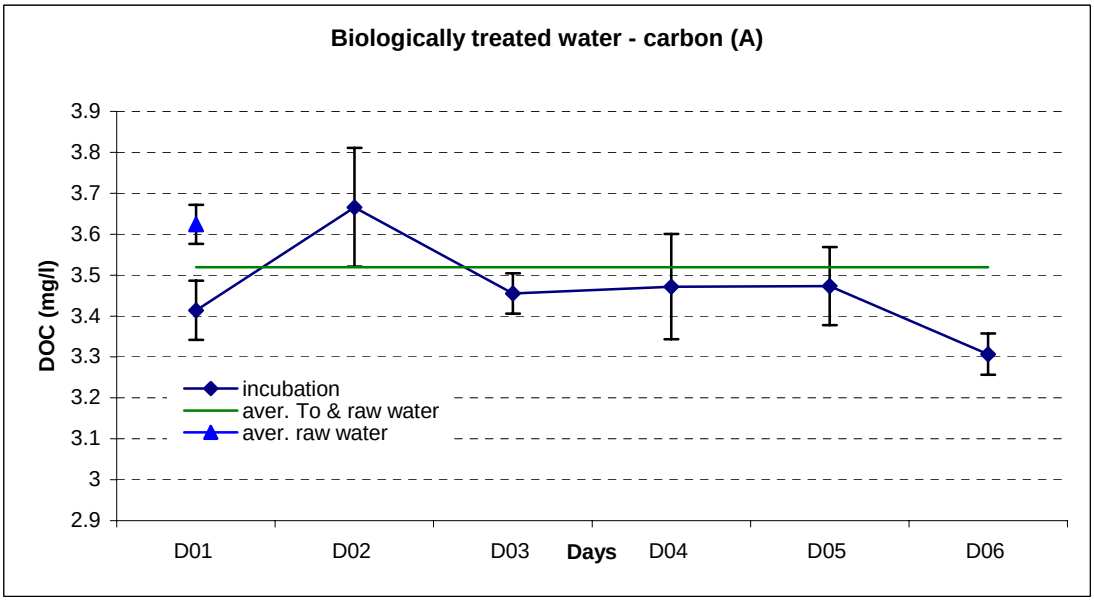

Figure: Flask A. DOC removal over time in biologically treated water with granulated active carbon material

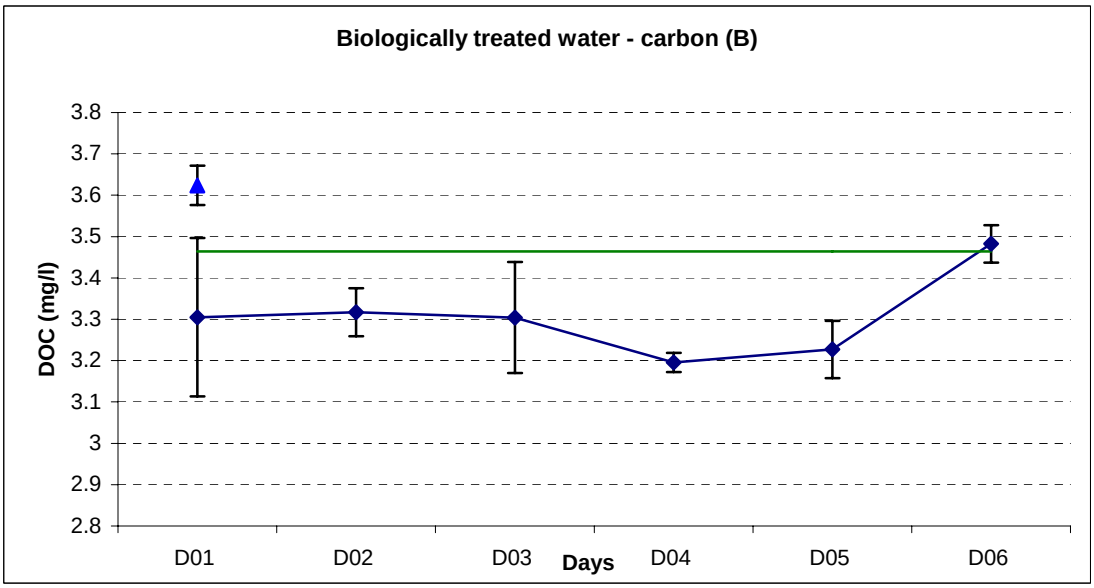

Figure: Flask B. DOC removal over time in biologically treated water with granulated active carbon material

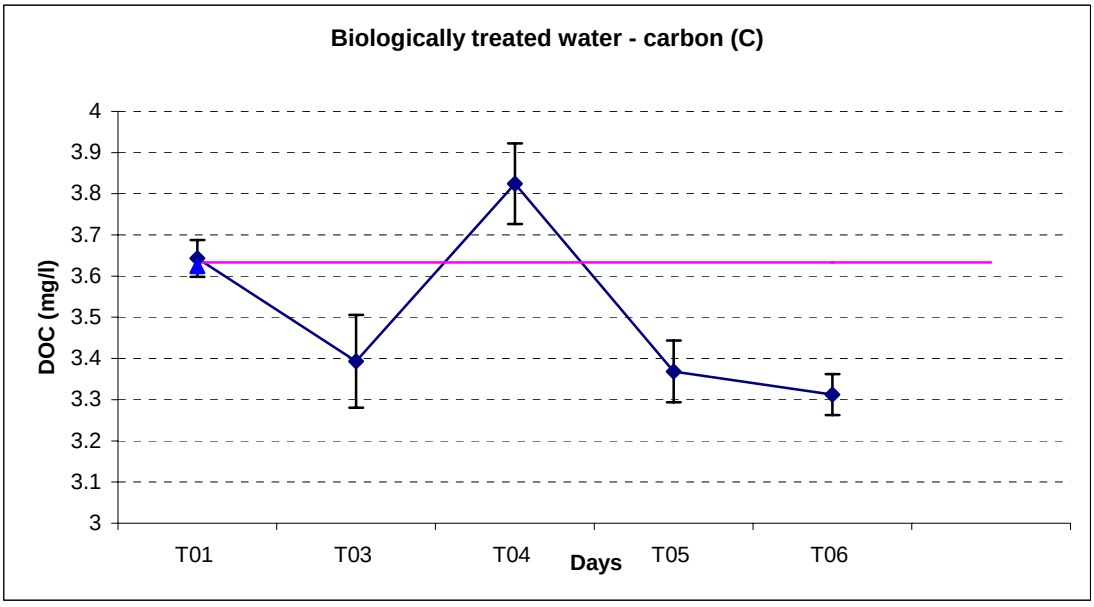

Figure: Flask B. DOC removal over time in biologically treated water with granulated active carbon material.

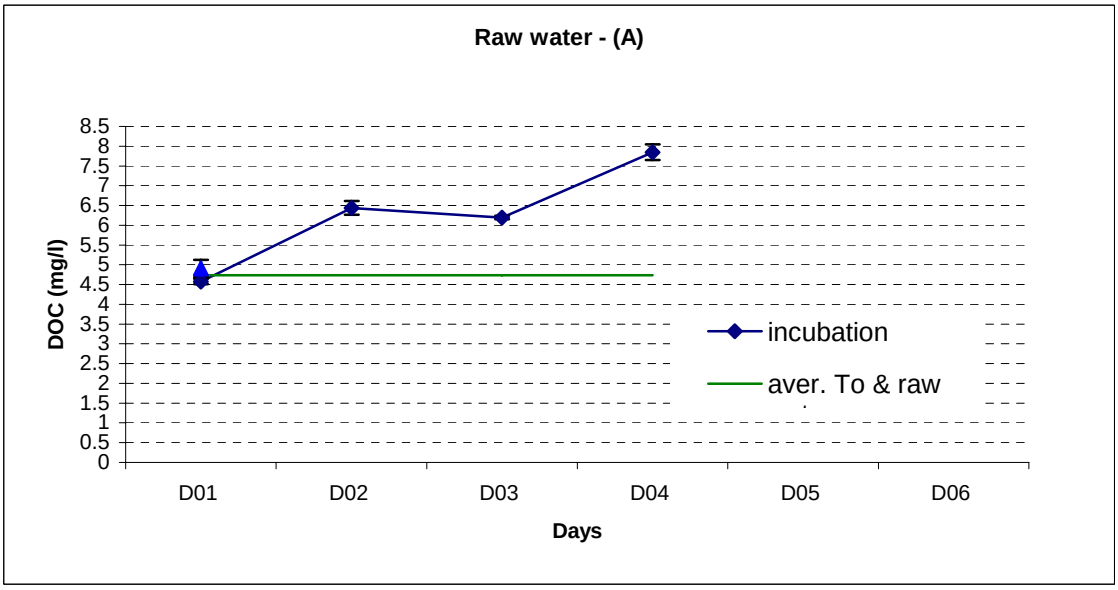

Figure: Flask A. DOC removal over time of raw water.

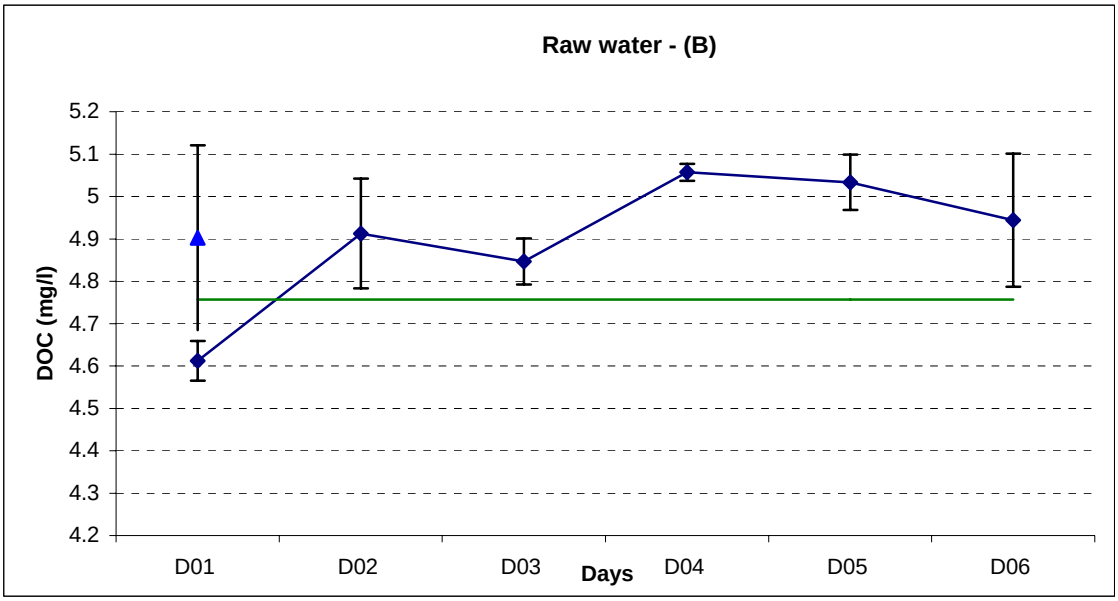

Figure: Flask B. DOC removal over time of raw water.

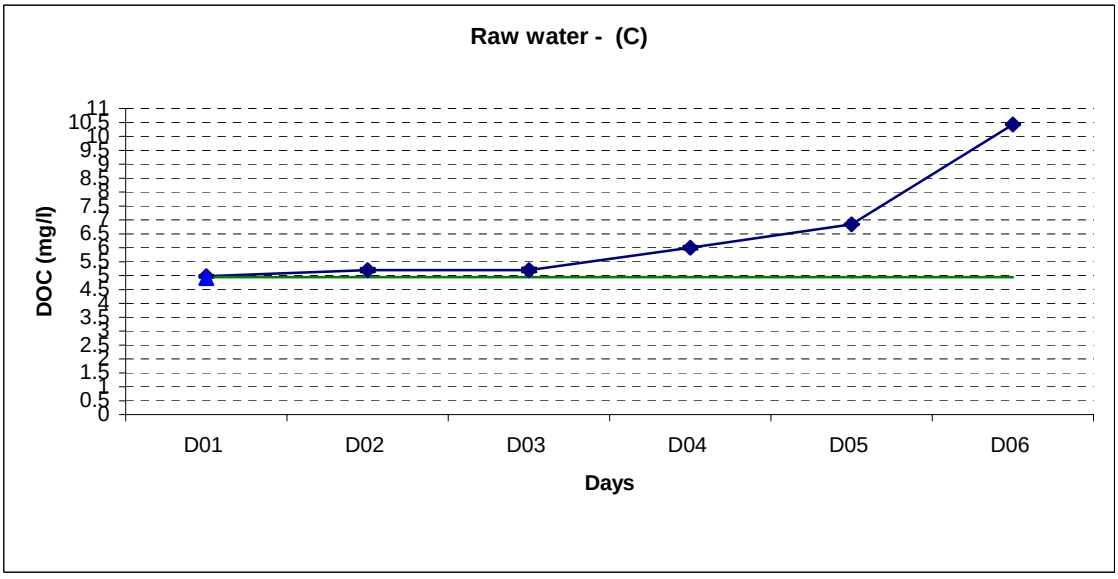

Figure: Flask C. DOC removal over time of raw water.