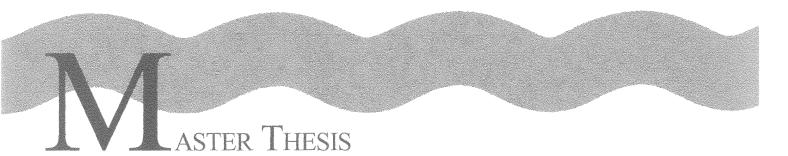


CHALMERS UNIVERSITY OF TECHNOLOGY Department of Sanitary Engineering Applied Environmental Measurement Techniques



Biological Drinking Water TreatmentEvaluation of a Pilot Plant Study at Varbergs Waterworks, Sweden

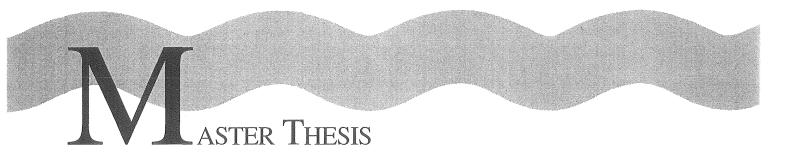
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Master Thesis 1999:1



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Abstract

The municipality of Varberg plans to build a large-scale facility for biological treatment of drinking water. The purpose of this thesis is to evaluate the pilot plant studies carried out at the local waterworks. Iron and manganese from a groundwater source are removed in bioreactors, followed by rapid sand filtration. The reactors consist of plastic pipes filled with a biofilm carrier medium. Iron and manganese concentrations in filtered water comply with the limits and recommendations of the Swedish drinking water standard. Surface water of good quality is cleaned by slow sand filtration, with subsequent filtration through granular activated carbon. Special emphasis is put on investigating the removal of natural organic matter in the pilot slow sand filters. A new, modified method for the measurement of Biodegradable Dissolved Organic Carbon (BDOC) is presented and applied in the experimental part of this work. Water samples were incubated in glass beakers, with bacteria fixed on a carrier medium with high specific surface area (Siran). Slow sand filtration was found to be a suitable treatment process for the lake water. The performance of the slow sand filters agreed well with what has been reported in the literature. The colour value of the raw water was much higher in winter. Therefore, ozonation prior to filtration is suggested for the cold season, to enhance the removal of humic substances.

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1 Introduction

In the past, biological activity in drinking water treatment facilities was often regarded with suspicion and concerns about microbial contamination. However, research has revealed that microorganisms growing on filter media can be very effective in removing contaminants from raw waters. With the growing interest for sustainable development and clean production, research in biological treatment of drinking water has been booming during the last two decades. From a sustainability point of view, biological treatment options have some appealing general features compared to physicochemical drinking water treatment. They tend to work without or with a minimised input of chemical reagents such as oxidants or flocculants. This is usually accompanied by a reduction in generated waste, particularly sludge. A further advantage is that with biological treatment it is possible to produce biologically stable water that only demands a small disinfectant dose prior to delivering it to the consumers. There are even examples of biological treatment facilities without a final disinfection step. The so-called conventional process of flocculation with subsequent rapid sand filtration cannot comply with such demands (Hambsch & Werner, 1996). These issues are expected to be even more important in the future, and there will certainly be a growing interest in sustainable drinking water treatment technologies.

The municipality of Varberg (Sweden) wishes to improve the quality of the water delivered to the consumers. This is why the local waterworks is planning to build a large-scale biological treatment facility for drinking water in the close future. The processes applied will comprise slow sand filtration and biological filtration for removal of iron and manganese. To insure the applicability of the chosen processes under the local circumstances and provide backup information for an optimal design of the future facility, pilot plant studies were initiated. In the spring of 1998, in co-operation of Varberg waterworks and a consulting company, pilot scale reactors were set up for both slow sand filtration and biological removal of iron and manganese.

2 Purpose and scope

The purpose of this thesis work is to evaluate the pilot plant studies carried out at Varberg waterworks, using analytical results available from the waterworks and a commercial lab, as well as own measurements. This is done as far as the limited time of a master thesis allows, since the pilot plant study will be continued until March/April 1999. Secondly, a new, modified method for the measurement for Biodegradable Dissolved Organic Carbon (BDOC) is tested and applied to the problem. Thirdly, a literature study is done, covering the fields of slow sand filtration, biological removal of iron and manganese and the measurement of BDOC.

3 Scientific background

The literature study presented in the following, aims at giving the necessary background knowledge for understanding the processes involved in the Varberg pilot plant study. Information has been selected in terms of significance for the evaluation of the pilot plant study and the experimental part of this work.

3.1 Natural organic matter in drinking water

Investigating Natural Organic Matter (NOM) in water is a complex and difficult task. Due to the large variety of substances that can be present, it is virtually impossible to identify and quantify them all in a water analysis. Instead, bulk parameters are commonly used to either estimate the amount of natural organic matter or quantify certain groups of substances with similar character. Knowledge about the type and amount of organic matter in a drinking water is important for assessing its quality.

3.1.1 Common bulk parameters

The measure of Chemical Oxygen Demand (COD) originally derives from wastewater treatment. The COD states how much oxygen is needed to chemically oxidise all organic matter in a water sample. The concept is applied to drinking water as well, as an indicator of the NOM content. In Sweden, the common dichromate method is banned because of its need for mercury. Instead, potassium permanganate is used as oxidant. The disadvantage with potassium permanganate is that it does not accomplish sufficient oxidation of certain types of organic matter and might therefore produce inconsistent results (Morrison, 1998).

The measurement of Total Organic Carbon (TOC) is a widespread method and gives the total amount of organic carbon in a water sample as mgC/l. Dissolved Organic Carbon (DOC) implies that the sample has been run through a filter with 0.45 μ m pore size prior to analysis, to exclude particles. The term *dissolved* is operationally defined in this context. The limit of 0.45 μ m does not have any chemical meaning except that the filter medium is supposed to retain bacteria.

There is no direct correlation between the above parameters of COD and TOC/DOC. Two organic molecules containing the same number of carbon atoms may differ in their oxygen demand during mineralisation, depending on how many oxygen atoms are in the molecule. For example, a hydrocarbon molecule without any O-atoms demands more oxygen than a sugar molecule with the same amount of carbon, but several O-atoms (Morrison, 1998).

The measurement of UV-absorbance at 254 nm is a common and easy method to estimate the organics content in a water sample. This UV wavelength is absorbed by aromatic and aliphatic compounds with double bonds (Haarhoff & Claesby, 1991). It is frequently assumed that a correlation exists between the parameters of UV_{254} -absorbance and the content of TOC or DOC. This is not necessarily true, as the UV_{254} measurement mainly covers aromatic compounds, whereas TOC and DOC do not depend on the type of organic matter. Therefore this correlation cannot be applied if the organic carbon composition changes over time or different types of water are being compared (Morrison, 1998; Eaton, 1995).

The measure of *colour* is defined as the absorption of light in the visible range at 400 nm. Similar to UV_{254} , colour is often used as a general indicator for the amount of organic matter. Organic matter absorbing such low energy radiation as 400 nm is more aromatic than molecules absorbing at 254 nm, thus colour is mainly an indicator for the content of humic substances. Natural river waters with DOC concentrations above about 10 mg/l, especially in lowlands, are distinctly coloured (Drever, 1997). To be more correct, the above, widespread application of colour should be called *apparent colour*. It has been recommended to filter the water sample through a membrane filter to exclude interference of suspended particles which also absorb this wavelength. The parameter of *true colour* then only takes into account the absorbance of dissolved and colloidal substances (Claesby, 1991).

3.1.2 The relevance of biodegradable organic matter

The growth of bacteria in water supply systems is a very widespread problem. Biofilm formed on the walls of pipes can lead to poor tap water quality in form of bad odour and taste. Even pathogenic microorganisms may be spread under such conditions. Commonly the water quality deteriorates with increasing residence time in the supply system. The extent of bacterial regrowth is related to the presence of Biodegradable Organic Matter (BOM), since heterotrophic microorganisms utilise BOM for life (dissimilation) and growth (assimilation). The traditional solution for such problems is to keep a carefully dosed disinfectant residual in the water to prevent growth. Most commonly, chlorine is used for this purpose.

Unfortunately, chlorination has some side-effects. Chlorine not only inhibits microbial growth by oxidation, but also reacts with organic molecules. Eventually halogenated organics are formed, many of which are carcinogens or mutagens. Of major concern is the possible formation of trihalomethanes¹ (THM). Chloroform (CHCl₃) for instance is a suspected carcinogen (Harrison, 1990). Particularly, humic substances in raw water are regarded as precursors for the formation of chlorination by-products.

Bulk parameters like DOC or UV-absorption are very rough measures of organic carbon and do not give reliable information about the biological stability of the water, i.e. the ability of the water to support microbial growth. There is no general relationship between the contents of Biodegradable Organic Matter and the DOC of a water. The ratio will depend on the type of organic matter. It is generally accepted that the large organic molecules like humic substances are almost resistant to biodegradation. Most bacteria seem to prefer the fractions of relatively small molecules with molecular weights less than maybe 1000 amu² (Klevens et al., 1996; Collins et al., 1994, Eighmy et al., 1994).

Even in raw water from the same source, the proportion of BOM can vary seasonally. Often the proportion of the smaller, more biodegradable fractions are higher in the warm season than in the cold water of winter or spring (Klevens et al., 1996, Welté & Montiel, 1996). Therefore, TOC, DOC, UV_{254} or colour are hardly suitable to assess Biodegradable Organic Matter, and more specific parameters are needed.

The measure of *Specific UV-Absorbance* (SUVA) is defined as the ratio of UV_{254} /TOC. It thus indicates the proportion of aromatic compounds in the organic carbon fraction (degree of

¹ Trihalomethanes: derivatives of methane in which three hydrogen atoms are substituted by bromine or chlorine ² atomic mass units

aromaticity) (Klevens et al., 1996). There is some evidence that the compounds of Biodegradable Organic Matter do not absorb in the UV (Welté & Montiel, 1996). In this respect, SUVA can be helpful as an indicator for the proportion of BOM in a water.

In recent years, initiatives have been taken in several countries to provide a biologically stable¹ drinking water which does not support the growth of microorganisms in the supply-system. At the same time, attempts to reduce the formation of chlorination by-products have been made. This inevitably requires a reduction of Biodegradable Organic Matter. For example in the US, the Disinfectant / Disinfectant by-product rule puts maximum values on some specific chlorination by-products and limits the content of TOC to < 4 mg/l prior to chlorination. The latter is anticipated to be reduced to < 2 mg/l (Bauer et al., 1996). Good qualitative correlations have been found between biodegradability parameters to the demand of chlorine to disinfect waters (Huck, 1990).

It can be concluded from the above paragraphs that the measurement of Biodegradable Organic Matter can give important information about the quality of raw and finished water in drinking water treatment.

3.2 Measurements of Biodegradable Dissolved Organic Carbon (BDOC)

There are basically two different approaches for the measurement of Biodegradable Organic Matter in water samples.

Biomass-based methods determine the amount of cell-mass that can be formed from the carbon in the water sample as substrate. The bacteria added as an inoculum are either the indigenous bacterial community from a surface water or a special, known species. Commonly, the actual measure of Biodegradable Organic Matter would then be *colony forming units*² (cfu) or concentration of adenosintriphosphate (ATP) in the biomass. By conversion factors, those measures can be expressed in terms of Assimilable Organic Carbon (AOC) in the water sample (Huck, 1990). Biomass-based methods will not be discussed in detail here.

The other group of methods is based on the difference of DOC before and after incubation of the water sample. The result is expressed as Biodegradable Dissolved Organic Carbon (BDOC), which can be defined as follows: The BDOC is that portion of the organic carbon in water that can be mineralised by heterotrophic microorganisms (Huck, 1990).

Some authors have pointed out that BDOC and AOC measure quite different parameters, since no correlations between the parameters could be established (Jago et al., 1994) It has been recommended to apply the two approaches to different kind of objectives. For the assessment of bacterial regrowth and coliform growth in water supply systems, biomass-methods are expected to be more suitable. To determine the chlorine demand of a water sample or the potential formation of disinfection by-products, DOC-based methods are said to be more appropriate (Huck, 1990). In contrast to this, it has been stated that the primary objective of BDOC measurements is to predict the potential for bacterial growth (Frias et al., 1992).

¹ Operationally defined as a water with <10 μ g/l Assimilable Organic Carbon (AOC) or <0.15 mg/l Biodegradable Dissolved Organic Carbon (BDOC) (Lambert & Graham, 1995). Definitions see below.

² Colony forming units: measure of bacteria concentration, the number of colonies formed on agar plates

Unfortunately there is no standard method so far for the measurement of BDOC. A number of methods have been proposed by different authors. However, some general limitations and necessities apply. It has been pointed out that sampling containers should, if possible, be made of glass. For proper cleaning, glassware should be heated to 550 °C for several hours. The DOC-based methods are applicable to waters containing more than 0.2 mg/l BDOC. This is because in many cases, a difference of 0.1 or 0.2 mg/l cannot be reliably differentiated by TOC/DOC analysis (Huck, 1990).

3.2.1 BDOC analysis using suspended bacteria

Batch-methods that incubate a water sample with suspended bacteria for a specific duration are based on the method of Billen-Servais (Servais et al., 1987). The sterile filtered water sample is seeded with unknown, indigenous bacteria from surface water and kept in the dark for 10, 21 or 28 days. The BDOC can be determined by two different analytical approaches. The normal, simple one consists of measuring the DOC of the sample until it has reached a stable level. The BDOC is then the difference between initial and final DOC.

The other procedure is more sensitive, but requires high analytical effort. The mortality of the suspended bacteria is monitored over the whole period of incubation. Then bacterial mortality is integrated over time, which equals the sum of produced biomass. Finally the sum of produced biomass is divided by the growth yield, commonly called Y. The result equals BDOC, since Y is defined as produced biomass per gram of substrate (Huck, 1990, Volk et al., 1994).

3.2.2 BDOC analysis using fixed bacteria

Different methods take advantage of a biofilm on an inert support medium. The most common one uses sand colonised with bacteria as inoculum (Joret and Lévi, 1986). The sand is taken from sand filters at water treatment plants which do not chlorinate their water prior to filtering. The sand is washed until no release of carbon is detectable in the wash water. Normally, 100 g of sand and 300 ml of water sample are incubated in a 500 ml flask for 5-7 days with aeration. The DOC of the water sample is checked before and after putting it into the flask and the mean of those two measurements defined as initial DOC. During the incubation period, DOC is measured daily until a plateau is reached. Finally, BDOC is calculated as the difference between initial and minimum DOC.

The use of a biofilm has some apparent disadvantages. Carbon can be released from the inoculum or adsorbed to the surface, without being degraded. The effect of different parameters on the results of the method has been investigated. Unfortunately it was shown that BDOC results depend on factors like the ratio of sand/sample volume, the incubation time and use of aeration. The most appropriate sand/water ratio seems to be the one most commonly used, namely 1:3. Use of smaller amounts of sand, e.g. 10 g per 300 ml water, leads to a serious underestimation of BDOC. The use of more sand aggravates the problems of carbon release and carbon adsorption. From aerated samples, higher BDOC values are calculated than from non-aerated ones, especially if the BDOC content in the sample is high. If the incubation time is extended, DOC levels in the flask may increase again, which could be due to bacterial lysis or desorption of DOC from the biofilm. It has also been pointed out that stirring the sample speeds up the biodegradation process. This is due to higher oxygen supply and better transport of carbon and nutrients to the biofilm (Volk at al., 1994).

The initial idea of filling support material in a glass tube to create a column with fixed bacteria inside, was to run the measurement continuously. The DOC of the sample is then measured before the water enters the column, and after it exits. Even discrete water samples can be analysed, by recirculating the sample through the column. Both possibilities are illustrated in Figure 1. Before the column is ready to use, the support medium has to be colonised with bacteria. For this purpose, natural lake or river water is pumped through the column. The duration of the colonisation period that authors believe to be necessary varies substantially, from 5 days (Frias et al., 1992) to 2 months (Lütkens, 1996).

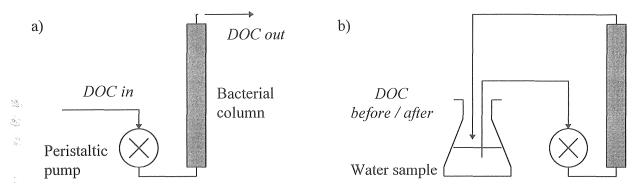


Figure 1: Continuous (a) and batch (b) operation of bacterial columns

The high surface area of the support material decreases the contact time necessary to achieve biodegradation of the organic material in the sample water. Working flows between 3.5 and 7 ml/min correspond to retention times of 45 min to 2 h in the column. Discrete samples are commonly recirculated for 5 days (Frias et al., 1992).

However, there seem to be some inherent problems of bacterial columns. Small molecules can diffuse into the pores of the support medium and the biofilm, whereas for larger molecules, this effect is negligible. Thus the bacterial column might work as a chromatography column, with small molecules leaving the system with a delay of up to 50 hours (Lütkens, 1996). With recirculation of discrete samples and therefore long contact times, there could be problems with carbon release from the tubing.

3.2.3 Comparison of methods

The variety of methods that are used poses a major problem when data from different studies have to be compared. Studies have been conducted which compare the different methods and their results when applied to the same kind of water.

It has been reported that all the methods described above do produce similar results, from a statistical point of view. Table 1 shows the results of BDOC analysis on raw and finished waters from the Llobregat River (Spain), and gives an idea about the inherent variability of BDOC measurements.

Table 1: Comparison of BDOC methods for River and finished water, in % BDOC/DOC.Standard deviations in brackets.Summarised from Frias et al., 1995

Method	Authors, year	Time	%BDOC/DOC River	% BDOC/DOC Finished
Suspended bacteria	Servais et al., 1987	21 d	39.17 (11.09)	16.17 (9.17)
Bacteria on sand	Joret & Lévi, 1986	10 d	36.74 (14.22)	27.01 (12.08)
Column (continuous)	Ribas et al., 1991	2 h	25.8 (9.2)	31.9 (17.0)
Col. (recirculated)	Frias et al., 1992	5 d	36.07 (14.35)	27.01 (11.54)

Other works show that the method with bacteria on sand gives substantially higher BDOC results than the method using suspended bacteria. For a given kind of water, a good correlation could be found between the results of these two methods (Volk et al., 1994). In that specific case, the method with fixed bacteria produced about twice as high results. A population of fixed bacteria is obviously able to degrade a wider range of organic molecules. Possible reasons are

- a higher biological diversity among the fixed bacteria compared with suspended ones
- ecological advantages due to fixation in a biofilm
- more bacteria in the sample flask from the beginning, due to the high bacterial density in the biofilm

From other comparative studies, problems have been reported with the column method. Recirculation of discrete samples through the column produced results that were inconsistent with those from the fixed bacteria method after Lévi. The column method for example indicated that a finished drinking water had higher BDOC than the raw water, and had a poor reproducibility (Jago et al., 1994).

3.3 Slow sand filtration

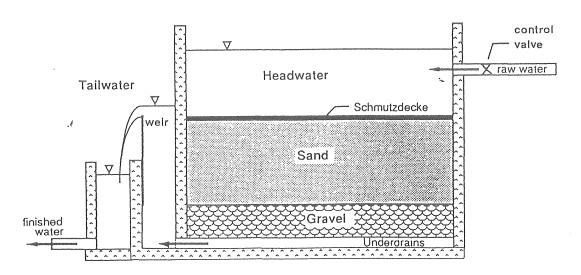
The first modern slow sand filter was installed in 1829 in London, and the basic design of those built today is still the same. Since the process requires a relatively large area, many authors see it as a solution for small waterworks supplying up to a few thousand of people. On the other hand, London receives 85 % of its water from slow sand filters (Hendricks, 1991). There is a vast amount of literature available on the subject. In several cases, results of different studies are contradictory, especially when it comes to the influence of different parameters on a slow sand filter's performance. This section will try to give an overview and incorporate recent research.

3.3.1 General principles

The set-up of a slow sand filter is remarkably easy, as illustrated in Figure 2. The unit consists of a filter box, in which a bed of sand is supported by a layer of gravel. The raw water enters the filter and makes up the headwater above the sand layer. Through so-called underdrains within the gravel support, consisting of perforated pipes, the clean water is leaving the filter. The walls of full-scale filters are usually made of concrete, or alternatively of sloped soil.

The cleaning process takes place while the water is slowly percolating through the sand. There are two different approaches to regulate the flow. With inflow controlled filters, the desired flow is set with an inflow valve, so that with increasing build-up of headloss, the height of the supernatant water layer increases. Outflow controlled filters have a constant headwater level, but the outflow valve situated after the filter requires further opening with ongoing clogging of the filter.

On top of the sand bed, a layer of debris and high microbial activity forms after some time of operation. In the literature it is traditionally called *Schmutzdecke*, a German word meaning "dirty blanket". This term seems to be too negative, considering an important part of the cleaning process takes place in this layer. However, the term *Schmutzdecke* will be used in this report to be consistent with the usual terminology in this area of study.



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Figure 2: Schematic cross section of a slow sand filter (Hendricks, 1991)

The filter run is ended when the headloss is such that either the supernatant water reaches its maximum allowable height (inflow controlled filters) or the desired flow cannot be maintained (if outflow controlled). Filters are normally run continuously, 24 hours a day, since downtimes can negatively affect the biology. Slow sand filters are not backwashed. The traditional cleaning procedure implies lowering the water table under the sand surface and subsequent removal of the *Schmutzdecke* plus the adjacent 1-3 cm of sand. Since this procedure removes sand, the filter bed has to be renewed after a few years, when the filter bed depth has become insufficient (Hendricks, 1991). As water has to be supplied continuously to the consumers, even when a filter is cleaned, slow sand filtration facilities need to consist of at least 2 filter units.

3.3.2 Mechanisms of pollutant removal

The theory of physical particle removal in *rapid sand filters* without microbial life has been described in detail by other authors (Hendricks, 1991). Although mechanisms such as interception and sedimentation certainly also occur in slow sand filters, the main factor for removal of pollutants seems to be biological. This is shown by the fact that new slow sand filters tend to have a poor removal efficiency, which improves with the first filter run. During this start-up phase called maturation, a dense microbial community forms, not unlike those found in a natural environment, e.g. a sandy lake bottom. In literature, maturation times of 35 to over 100 days have been reported (Haarhoff & Claesby, 1991).

Several biological mechanisms have been attributed to contaminant removal in slow sand filters, for example predation of bacteria by protozoa, metabolic breakdown and an increased stickiness of the sand surface (Haarhoff & Claesby, 1991; Weber-Shirk & Dick, 1997). The mechanisms by which different fractions of organic matter are removed in slow sand filters are not yet fully understood. The general perception is that smaller and simpler organic molecules with molecular weights about <5000 amu are removed by biodegradation. In contrast, humic material is probably rather adsorbed to the surface of the filter medium (Collins et al., 1994).

Since scraping the filter bed for cleaning removes the biologically very active *Schmutzdecke*, and disturbs the top of the sand by dewatering, another ripening period of 6 hours to 2 weeks

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occurs and the effluent quality may deteriorate for a while. This problem tends to appear with cold water or immature filter beds.

3.3.3 Design parameters

One of the most appealing characteristics of slow sand filtration is its simplicity. Therefore it has been recommended to keep things simple throughout the design, easy to maintain and operate (Hendricks, 1991). Recommended values for important design parameters are summarised in Table 2.

Filtration rate [m/h]	0.1 - 0.4	Depth of supernatant water [m]	1-1-5
initial depth of sand bed [m]	1.2	Effective size* of sand [mm]	0.15-0.35
minimum depth of sand	0.7	Uniformity Coefficient** (UC)	<3 (preferred <2)

Table 2: Recommended desig	criteria for slow sand filtration	by (Huisman & Wood, 1974)
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* Defined as the sieve size at which 10 mass-% of a sand pass (d_{10}) ** Ratio d_{60}/d_{10}

The most important design parameter is the filtration rate, commonly stated as m/h, since it decides about the filter bed area needed to treat a certain amount of water. When choosing a design filtration rate, one should consider that while one slow sand filtration unit is down for cleaning, the other filters have to take over some extra flow to compensate. Uncertainties and possible unexpected events, such as a deterioration of raw water quality can easier be coped with if a conservative approach is taken concerning the rate. Anyhow, high filtration rates are often not economical since they result in a faster build-up of headloss and significantly shorter filter runs. Runs shorter than a month are normally regarded as unacceptable because of the high labour cost for cleaning.

The effective size of the sand has to be chosen carefully. Too fine sands have a lower permeability and cause much headloss. Too coarse media compromise the effluent quality. Authors stated that larger sizes than usually recommended may be used, but preferably in warm climates where the biological activity is sufficient year round. The suitable uniformity coefficient of the sand is limited. Sands with a wide grain size distribution have a lower permeability, because finer grains block the interstices between the large ones. It is important to make sure that the purchased sand has been carefully washed to remove the fine fractions. Otherwise, fines may cause effluent turbidity to be higher than raw water turbidity for several months during operation (Pyper & Logsdon, 1991, Hendricks, 1991).

For climates with longer periods of frost, the question of covering the filter with a roof has to be addressed. There are two approaches to cope with the problem. It is possible to accept the occurrence of an ice-block on top of the filter, if the side walls are designed to resist the pressure of the expanding ice. Usually the sand bed itself does not freeze and the ice block is floating on top of the supernatant water. A problem is that with a thick layer of solid ice on top, filters practically cannot be scraped. Open filters in Nordic climate are only possible to operate if it is certain that the filter run between two scrapings exceeds the length of the frost period. This requires excellent raw waters and and/or a moderate filtration rate. In this case, the filters have to be scraped just before the beginning of the cold season. Since this policy involves certain uncertainties and nuisance, most authors recommend covered filters in cold climates. Covered filters usually do not need additional heating, and a small pump which keeps the headwater circulating is an inexpensive means to help prevent freezing. A roof has several other advantages. In summer, the filter is shaded which prevents the growth of algae that might otherwise clog the sand. It furthermore protects the filter from wind-blown debris and vandalism. Generally, covering the filters will result in longer filter runs. The disadvantage of a roof is certainly the additional investment costs (Claesby, 1991; Hendricks, 1991).

3.3.4 Performance of slow sand filters

The performance of different slow sand filters is relatively difficult to compare, since published studies include filters with totally different prerequisites in terms of climate, raw water quality etc. Nevertheless, a compilation of available performance data is presented in the following, particularly concerning the removal of Natural Organic Matter.

Slow sand filtration has a reputation for being able to remove Natural Organic Matter from raw waters. The extent to which components making up organic carbon and colour are removed is however very limited. Because of different raw waters and the crudeness of the used bulk parameters, results tend to be site-specific. Reported organics removals in terms of DOC are commonly in the range of 5-40 %, see Table 3. The average DOC removal of the filters included in this table was only 160

filters included in this table was only 16%.

 Table 3: DOC removals typically achieved by slow sand filtration

 (Lambert & Graham, 1995, see there for detailed references of the studies included in this table)

Water source	DOC [mg/l]	rate [m/h]	Rem.[%]	Water source	DOC [mg/l]	rate	Rem.[%]
Springfield (US)	2.3 (winter)	0.04	15	River Ohio (US)	1.5 - 3.2	0.12	5-24
Springfield (US)	3.0 (autumn)	0.05	12	River Avon (UK)	4.8	0.20	23
Portsmouth (US)	5.3 - 7.0	0.05	8-30	Ivry (France)	2.2 - 2.3	0.20	18-20
Portsmouth (US)	8.0	0.10	12	River Thames (UK)	3.7	0.25	15
Ashland (US)	2.8	0.05	12	Leng (Switzerland)	0.95	0.67	16
Ashland (US)	2.8	0.10	9				

Slow sand filters tend to remove 5-35 % of the UV_{254} -absorbing substances (Table 4), with a mean of 17 %. Colour removals reported are in the range of 15-80 %, the mean being 34 % (Table 5). It has been stated elsewhere that the removal of *true colour*, caused by humic substances, is only around 25 %. As the parameter of a*pparent colour* includes a contribution from suspended particles which are effectively retained in slow sand filters, the removal of apparent colour may be higher. Unfortunately it is rarely stated in literature, which of these two colour parameters was measured (Claesby, 1991).

Water source	UV-abs [m ⁻¹]	rate[m/h]	Rem.[%]	Water source	UV-abs	rate	Rem.[%]
Springfield (US)	8.1	0.04	33	River Avon (UK)	13.3	0.2	32
Springfield (US)	9.3	0.05	22	Ivry (France)	4.9-5.2	0.2	2-20
Portsmouth (US)	20-30	0.05	20-30	River Thames (UK)	10.0	0.25	12
Portsmouth (US)	28	0.1	8	Leng (Switzerland)		0.7	16

Table 5: Colour removals typically achieved by slow sand filtration (Lambert & Graham, 1995)

Water source	Colour	rate[m/h]	Rem.[%]	Water source	Colour	rate	Rem.[%]
Springfield (US)	16°H* (winter)	0.04	44	Seagahan (US)	20-55 °H	0.15	15-20
Springfield (US)	12⁰H (autumn)	0.05	42	River Avon (UK)	1.63 m ⁻¹	0.2	38
Lake Vyrnvy	20-30 °Н	0.15	20-30	River Thames (UK)	0.90 m ⁻¹	0.25	23

* degree Hazen

Biological drinking water treatment - Evaluation of a pilot plant study at Varberg waterworks, SwedenMaster thesisAEMT 97/98Gerald Heinicke

To assess the finished water quality in terms of potential bacterial regrowth, measurements of Biodegradable Organic Matter are more suitable than the above parameters. Slow sand filtration is much more efficient at removing BOM than general organic bulk parameters. That is the reason for filtrates generally having a good biological stability, leading to reduced bacterial growth in the supply system. Removals of Assimilable Organic Carbon (AOC) range from 14-40 % (Table 6). BDOC removals are typically higher, from 46-75 %, with a mean of 60 %.

Table 6: AOC and BDOC	removals typically a	chieved by slow say	nd filtration (Lamber	& Graham, 1995)
			and ARACA GOLORA (AMOUNT OF)	. co Growing assoy

Water source	AOC [µgC/l]	rate[m/h]	Rem.[%]	Water source	BDOC [mg C/l]	Rem.[%]
Leidun (Netherlands)	8		25	Ivry (France)	0.4 - 0.65	46-75
Weesperkarspel (NL)	16		25	New Hampshire	0.7	57
Weesperkarspel (NL)		0.7	40			

The influence of the filtration rate on effluent quality has long been subject to controversy. To achieve better filtrate at low filtration rates with longer contact times seems to be logical. However, the results presented in the above tables suggest that the rate does not have any major effects on the percentage organics removal. Slow sand filters are apparently able to adjusts to higher organics load which might occur due to either a higher concentration in the raw water or a higher filtration rate (Lambert & Graham, 1995). Recent studies have been published where filtration rates were increased from 0.1 to at least 0.5 m/h without deterioration of effluent quality, taking into account any currently available parameter (Rachwal et al., 1996).

On the other hand, there are examples indicating a decreasing efficiency with higher filtration rates, as illustrated in Figure 3. Both the removals of DOC and permanganate-COD seem to depend on the filtration rate to a significant extent. In most studies however, there was only a slight negative trend with higher filtration rates and the difference was not statistically significant (Lambert & Graham, 1995; Collins et al., 1994).

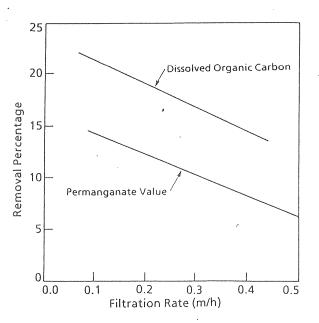


Figure 3: Removal of organic carbon during slow sand filtration (Haarhoff & Claesby, 1991)

Several authors reported that low temperatures have a much more detrimental effect on slow sand filter performance than high filtration rates. An example for the dependence of organic carbon removal on water temperature is given in Figure 4.

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In addition to less favourable temperatures for microbial life, a smaller proportion of Biodegradable Organic Matter in winter raw waters contributes to low removals of TOC. Figure 5 gives an example for this phenomenon from France. In the same study it was shown that the percentage of BDOC removal in a slow sand filter deteriorated drastically at water' temperatures below 8 °C.

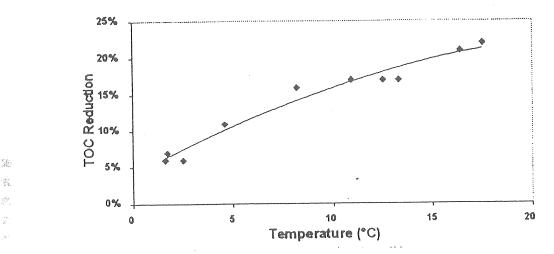


Figure 4: Removal of organic matter measured as TOC reduction at different raw water temperatures in a slow sand filter at a rate of 0.13 m/h (Seger & Rothman, 1996)

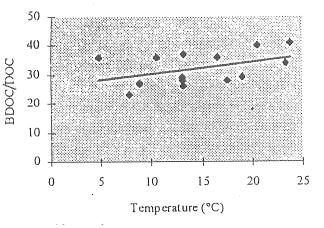


Figure 5: Ratio between BDOC/DOC and water temperature (Welté & Montiel, 1996)

3.4 Improvements of slow sand filtration

Several modifications have been suggested to classical slow sand filtration that either increase the performance or improve operational conditions.

3.4.1 Alternative filter cleaning technique

Before a slow sand filter is cleaned by scraping, the water table has to be lowered, and the top centimetres of the sand fall dry. This has been shown to be more detrimental to the biology than the scraping procedure itself. To avoid this problem and at the same time save some work, a new cleaning technique has been developed at the West Hartford (USA) slow sand filter.

When terminal headloss is reached at this slow sand filter, the water table is only lowered to about 30 cm above the sand bed. A tractor with rubber tires drags a rake over the sand surface, loosening the debris which caused the headloss. At the same time, the supernatant water is

drained horizontally, thus removing the particles with the flow. After a period of 8-10 years, the sand bed is totally removed for cleaning. There is evidence that the harrowed filter sustained a greater bacterial biomass compared to scraped filters and thus had an improved performance. The wet harrowing technique has been evaluated on full-scale facilities and is recommended for low turbidity raw waters (Hendricks, 1991, Sims & Slezak, 1991, Brink & Parks, 1996).

3.4.2 Fabric protected slow sand filtration

The general idea of placing a layer of fabric on top of the sand bed is to facilitate cleaning. Suspended particles are retained on the filter mat, so that the sand surface would not have to be scraped. Instead, the cleaning procedure consists of the removal and washing of the fabric. Furthermore, a non-woven fabric is considered to be a more effective filtration medium than sand, due to its higher porosity and specific surface area. Thus, the necessary filter bed depth is lower, resulting in less headloss than for an unprotected sand bed. Available and suitable fabrics are between 0.36-20 mm thick and their properties have been summarised (Hendricks, 1991). Pilot plant studies with fabric protected slow sand filters showed encouraging results (Graham et al, 1996). Filter mat cleaning was easy for pilot-scale facilities, but a suitable method for cleaning very large pieces of fabric does not exist so far.

3.4.3 Slow sand filtration through iron-oxide-coated-olivine

Olivine sand is a mixture of iron and magnesium silicates which occurs naturally. The mineral has a more positive surface charge than common quartz. This is particularly advantageous as aquatic organic matter generally has a negative surface charge. Furthermore the olivine sand grains can be artificially coated with iron oxide. Such a surface enhances the adsorption of organic matter to the grains. Subsequently, the adsorbed substrate is mineralised by the bacteria on the surface (McMeen & Benjamin, 1996).

In a pilot plant study, iron-oxide-coated-olivine was tested as a slow sand filter medium and compared with uncoated olivine and ordinary sand. With good quality river water as feed, the iron-oxide-coated-olivine filter achieved consistently higher organics removal. Removal of DOC was 20-50 %, compared to 5-12 % by sand or uncoated olivine. Absorption of UV_{254} was reduced by 44-70 % in the iron-oxide-coated-olivine, but only 8-28 % by the other two filters. After 6 months of pilot plant operation, there were no signs that the adsorptive capacity of the grain surfaces would be exhausted. Probably the adsorption sites are regenerated biologically.

The drawback with the medium is that no established industrial manufacturing process exists to coat sufficient amounts of olivine. Thus the costs for building a full-scale plant cannot yet be assessed (McMeen & Benjamin, 1996).

3.4.4 Pre-ozonation

Ozonation is a well-known pre-treatment option for coloured raw waters rich in humic substances. By adding ozone to the water, the biodegradability of aquatic matter is increased. The oxidant breaks down large, refractory organic molecules such as humic substances to lower molecular weight compounds. This can be measured as a decrease in UV_{254} -absorbance and a corresponding increase in biodegradable organic matter. After ozonation, the bacteria in

the slow sand filter are able to remove a far higher proportion of organic matter from the water (Hendricks, 1991). If properly dosed, the oxidant in the water does not inhibit the bacterial activity in the slow sand filter. The enhancement of NOM removal increases with the ozone dose. The positive effect of ozonation has been found to be most pronounced for cold raw waters (Seger & Rothman, 1996).

One of the drawbacks with ozonation is a typically faster build-up of headloss, since more substrate for bacterial growth is available (Hendricks, 1991). The denser bacterial population tends to clog the filter. Secondly, the additional biodegradable matter in the water can be of concern. If the substrate is not properly removed during filtration, the biologically unstable water may sustain substantial regrowth in the supply system.

3.5 Advanced biological treatment

The immense extent of research carried out in the field of biological drinking water treatment has resulted in some new developments which can achieve better effluent qualities than slow sand filtration. Some of these new technologies are mentioned here briefly. However, they generally lack the simplicity of slow sand filtration.

3.5.1 Biological Activated Carbon (BAC)

Filters containing Granular Activated Carbon (GAC) have been used for the removal of organic carbon from water, especially for trace pollutants such as pesticides. If the raw water is subjected to ozonation, extensive biological life forms in the filter medium. The combination of GAC with pre-ozonation is often called Biological Activated Carbon (BAC). Several advantages have been attributed to GAC as a biofilm carrier material:

- Bacteria grow best in places where they are protected from being eaten or washed away. The amount of pores in GAC, with its extremely large specific surface area provides ideal support for bacterial growth.
- GAC tends to adsorb substrate, nutrients and oxygen, so that the bacteria living on the surface are better supplied. This allows bacterial growth and biodegradation even at very low influent substrate concentrations. Furthermore, the contact time between the bacteria and substrate/nutrients is extended.
- The variety of functional groups of the surface of activated carbon obviously improves the attachment of microorganisms (for example -OH and carboxylic groups -COOH).

At water temperatures higher than about 15°C, BAC and slow sand filtration with preozonation achieve similar removals of Biodegradable Organic Matter. At low temperatures, BAC outperforms slow sand filtration. At the beginning of the filter run, the removal of organic matter by BAC filtration is much better than by slow sand filtration. Initially the activated carbon has its full adsorption capacity, while the sand becomes slowly colonised by bacteria. After some months, when the adsorption capacity is exhausted, the BAC was shown to decrease the DOC of a water only slightly better than sand (Dussert & Tramposch, 1996).

3.5.2 Combined treatment

Waterworks in several European cities accomplish drinking water treatment without chlorine disinfection. By means of an extensive treatment chain, biologically stable water can be produced. This is particularly impressive if considering the, in many cases, relatively poor raw water qualities in the densely populated Central Europe. Figure 6 describes the combination of physical, chemical and biological treatment processes used for the drinking water supply of Amsterdam. Surface water is pre-treated by means of coagulation, sedimentation and filtration. Rapid sand filtration mainly removes suspended solids and accomplishes nitrification of ammonium. Ozonation and Granular Activated Carbon filtration make up the BAC treatment and remove most of the organic matter. At this point, the DOC has already been diminished to less than 1 mg/l. After the final step of slow sand filtration, the Assimilable Organic Carbon (AOC) is reduced to less than 10 μ g/l, so that the water can be supplied to the consumers without chlorination (van der Hoek et al., 1996). This kind of extensive treatment is certainly a very costly alternative.

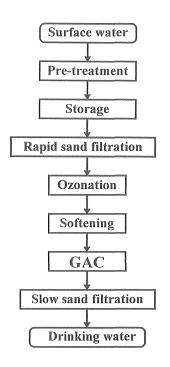


Figure 6: Process scheme for the water supply of Amsderdam (van der Hoek et. al, 1996)

3.6 Biofilters for removal of iron and manganese

3.6.1 Iron and manganese in drinking water

Iron and manganese in surface waters are generally found in their precipitated, oxidised forms. In waters lacking oxygen, which means groundwater and at times the deep layers of lakes, both metals may occur in their soluble forms.

Dissolved iron is mainly in the form of Fe^{2+} and often chelated¹, dissolved manganese occurs as Mn^{2+} . By increasing the redox potential of the water, or the pH, a chemical oxidation of iron and manganese is obtained. The oxidised and thereby precipitated Fe (III) occurs in form of FeCO₃ and iron hydroxides such as Fe(OH)₂ or Fe(OH)₃, while oxidised Mn (IV) exists as manganese dioxide MnO₂.

Dissolved iron in drinking water does not have to be limited for toxicological reasons. However, it poses other problems. If iron is present at levels above about 0.2 mg/l, some of the following undesirable effects can occur (Lyberatos et al., 1997):

- reddish-brown colour of the water due to iron precipitation if exposed to air
- reduction of effective pipe diameter because of iron precipitation
- unpleasant odour and taste, caused by iron bacteria that grow in the pipes and eventually die and get washed out.

The Swedish drinking water standard for iron is 0.1 mg/l, and 0.05 mg/l for manganese. In the same paper, it is recommended to keep the concentrations below 0.05 mg/l Fe and 0.02 mg/l Mn (Livsmedelsverket, 1993).

¹ Chelate: Complex involving a multidentate organic ligand. The cation is bonded from more than one side.

3.6.2 Physicochemical and biological removal

In technical systems, physicochemical removal of iron and manganese can be achieved by aeration followed by solid-liquid separation. The solid-liquid separation is generally performed by sedimentation of the precipitate and/or filtration (Lyberatos et al., 1997). If aeration with solid-liquid separation is insufficient to reach the demanded quality, additional treatments are possible, such as pH correction, use of chemical oxidants (chlorine, potassium permanganate or ozone) or ion exchangers.

However, there can be problems with the physicochemical methods. In the USA, 40-50% of the waterworks that were checked did not meet the drinking water standards for Fe and Mn. In France, this figure was about one third (Mouchet, 1992). Also some Swedish waterworks reported increasing demands of oxidants to ensure manganese reduction, and still the levels could not be kept according to the standards (Hedberg and Wahlberg, 1998). The most common reason for problems with conventional iron removal is iron complexation, by silica or humic substances.

The activity of certain microorganisms is known to enhance the oxidation of iron and manganese in water. Based on that knowledge, a number of removal systems have been developed which take advantage of iron and manganese bacteria. Several different technical applications for biological removal are available and have been summarised (Seppänen, 1992). They comprise, among others, slow sand filtration. However, the most promising technical solution seems to be oxidation in a bioreactor. Such a bioreactor can have different dimensions, from solutions for single houses to large treatment plants supplying thousands of people.

3.6.3 Biological processes

There are several genera of bacteria that oxidise iron and manganese in different ways. Some of them can be identified under a microscope due to their characteristic forms. One group comes in form of sheaths, while the most common iron bacterium *Gallionella ferruginea*, grows in spirally twisted stalks (Mouchet, 1992). The different species involved in the process will not be discussed in detail.

Except for some specialists that only oxidise iron or manganese, the bacterial population of biofilters contain groups of bacteria which can utilise both metals. For most of the bacteria, the environmental conditions decide whether they oxidise iron or manganese.

Intracellular oxidation is performed by enzymes, while many bacteria excrete extracellular polymers that cause oxidation outside the cell as well. The polymers have a negative surface charge that attracts the positive ions.

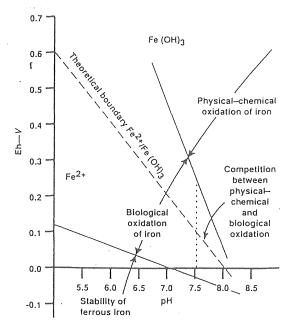
There are several possible reasons for the bacteria to oxidise iron and manganese. Autotrophs¹ utilise the energy from the exothermic reaction in order to assimilate organic carbon from CO_2 . However, the oxidation of iron and manganese sets free only minute amounts of energy, so that for example 600 mol of Fe^{2+} are required to assimilate one mol of carbon. Most iron and manganese bacteria are heterotrophic. The oxidation might be a mechanism to detoxify their ambient medium. Additionally, the micro-climate surrounding bacteria has a higher pH than the ambient, which may be another, indirect reason for oxidation (Mouchet, 1992).

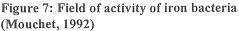
¹ autotrophic micro-organisms: do not depend on organic carbon for food (opposite of heterotrophic)

3.6.4 Demands of iron and manganese bacteria

In nature, iron and manganese bacteria are widespread. Parameters like temperature, salinity, contents of iron or organics do not inhibit their activity in the range found in natural ground and surface waters. However, these parameters may have an impact on species composition. Since iron and manganese bacteria are involved in redox processes, their main limitations are the ambient conditions of pH and redox potential. It has been shown that the gradient zone between anoxic and oxic environments is suitable for growth.

Figure 7 illustrates the activity field of iron bacteria. The redox potentials are defined as the difference in potential to a standard hydrogen electrode. Biological iron oxidation takes place in a field of environmental conditions situated around the theoretical boundary between Fe(II) and Fe(III). At higher pH and redox values, iron is chemically oxidised. If the pH value exceeds about 7.5, chemical oxidation easily becomes preponderant, as indicated by the thin broken line in the diagram.





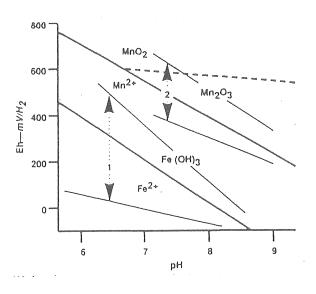


Figure 8: Comparison of requirements of iron and manganese bacteria (Mouchet, 1992) 1 – field of bacterial iron oxidation 2 – field of bacterial manganese oxidation

Figure 8 compares the pH and redox requirements of iron and manganese bacteria. The two bold lines describe the thermodynamic boundaries between oxidised and reduced forms of iron and manganese. The two thinner lines which arrow 1 points at, describe the limits of bacterial iron oxidation. In contrast, biological manganese oxidation takes place within the area defined by the two lines between the points of arrow 2. The broken line denotes the theoretical boundary between the two oxidised manganese species MnO_2 and Mn_2O_3 . To oxidise manganese, the bacteria need dissolved oxygen >5 mg/l, corresponding to a redox potential of +300-400 mV. Optimal conditions for both processes cannot be achieved in the same bioreactor, with the exception of very low filtration rates (Mouchet, 1992).

3.6.5 Performance of the biological process

If compared to physicochemical removal, biooxidation has some important advantages. First of all, the process is rapid, thus allowing high filtration rates. In coarse sand filters used in France, rates are commonly 10-70 m/h for iron and 10-40 m/h for manganese. Secondly,

biological iron precipitates are crystalline iron oxides, which are more compact than the amorphous products of chemical oxidation. Therefore the precipitate is denser and has a lower tendency to clog filters. The capture of biological precipitate can be about five times higher before the filter has to be backwashed. Similar advantages have been observed with biological manganese precipitates. Thirdly, no chemicals need to be added during the process, except for a final chlorination before the water is distributed to the consumers, and possibly pH adjustment. In fact, adding for example oxidants, would only inhibit the biology. Iron and manganese are generally removed down to trace concentrations. If iron is present in form of chelate complexes, bacteria are able to use the organic fraction, thereby releasing the iron for subsequent oxidation (Mouchet, 1992).

3.6.6 Application of biological removal in bioreactors

The main task in designing a facility for biological removal is to provide the bacteria with optimal conditions for growth. It is therefore essential that the redox potential of the water is controlled during the process, through aeration. The design of the facility will depend on the raw water quality, for example if both iron and manganese are to be treated. The successive treatment steps for ground water containing dissolved iron and manganese, as well as ammonium, are illustrated in Figure 9. It has been shown that, if water contains high amounts of ammonium, biological oxidation of Mn(II) can only take place after nitrification. The links between biological Mn oxidation and ammonium/nitrate have been investigated further (Verstraete et al., 1995), but will not be discussed here. The treatment for water containing iron and manganese, but no significant amount of ammonium, comprises two separate filtration steps:

- initial aeration and primary filtration for biological Fe removal,
- secondary aeration, pH adjustment and secondary filtration for manganese removal.

The form of bioreactor can vary depending on the dimensions of the facility. In France, largescale plants (up to 1200 m³/h) operate bioreactors based on rapid sand filters, with coarse sand (0.95-1.35 mm). The basic set-up for one filtration step, thus used for either iron or manganese, is illustrated in Figure 11. The two processes of biooxidation and retaining the precipitate take place in the same reactor. The pressurised aeration is controlled by means of flow meters and valves. Alternatively, aeration can be done by letting the water drop over cascades. The oxygen content would then be regulated by a partial bypass of non-aerated raw water. It has been reported that the seeding time of a bioreactor is much longer for biological manganese removal than for iron, and can take up to 2 months. Adding backwash sludge from other biofilters can speed up the seeding process (Mouchet, 1992).

Another type of bioreactor is filled with biofilm carrier material of plastic, which has a large surface area. The bioreactor is followed by rapid sand filtration to retain the precipitate, see Figure 10. During a pilot plant study in Sweden, manganese was biologically oxidised and removed so that Mn levels were complying to drinking water standards. In this case, hydraulic loading rates were relatively low, equivalent to a residence time of 1.3 hours. The same low Mn concentrations could be achieved in the outflow when the detention time was halved, but the rapid sand filter needed more frequent backwashing (Hedberg & Wahlberg, 1998).

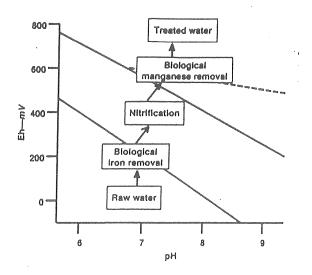
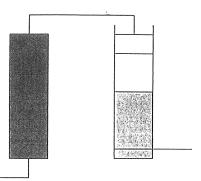


Figure 9: Successive treatment steps for water containing Fe(II), Mn(II) and NH₄. (Mouchet, 1992)



Biooxidation Rapi

Rapid sand filtration

Figure 10: Pilot plant set-up for biooxidation and filtration (Hedberg & Wahlberg, 1998)

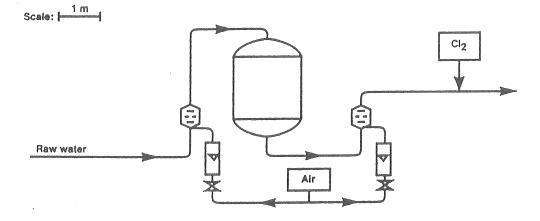


Figure 11: Basic design of a biological unit for a flow rate of 100 m³/h (Mouchet, 1992)

Trickling filters are known from waste water treatment. In such a filter, the water trickles slowly downwards over the support medium. A pilot scale trickling filter, filled with gravel of a mean diameter of 5 mm, has been used to remove iron from raw water. Since air is naturally convected through the filter because of the temperature difference inside/outside, no additional aeration was necessary. The pilot plant trickling filter showed good removal efficiency. Redox and pH measurements indicated that both biological and physicochemical iron oxidation took place (Lyberatos et al, 1997).

For small water supplies, even individual houses, yet another type of bioreactor has been described. It consists of a so-called pre-treatment unit (= the bioreactor), divided in partitions. The water has to pass through a layer of lightweight filter material floating on the surface when flowing from one partition to the next, driven by gravity. Finally, a small, integrated slow sand filter unit completes the treatment (Seppänen, 1992).

4 Varberg waterworks

Varberg waterworks is supplying 40 thousand people and a number of industries, including a nuclear power plant. The waterworks utilises raw water from two different sources. Very soft water is taken from Lake Stora Neden. This surface water is of good quality, with low content of organic matter and low turbidity. Comparatively hard groundwater is taken from wells at Ragnhilds Källa, also containing considerable amounts of iron and manganese. After treatment, both waters are mixed to ensure a suitable hardness. The mixing ratio will be about 70-80 % surface water and 20-30 % groundwater.

Based on these premises, a biological treatment chain was suggested by the engineering consultant (VA-Ingenjörerna AB, 1998). This is illustrated in Figure 12. Both raw waters will be treated biologically without adding any chemical oxidant, and subsequently mixed. Alkalinity is increased by adding carbon dioxide and NaOH. The activated carbon treatment is supposed to be an additional barrier against breakthrough of contaminants and should furthermore decrease organic carbon.

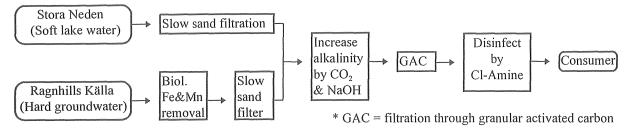


Figure 12: Schematic description of suggested future treatment at Varberg waterworks

4.1 Pilot scale slow sand filters

To investigate the treatment of lake water, three pilot plant scale slow sand filters without roof were built. The filters are made up by tubes of stainless steel with a diameter of 1.5 m, see Figure 13. The height of the sand bed is 1 m for all filters. The height of the supernatant water is 1 m for filters 1 & 2 and 2 m for filter 3, eventually allowing for a higher rate. Piezometers are installed to keep track of the headloss. They are arranged more densely in the upper part of the sand layer, the spacings between them are 30, 40, 100, 300, and 800 mm. The first one is supposed to be just under the sand surface, the last one is situated in the underdrain pipe. The hydraulic loading rate is outflow controlled. By means of a simple mechanic device, it is possible to keep the flow constant, even though the slow sand filter upstream builds up headloss over time (Figure 14). The flexible inflow tube is pressed against a solid block which limits the flow. In this way the water level in the box is kept constant and so is the filtration rate. The regulation boxes were developed for this project by the consulting engineers. The height of the supernatant water layer is constant as well since exceeding feed water for the filters is discharged into an overflow.

Downstream of the slow sand filter and the regulation box, an activated carbon filter is installed. Since the carbon filter was only used since October 1998, the effects of it will not be discussed in this thesis. Fresh activated carbon is in a pre-loading phase for at least six weeks, giving too high absorption values compared with the realistic performance in the long run.

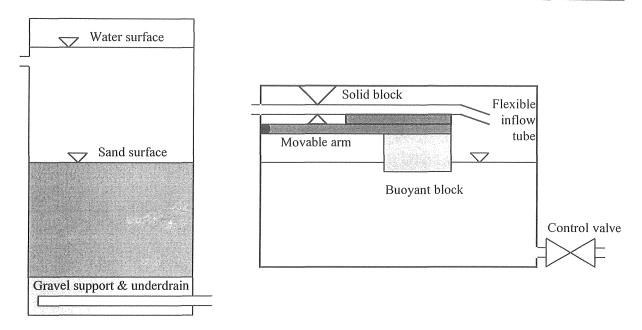
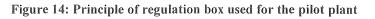


Figure 13: Pilot plant slow sand filter



4.1.1 Operation

The filters started to operate in spring 1998. Filter 1 is a reference filter and supposed to be kept at a low, constant filtration rate. On filters 2 & 3, different filtration rates are applied to investigate the effects thereof on filtrate quality and headloss development. An overview of the filtration rates of the 3 filters is given in Table 7. Due to a misunderstanding, all filters were run on a higher rate than what was planned over summer. In August, the rates were lowered on all filters. From September on, filters 2 & 3 have been run on an increased rate of 0.45 m/h while the reference filter 1 was kept at a low rate.

Time span	reference Filter 1	Filter 2	Filter 3
until 9-Aug	0.4 - 0.42	0.6 - 0.72	0.6 - 0.72
10-Aug until 2-Sep	0.2	0.3	0.3
from 3-Sep	0.2	0.45	0.45
from 20-Oct	0.2	0.35	0.35

 Table 7: Approximate hydraulic loading rates on the slow sand filters [m/h]

Until August 24, the sand surface was scratched with a rake three times a week to decrease headloss and facilitate the flow. From then on, filters were no longer scratched, to see how the headloss develops undisturbed. Finally the headloss became too high, and thus the top 3 cm were removed on October 20. Because of the cleaning, the flow in the filters was interrupted for about a day.

4.1.2 Sampling and analysis

Regular samples were taken on the raw water as well as after each filter, continuously since June 24 1998. The sampling and analysis programme is summarised in Table 8. On site, headloss was monitored three times a week. As long as the sand surface was scratched, the headloss was determined both before and after the procedure. At the waterworks' lab, UV

absorption and the colour value were measured. Samples were sent to a commercial lab for analysis of common chemical parameters, major constituents as well as TOC and microbiological parameters. Samples for BDOC were taken weekly in August and September and frozen until analysis. After the scraping on October 20, no samples were taken for about four weeks.

Parameter	Frequency*	Place**	Method	remarks
Flow	3	S	flow meter	
pH and temperature	3	S	electrode	
Headloss	3	S	piezometers	twice if scratched
Colour	3	WL & CL	НАСН	
UV-absorption 254nm	3	WL & CL	photometer	
Chemical analysis***	3	CL	ICP, IC and various	standard analysis
TOC	3	CL	TOC-analyser	
BDOC	1	0	see chapter 5	10-Aug to 28-Sep
Bacteria	1	CL		

 Table 8: Sampling and analysis programme for the slow sand filters

* times per week ** S = on site, WL = waterworks' lab, CL = commercial lab, O = own measurement

*** comprises: pH, turbidity, conductivity, alkalinity, hardness, smell, colour, COD, NO₃-N, NO₂-N, NH₄-N Ca, Mg, Fe, Mn, Na, K, Al, PO₄-P, F⁻, Cl, SO₄

4.2 Pilot scale biofilters for removal of Fe and Mn

For the treatment of groundwater two pilot plant biofilters were installed. The system comprises the actual bioreactor and subsequent rapid sand filter, see Figure 15. The biofilters consist of plastic pipes of 2.8 m length and 155 mm inner diameter, which are filled with a biofilm carrier media of plastic as shown in Figure 16.

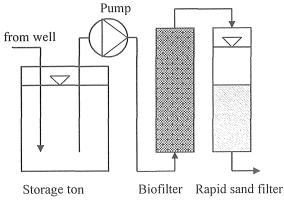


Figure 15: Set-up of pilot plant biofiltration

Figure 16: Photo of biofilm carrier media in size comparison to a Swedish 1Kr coin

The filters have been continuously operating since early February 1998. Until January 1999, both filters had a flow rate of 0,3 l/min, equivalent to 0.95 m/h and a residence time of about 3 hours. The incoming ground water originates from two different wells which were changed once in a while. The water from these boreholes differs in quality concerning iron and manganese contents. The rapid sand filters were backwashed 3 times a week. At the end of week 41/1998, such an amount of sludge had been accumulated that the bioreactors had to be backwashed.

4.2.1 Sampling and analysis

Weekly analysis was done on both filters of pH, influent and effluent, sometimes temperature. Iron and manganese were checked in raw water, after the biofilter and finally after the sand filter. On biofilter 1, the same was done for samples filtered through double paper filters, to retain precipitates and only analyse the dissolved metals. HACH methods were used to quantify iron and manganese in the waterworks' lab. At irregular intervals, samples were given to a commercial lab to double-check the results.

On one occasion in September the redox potential was measured in four different locations of the system, in the raw water pipe, in the storage ton, after the bioreactor and in the outflow of the sand filter.

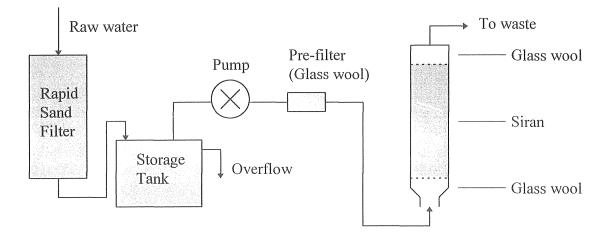
5 Experimental

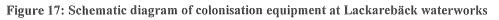
The technique for BDOC analysis described here can be seen as a modification of the Joret and Lévi - method that was explained above. The main difference is that an inert support medium with high a surface area is used instead of sand. The idea was that with the higher surface area of the medium, less material is needed as inoculum compared to sand. This would result in a faster biodegradation and fewer problems with adsorption or desorption of carbon on/from the inoculum.

5.1 Colonisation of Siran

The colonisation of the Siran material was done at Lackarebäck waterworks, Göteborg, using raw water from lake Delsjön. As inert support medium, Siran (Schott, Ref. SIKUG 012/02/300/A) was used. Siran is a sintered porous glass in form of balls with 1-2 mm diameter, 60-70 μ m pore diameter, 55-60% pore volume, bulk density of 0.57 g/cm³ and a surface area of 0.15 m³/g. It was kept in a glass tube (630mm, internal Ø 20mm) with glass wool in the bottom and top of the column, as used in previous studies (Lütkens, 1996). To prevent the inflow of particles, the raw water was passed through a rapid sand filter.

It has been suggested that the Siran was properly colonised with biofilm after a period of 2-3 months (Lütkens, 1996). The equipment with 2 identical columns was set up and started on July 1st, 1998, using a flow of about 8 ml/min per column. After a few weeks of operation it was discovered that the glass wool in the column tended to clog. This resulted in some periods of decreased flow and once the carrier material was driven out of the column by pump pressure. These problems made it necessary to install an easily renewable pre-filter to protect the columns, consisting of a thicker piece of plastic tube filled with glass wool. The final set-up of the equipment is illustrated in Figure 17.





The Siran material that had been used for experiments had to be put back into the columns afterwards to keep the biofilm in good shape. The best method of putting the wet and sticky material back seems to be to wash it into the column with water. To avoid the formation of air bubbles during this process, it is advisable to keep the Siran surface in the tube under water at all times. In that way, Siran balls falling into the column have to pass the water layer prior to settling onto the Siran surface. Several times during the refilling of used carrier material, the tube should be carefully hit with e.g. a screwdriver to compact the filling.

5.2 Set-up of equipment for BDOC experiments

For the analysis of BDOC, a paddle equipment common for flocculation experiments was used, see Figure 18. Glasses were covered with plastic sheets to prevent dust from falling in. The colonised Siran was washed at least 10 times with nanopure water to avoid or at least minimise leakage of carbon. All equipment in contact with water samples or carrier material was cleaned in a laboratory dishing machine and rinsed 3 times with nanopure water. The water in the glasses was stirred in order to maintain a sufficient supply of the biofilm with food, nutrients and oxygen. The paddles were adjusted to an appropriate velocity to avoid the Siran being moved around by the flow.

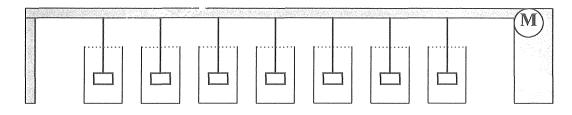


Figure 18: Set-up of equipment for BDOC analysis M = engine

Two sets of initial experiments were run to test the proposed measurement method, and summarised in:

1 st Experiment (August 98)			2 nd Experiment (September 98)			
Glass	Tested water	Siran [g]	Glass	Tested water	Siran [g]	from
1	raw water	0	1	raw water	0	
2	raw water	0.1	2	raw water	10.0	top
3	raw water	1.0	3	raw water	10.0	bottom
4	raw water	10.0	4	synthetic soft	10.0	top
5	nanopure + 10 mg C/l	0.1	5	synthetic soft	10.0	bottom
6	nanopure + 10 mg C/l	1.0	6	raw + 10 mg C/l	10.0	top
7	nanopure + 10 mg C/l	10.0	7	raw + 10 mg C/l	10.0	bottom

Table 9: Summary of BDOC experiments to test the method

During the first experiment, 4 glasses of raw water from Lake Stora Neden (near Varberg), were tested. The water was filtered through 55 mm glass fibre filters (MCG, pore-size $\approx 1 \mu m$, Munktell). Then 0, 0.1, 1, and 10 g (wet weight) of colonised Siran were added to 400 ml of water sample, in order to determine the necessary amount of biofilm. In addition, 3 glassed of nanopure water with 10 mg/l carbon (in form of 25 mg/l Glucose) were tested with 0.1, 1 and 10 g of Siran.

The second experiment comprised 3 glasses with 450 ml of filtered raw water, one without Siran, one with 10 g from the bottom of the column and the third with 10g Siran from the top of the column. Two more glasses contained the same raw water, but spiked with 10 mg C/l (Glucose). One was tested with 10 g of Siran from the bottom, the other one from the top. Finally, 2 glasses applied synthetic soft water (Morrison, 1998). This contains nanopure water and common salts to provide for electrolyte and nutrients. Ten mg/l of carbon were added as well as 10 g of Siran from the bottom/top as above. For the exact composition of synthetic soft water, see Appendix A. Taking the Siran from different places in the column was to investigate if the biofilm at the inflow of the column would be more active than at the top.

5.3 Sampling

Sampling was done directly from the glasses, using a syringe equipped with round 25mm glass-fibre filters (pore-size 1.2 μ m, GF/C, Whatman). Syringe, filter holder and each new filter were carefully rinsed with nanopure water prior to sampling. Then, the equipment was rinsed with the sample water (not 1st experiment) before taking the actual sample of about 20ml. For the first experiment, samples were taken at 0 hours, 1 hour, 5 hours, 1 day, 3 days and about a week. In the second experiment, an additional sample was taken of the 3 different waters before they were poured into the glasses.

5.4 TOC analysis

The analysis of DOC was carried out on a Shimadzu 5000 TOC-analyser, equipped with an autosampler. In the mode used for this study, DOC was calculated from the contents of Total Carbon (TC) and Inorganic Carbon (IC):

DOC= TC-IC

Different calibration curves were used for sample analysis. Samples from the initial experiments were analysed using a common calibration with TC= 15, 5, 1 ppm. For the actual Varberg samples, calibration was done specially for the expected low values of DOC. Three-point calibration was applied with 5, 3, 1 ppm for TC and 4, 2, 0.5 ppm for IC.

5.5 Modifications of the method for the analysis of the Varberg samples

Based on the results of the initial experiments conducted to develop a reliable method for the measurement of BDOC, some modifications were done to the technique.

- The colonised carrier material taken from the columns was now washed 15 times in nanopure water, the last wash water sampled for analysis of DOC.
- 10 g of colonised Siran were added to each water sample.
- The duration of the measurement was decided to be 5 days.
- Filters used for sampling were changed to a smaller pore-size of 0.7 μ m (GF/F).
- Duplicate DOC samples were taken before the water was poured into the glass and just after that (0 hours), in addition to the final duplicate sample after 5 days.
- 360 ml of sample were poured into each glass, which left an amount of 300 ml after taking out 60 ml for the duplicate 0 hour-samples.
- The salts included in the synthetic soft water (except for the sodium bicarbonate) were added to the glass after taking the 0 hour samples. 10 ml of a 30-fold salt concentrate were added to the remaining 300 ml. The mistake introduced by diluting the water sample was taken into account when calculating BDOC.

The 56 samples from the Varberg pilot plant were analysed in 4 series with 14 glasses each. During the first series, the paddles were relatively deep in the water. In contrast to the paddles itself, the axles were not chrome-plated. Development of rust made it necessary to reduce the depths for the second series. For the third and fourth series, the depth was increased again by several mm, and the paddle speed was increased to about 28 rotations per minute.

6 Results and Discussion

6.1 Slow sand filters

6.1.1 Raw water quality

Some important parameters of the raw water from Lake Stora Neden and their seasonal variation are summarised in Table 10. Apart from the low alkalinity and pH, which can be easily adjusted, this excellent quality raw water already complies with the Swedish drinking water standard. Turbidity, conductivity and nutrients are very low and do not show much seasonal variation. The more or less constant temperature throughout the year is due to the intake of lake water at a depth of 20 m.

The microbial quality of the water is excellent, even in summer the standard was fulfilled at all sampling occasions. As could be expected, the bacterial numbers are lower in winter.

Parameter	unit	Jul-Aug	Nov-Dec	Swedish limit	recommended
Temperature	°C	7.4	5.4		an to ta
pH		6.7	6.9	7.5 - 9.0	6 6 E
Turbidity	NTU	0.24	0.32	0.5	
Conductivity	mS/m	7.6	7.6	6 6 6	40
Hardness	°dH **	0.94	0.94	15	an 666 657
Alkalinity	mg/l HCO ₃	8.2	9.0	6 is 6	60
NH ₄ -N	mg/l	0.03	0.03	0.4	0.05
NO ₃ -N	mg/l	< 0.5	< 0.5	5	1
NO ₂ -N	mg/l	0.001	< 0.001	0.005	60 KM 60
PO ₄ -P	mg/l	< 0.01	< 0.01	0.2	
UV-abs. 254 nm	m ⁻¹	5.68	8.64	60 Hill Str.	100 000 CO
Colour	mg/l Pt	6.5	12.9	15	5
COD	mg/l	2.2	3.5	4	2
TOC	mg/l	2.79	3.86	For Edit Link	
DOC*	mg/l	2.33***	···· co co	EI3 60 EN7	100 ED 60
SUVA (UV/TOC)	m ⁻¹ mg ⁻¹	2.04	2.24	4a 65 80	un an
Heterotr. bacteria 2d	1/ml	48	12	100	50 KM 80
Heterotr. bacteria 7d	1/ml	84	63	5000	
Coliforms	1/100 ml	5	3	100	

 Table 10: Selected seasonal characteristics of raw water from Lake Stora Neden (mean values)

 Swedish drinking water limits and recommendations by (Livsmedelsverket, 1993)

* own measurements, see chapter 6.4.2. ** German degrees of hardness *** Aug-Sep

All indicators of natural organic matter show higher contents during November-December compared to the summer. The average TOC is 38 % higher, the COD 59 %. In accordance with the literature, the ratio between UV_{254} -absorption and TOC known as SUVA is higher during the cold season, suggesting a larger proportion of aromatic molecules. This finding is supported by the almost doubled colour value in winter, indicating an increased content of humic substances. There are several naturally occurring factors responsible for this seasonal pattern. More rain and less biological activity in the soil enhance the transport of humic

substances into the lake. Furthermore, the lack of sunlight that could destabilise the large molecules, together with the low water temperature, inhibits their biodegradation in the lake. In fact, the average colour value for November-December clearly exceeds the recommended level and is close to the Swedish drinking water standard. Nevertheless, the content of DOC in natural surface waters (rivers and lakes) usually varies between 2-15 mg/l (Drever, 1997). This raw water is at the lower end of the range.

6.1.2 Headloss

Since the procedure of raking the sand surface was stopped in the end of August, the undisturbed headloss development could be monitored (Figure 19). The first cycle, August-October, produced headloss curves in which the effect of the filtration rate is clearly visible. Both filters 2 & 3, run at 0.45 m/h, built up headloss more rapidly than the reference filter 1 at 0.2 m/h. It seems that filter 1 could have been run much longer when the scraping was done in October. Unfortunately, the length of the first filter run cannot be determined precisely since the beginning of it was disturbed by the raking. The possible length of run seemed to be in excess of 2 months, even for filters 2 & 3. For an overview of the different filtration rates over time, compare Table 7.

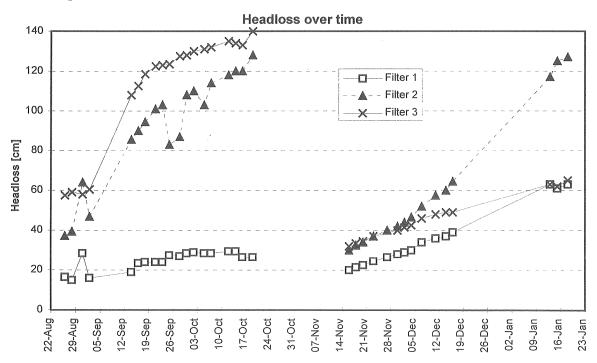
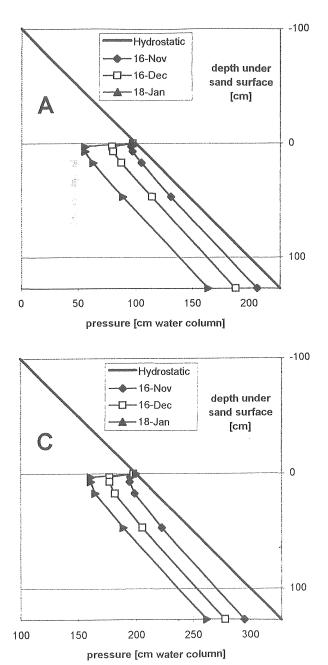


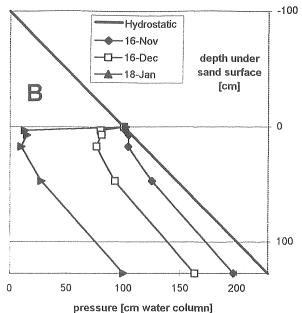
Figure 19: Development of total headloss since the raking was stopped. Scraping was done on October 20.

The second cycle started after the scraping in October, with filtration rates of 0.20 - 0.24 m/h at the reference filter and about 0.35 m/h for filters 2 & 3. In November, the total headloss was again determined by the filtration rate. Then, somewhat unexpected results occurred. In January, filter 3 did not suffer from more headloss than the reference filter 1.

To gain further insight, the headloss development in different depths of the 3 filter beds is compared in Figure 20. Some weeks after the scraping was done, there was no significant headloss from the top of the filter bed (curves for November 16). With time, most of the headloss increase took place at the very top, indicating the development of a *Schmutzdecke* layer. Further down in the filter bed, the pressure curves are almost parallel to the hydrostatic pressure, showing that only little headloss is caused by this part of the filter beds.

On January 18, the filters 1 (diagram A) and 3 (diagram C) had almost the same headloss distribution over the filter beds. The large total headloss of filter 2 is caused by a layer on top of the sand. Furthermore, in filter 2, there seems to be a further increase of headloss between the second and third piezometer, that is 7-17 cm under the sand surface (diagram B).





Legend:

Diagram	Filter	Filtration rate [m/h]
A	1 (reference)	0.20 - 0.24
В	2	about 0.35
С	3	about 0.35

In the diagrams, the headloss in different depths of the filter bed is the difference between the hydrostatic pressure and the pressure measured by the piezometer tubes. The total headloss over the filter is represented by the lowest tube, which is situated within the gravel support.

The sand surface and the surface of the gravel support are indicated by the two horizontal lines.

It should be noted that filters 1 & 2 have 1m of water above the sand, whereas filter 3 has 2m.

Figure 20 A-C: Headloss in different depths of the filter bed, after the scraping on October 20 There are at least 2 possible reasons for the differences in headloss of Filter 2 and 3:

• Maybe the two filters have developed a different biological community. Mass production of certain species in filter 2 could have caused clogging of the sand surface. The absence of higher organisms that otherwise mix the sand and loosen the *Schmutzdecke* could have a similar effect. Already when the first scraping was done in October, the filters obviously had different biological characters. Filters one and two only had a thin green layer on top of the sand, probably algae. In contrast to that, filter 3 had a fully developed *Schmutzdecke*.

• Another possibility is that the flow through the top layer of filter 3 is no longer evenly distributed over the surface. Especially in small filters like these, it is not uncommon to find short-cut flows along the walls. In this case, the *Schmutzdecke* would not exert its full headloss.

The filtration rate is obviously not the only factor determining headloss development, even for slow sand filters receiving the same raw water. However, there is no reason to believe that such a slow build-up of headloss as in filter 3 is common for the filtration rate of 0.35 m/h. For the design of a full-scale slow sand filters, it is safer to consider the faster headloss development of filter 2 to be normal.

6.1.3 General parameters of water quality

In average, the slow sand filters removed raw water turbidity by 50 % (data not shown). The removal efficiency did not depend on the filtration rate. Due to the very clear raw water from Lake Stora Neden, turbidity is no critical parameter for this pilot plant study.

Most common chemical parameters, such as hardness, alkalinity and conductivity as well as the concentrations of major ions like sulphate, remained practically unchanged by slow sand filtration.

As could be expected, the already low ammonium content of the raw water was further reduced in the filters. This is due the natural process of nitrification. Anyhow, effluent nitrate concentrations were always below 0.5 mg/l, which seemed to be the detection limit of the applied method. In summer, there were a few examples of increased nitrite contents after the filters, probably due to incomplete nitrification. On two sampling occasions in early summer, the effluent nitrite concentrations were slightly higher than allowed by the Swedish drinking water standard. After the beginning of July, this problem did not occur again (data not shown). A possible explanation is that the filter bed was not entirely mature in early summer, so that the number of nitrifying bacteria was insufficient.

6.1.4 Parameters of natural organic matter

Apart from the BDOC, four parameters of organic matter have been measured. In the following, the results for TOC, UV_{254} -absorbance, COD and colour are presented.

6.1.4.1 Total Organic Carbon

In summer, the TOC of the raw water was relatively stable between 2.5 and 3 mg/l. A diagram showing raw water and filtrate TOC concentrations over time can be found in Appendix B. For all other diagrams in the following, the TOC results from September 14 and 16 were removed from the data. Around that time, maintenance was done on the raw water pipe upstream from the pilot-plant, which was probably the reason for the extremely high raw water TOC on September 14 (=16 mg/l).

The ratio of effluent to influent TOC (C/C₀) for all three filters is shown in Figure 21. Most of the time, the TOC of the filtrate is around 90 % of the raw water value. Overall, the curves for the three filters are similar. Some single points with very high or low C/C₀ stick out from the average range. Two possible explanations are:

- C/C_o ratios higher than 1.0 indicate a net release of organic carbon from the filter. This is certainly possible, if particles high in organic carbon, e.g. parts of biofilm, get into the filtrate sample by coincidence.
- On the other hand, single errors during analysis can also cause distorted results. For example on November 18, all filters removed about half of the TOC from the water. The reason is a very high result for the raw water TOC. This single high value might be wrong.

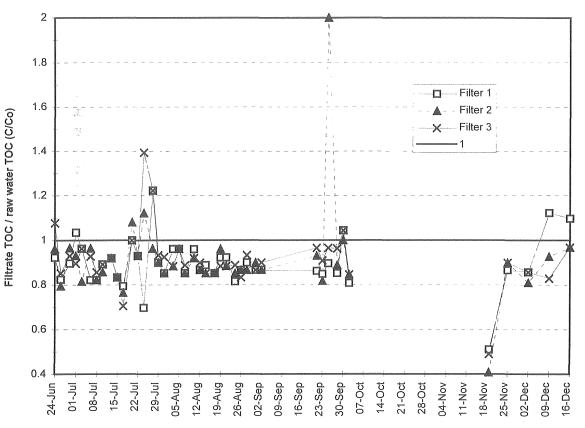


Figure 21: Ratio between filtered water and raw water TOC concentrations (C/C_{o})

滅論

Furthermore it has been investigated which parameters influence the TOC removal of the pilot plant slow sand filters. Figure 22 shows the relation between the percentage of TOC removal and the filtration rate, including data for all three filters. There seems to be a trend towards slightly lower removal efficiency at high rates, but the scattering of the data is substantial. Over the whole range of filtration rates from 0.2 to 0.72 m/h, the average TOC removal only decreases from 11% to 8 %. These values correspond well with those reported in literature, for cold water. Diagrams showing the same relation, for each filter separately, can be found in Appendix C.

The average efficiency for TOC removal is not significantly influenced by the filtration rate. If the biology of the slow sand filters adapts to the filtration rate, it can be presumed that it also adapts to different raw water TOC contents. In that case, the removed amount of organic carbon should be linearly correlated with the carbon load on the filter. In Figure 23, the TOC load has been calculated by multiplication of raw water TOC, filtration rate, filter bed area and hours per day. For TOC removal, it can be said that the filters seem to adapt to a high filtration rate, rather than being negatively affected by it. Similar diagrams, separately for each filter, can be found in Appendix D.

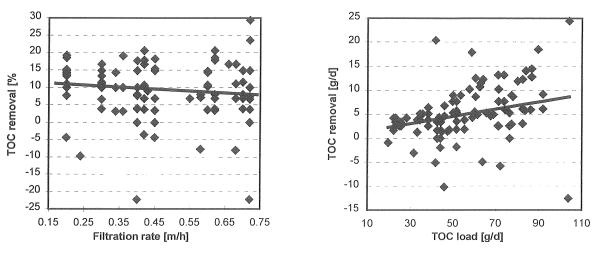


Figure 22: TOC removal in all slow sand filters versus filtration rate

Figure 23: TOC removal versus TOC load. (A few values far out in the + or - not visible)

The seasonal differences in raw water temperature are small. They do not have any noticeable effect on TOC removal (data not shown).

6.1.4.2 UV-absorbance at 254 nm

The ratio between raw water and filtrate UV_{254} -absorbance is presented in Figure 24. Until August, the UV-absorbance of the filtrate is around 90 % of the raw water value. From then on, the average removal is slightly better. In contrast to the parameter of TOC, UV-absorbance is consistently removed from the raw water. Not a single measurement indicates an increase of the organic matter content during slow sand filtration. In this study, the UV-absorbance in raw and filtrate waters is a very stable parameter, without any extreme values as experienced for the TOC. This can be also seen in the diagram showing raw water and filtrate UV-absorbance, in absolute numbers (Appendix B).

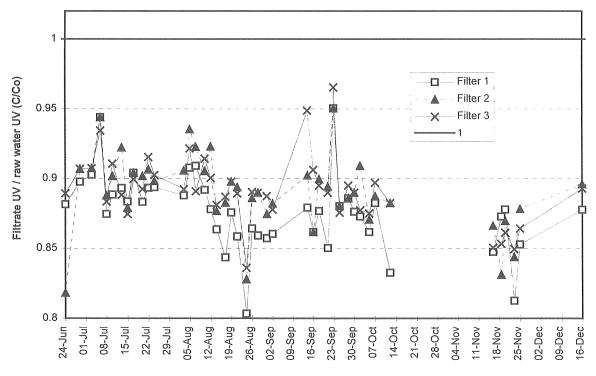


Figure 24: Ratio between filtered water and raw water UV-absorbance

The influence of the filtration rate on UV-absorbance is shown in Figure 25. A trend to lower removal efficiency with high filtration rates can be identified. In average, the filters remove 13 % at 0.2 m/h, but only 8 % at 0.72 m/h. Diagrams showing this data for each filter separately are found in Appendix E.

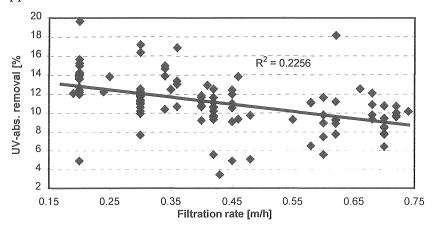


Figure 25: Removal of UV-absorbance in all three slow sand filters versus filtration rate

6.1.4.3 Absorption of visible light at 400 nm (Colour)

In winter, as mentioned above, the colour value of the raw water is relatively high. The curves for raw water and filtrate colour over time can be found in Appendix B.

Colour is, with a few exceptions, consistently reduced by the filters (Figure 26). The scattering of the colour data is more pronounced, compared to the parameter of UV-absorbance.

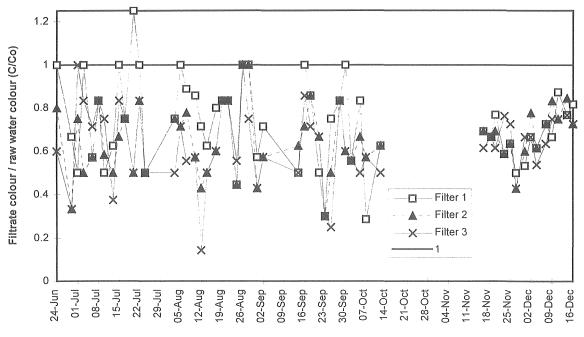


Figure 26: Ratio between filtered and raw water colour value

In contrast to the other two organic parameters discussed above, the removal of colour does not seem to depend at all on the filtration rate. The data for this relation is totally scattered (Appendix F). Unfortunately, the efficiency of colour removal does not seem to increase with

high raw water concentrations. Thus, with the high concentration of humic substances in winter, colour values in filtered water of up to 14 mg Pt/l were measured. This is more than recommended (5 mg Pt/l), and comes close to the drinking water standard (15 mg Pt/l).

6.1.4.4 Chemical Oxygen Demand

The ratio of filtered water COD to raw water COD is shown in Figure 27. The bulk of the measurements indicate a C/C_o between 60 and 100 %. At a couple of occasions, the COD in the filtered water sample was higher than in the raw water. Several times, the Swedish limit of 4 mg/l is violated by the filtrate (see the curves of COD over time in Appendix B). The recommended value of 2 mg/l is exceeded most of the time.

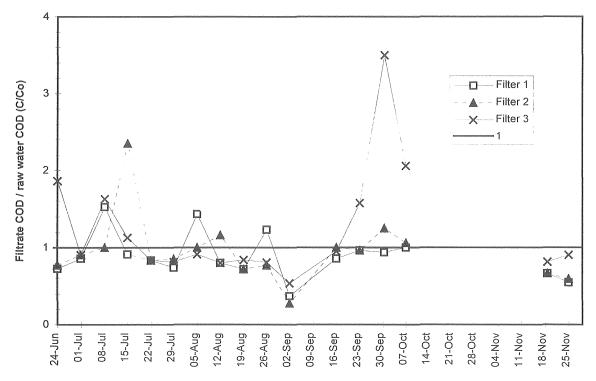
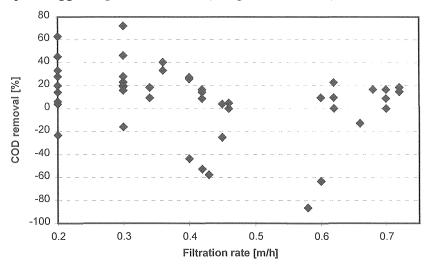


Figure 27: Ratio between filtered and raw water COD

The percentage of COD removal seems to be higher for low filtration rates (Figure 28), at least if the samples suggesting a net increase (=negative removal) are not taken into account.





6.1.4.5 Comparison of the four parameters of organic matter

The results of the four available parameters show some differences in character. Most obvious is the different scattering of the analysis data. Table 11 compares the Coefficient of Variation, which is defined as Standard Deviation divided by mean. The period of July-September was chosen to avoid interference from the seasonal changes in raw water composition.

 Table 11: Organic parameters of raw water - Coefficient of Variation (CV) for July-September

TOC	UV-absorption	Colour	COD	
8.8 %	3.4 %	31.7 %	40.3 %	

The most stable parameter is UV-absorbance, while the COD is very variable. Since the quantity and composition of organic matter in this raw water probably does not change that much over short periods of time, it can be deduced that especially the COD measurement had a poor precision. It has been investigated if there are correlations between the four parameters. Figure 29 shows the scatter-plot for UV-absorbance and TOC in the raw water. It is hard to say if they are correlated, since the bulk of the measurements is concentrated in a cluster, without much variation in both parameters. Figure 30 shows a similar representation of COD and TOC values. Apart from the single very high COD value, there is some trend to higher COD with increasing TOC.

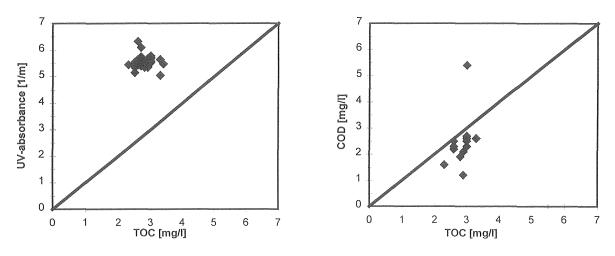


Figure 29: Scatter-plot for UV-absorbance and TOC in the raw water (July-Sep)

Figure 30 Scatter-plot for COD and TOC in the raw water.

The degree to which the pilot plant filters remove TOC, UV-absorption and colour, is presented in Table 12. The average removals agree well with results reported from other studies (compare section 3.3.4). According to the averaged results, COD is practically not removed in summer. Considering the data for the other three parameters, this is probably not true. The calculated average COD removal may be strongly influenced by some wrong, very high COD results. The meaningfulness of the COD data is thus questionable in this study. In contrast to what has been suggested in literature, the efficiency of organics removal of the Varberg slow sand filters is not lower in winter. The almost constant raw water temperature throughout the year provides an explanation for this.

Table 12: Seasonal variation in removal of parameters of organic matter (all three filters)

	TOC	UV	Colour	COD
Jul-Sep	9 %	11 %	32 %	-4 %
Nov-Dec	9%	13 %	36 %	30 %

In winter, the organics load of the raw water is considerable. Time will reveal if the activated carbon filters, situated after the sand filters, can ensure compliance with the standard. This will only be possible to decide in the long run, after the initial pre-loading phase of the GAC. If COD and colour values of the treated water are found to exceed the limits even with GAC filtration, the treatment has to be an extended. The obvious solution would be to ozonate the water prior to filtration. The filtration treatment would then be:

$\mathbf{Ozonation} \rightarrow \mathbf{Slow} \ \mathbf{sand} \ \mathbf{filtration} \rightarrow \mathbf{Granular} \ \mathbf{Activated} \ \mathbf{Carbon} \ \mathbf{filtration}$

It would be sufficient to run the ozonation facility only during the winter, to break down the humic substances which are responsible for the high colour values.

6.1.5 Microbial parameters

In summer and early autumn, heterotrophic bacteria which form colonies after 2 days of incubation were effectively removed, see Figure 31. After the scraping of the filters in October, the few available measurements indicate a massive growth of such microorganisms in the filters. In the effluent of reference filter 1, up to 260 of those 2-day heterotrophs per ml were recorded, which is violating the Swedish drinking water standard.

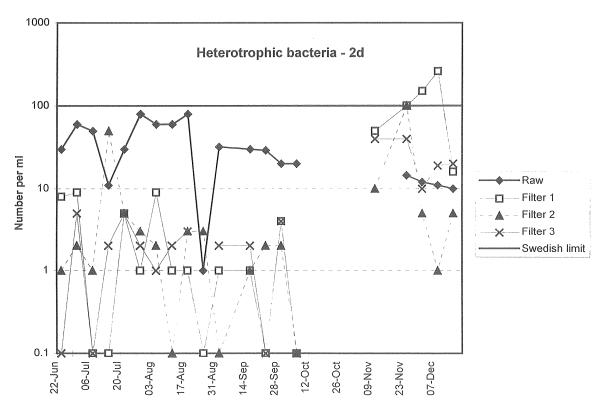


Figure 31: Concentration of heterotrophic bacteria after 2 days of incubation. The number of 0.1 in the logarithmic scale denotes occasions when statistically less than 1 bacterium per 100 ml was found.

Figure 32 shows the ratio of effluent to influent 2-day heterotrophs (C/C₀). The net growth in winter, especially in reference filter 1, is clearly visible in the diagram. The solid line of $C/C_0 = 1$ denotes the limit between removal and net growth of bacteria.

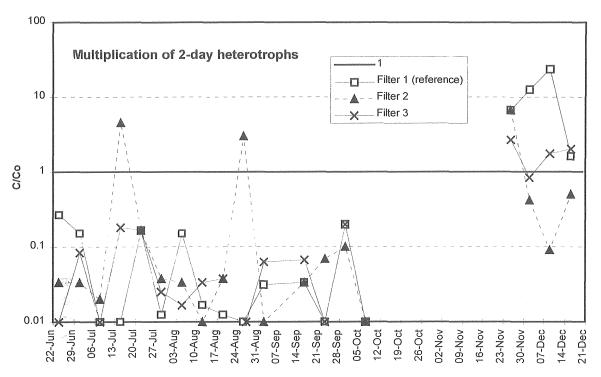
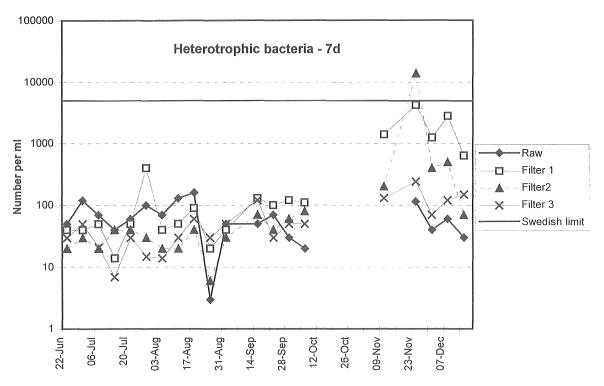


Figure 32: Multiplication factor (C/C₀) of 2-day heterotrophs

The data for 7-day-heterotrophic bacteria show similar patterns (Figure 33). Here, the removal efficiency was lower from the beginning, and already in autumn a net formation of bacteria took place. Filter 2 exceeded the standard when 13900 organisms per ml were measured. The ratio of effluent to influent 7-day heterotrophs (C/C_0) over time is shown in Figure 34.





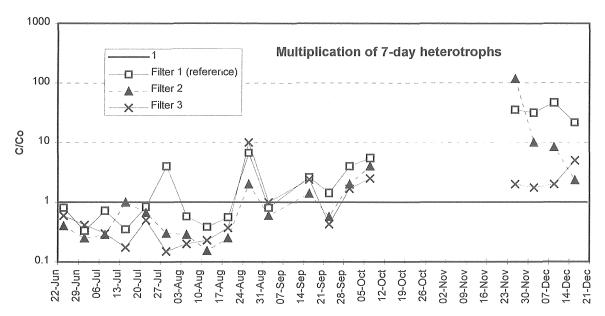


Figure 34: Multiplication factor (C/C₀) of 7-day heterotrophs (in logarithmic scale)

The highest measured effluent number of coliform bacteria was 2 per 100 ml, which does not even come close to the limit of 100 (see Appendix G). The species E.coli, which is not permitted in drinking water at all, was not found in any sample of the filtrate.

It is known that bacteria are washed out from slow sand filters. Their number is, however, expected to be small under normal circumstances. The above findings show that the bacterial water quality may actually be worse after a slow sand filter. Possibly the lower temperatures in winter inhibit the growth of bacteria-eating species such as protozoa which otherwise consume the bacteria that multiply in the upper part of the filter bed. The observed growth of heterotrophs does not present a major health risk, especially not at water temperatures of about 5°C. Pathogenic bacteria grow better at higher temperatures, closer to the human body temperature of 37°C. Anyhow, to ensure compliance with the standard, the water has to be disinfected before delivering it to the consumers.

6.2 Biofilters

The results of the investigation of iron and manganese removal are presented in the following. Unfortunately, the effects of a higher filtration rate could not be studied yet. The two filters have been run at the same, constant rate so far. As the filters tend to behave similarly, most results are just shown for one of them. Some results for the other filter can be found in the Appendix.

6.2.1 Iron removal

When the measurements began in week 10, the iron removal of the filters was already fully developed (Figure 35. For results for Filter 1, see Appendix H). Thus the start-up phase has been less than 4 weeks. Throughout the year, iron has been removed down to trace amounts. Until week 35, the concentration leaving the bioreactor closely followed the raw water iron content. From then on, at times very high concentrations were found in samples after the biofilter. This is most probably caused by the accumulation of iron sludge in the reactor. Even the backwashing of the reactor in October did not end the shedding of iron. The backwashing procedure was probably not effective enough to remove all the precipitate, as the tubing for

backwash water apparently had a too small diameter. It might be a good idea to regularly backwash the reactor, in order to avoid such large accumulations of sludge.

The analysis of 0.45 μ m-filtered samples indicate that in all cases, the iron occurs as particles. Almost no iron is in dissolved form (data not shown). The reason might be a chemical oxidation taking place already in the storage ton, since even the raw water samples do not seem to contain soluble iron.

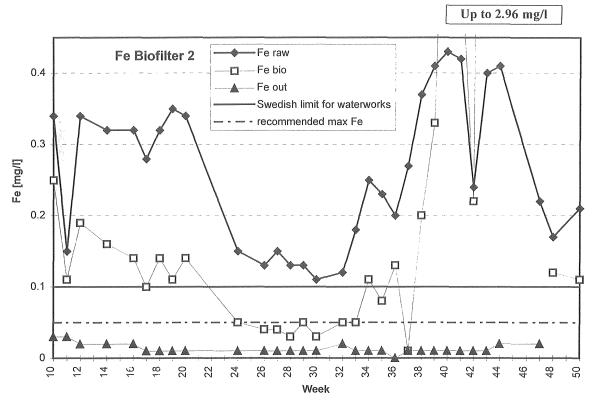
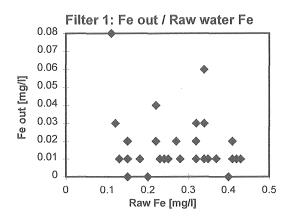
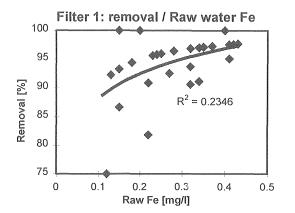


Figure 35: Iron concentrations for filter 2 - influent, after the bioreactor and effluent (unfiltered samples) The possible influence of different parameters on iron removal was investigated. Varying temperatures during the study did not seem to affect the removal. The percentage of removal over time is shown in Appendix H, as well as its relation to temperature.

The effluent concentration does not depend on the raw water concentration (Figure 36). Thus, logically, the percentage of removal is increasing with the influent concentration (Figure 37).









6.2.2 Manganese removal

Filter operation started in week 6. The start-up phase for manganese removal seems to be completed in week 18, when the effluent concentration reaches a plateau (Figure 38, for results of filter 2, see Appendix I). The seeding time of 12 weeks exceeds the 2-8 weeks reported from France (Mouchet, 1992). The low water temperatures during start-up may explain the difference. In Figure 39, the seeding time is clearly visible as well because of the low removal efficiencies. After week 18, the effluent concentration consistently complies with the drinking water standard and the recommendations.

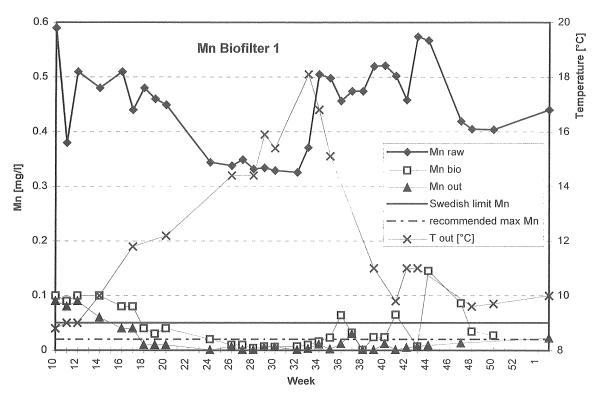


Figure 38: Mn concentrations for filter 1 - influent, after the bioreactor and effluent (unfiltered samples)

After the backwashing attempt, increased amounts of manganese are leaving the reactor. However, the effect is not as pronounced as for the iron described above. Analysis of the filtered samples revealed that most of the manganese in the raw water is soluble. After the bioreactor, the remaining manganese has strongly varying proportions of dissolved and particulate forms (data not shown).

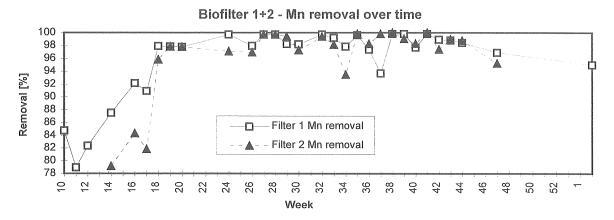


Figure 39: Development of manganese removal over time for both biofilters

For the calculation of possible correlations of the biofilters' performance with other parameters, results obtained during the seeding time are excluded to avoid interference from this factor. Removal efficiency is close to 100 % which makes it difficult to identify any external influences. Therefore there is no apparent correlation between the manganese removal efficiency and water temperature (See Appendix I). Possibly there is a slight trend of increasing effluent concentrations with higher contents in the raw water, although the scattering of the data is considerable (also Appendix I).

6.2.3 Redox and pH environment of the bioreactors

The results of my own redox measurements have been inserted into the Eh / pH diagram published by (Mouchet, 1992). In Figure 40, crosses denote the pH and redox position of the raw water from Ragnhilds Källa, both in the influent pipe coming from the well, and in the storage tank. The small arrow specifies the redox range of the effluents from both bioreactors, and both rapid sand filters. For a general description of the underlying diagram, consult Figure 8.

According to the measurements, the redox potential in the raw water pipe (+ 143 mV to standard hydrogen, as a mean of 3 measurements) is not very low and the iron should almost not be soluble under such conditions. In the storage tank, the redox potential is about 100 mV higher (+ 254 mV as mean of 3), and the iron is definitely precipitated. This finding is confirmed by the observed brown precipitate on the storage tank walls and the fact that no soluble iron has ever been detected during raw water analysis.

The environmental conditions are clearly not favourable for biological iron removal. The redox potential after raw water storage is already too high. Anyhow, chemical oxidation is dominant over biological oxidation at pH values over 7.5, as illustrated in Figure 7. After the bioreactor, and also after the rapid sand filters, the measured redox potentials were in the range of +394 - 419 mV. This is supposed to be a good environment for manganese bacteria and explains the excellent Mn removal.

The observed good removal of iron is most probably due to the increased oxygen content in the storage tank, leading to chemical oxidation. The long retention time of currently three hours, equivalent to a filtration rate of only 0.95 m/h, is unrealistic to have in a large-scale plant. The forthcoming experimental increase of filtration rate will show if sufficient iron removal can be maintained. It has been pointed out in the literature that chemical iron precipitates have a much higher tendency to clog filters than biologically oxidised iron oxides. Thus, even if the effluent iron concentrations comply with the recommendations, the chemical character of oxidation might cause unnecessarily short runs of the rapid sand filters. In a full-scale facility, the backwashing frequency is an important factor because of the labour cost implied.

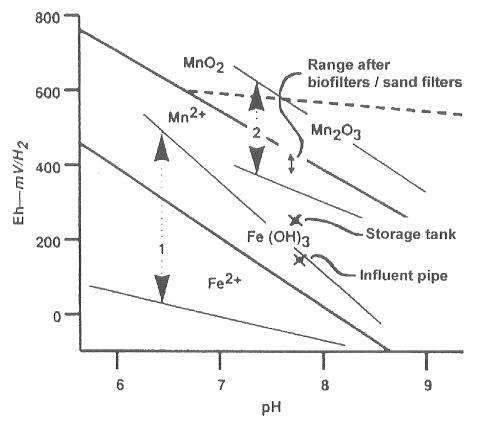


Figure 40: Measured Redox and pH values and their relation to the chart published by (Mouchet, 1992)1 – field of bacterial iron oxidation2 – field of bacterial manganese oxidation

An alternative would be a more advanced plant with controlled aeration and possibly pH adjustment. To optimise both biological iron and manganese removal, the use of 2 separate bioreactors with different environmental conditions is advisable. Another advantage is that with such technology, the process can be influenced and it is possible to react to e.g. changes in raw water character.

On the other hand, simplicity is an immense advantage for such a facility. If the pilot plant study reveals acceptable performance even at higher filtration rates, the current simple technology may be used for the full-scale facility as well.

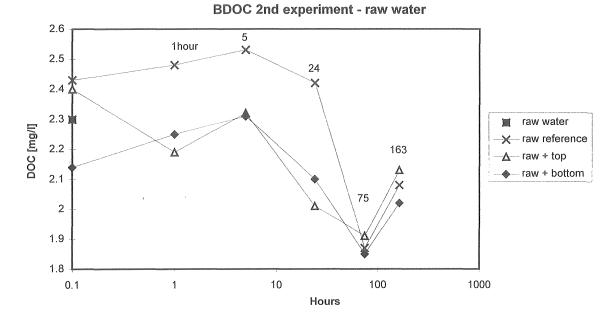
6.3 BDOC - Experiments and Measurements

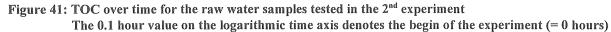
6.3.1 Experiments to test the method

The data obtained from the first experiment were not particularly promising. For the 4 raw water samples with different amounts of colonised Siran, no falling or rising trend of DOC was visible over time (data not shown). Values lie within the range of 2.2 and 2.75 mg/l and suggest that the sum of possible mistakes due to contamination or dilution was too high.

For the 3 glasses with nanopure and glucose, all values were closely around the initial 10 mg/l, even after a week of incubation (data not shown). Probably the absence of nutrients prevented the breakdown of organic carbon. The high accuracy and precision achieved for the blank and standard samples analysed during the TOC analysis indicated that the TOC machine was correctly calibrated and operated well.

The data for the 2nd experiment is shown in the following. When looking at these diagrams, one should consider the inherent variability in any TOC measurement which can be estimated to be at least 2%, rather more (Axén, 1998). Comprehensive results of the 2nd experiment can be found in Appendix J.



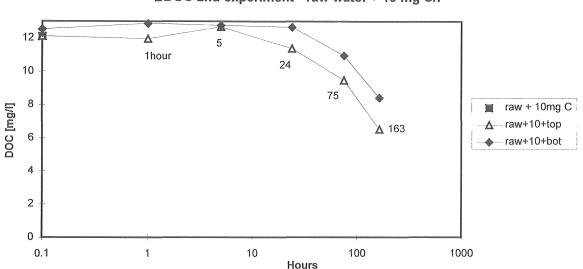


The single measurement called "raw water" is a sample that was taken before the water was put into any of the glasses. It could have been expected that the raw water used in the different glasses should have the same TOC content. Although this is roughly true, the raw water with Siran from the bottom starts somewhat lower than the others. The slight increase in one of the curves with Siran could possibly indicate some leakage of carbon from the biofilm, which should be kept in mind for the following diagrams. Until 5 hours, the curves show different patterns, but the overall level remains about the same.

From then on, there is clear falling trend for all the curves, even the one without any biofilm added. Probably, bacteria that passed the filtration are responsible for the removal of organic carbon. A minimum concentration was reached with the 75 hours measurement.

From 75 to 163 hours, a time span of about 4 days, all DOC concentrations increase by about 10%. This could be due to leakage of organic material from the biofilm.

With 10 mg/l of easily biodegradable carbon (as 25 mg/l glucose) added to the raw water, the initial DOC was about 12 mg/l, as could be expected. The data is shown in Figure 42. For the two glasses, with Siran from the top or bottom of the column, the DOC decreased within a week to 6.5 and 8.4 mg/l, respectively.

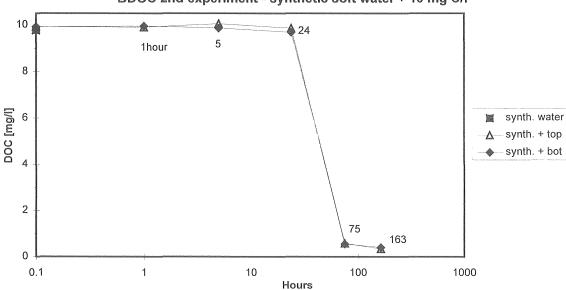


BDOC 2nd experiment - raw water + 10 mg C/I

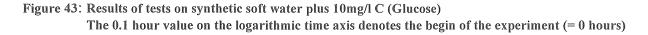
Figure 42: Results of tests on raw water plus 10mg/l C (Glucose) The 0.1 hour value on the logarithmic time axis denotes the begin of the experiment (= 0 hours)

In contrast to the raw water that was spiked with glucose, the DOC of the 2 glasses with synthetic soft water plus glucose practically decreased to zero within three days (Figure 43). Both glasses, with Siran from the bottom and the top, produced identical curves. The origin of Siran from the column does not seem to have any significance for the result of BDOC measurements.

Probably, bacterial growth in the glucose-spiked raw water is not primarily limited by carbon. The availability of nutrients might be an important factor. However, if this is also true for the raw water sample with its low carbon content, remains unknown so far. Nevertheless, the possible deficiency of nutrients in the Varberg raw water was the reason for adding the salt and nutrient mix of the synthetic soft water to all Varberg samples.



BDOC 2nd experiment - synthetic soft water + 10 mg C/I



6.3.2 BDOC of Varberg samples

The summarised results of the BDOC measurements on the Varberg samples are presented in Table 13.

A number of additional measurements was done to identify and avoid possible sources of error:

- All runs of the TOC-analyser showed acceptable accuracy and precision for the total carbon (TC) standards and the nanopure water blanks. There were no problems with the machine.
- The 15th wash-water did not contain any detectable amounts of carbon, so that it can be assumed that 15 washes of the Siran is enough to minimise carbon leakage.
- A number of filter blanks from the GF/F filters were taken and gave roughly the same values as nanopure water. The filters do not seem to be a source of contamination.
- The salt concentrate, kept in the refrigerator, was sampled after the 2nd series and contained a small amount of carbon. As only 10 ml of the concentrate are added to 300 ml of sample, the detected 0.3 mg/l were insignificant. In addition, its content of PO₄ was checked after the 3rd series and turned out to be exactly the amount that has been weighed in. Anyhow, to be on the safe side, the nutrient salt mix was renewed for series 4.

Date	Raw A	Raw B	Filter 1 A	Filt. 1 B	Filt. 2 A	Filt. 2 B	Filt. 3 A	Filt. 3 B
10-Aug	0.71	0.14	0.22	-0.01	0.47	0.01	0.56	0.03
17-Aug	0.56	0.15	0.42	0.02	0.45	0.05	0.66	0.10
24-Aug	0.82	0.02	0.25	0.00	0.68	0.11	0.31	0.08
31-Aug	1.00	0.05	0.30	0.05	0.01	0.08	0.30	0.13
07-Sept	0.15	0.23	0.03	-0.08	0.14	0.12	0.04	0.06
21-Sept	0.20	0.08	0.09	0.03	0.10	-0.04	0.19	-0.03
28-Sept	0.17	0.13	0.09	-0.06	0.01	-0.02	0.11	0.07

 Table 13: BDOC of Varberg samples as mg/l. Duplicate samples (A and B)

It is obvious in Table 13 that the first set of 14 glasses, series 1 which is printed with grey shading, produced much higher BDOC values than series 2-4. The duplicate samples, for example raw A and raw B, should have at least similar values. To try and find out the reason for this phenomenon, factors that might be responsible are compared in Table 14.

	e i i	C (1 C	• •	
Table 14: Comparison	of parameters	for the four	· series of measuremen	ts

Series	Salt mix	Siran	Paddling	ΔIC (St.Dev)	[mg/l]	Rust
1	fresh	from column	high	0.37	(0.10)	more or less in all glasses
2	1 week	used	low	0.10	(0.07)	no rust
3	2 weeks	from column	high	0.07	(0.07)	no rust
4	fresh	used	high	0.11	(0.11)	no rust

The differences in freshness of neither the colonised Siran nor the salt concentrate could explain the high BDOC results of series 1. There are only two factors which occur in series 1, but not in the others:

- a large increase in Inorganic Carbon (Δ IC) during the 5-day period and
- the presence of rust from the corroding axles

Contact with the atmosphere can cause an uptake of CO_2 during the 5 days of stirring, resulting in an increase of inorganic carbon until equilibrium conditions. However, the uptake of CO_2 from the air does not seem to be that relevant. Even the 3 glasses of nanopure water from the first experiment showed IC increases of 0.00, 0.03 and 0.28 mg/l after one whole week of being stirred. Since nanopure water basically does not contain any inorganic carbon, it had been expected that these samples would be eager to take up CO_2 from the air.

Another characteristic of the 3 nanopure water samples from the first experiment was that their BDOC was practically zero, probably because of the mentioned nutrient deficiency.

Therefore, another possible explanation for the observed differences in ΔIC is that mineralisation of organic matter causes an increase in Inorganic Carbon from within the water sample, by CO₂ production. A large ΔIC would then correspond to a higher BDOC in the water sample. The results of the second experiment have been investigated for a possible correlation, see Figure 44. All the seven samples were exposed to the air for the same time and stirred with the same velocity. The 2 samples with very high BDOC indeed have the largest increase in IC, although there is no clear linear correlation between both parameters. Especially remarkable is that most of this IC increase takes place between 24 and 75 hours of the incubation, which corresponds to the main decrease of organic carbon in the samples (compare Figure 43). This observation could indicate that the high BDOC results of the series 1 Varberg samples, with their clearly higher ΔIC , really stand for biodegradation of more organic matter.

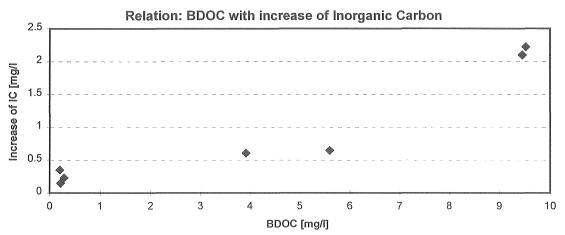


Figure 44: Relation of BDOC to the measured increase in Inorganic Carbon (IC) during incubation

The other factor, according to Table 14, is the presence of rust from the corroding axles in series 1, producing brown flocs more or less intensively covering the Siran after 5 days. Possible effects of the rust that decrease the DOC contents in the glass might be:

- a positive influence of the rust on biodegradation
- adsorption of some organic molecules to the rust, without being biodegraded
- complexes between dissolved iron and organics that were retained on the GF/F filter while sampling

As mentioned in the scientific background section, the presence of iron oxides can speed up the adsorption and subsequent degradation of organic matter (compare section 3.4.3). There is the possibility that the series 1 results show the real level of BDOC in the water samples, and that the biodegradation in the later measurements was inhibited in some way. Maybe the

added amount of colonised Siran - 10 g - is not enough to support sufficiently quick biodegradation without any iron oxides around.

Since none of the two datasets in Table 13 can be discarded for obvious errors, and since they are too different to average them, the results from series 1 and series 2-4 are discussed separately in the following.

6.3.2.1 Series 2-4

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The BDOC results of series 2-4 are indeed very low. As pointed out in the literature study above, the lower limit of applicability for DOC-based methods is about 0.2 mg/l BDOC. It is noticeable that the two injections from the same vial in the TOC-analyser are approved if their coefficient of variation is under 2%. That means that at a total carbon (TC) level of 3.2 mg/l, common in these measurements, two injections easily vary by 0.128 mg/l, without a third injection being started. Until the water sample is analysed in the TOC machine, it is subjected to many handling operations which bring it into contact with a number of containers, beakers etc. All of these may contribute to the error by contamination. If then the differences between initial and final DOC values are as minute as here, the BDOC results are very susceptible to mistake.

In this respect, the results displayed in Table 13 are not trustworthy as such. The standard deviations are high, negative values occur, and the filtered water BDOC is not always lower than the raw water. In principle this applies also for the mean of the duplicate samples presented in Table 15. However, the mean values for raw and filtered waters in the bottom of this table do have some more significance. It can be seen that the average content of BDOC in raw water is higher than after the slow sand filters. In addition, the reference filter 1, run at a lower rate, produces water with a lower mean BDOC than the other filters do.

Date	Raw	Filter 1	Filter 2	Filter 3
10-Aug	0.14	0.00	0.11	0.03
17-Aug	0.15	0.02	0.05	0.10
24-Aug	0.02	0.00	0.11	0.08
31-Aug	0.05	0.05	0.04	0.22
07-Sept	0.19	0.01	0.13	0.05
21-Sept	0.14	0.06	0.05	0.09
28-Sept	0.15	0.05	0.01	0.09
mean	0.12	0.03	0.07	0.09
Std. Dev.	0.06	0.02	0.04	0.06

Table 15. Moon RDOC	volues from sories 7-A	Nonativo values were	orar se habrenar i	for this calculation
Table 15: Mean BDOC	values nom series 2-4.	a regative values were	i i i gai ucu as zeio	ior this calculation

The mean initial DOC in raw water from Stora Neden was 2.33 mg/l. Thus, the ratio BDOC/DOC is 5.2% for the raw water, which is several times lower than the ratios for surface waters reported in the literature, compare Table 1 and Figure 5.

According to the values in Table 15, the water from Lake Stora Neden is already biologically stable (BDOC < 0.15 mg/l). This is very improbable. A thick layer of biofilm was found on the walls of the main raw water pipe coming from the lake, when it recently had to be opened for repairs.

6.3.2.2 Series 1

According to the results of the first series, BDOC in raw water is clearly higher than in filtered water (Table 16).

Date	Raw	Filter 1	Filter 2	Filter 3
10-Aug	0.71	0.22	0.47	0.56
17-Aug	0.56	0.42	0.45	0.66
24-Aug	0.82	0.25	0.68	0.31
31-Aug	1.00	0.30		
mean	0.77	0.29	0.53	0.51
Std. Dev.	0.16	0.08	0.11	0.15

Table 16: BDOC results of series 1 [mg/l]

A student-t-test was done to determine if the BDOC values for raw and filtered waters are really different from a statistical point of view. In spite of the few available values to compare, it was shown that each filter produced a water with a lower BDOC than the raw water, at an $\alpha = 0.1$ level of significance. Additionally the reference filter decreased the BDOC more than the other filters which were run at a higher filtration rate, at the same level of significance. For details about the statistics, see Appendix K

If the mean value of 0.77 mg/l for raw water is taken for real, the ratio BDOC/DOC becomes 33 %. This agrees well with the levels reported for natural surface waters, compare Table 1 and Figure 5.

7 Conclusions

7.1 Slow sand filters

The following conclusions can be drawn, so far, from the pilot plant study at Varberg waterworks:

- Slow sand filtration was found to be a suitable treatment method for water from Lake Stora Neden. This is due to the excellent quality of the raw water.
- The only critical parameters that may at times not comply with the Swedish standards are Chemical Oxygen Demand (COD), colour and content of heterotrophic bacteria.
- The results of the COD measurements, indicating some violations of the drinking water standard in filtered water, should be regarded with suspicion. To be able to identify errors, the COD analysis, performed by a commercial lab, should rather be done in triplicates.
- In accordance with the literature, the removal of organic bulk parameters by slow sand filtration is relatively poor.
- If the combination of slow sand filtration with Granular Activated Carbon filtration does not sufficiently reduce the colour and COD values in the long run, pre-ozonation should be considered during the cold season. If necessary, this option can be installed even after the construction of the full-scale slow sand filters. In that case, the typically faster headloss development of filters receiving ozonated water should be considered in the design, by choosing a more conservative filtration rate.
- High filtration rates seemed to cause deterioration of treatment efficiency for several parameters related to organic matter, such as TOC, UV_{254} -absorbance and COD. This trend is however very slight, so that the effects thereof are not dramatic.
- Headloss development turned out to be relatively unpredictable. However, there is some evidence for a faster build-up of headloss at higher filtration rates. With a high filtration rate of 0.35 m/h, filters obviously can be run for around 3 months between cleaning procedures. Filtration rates around 0.2 m/h promise even longer filter runs.
- Contents of Biodegradable Dissolved Organic Carbon (BDOC) in the raw water are either very low around 0.1, or more probably, around 0.8 mg/l. Biodegradable Organic Matter was removed to a significantly higher extent at lower filtration rates.

Considering the above findings, design filtration rates between 0.2 and 0.35 m/h are possible, without compromising filtrate quality or operational feasibility.

7.2 Biofilters for removal of iron and manganese

- Under the present conditions with a very long retention time, the biofilters show excellent iron and manganese removal. The effluent concentrations consistently comply with the Swedish standard as well as the recommendations.
- The pH and redox conditions in the biofilters seem to be optimal for biological manganese removal, and therefore not optimal for biological iron precipitation.
- If the pilot facility does not support sufficiently high filtration rates, a technologically more advanced solution with two separate bioreactors, controlled aeration and pH adjustment should be considered.

8 Recommendations for further studies

The suggested Siran batch method for measuring BDOC needs to be developed properly. Questions which have to be addressed comprise:

- How long time does it take to colonise a column of Siran with a biofilm ? If the duration of 5 days, suggested by some authors, is enough, the preparation for such BDOC measurements would be much simpler.
- How does the amount of colonised Siran, that is added to the water sample, influence the BDOC result ? Are 10g in 300 ml of sample really enough, and what is the ideal amount ?
- Are 5 days of incubation sufficient for BDOC analysis with the investigated method ? How long should the duration of the measurement be ?
- Finally it should be investigated how iron oxides influence biodegradation. Do they only remove organic matter from the sample by adsorption, or is the mineralisation really enhanced, as suggested in the literature. If the latter is true, additions of iron oxides could possibly even be used to speed up BDOC measurements.

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10 References

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- (1) Axén E., 1998: Personal communication, Chalmers University of Technology, Sanitary Engineering
- (2) Bauer M.J. et al., 1996: GAC enhanced slow sand filtration (GAC Sandwich[™]), in: Graham N., Collins R., (editors): Advances in slow sand and alternative biological filtration, Wiley, Chicester
- (3) Brink D.R., Parks S., 1996: *Update on slow sand/advanced biological filtration research*, in: Graham N., Collins R., (editors): Advances in slow sand and alternative biological filtration, Wiley, Chicester
- (4) Claesby J.L., 1991: Source water quality and pretreatment options for slow sand filters, in: Logsdon G.S. (editor): Slow sand filtration, American society of civil engineers, New York
- (5) Collins M.R. et al, 1994: *Removal of natural organic matter by slow sand filtration*, in: Collins M.R., Graham N.J.D. (editors): Slow sand filtration *An international compilation of recent scientific and operational developments*, American Water Works Association, Denver
- (6) Drever J.I., 1997: *The geochemistry of natural waters*, 3rd ed., Prentice-Hall, Upper Saddle River
- (7) Dussert B.W. & Tramposch W.G., 1996: *Impact of support media and properties on the biological treatment of drinking water*, in: Graham N., Collins R., (editors): Advances in slow sand and alternative biological filtration, Wiley, Chicester
- (8) Eaton A., 1995: *Measuring UV-absorbing organics: A standard method*, Journal of the American Waterworks Association (AWWA), Vol. 87, No. 2, pp. 86-90
- (9) Eighmy T.T. et al., 1994: Microbial activity in slow sand filters, in: Collins M.R., Graham N.J.D.
 (editors): Slow sand filtration An international compilation of recent scientific and operational developments, American Water Works Association, Denver
- (10) Frias J., Ribas F., Lucena F., 1992: A method for the measurement of biodegradable organic carbon in waters, Water Research, Vol. 26, No. 2, pp. 255-258
- (11) Frias J., Ribas F., Lucena F., 1995: Comparison of methods for the measurement of biodegradable organic carbon and assimilable organic carbon in water, Water Research, Vol. 29, No. 12, pp. 2785-2788
- (12) Graham N.J.D. et al, 1996: *Effect of reduced depth, fabric-protected slow sand filters on treated water quality*, in: Graham N., Collins R., (editors): Advances in slow sand and alternative biological filtration, Wiley, Chicester
- (13) Haarhoff J., Claesby, J.L., 1991: *Biological and physical mechanisms in slow sand filtration*, in: Logsdon G.S. (editor): *Slow sand filtration*, American society of civil engineers, New York
- (14) Hambsch B., Werner P., 1996: *The removal of regrowth enhancing organic matter by slow sand filtration*, in: Graham N., Collins R., (editors): Advances in slow sand and alternative biological filtration, Wiley, Chicester
- (15) Harrison R.M., 1990: *Pollution: Causes, effects, and control*, 2nd ed., The royal society of chemistry, Cambridge
- (16) Hedberg T. and Wahlberg T.A., 1998: *Upgrading of waterworks with a new biooxidation process for removal of iron and manganese*, Water Science and Technology, Vol. 37 No. 9 pp. 121-126
- (17) Hendricks D. (editor), 1991: Manual of design for slow sand filtration,
 AWWA Research Foundation and American Waterworks Association, Denver, Colorado

- (18) van der Hoek J.P., Bonné P.A.C., Kors L.J., te Welscher R.A.G., 1996: *Slow sand filtration: Effect of grain size and filtration rate on operation and performance*, in: Graham N., Collins R., (editors): Advances in slow sand and alternative biological filtration, Wiley, Chicester
- (19) Huck P.M., 1990, *Measurement of Biodegradable Organic Matter and bacterial growth potential in drinking water*, Journal of the American Waterworks Association (AWWA), Vol. 82, No. 9, pp. 78-86
- (20) Huisman L., Wood W.E., 1974: Slow sand filtration, WHO, Geneva
- (21) Jago P. and Sidorowicz S., 1994: *Final report on the association between AOC and BDOC, and an evaluation of the LUMAC/KIWA biofilm monitor*, Foundation for Water Research, Medmenham (UK)
- (22) Joret J.C. and Lévi Y., 1986: *Méthode rapide d'évaluation du carbone éliminable des eaux par voie biologique*, Trib. Cebedeau. Vol. 39, pp. 3-9
- (23) Klevens C.M., Collins M.R., Negm R., Farrar M.F., 1996: *Characterization of NOM removal by biological activated carbon*, in: Graham N., Collins R., (editors): Advances in slow sand and alternative biological filtration, Wiley, Chicester
- (24) Lambert S.D., Graham N.J.D., 1995: *A comparative evaluation of the effectiveness of potable water filtration processes*, J Water SRT Aqua, Vol. 44, No. 1, pp. 38-51
- (25) Livsmedelsverket, 1993: *Livsmedelsverkets kungörelse om dricksvatten*, Statens Livsmedelsverkets författningssamling
- (26) Lyberatos G. et al.,1997, *Removal of iron from potable water using a trickling filter*, Water Research Vol.32, No. 5, pp. 991-996
- (27) Larsen R.J. and Marx M.L.: Statistics, Prentice-Hall, Englewood Cliffs (New Jersey), 1990
- (28) Lütkens J., 1996: *Evaluation of a technique for measuring BDOC in a continuous bioreactor*, Master thesis in Applied Environmental Measurement Techniques, Department of Sanitary Engineering, Chalmers University of Technology, Göteborg
- (29) McMeen C.R, 'Benjamin M.M., 1996: *Removal of natural organic matter by slow sand filtration through iron-oxide-coated-olivine*, in: Graham N., Collins R., (editors): Advances in slow sand and alternative biological filtration, Wiley, Chicester
- (30) Morrison G., 1998: *Personal communication*, Chalmers University of Technology, Technical environmental planning
- (31) Mouchet P., 1992, *From conventional to biological removal of iron and manganese in France*, Journal of the American Waterworks Association (AWWA), Vol. 84, No. 4, pp. 158-167
- (32) Pyper G.R., Logsdon G.S., 1991: *Slow sand filter design*, in: Logsdon G.S. (editor): *Slow sand filtration*, American society of civil engineers, New York
- (33) Rachwal A.J. et al., 1996: *Comparison between slow sand and high rate biofiltration*, in: Graham N., Collins R., (editors): Advances in slow sand and alternative biological filtration, Wiley, Chicester
- (34) Ribas F., Frias J., Lucena F., 1991: *A new dynamic method for the rapid determination of biodegradable dissolved organic carbon in drinking water*, J. Applied Bacteriology, (71), pp. 371-378
- (35) Seger A., Rothman M., 1996: *Slow sand filtration with and without ozonation in Nordic climate*, in: Graham N., Collins R., (editors): *Advances in slow sand and alternative biological filtration*, Wiley
- (36) Seppänen H.T., 1992: *Experiences of biological iron and manganese removal in Finland*, Journal of the Institution of Water and Environmental Management, Vol. 6, No. 3, pp. 333-341

- (37) Servais P., Billen G., Hascoet M.C., 1987: Determination of the biodegradable fraction of dissolved organic matter in waters, Water Research, Vol. 21, pp. 445-450
- (38) Sims R.C. and Slezak L.A., 1991: *Slow Sand Filtration Present practice in the US*, in: Logsdon G.S. (editor): *Slow sand filtration*, American society of civil engineers, New York
- (39) VA-Ingenjörerna AB, 1998: Projektbeskrivning: Långsamfilters effekt på reducerad återväxt i Ledningssystem i samband med försök vid Varbergs vattenverk, unpublished
- (40) Verstraete W. et al., 1995: Influence of nitrate on manganese removing microbial consortia from sand filters, Water Research, Vol. 29, No. 2, pp. 579-587
- (41) Volk C., Rennner C., Robert C., Joret J.C., 1994, *Comparison of two techniques for measuring Biodegradable Dissolved Organic Carbon in water*, Environmental Technology, Vol. 15, pp. 545-556
- (42) Weber-Shirk M.L., Dick R.I., 1997: Biological mechanisms in slow sand filters, Journal of the American Waterworks Association (AWWA), Vol. 89, No. 2, pp. 72-83
- (43) Welté B., Montiel A., 1996: *Removal of BDOC by slow sand filtration: Comparison with Granular Activated Carbon and effect of temperature*, in: Graham N., Collins R., (editors): Advances in slow sand and alternative biological filtration, Wiley, Chicester

11 Appendix

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Appendix	A: Synthetic soft water	I
	B: Organic parameters over time (TOC, UV, colour, COD)	II
	C: Percentage of TOC removal versus filtration rate	VII
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Appendix A Synthetic soft water

Recipe of synthetic soft water used for the BDOC experiments (Morrison, 1998).

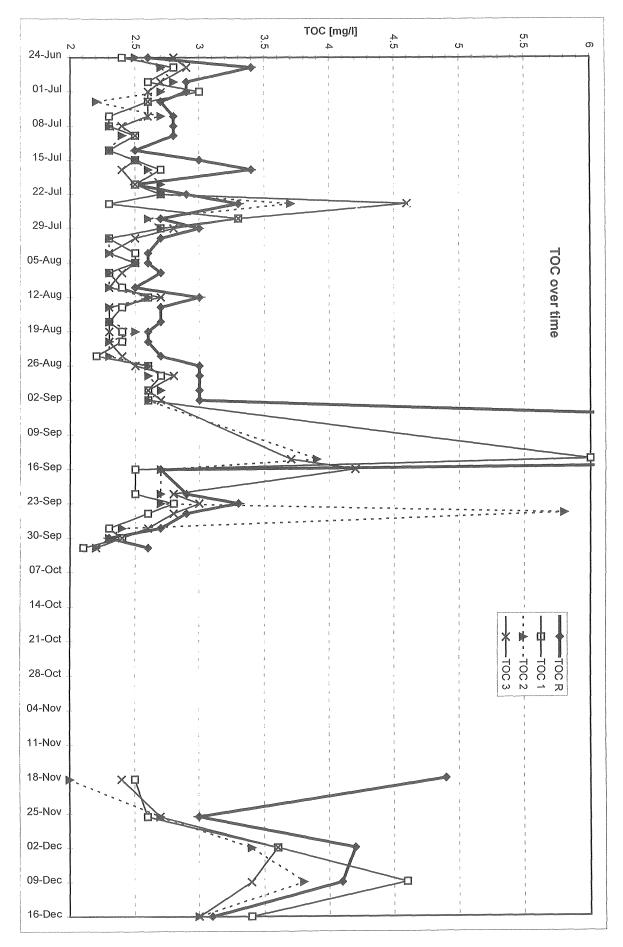
NaHCO ₃	48 mg/l
$CaSO_4 \cdot 2 H_2O$	30 mg/l
MgSO ₄	30 mg/l
KC1	25 mg/l
NaNO ₃	$2.60 \cdot 10^{-4} \mathrm{M}$
$K_2HPO_4 \cdot 3 H_2O$	$1.28 \cdot 10^{-5} \mathrm{M}$

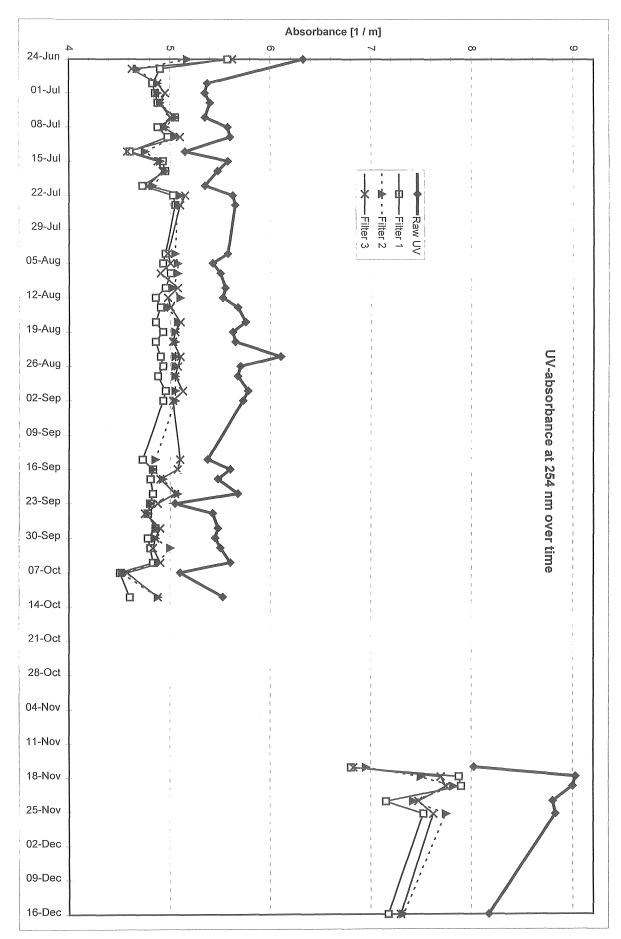
Appendix B

Organic parameters over time

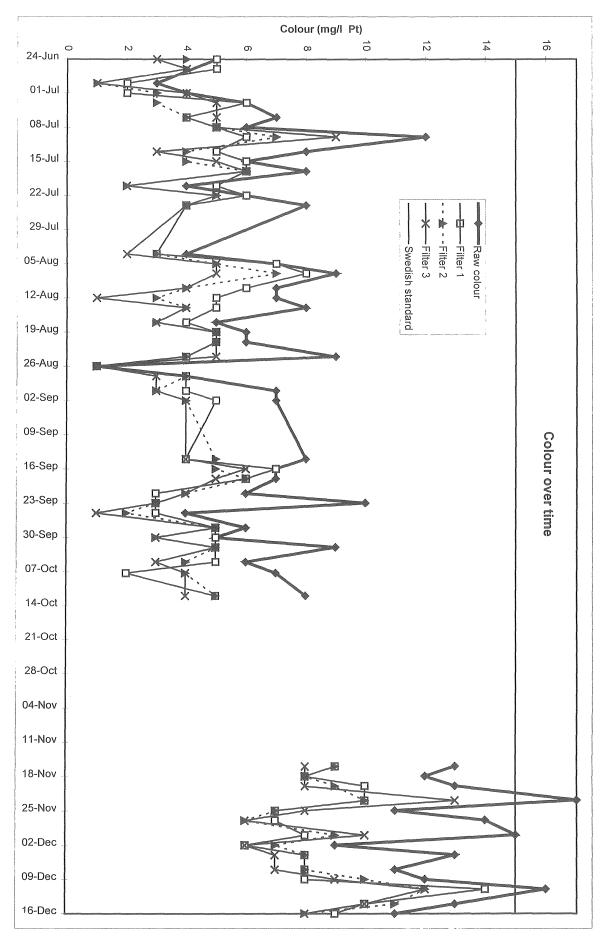
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TOC – UV – Apparent Colour – COD

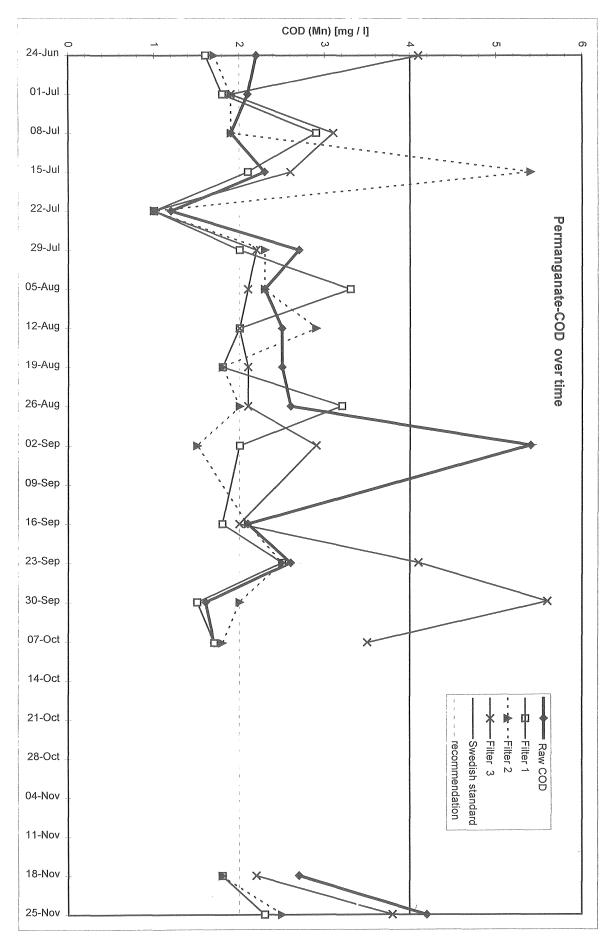




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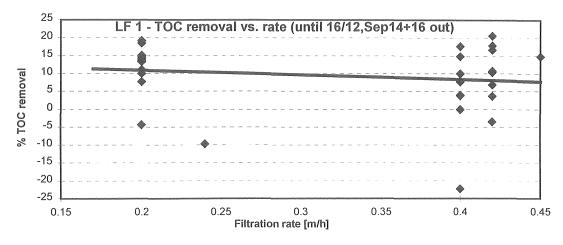


Figure: Filter 1 TOC removal versus filtration rate

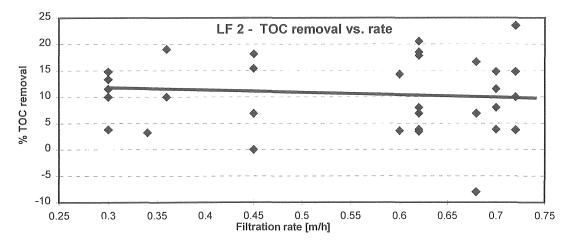


Figure: Filter 2 TOC removal versus filtration rate

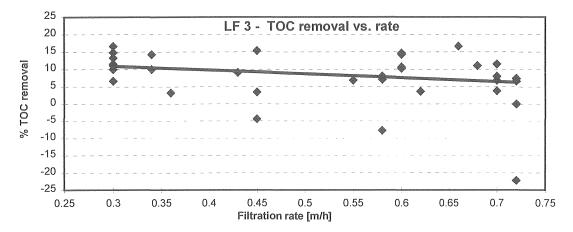


Figure: Filter 3 TOC removal versus filtration rate



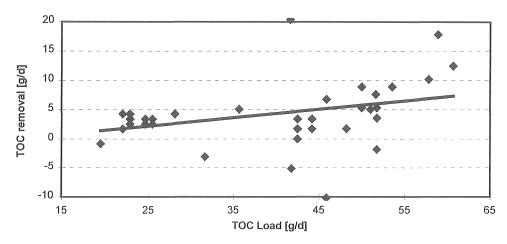


Figure: Filter 1 - TOC removal versus TOC load (both in grams per day)

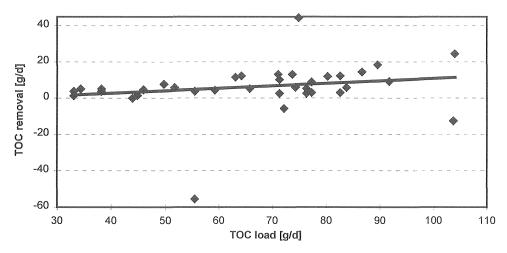


Figure: Filter 2 - TOC removal versus TOC load (both in grams per day)

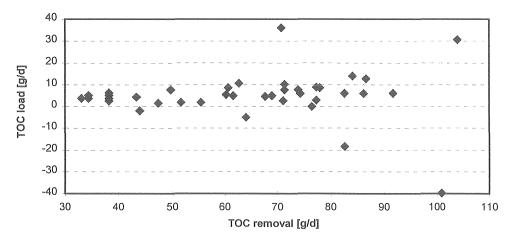


Figure: Filter 3 - TOC removal versus TOC load (both in grams per day)



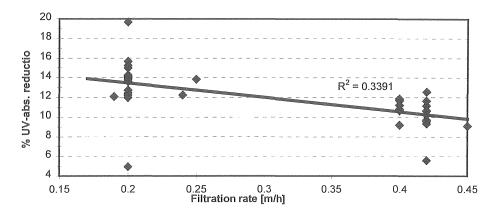


Figure: Filter 1 - Reduction of UV-absorbance versus filtration rate

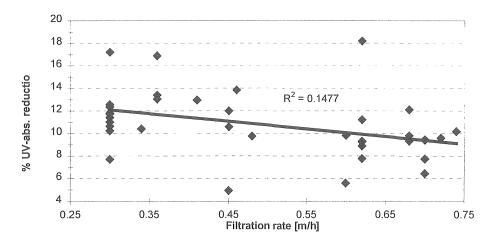


Figure: Filter 2 - Reduction of UV-absorbance versus filtration rate

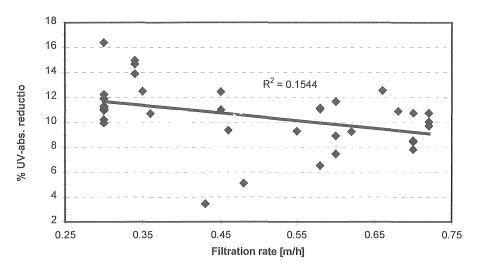
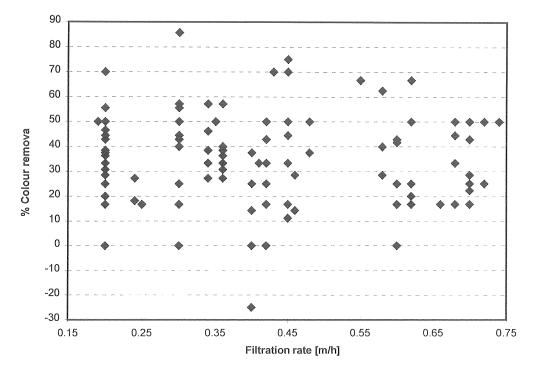
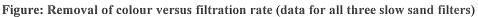


Figure: Filter 3 - Reduction of UV-absorbance versus filtration rate







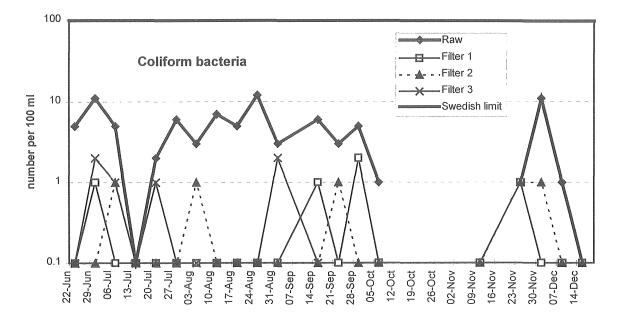


Figure: Number of coliform bacteria over time - in raw water and after the slow sand filters (log-scale)



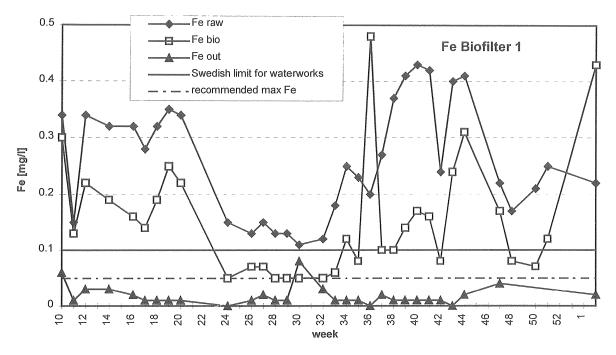


Figure: Iron concentrations for filter 1 - influent, after the bioreactor and effluent (unfiltered samples)

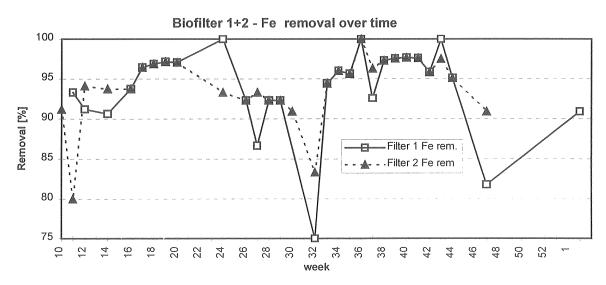


Figure: Development of manganese removal over time for both biofilters

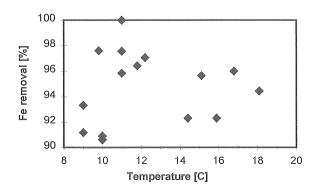


Figure: Relation between Fe removal and temperature



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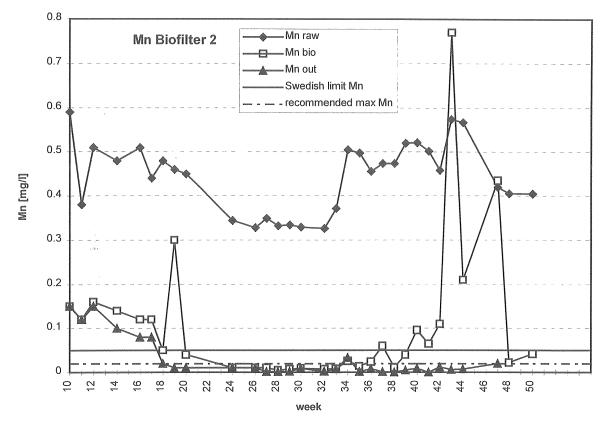


Figure: Mn concentrations for filter 1 - influent, after the bioreactor and effluent (unfiltered samples)

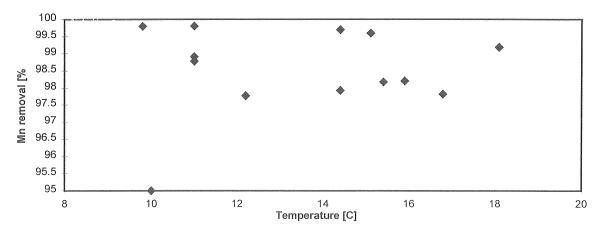
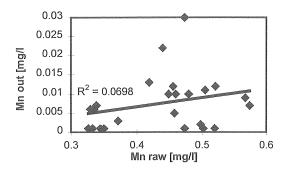
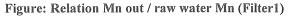


Figure: Relation of Mn removal to water temperature (Filter 1, data during seeding time removed)





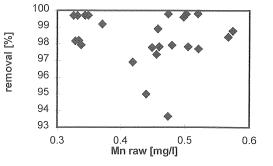


Figure: Relation Mn removal / raw water Mn

Appendix J Results of second BDOC experiment

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3.45

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Raw water	3.35	1.05	2.3	
Raw water reference				no Siran added
0 hours	3.53	1.11	2.42	
1	3.52	1.04	2.48	
5	3.67	1.14	2.53	
24	3.49	1.07	2.42	
75	3.1	1.23	1.87	·
163	3.39	1.31	2.08	
Raw water + top				Siran from the top of the column
0 hours	3.45	1.05	2.4	
1	3.39	1.2	2.19	
5	3.41	1.09	2.32	
24	3.17	1.16	2.01	
75	3.15	1.24	1.91	
163	3.33	1.2	2.13	
Raw water + bottom				Siran from the bottom of the column
0 hours	3.24	1.11	2.13	
1	3.39	1.13	2.26	
5	3.46	1.16	2.3	
24	3.29	1.18	2.11	
75	3.11	1.26	1.85	

2.02

TOC mg/l Remarks

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IC

TOC mg/l Remarks

<u> </u>				
D () 10 0/1	12.01	1 1 1	10.11	
Raw water + 10 mg C/l	13.21	1.1	12.11	25 mg/l glucose added
P				
Raw $+ 10 \text{ mg C} + \text{top}$				Siran from the top of the column
0 hours	13.11	1	12.11	
1	13.06	1.09	11.97	
5	13.83	1.15	12.68	
24	12.54	1.18	11.36	
75	10.85	1.4	9.45	
163	8.21	1.7	6.51	
Raw + 10 mg C +bottom				Siran from the bottom of the column
0 hours	13.56	1.03	12.53	
1	13.99	1.11	12.88	
5	14	1.24	12.76	
24	13.88	1.22	12.66	
75	12.31	1.37	10.94	
163	10.07	1.67	8.4	

Synth. water + 10 mg C/l 16.41 6.63 9.78 Salt & nutrient mix + Glu	ucose
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Synth. + 10 mg C + top				Siran from the top of the column
0 hours	16.49	6.56	9.93	
1	16.6	6.7	9.9	
5	16.87	6.81	10.06	
24	16.82	6.96	9.86	
75	8.85	8.28	0.57	
163	9.14	8.81	0.33	

Synth.+10 mg C +bottom				Siran from the bottom of the column
0 hours	16.54	6.62	9.92	
1	16.64	6.69	9.95	
5	16.66	6.79	9.87	
24	16.59	6.9	9.69	
75	8.94	8.39	0.55	
163	9.11	8.72	0.39	

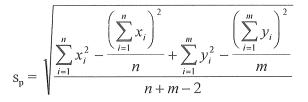
Appendix K Student-t-test for the data of the second BDOC experiment

A t-test is used to check if two populations of data are probable to have the same mean, by regarding random samples of them. A paired t-test regards the differences between the pairs and would have been the logical choice since it is especially suitable for data that represents a parameter before and after a treatment process. As the data for raw water and filter 1 consist of four measurements and the others of only three, the comparisons had to be done by the two-sample t-test which does not require the same number of values in both samples

The data should consist of independent random samples from two normal distributions, each having the same variance (Larsen & Marx, 1990). For the regarded data (Table 16), the standard deviations, and thus the variances, are roughly the same.

The parameter t for the two-sample test is defined as

with



x_i, y_i = values in first (second) sample n, m = number of values in the first (second) sample

 s_p = pooled standard deviation μ_X , μ_Y mean of first (second) population

 $t = \frac{\overline{x} - \overline{y}}{s_p \sqrt{\frac{1}{n} + \frac{1}{m}}}$

The number of degrees of freedom for the two-sample t-test is n + m - 2. The null hypothesis is that the two waters have the same mean. In this case, the alternative is that the second water has a lower BDOC, which results in a one-sided test. The critical t-values, quantiles of the t distribution, are tabled.

To test $H_0: \mu_X = \mu_Y$ versus $H_1: \mu_X > \mu_Y$

at the α level of significance, reject H₀ if $t \ge t_{\alpha, n+m-2}$

Table 1: Results of the t-test

data	Raw - Filter 1	Raw - Filter 2	Raw - Filter 3	Filter 2 - Filter 1	Filter 3 - Filter 1
t	3.96	1.90	1.90	2.90	2.08
t _{0.1,n+m-2}	1.44	1.47	1.47	1.47	1.47

An α of 0.1 means that there is a 10% probability that H₀ is rejected although it is true.