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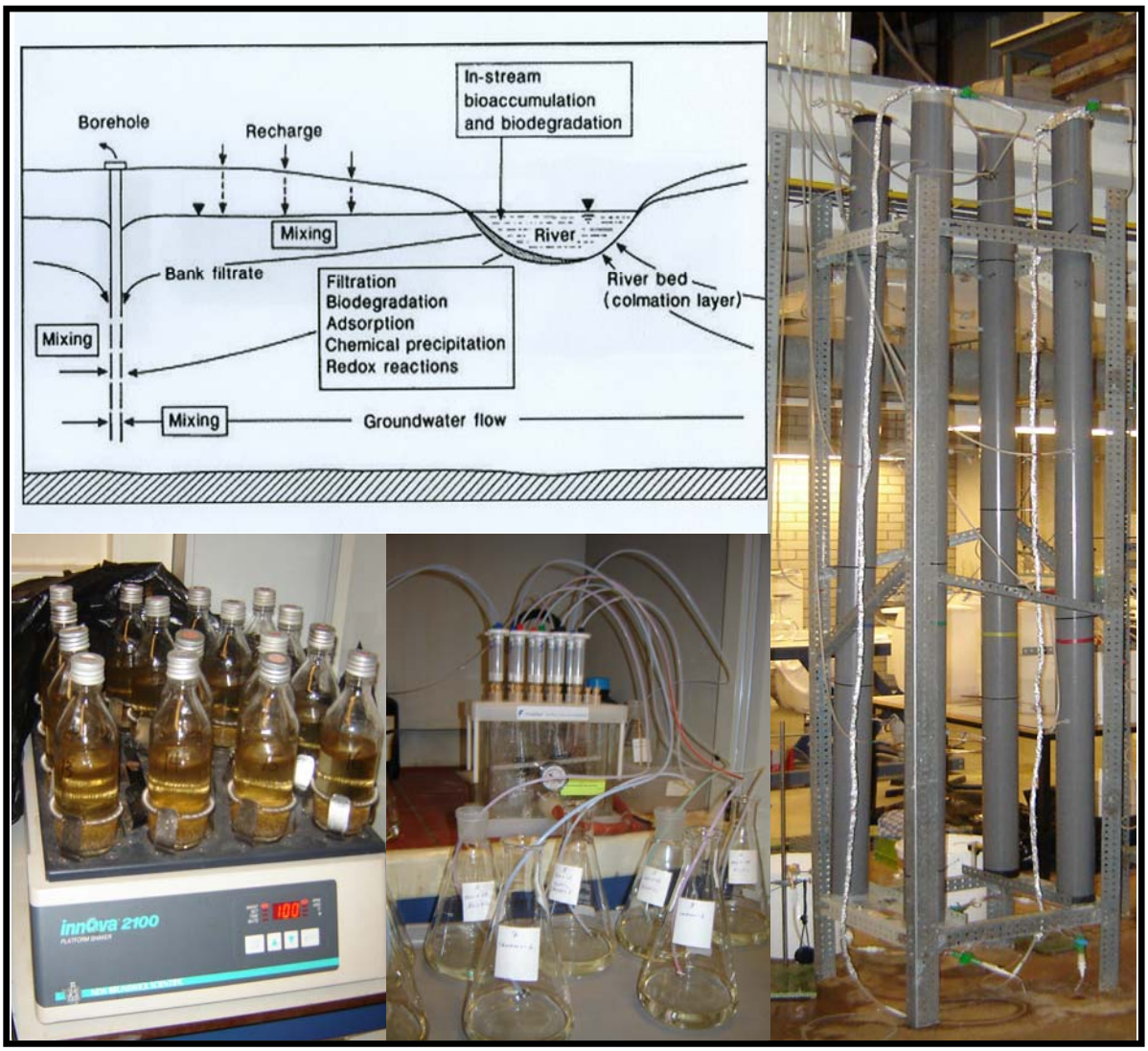

Organic Matter Characterization and EDCs Removal during Riverbank Filtration

Mohammed Oumer Ibrahim

MSc Thesis MWI-2007-16
May 2007

UNESCO-IHE
Institute for Water Education

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Organic Matter Characterization and EDCs Removal during Riverbank Filtration

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Abstract

Natural treatment system like river bankfiltration (RBF) is attractive for drinking water production because of its low cost, sustainability, performance, and relevance to both developed and developing countries. Its effectiveness has been proved in Europe and USA where it has been utilized for decades. Filtration, biodegradation, adsorption, and dilution are the main processes to produce significant improvements in raw water quality during RBF.

Detailed information on organic matter removal by RBF systems subjected to different processes and hydrogeological conditions is essential for rational design of RBF systems and to predict degree of purification provided by RBF at various sites. Therefore, as part of the ongoing effort, this study was focused on characterization of organic matter (OM) and removal of three endocrine disrupting compounds (EDCs) (Estrone (E1), 17β-Estradiol (E2), and Ethynlestradiol (EE2)) during RBF under different process conditions.

Laboratory based soil column and batch experiments were conducted to characterize OM and to study removal of EDCs during RBF. Investigation of the main process responsible for the removal was also carried out. Delft canal water (DCW) and secondary effluent (SE) from Hoek Van Holland wastewater treatment plant were used as an influent. Silica sand of size 0.8-1.25 mm was used as a filter media. Steroid estrogens were quantified using a biological technique called enzyme linked immunosorbent assay (ELISA). Solid phase extraction (SPE) was applied as a sample pre-treatment technique for ELISA.

A DOC removal of 13 and 20 % was found in 5 m long soil column with DCW and DCW mixed with SE (1:1) respectively at HLR of 1.25 m/d. The lower DOC removal from DCW was attributed to its lower BDOC content. Decreasing HLR to 0.625 m/d reduced the removal efficiency to 10 and 17 % for DCW and DCW mixed with SE respectively. A maximum achievable removal efficiency of 44 % from DCW and 53 % from the mixed sample were estimated at HLR 1.25 m/d. Batch studies showed better removal efficiency as compared to soil column at HLR of 1.25 m/d. A DOC removal of 20 and 24 % was achieved in batch studies with DCW and mixed sample respectively. It was also found that organic matter decomposition under aerobic condition was faster as compared to anoxic condition. A good positive correlation was observed between organic matter removal, biomass development and oxygen consumption.

Batch studies showed removal of EDCs ranging from 47 to 98 % with ELISA recovery from 45 to 118 %. Bioadsorption was identified as the main removal mechanism for steroid estrogens. The overall EDC removal from DCW mixed with SE under aerobic condition was 96, 93 and 79 % for E1, E2 and EE2 respectively.

Characterization of organic matter in DCW and SE revealed that DCW has more DOC with less BDOC component as compared to SE. SUVA values of both DCW and SE indicated the presence of a mixture of high and low molecular weight, humic and non humic, and hydrophobic and hydrophilic OM in the samples. However, relatively DCW is more humic and hydrophobic than SE.

Keywords: *Riverbank Filtration, Organic Matter, Endocrine Disrupting Compounds, Removal Efficiency, Characterization, Biodegradation, Adsorption.*

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List of Acronyms and Abbreviations

AOC	Assimilable Organic Carbon
ATP	Adenosine triphosphate
BDOC	Bio-Degradable Organic Carbon
DCW	Delft Canal Water
DBPs	Disinfection By-Products
DN	Nominal Diameter
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
EBCT	Empty Bed Contact Time
EC	Electrical Conductivity
EDCs	Endocrine Disrupting Compounds
EEM	Excitation-Emission Matrix
E1	Estrone
E2	Estradiol
EE2	Ethynlestradiol
HAAs	Haloacetic Acids
HLR	Hydraulic Loading Rate
HPSEC	High performance size exclusion chromatography
HRT	Hydraulic Residence Time
NOM	Natural Organic Matter
PhACs	Pharmaceutically Active Compounds
PVC	Polyvinyl Chloride
RBF	Riverbank Filtration
SE	Secondary Effluent
SP	Sampling point
SSF	Slow Sand Filters
THMs	Trihalomethanes
TOC	Total Organic Carbon
UVA	Ultraviolet absorbance

1 INTRODUCTION

1.1 Background

Drinking-water quality is an issue of concern for human health in developing and developed countries. Cities are growing at an incredible rate worldwide. The current urban population of 2.8 billion people will increase to 3.8 billion in 2015 and to 4.5 billion in 2025 (WHO/UNICEF, 2001). Mega cities create tremendous demand for water and act as dense sources of pollution. This challenges the ability of those in charge of water management to provide for the needs of all inhabitants. More than 2.2 million people, mostly in developing countries, die each year from diseases associated with poor water and sanitary conditions (WHO/UNICEF/WSSCC, 2000). There are 1.1 billion people, or 18 per cent of the world's population, who lack access to safe drinking water. About 2.6 billion people or 42 per cent of the total, lack access to basic sanitation (WHO/UNICEF, 2001).

Nowadays water companies are facing a number of challenges in the conventional treatment of surface water. These challenges include more stringent regulations, demands for sustainable production, the discovery of new chemical and microbial threats, changes in raw water quality, and high demands from the consumer regarding the aesthetic quality of tap water.

In addition, the use of low cost techniques to enhance the capabilities of existing water treatment infrastructures is also an issue. Many developed and developing countries need appropriate technologies that can bring about sustainable low cost water supply services. One of the technologies that can offer such an advantage is Riverbank Filtration (RBF). This technology takes advantage of the capacity of alluvial sediments to effectively filter and remove physical, chemical, and biological contaminants from surface water recharging alluvial aquifers (McClain, 2004). It is a multi-objective technology which provides sustainable treatment and pre-treatment services of use both in the developed and the developing world (Amy, 2006). It can provide opportunity for a complete treatment system and avoids the use of chemicals.

The effectiveness of bank filtration has long been recognized in Europe. Many utilities in North America are also interested in the technology. However, their treatment objectives are different. In North America RBF is considered as only a pre-treatment for microorganisms, particles, and some DOC in a multiple barrier concept whereas, in Europe, it often is considered as a major part of the overall treatment that produces a biostable, high quality water that can be distributed after little additional treatment without chlorine addition (Grunheid *et al.*, 2005).

During underground passage of water, processes such as filtration, sorption and biodegradation produce significant improvements in raw water quality (Schmidt *et al.*, 2003). These treatment processes result in particle removal, organic and inorganic chemical removal, peak smoothing in spills, temperature equalization, reduction in DBP formation and production of biologically stable water.

Increasing concern regarding the impact of surface water contamination is driving many utilities to seek a higher quality of source water, and many are investigating RBF. In addition, many cities in developed and developing countries are looking for low cost solutions to source water contamination problems. It is stated in many literatures (Dillon *et al.*, 2002; Hiscock and Grischek, 2002; IWA, 2006; Kim and Corapcioglu, 2002; Ray *et al.*, 2002; Weiss *et al.*, 2005; Worch *et al.*, 2002) that the need for better understanding of contaminant removal in RBF system is one of the issues to be addressed nowadays. Although much work has been done in some countries of Europe, there is still knowledge gap among other developed and developing countries. There is no a reliable tool or methodology for transfer of RBF experience to other parts of the world.

1.2 Problem Identification

For more than one hundred years, RBF has been used in Europe to produce drinking water by inducing surface water to flow downward through sediment and into a pumping well (Tufenkji *et al.*, 2002). During this process, potential contaminants are filtered from the water, significantly improving water quality.

Due to the practice of water recycling through a semi-closed urban water cycle, the introduction of effluent organic matter and persistent trace organic pollutants in the drinking water is of potential concern. Point source and non-point source pollutions of surface water are also of big concern. Organic matter (OM) affects drinking water quality. Organic carbon present in surface and ground water may affect negatively subsequent treatment unit operations through formation of disinfection byproducts (DBPs), membrane fouling and biological growth in the distribution systems.

Although there are evidences of a substantial removal of OM, DBPs precursors, and organic micropollutants during percolation through subsurface systems, a lack of knowledge exists with respect to the relative changes of organic matter composition during RBF and factors responsible for those changes (Ray *et al.*, 2002). Therefore research is needed for more complete description of removal processes for the non-humic and humic fractions of OM.

Recently, several research studies have been carried out in Europe and USA to show how contaminants are removed (NWRI, 2003; Ray *et al.*, 2002; Schubert, 2002).

However, further researches are still needed to improve the understanding of RBF for contaminant removal. Due to lack of knowledge on the removal mechanism of pathogenic microbes and other key contaminants in the river bank environment, the technology has not been used in many parts of both developing and developed countries. Though it is relatively simple, natural and low cost water treatment system, there is no transfer of technology to developing countries.

Therefore, there is a need to assemble a robust data base on RBF performance in removing particles and turbidity; organic matter (OM); biodegradable dissolved organic carbon (BDOC) and assimilable organic carbon (AOC); trace organics such as pharmaceutically active compounds (PhACs) and endocrine disrupting chemicals (EDCs); nitrogen (organic, ammonia, and nitrate); and microbes (viruses, bacteria, and protozoa).

This thesis work addressed some of the above mentioned issues by adding knowledge on the ongoing research on the understanding of contaminant removal processes under various process conditions (influent water quality, soil properties, retention time, hydraulic loading rate, aerobic and anoxic conditions). The study was carried out by using laboratory based soil column and batch tests to simulate the performance of RBF with regard to the relative changes of organic matter composition (OM fractions) and EDCs removal. The study also included investigation of the main process responsible for the removal.

1.3 Goal and Objectives

The main goal of this MSc study is to evaluate the performance of RBF with regard to the attenuation of OM and EDCs (Estrogens) with attention to the role of biomass in the process.

The specific objectives to achieve this goal are:

1. To study OM removal efficiency of RBF for various process conditions using batch reactors and soil column set up
2. To investigate EDCs removal efficiency of RBF using soil batch reactors
3. To characterize OM in water samples (Delft Canal water and wastewater secondary effluent) before and after treatment by RBF
4. To analyse the relative performance of biodegradation and adsorption processes for the removal of three different types of estrogens compounds (Estrone (E1), 17β-Estradiol (E2) and Ethynlestradiol (EE2)).

1.4 Outline of the Report

This thesis contains five chapters. Chapter one gives background information, problem identification and goals & objectives of the MSc research work.

Chapter two of the report presents a critical literature review on the concept, experience, historical background, and performance of RBF systems. In addition, it discusses about OM and EDCs which are the main areas of interest for this research work. Based on literature review, the issues which need research in the future are also identified.

Chapter three explains the research methodology followed to accomplish this study. It describes the experimental setups in the laboratory, experimental procedures needed to collect data and how data was analysed & interpreted.

Chapter four presents results of the study and discusses the outcomes. Finally conclusions and recommendations are presented in chapter five of the report.

2 LITERATURE REVIEW

2.1 Concept of Riverbank Filtration System (RBF)

RBF is a process for producing drinking water. It takes advantage of existing geologic formations adjacent to the water body to filter drinking water. River water is induced to flow through riverbed soils to pumping wells located on the banks of the river. During the passage of this water through the riverbed and aquifer, dissolved and suspended contaminants as well as pathogens are removed due to a combination of physical, chemical, and biological processes (Amy, 2006; Huisman, 1989). The aquifer materials can effectively filter out waterborne bacteria and contaminants and produce water of superior quality and consistency. Figure 2-1 shows the schematic representation of the attenuation processes of RBF system.

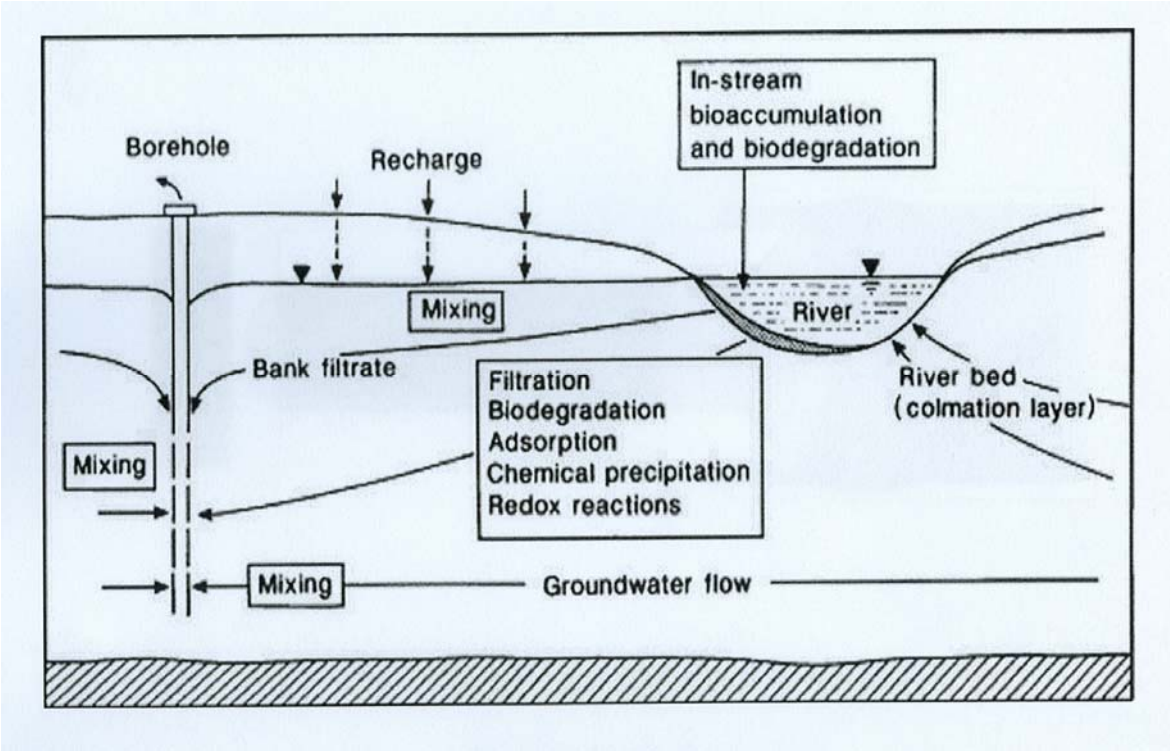


Figure 2-1 Schematic diagram of processes affecting water quality during RBF *(Source: Amy, 2006)*

Mixing, biodegradation and sorption are the main beneficial attenuation processes. These processes take place within two main zones: the biologically active colmation layer, where intensive degradation and adsorption processes occur within a short residence time; and along the main flow path between the river and abstraction borehole

where degradation rates and sorption capacities are lower and mixing processes are greater (Hiscock and Grischek, 2002).

2.2 Experience with Riverbank Filtration (Historical background)

The concept of RBF began in 1870's in Germany, and it is a common water production technology in Europe (Ray *et al.*, 2002). In Western Europe, one of the first RBF plant was established in the lower Rhine Valley region in Dusseldorf, Germany which is located on both sides of the Rhine River. It was because of limited ground water resources that water works in the Lower Rhine Valley Region preferred to use RBF to supply drinking water to their population. In the Netherlands as well RBF has been applied for more than 100 years (Hiemstra and Buiteman, 2006).

In the early years of RBF construction, enhanced well yield through induced infiltration was the primary goal. More recently, improvements in the water quality have become equally important. In 1892/93, there was an outbreak of epidemic cholera in Hamburg, Germany, that was caused by drinking water from a water works with direct intake from the Elbe River. This led to the use of artificial or natural subsoil passage of raw water as a replacement or supplement to direct intake for public water supply (NWRI, 2003; Schmidt *et al.*, 2003).

In some countries of Europe, RBF is used as a pre-treatment technology preceding more advanced treatment operations. Table 2-1 summarises the contribution (in percentage) of drinking water production from bank filtrate in some European countries.

Table 2-1 Percentage of drinking water production from bank filtration

No.	Country	Percentage
1	Slovak Republic	50
2	Hungary	45
3	Germany	16 (Berlin 60%)
4	Netherlands	5
5	Finland	48
6	Switzerland	80
7	France	50

Source: Compiled from Amy, 2006; and Tufenkji et al, 2002

In the United States, RBF systems have been operating for about half a century (NATO, 2004). According to a conservative estimate, potential exists for 67 million people to be served by RBF in the US. Increasing concern regarding the impact of surface water contamination is driving many utilities to seek a higher quality of source water, and many are investigating RBF.

The design and operation of RBF sites vary around the world depending on the objectives of the Water Authorities. The European practice of design is to use retention times of several weeks or even months (Grunheid *et al.*, 2005). Here, the target is to eliminate biodegradable dissolved organic carbon (BDOC), pathogens and degradable trace organic pollutants from the surface water to produce a biostable, high quality water that can be distributed after little additional treatment without chlorine addition. A relatively less retention times ranging from several hours, to days, to at most a few weeks is practiced in the design of RBF sites in North America (Grunheid *et al.*, 2005). Here, the primary treatment objective is the removal of pathogenic microbes from the raw water, with a particular emphasis on cysts and oocysts, and the reduction of cost for the conventional drinking water treatment. A secondary objective is the removal of turbidity and some dissolved organic carbon (DOC). The possibility of removal of degradable trace organic pollutants by bank filtration is often not addressed by facility designs in North America. Thus, a philosophical difference is that North American practice envisions bank filtration as only a pre-treatment for microorganisms, particles, and some DOC removal in a multiple barrier concept whereas, in Europe, it often is considered as a major part of the overall treatment.

Motivation for increasing interest in RBF in the U.S are (Bouwer *et al.*, 2003)

- Increased regulations on the direct use of surface water. Principal concerns:
  - DBPs (Dissolved organic matter in surface waters)
  - Giardia and Cryptosporidium (resistance to conventional disinfection)
- Potential to reduce treatment costs
- Buffer against spills and terrorist events

2.3 Factors affecting RBF System

a) Raw water quality

Rivers, reservoirs and lakes experience seasonal fluctuations in water quality. Farm fields contribute to the peak concentration of agricultural chemicals into the stream flow during the rainy season through runoff. Similarly, most rivers and lakes in temperate climates experience high concentrations of dissolved organic carbon in late fall when decomposed leaf litter finds its way to streams and rivers. In addition to these seasonal variations in chemical concentrations, water utilities have to deal with point and non point pollution sources.

Raw water quality is one of the main factors affecting the performance of RBF systems. Rivers carrying less polluted water in terms of suspended matters, turbidity, NOM, industrial discharge, wastewater discharge, pesticides etc. will be easier to treat than heavily polluted rivers. Heavily polluted river water requires higher travel length and

residence time. In addition, RBF systems with heavily polluted river water are more susceptible to riverbed clogging.

b) Well types and distance from the river

RBF wells can either be horizontal or vertical depending on the hydrogeologic setting, required production rate, and the utilities preference. Shallow alluvial deposits and a higher rate of pumping from a given location often favour horizontal wells, sometimes called Ranny wells or laterals. The laterals of the collector wells can all be directed towards the river or distributed in all directions. Horizontal wells have the advantage of yielding more water with a disadvantage of more contaminant breakthrough as compared to vertical wells (Amy, 2006). Vertical wells have more control over residence time. Figure 2-2 shows the configurations for the two types of bank filtration wells.

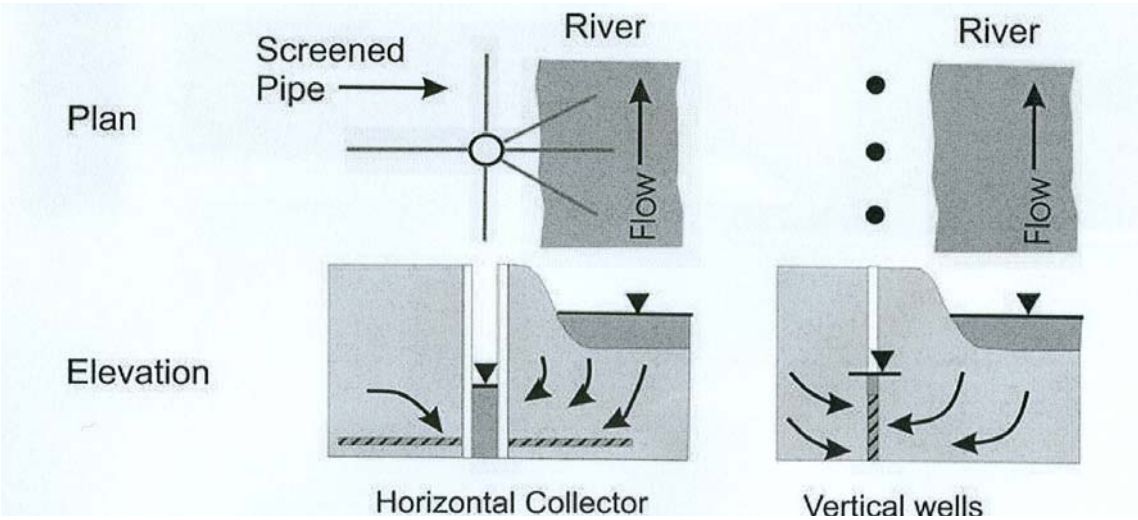


Figure 2-2 Schematic representation of Horizontal and Vertical Wells (*Source: Amy, 2006)*

Though biologically mediated degradation processes mainly occur at the first meters of the flow path from the river to the well, distance of the production well from the river also plays an important role in the water quality improvement of the bank filtrate through the process of filtration and adsorption. A longer flow distance (long travel time) provides more contact between the contaminants and aquifers. Also the development of redox zones between the river and the pumping wells depends on the travel distance, the amount of organic carbon present in the river water and the aquifer, and the oxygen content of river water. The natural organic matter present in river water and the aquifer is consumed by bacteria present in the subsurface. This causes a reduction, and eventual depletion, of oxygen in the ground water. Once the oxygen is completely depleted, denitrifying bacteria use nitrate as the energy source to reduce it to

nitrite. Further development of the redox conditions causes dissolution of iron and manganese. Therefore, water utilities should be able to optimize the placement of the wells in such a way that nitrate is adequately reduced, while the reduction of iron and manganese (or even sulphur) is minimized.

The trend among large utilities in the United States has been to design and build horizontal collector wells. However, both horizontal and vertical wells are used in the western part of the United States where a number of utilities use spreading basins to recharge aquifers with surface water (Ray, 2002). The length of radials in a horizontal well system is typically about 100 m or less. The number of laterals can typically range between 5 and 7. Utilities in Germany and other parts of Europe use horizontal as well as vertical wells. Construction of filter wells are carried out at some distance away from the river and, unlike the horizontal collector wells used in the United States, their laterals do not go under the riverbed.

c) Variation of water level in rivers

The direction of natural water flow depends on the relative water levels of ground water and river water. During low flow period, rivers can have water levels below the ground water table, in which case water flows towards the river and percolates in to the flowing wave of the river. In times of high flows, however, river water infiltrates vice versa into the aquifer. Thus, the flow direction of the groundwater is variable under natural conditions even without any anthropogenic extraction of groundwater.

River–aquifer interactions are governed by the fluctuating water level of the river. The resulting gradients between the quickly changing river level and the gradual variation of the groundwater table in the adjacent aquifer control flow and transport in riverbank filtration. The dynamic behaviour of the river level does not only influence clogging of the riverbed, flow and transport phenomena but also water quality, both in the river and production wells.

Pumping action creates a pressure head difference between the river and the aquifer and induces the river water to flow through the riverbed towards the pumping well that consequently extracts a mixture of groundwater originally present in the aquifer and bank filtrated surface water from the river. The proportions of both kinds of water in the extracted water can vary depending on both extraction rate and river flow.

Figure 2-3 shows the typical flow conditions associated with different types of bank filtration schemes. The majority of river bank filtration schemes are of Type 1. Groundwater flow beneath the river (Types 3, 4 and 6) is typically neglected at most sites. The formation of unsaturated conditions beneath the river occurs if groundwater abstraction rates are not adapted to the hydraulic conductivity of the river bed or if the

hydraulic conductivity of the river bed material becomes clogged due to surface water pollution inputs (Type 4). At some sites, the river bed cuts into the confining layer (Type 5). Collector wells are used with laterals at different depths, of different lengths and directions. Type 6 gives only one example with a lateral towards the river (Hiscock and Grischek, 2002).

d) Local ground water table

Mixing with ground water (dilution) is one of the processes that improve the water quality during RBF system operation. The efficiency of this process depends on the elevation of ground water table. Table 2-2 shows the results of a study made on RBF sites in Reston, Virginia to investigate the effect of dilution process on water quality improvement in riverbank filtrate.

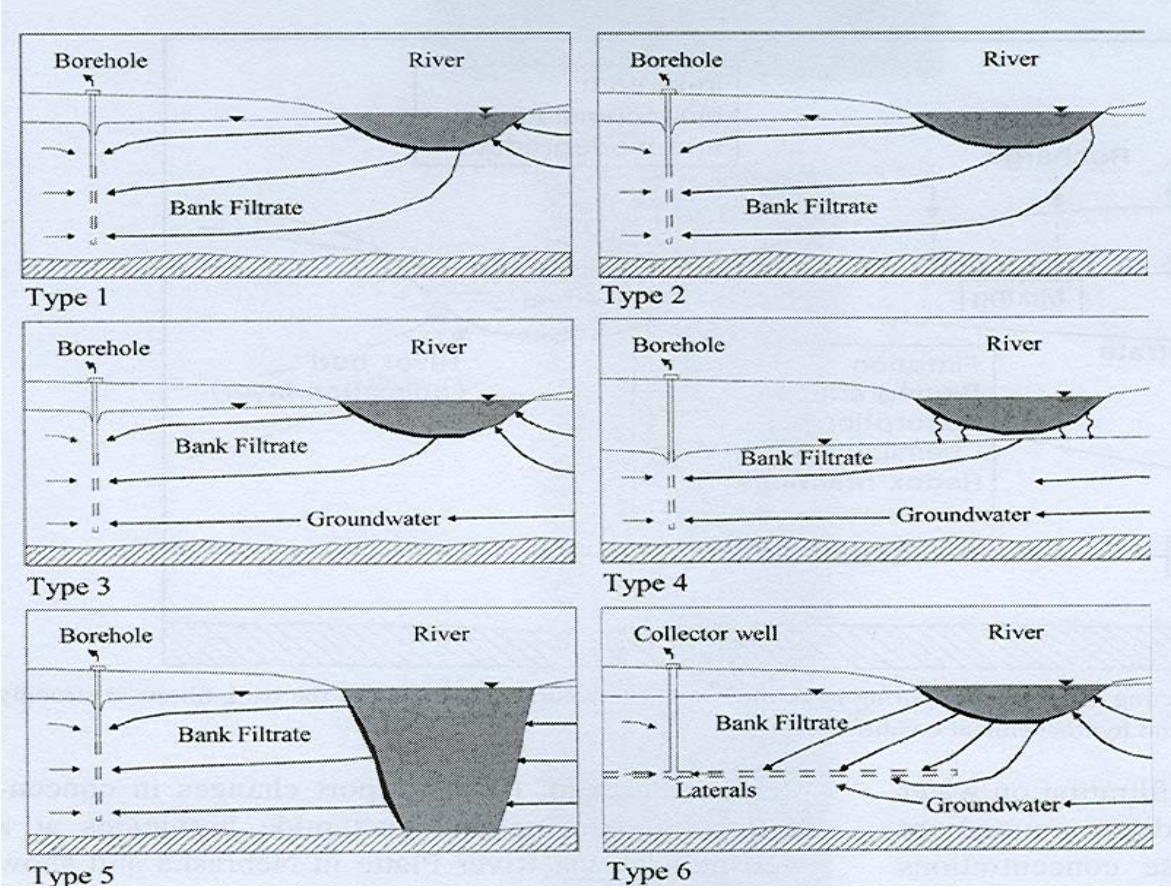


Figure 2-3 Schematic representation of types of flow conditions at RBF sites (*Source: Hiscock, 2002)*

Table 2-2 The effect of dilution process on water quality improvement of riverbank filtrate

Parameters	% total removal	% removal due to dilution	% removal due to subsurface filtration
Turbidity	87	10	77
DOC	63	29	34

Source: (Partinoudi *et al.*, 2003)

e) Site hydrogeology

The local hydrogeology of a site affects the quality of surface water. In alluvial aquifers with coarse-grained materials, a significant amount of dissolved chemicals can be stored when the river level is high. However, the water and associated chemicals drain back to the river when the floods in the river recede.

The characteristics of sediment found at the river-aquifer interface affect the quantity and quality of water entering the aquifer. The sediments present on the banks and riverbed affect the infiltration of water in to the aquifer. The bank material plays an important role during flood seasons. If the sediments on the banks and beds are fine grained and thick, they can retard the flow of river water into the aquifer. Coarse-grained sediments at the river-aquifer interface may not retard the migration of dissolved chemicals and pathogens to the same degree as thick, low permeability sediments. One may also expect the low permeability fine sediments to wash off or be redeposited on the riverbed, depending upon flow conditions in the river. Such dynamics of the sediments can also affect filtrate quality to some extent.

f) Schmutzdecke and riverbed clogging

The "Schmutzdecke" in RBF is a biofilm formed at the river bed/bank - water interface. In general, it consists of numerous forms of life including algae, plankton, diatoms, protozoa, and bacteria. The schmutzdecke layer is a place where inert suspended particles can be mechanically strained, organic matter and nitrogenous compounds broken down, and microorganisms entrapped (Huisman, 1989).

Riverbed clogging is one of the issues of research on the performance of RBF system. Clogging reduces aquifer recharge rates and may therefore be perceived as a problem in water supply systems, but it also increases the efficiency of filtration processes. Recent investigations have indicated that riverbed conductance is likely the capacity-limiting factor in high-capacity RBF systems (NWRI, 2003). However, the impact of riverbed conductance and its change with time on long-term sustainable yield has not been thoroughly evaluated. It has been observed that riverbed conductance varies as a function of time, which is likely the result of riverbed clogging. This clogging can be

caused by mechanical particle impingement, biological growth, or geochemical reactions within the aquifer/riverbed interface. All three of these processes can be impacted by dynamic and static hydraulic forces. However, the impact of these factors on the long-term specific capacity of a wellfield is poorly understood.

The need to establish or re-establish a Schmutzdecke layer after riverbed scouring events in order to once again provide water of acceptable quality needs to be ascertained so that appropriate operational methods can be implemented if required. For example, after scouring events, RBF extraction well pumping rates could be decreased or stopped, or laterals further from the river could be selected, until the riverbed Schmutzdecke is re-established. Such operating techniques are needed to ensure public health risks are minimized(IWA, 2006).

2.4 Performance of RBF

2.4.1 Contaminant Removal

a) Microorganisms and turbidity

Surface waters are often contaminated with pathogenic microorganisms excreted by humans, cattle, and various domestic and wild animals; however, the main sources are discharges of municipal wastewater effluents and runoff of livestock wastes and from fields receiving manure. Biological contaminants in surface water include protozoa, bacteria, and viruses. Underground passage for the removal of biological contaminants is, in principle, an efficient system. During the passage of pathogens through soil, their numbers are reduced by a combination of processes including adsorption to aquifer materials and inactivation.

The removal process is most efficient when groundwater velocity is slow and there is sufficient flow path length and time. Under optimal conditions, underground passage can achieve up to 8-log virus removal over a distance of 30 m in about 25 days (Schmidt *et al.*, 2003). However, efficiency will be diminished by short path lengths, high heterogeneity, coarse matrices, high gradients, and accompanying high velocities. Thus, to assure an efficient removal of pathogenic organisms, water suppliers should favourably install or establish underground passages with high flow path lengths and residence times. In general, the recommended minimum travel distance and time is 10 m and 1 day respectively (IWA, 2006).

A consistent 4-log removal of human enteric viruses was observed (Havelaar *et al.*, 1995) at RBF facility in the Netherlands. Berger (Berger, 2002) has compiled the removal studies of bacteria and spores at RBF sites. A 2-log removal of aerobic endospores at a travel distance of 0.6 m was observed at a site in Louisville. A 3.4-log

removal for sulfite reducing *Clostridia* was observed at a site in Terre Haute, Indiana, and 3 to 5-log removal at a site in the Netherlands, where total coliform removal easily exceeds 5- logs.

Turbidity of surface water is a measure of colloidal particle concentration. High turbidity is usually associated with poor microbial quality of water. RBF systems have been reported to remove turbidity anywhere from 1-log unit to nearly 3-log units. Microscopic particles removal of 2.4-log was reported (Wang *et al.*, 1995) at an experimental bank filtration facility in Louisville, Kentucky, where vertical well puming at 0.085 m3/s was used. Mikels showed filtrate turbidity between 0.3 and 0.4 NTUs for a river turbidity varying between 1 and 5 NTU (Mikels, 1992). The study was carried out in a horizontal collector well site in Kalama, Washington, where the laterals were only 6 m below the riverbed.

b) Natural organic matter

NOM in surface water is also a major concern for water utilities, since it contributes to colour, odour and deterioration of taste in drinking water and is the main precursor for disinfection byproducts, such as trihalomethanes (THMs) and haloacetic acids (HAAs), which are potentially carcinogenic.

Removal of NOM by RBF is described by measuring various sum parameters such as total organic carbon (TOC), dissolved organic carbon (DOC), biodegradable organic carbon, and assimilable organic cabon (AOC). The removal potential of RBF for these parameters is presented in Table 2-6 under section 2.4.3.

c) Trace elements

Trace elements such as iron, manganese, and various heavy metals are eliminated during ground passage, mainly by sorption processes. The performance of RBF system for heavy metals removal varies widely for different elements. Removal efficiencies for heavy metals during riverbank filtration at the River Rhine are presented in Table 2-3.

In aerobic aquifers, removal is achieved by ion exchange processes at negatively loaded surfaces of clay minerals, amorphous ferric oxides and alumina, and organic solid matter. In anoxic aquifers, the removal of metal ions is dominated by precipitation reactions with sulphide. In addition, heavy metals can be removed by ground filtration for a long time and they cannot be easily remobilized. However, if conditions in the aquifer become anaerobic, iron and manganese undergo chemical reduction and appear in the water, necessitating their elimination by treatment.

Table 2-3 Heavy metal removal by RBF at the lower Rhine (mean values 1975 – 1978)

Metal	Concentration in µg/L		Percentage Removal
	Rhine River	Bank Filtrate	
Zn	180	33	82
Cu	31.8	7.5	51
Pb	12.6	3.2	75
Ni	9.5	4.7	51
Cr	7.9	0.5	94
Sn	4.5	3.6	20
As	4.2	0.3	93
Cd	2.0	0.5	75
Se	1.8	1.6	11
Ag	0.5	0.5	0
Hg	0.3	0.2	33
Be	0.1	0.1	0

Source: (Schmidt et al., 2003)

2.4.2 Shock Loads and Temperature Equalization

In addition to contaminant removal, RBF is an excellent protection against shock loads and temperature equalization (Schmidt *et al.*, 2003). It plays very important role in smoothening peak concentrations and shock loads resulting from chemical spills or defects in industrial wastewater plant. It also provides the only possibility to attain a cost effective equalization of surface water temperatures. It results in a more constant water temperature. This is especially important for rivers receiving, even during the warm season, cooling water from power stations. Figure 2-4 below gives an example of how RBF is effective in dampening peak concentration, the case in the 1998 contamination of 1,2-dichloroethane in Rhine River. The example demonstrate how a short term peak pollution in the river turns into a longer lasting pollution of very low concentration in the aquifer bank filtrate.

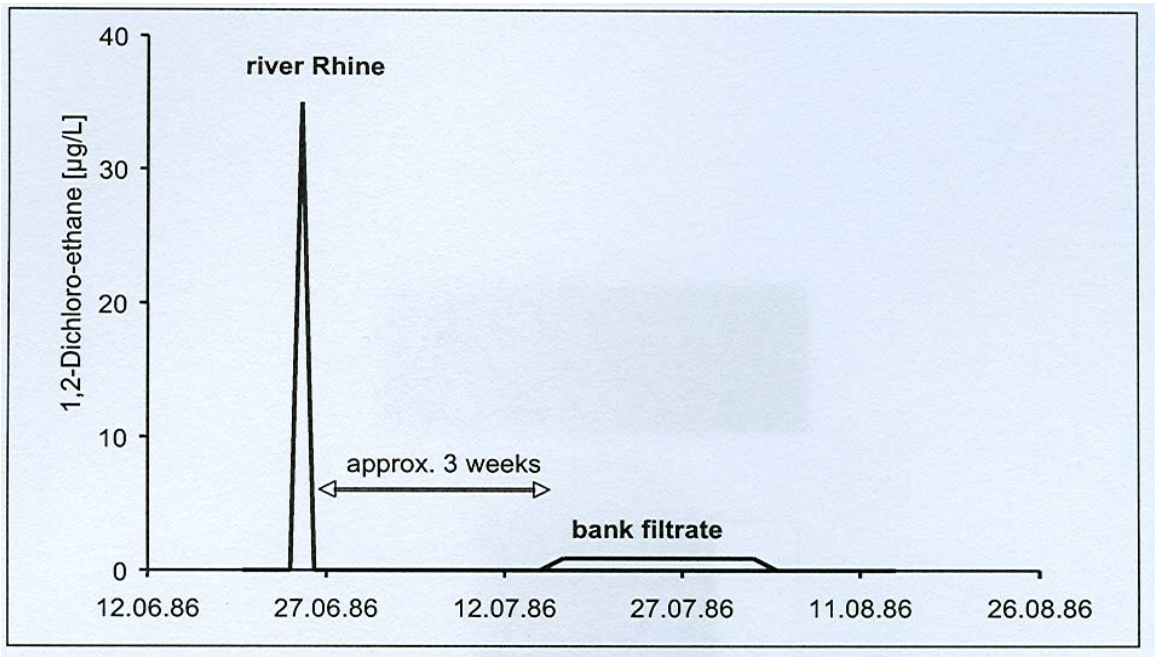


Figure 2-4 Examples of the protection against shock loads by bank filtration (*Source: Schmidt et al., 2003)*

2.4.3 Comparison with Slow Sand Filtration System

The mechanism for particulate, organic precursors and microbial removal by Slow Sand Filtration (SSF) and RBF systems are similar and rely on biological filtration processes involving biodegradation and bioadsorption. However, RBF is natural process whereas SSF is engineered/mechanical process. There are differences in design/operations as well as water quality performance (IWA, 2006).

SSF is effective in the removal of turbidity and microorganisms, with more limited removal of NOM, measured as DOC, and biodegradable DOC (BDOC) or assimilable organic carbon (AOC). SSF performance is influenced by source water characterstics, temperature, and the extent of surface ripening. As a consequence of the biologically active Schmutzdecke, the SSF can be considered as both a bilological as well as physical process. Attributes of the SSF process are its low cost, operational simplicity, and the possibility of it functioning as a stand alone treatment system (except for the option of post disinfection). Limitations of the SSF process are high land requirements (constraining its large system/centralized system applicability), and need for the occasional removal/restoration of the Schmutzdecke (a required operational intervention making SSF initially less effective until reestablishment of the Schmutzdecke). Table 2-4 presents a performance summary of SSF.

Table 2-4 Slow Sand Filter performance Summary

Water quality parameter	**Removal capacity**
Turbidity	<1 NTU
Coliform bacteria	1 – 3 log units
Enteric viruses	2 – 4 log units
Giardia cysts	2 – 4+ log units
Cryptosporidium Oocysts	>4 log units
DOC	<15 – 30%
BDOC	<80%
AOC	<65%
THM Precursors	<20 – 35%
Iron/Manganese	>67%

Source: (IWA, 2006)

The fundamental design/operational parameters describing SSF are media depth (D), hydraulic loading rate (HLR), and empty bed contact time (EBCT), with these three parameters related according to: HLR = D/EBCT. This engineered/mechanical filtration system requires some operational intervention in the form of less frequent periodic removal of the Schmutzdecke. While SSF may not provide true biostability, it can significantly reduce chlorine demand, permitting maintenance of a chlorine residual with a lower chlorine dose.

RBF, as a natural drinking water treatment process, is capable of removal of microorganisms, DOC, nitrogen (N), and trace organic compounds. In lakes and slow flowing (low turbulence) rivers, a clogging layer (Schmutzdeke) develops which is periodically removed during scouring. While straining and/or die-off (inactivation) of microorganisms occur during saturated flow of bank filtrate through an aquifer, biodegradation is the primary removal mechanism for organic contaminants. Thus, RBF is a sustainable treatment system that doesn't require operational intervention to restore its capacity.

In RBF, important design/operational factors include travel distance and travel time (or hydraulic residence time (HRT); these factors are analogs of D and EBCT for the SSF process. EBCT is related to HRT through porosity (ϕ): HRT=EBCT*ϕ. In RBF, the pumping rate at the recovery well(s) together with the resultant hydraulic gradient establish a Darcy flow velocity, which is analog of HLR for the SSF processes. The Darcy velocity or HLR are related to the interstitial velocity (v) through porosity ϕ: v=HLR/ϕ.

Tables 2.5 and 2.6 present the Comparative assessment of RBF and SSF in terms of (i) design/operational parameters/conditions, and (ii) quantitative performance of the two systems in terms of water quality.

Table 2-5 Design/operational parameters/conditions

Parameters or condition/process	**SSF**	**RBF**
Depth/travel distance	≈1 m	≥10 m
Residence/travel time	≥2 hours (≥ ≈0.1 day)	≥1 day
Hydraulic loading/infiltration rate	≤0.5 m/hour (≤12 m/day)	≤1 m/day
Schmutzdecke/Clogging layer	yes	yes
Flow regime	saturated	Unsaturated and saturated
Redox	Oxic (aerobic)	Oxic (aerobic) and anoxic

Source: (IWA, 2006)

Table 2-6 Quantitative Performance Comparison

Parameter/process	**SSF**	**RBF**
Turbidity (NTU)	≤ 1 NTU	≤1NTU
DOC removal	≥ 15%	≥50%
Biostability: BDOC removal	≥ 50%	< MDL
Trace Organics removal	-	≥50% (except for few persistent PhACs)
(Total) Nitrogen Achievable	-	≤2 mg/L
Microbial removal (Viruses)	≥ 2-log	≥4-log

Source: (IWA, 2006)

2.5 Natural Organic Matter (NOM)

2.5.1 Chemistry of NOM

Natural Organic Material (NOM) is a heterogeneous mixture of organic compounds that enter into water bodies from decaying vegetation, organic soils, and biological activity (Thurman, 1985). NOM from different source materials has different characteristics. In general, NOM molecules are large and contain many functional groups that affect their chemical behaviour. A typical structure of NOM is shown in Figure 2-5, which highlights some of the common functional groups present.

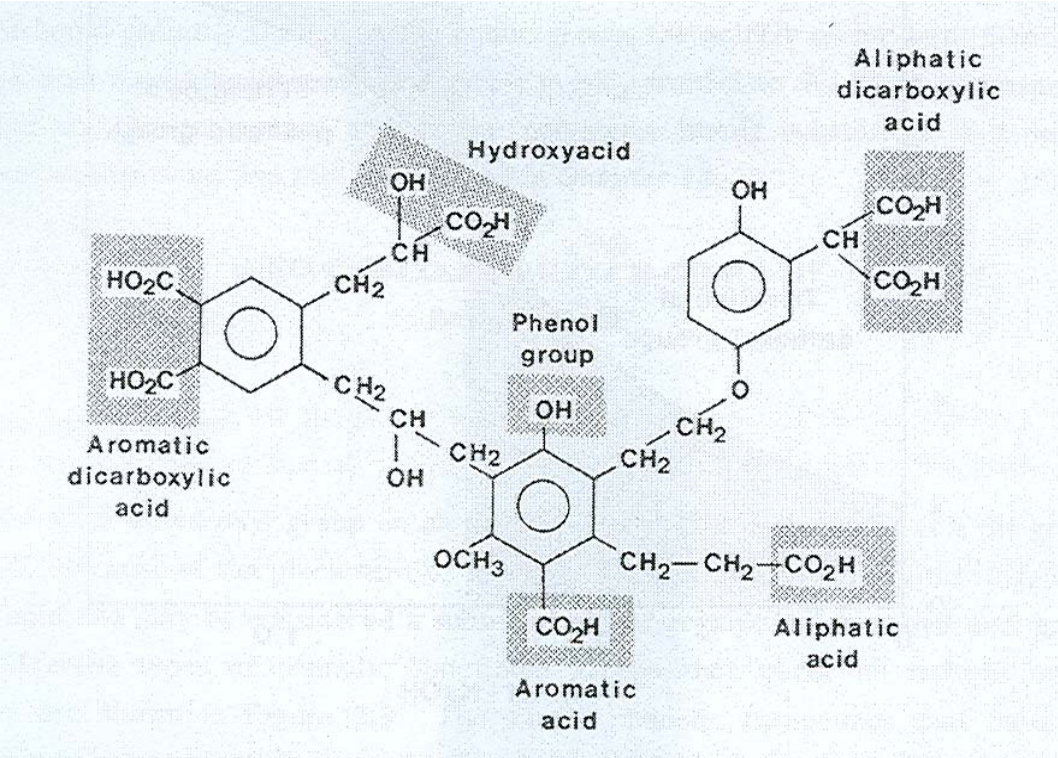


Figure 2-5 Typical NOM structure *(Source: Thurman, 1985)*

NOM is a complex mixture of dissolved and particulate humic and non-humic organic substances that occur in both surface and groundwater. It contains significant levels of DOC, which constitutes the reactive organic content and is responsible for the majority of reactions of interest in water treatment processes. It contributes to odour, colour and the deterioration of taste in drinking water, can facilitate the transport of toxic contaminants in groundwater, and is the main precursor for disinfection and oxidation byproducts (Ray *et al.*, 2002).

DOC consists of both humic (i.e humic and fulvic acids) and non humic components. Fulvic acids represent the most water soluble fraction of humic material and contribute 90 % of the dissolved humic substances in most natural waters (Ray *et al.*, 2002). Colors in water are caused by fulvic acids. The molecular weight of fulvic acids typically ranges between 500 and 2000 Daltons. Humic acids have molecular weights greater than 2000 Daltons. Humic molecules contain aromatic, carbonyl, carboxyl, methoxyl, and aliphatic units, with the phenolic and carboxylic functional groups providing most of the protonation and metal complexation sites. The non-humic fractions of DOC includes hydrophilic acids, proteins, amino acids, amino sugars and carbohydrates

The amount of DOC in natural water varies depending on the type of water from approximately 0.5 mg/l for groundwater and sea water to over 30 mg/l for colored water

from swamps. Figure 2-6 shows the average concentration of dissolved and particulate organic carbon in natural waters.

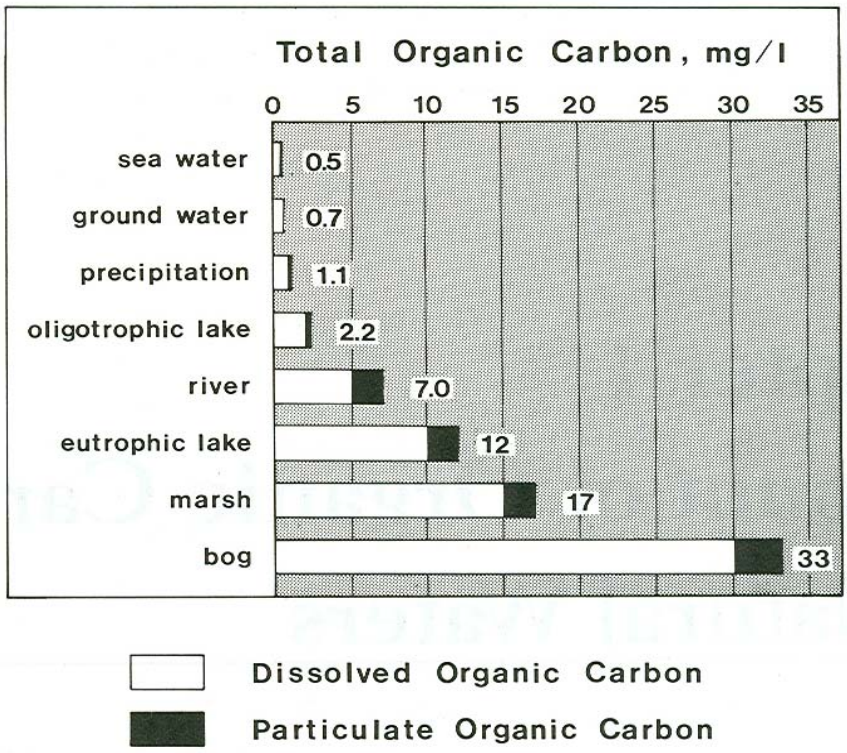


Figure 2-6 Approximate concentrations of dissolved and particulate organic carbon in natural waters *(Source: Thurman, 1985)*

Different components of NOM exhibit different transport behaviour during surface water infiltration. Several studies have indeed demonstrated that the mobility of NOM increases with decreasing molecular weight and hydrophobicity (Tufenkji *et al.*, 2002). These results suggest that the smaller and more hydrophilic fraction of NOM facilitate transport of contaminants in groundwater.

An average DOC composition of natural water is shown in Figure 2-7. 50 % of the DOC is aquatic fulvic and humic acids, the dominant group of natural organic compounds in water, and 30 % of the DOC is hydrophilic acids, a relatively unknown yet large fraction of the DOC. The remaining 20 % of the DOC are identifiable compounds (carbohydrates 10%, caboxylic acids 7 %, aminoacids 3 %, and hydrocarbons less than 1 %). Natural organics, especially humic acid (HA) and fulvic acid (FA) contribute to the natural colour of water, which becomes visible if the dissolved organic carbon (DOC) concentration is higher than approximately 5 mg/l. It is for that reason that natural organics removal is often referred to as colour removal.

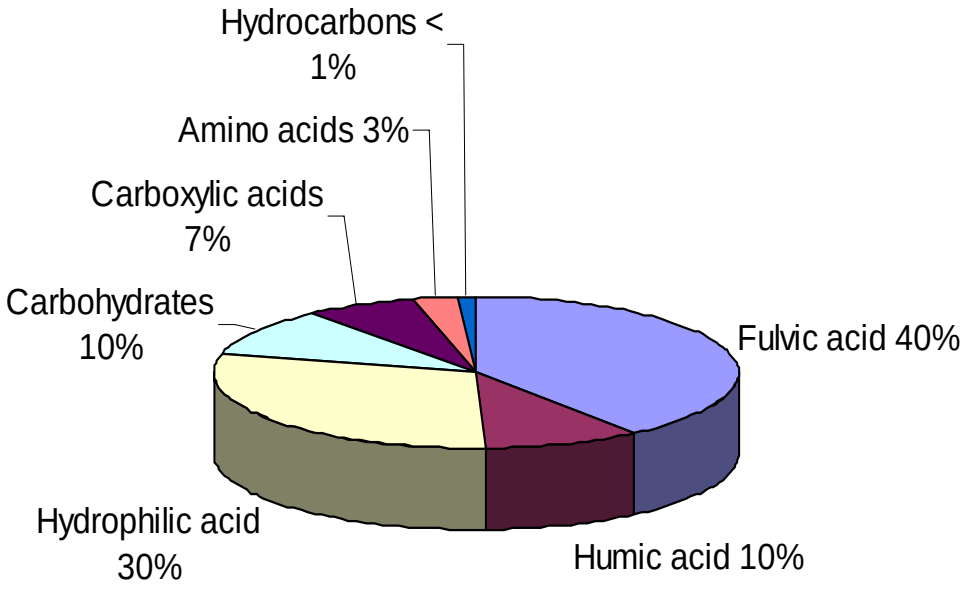


Figure 2-7 Composition of dissolved organic carbon for an average river water with a DOC of 5 mg/L *(Source: Thurman, 1985)*

Three different compounds make up humic substances (HSs): Humin (defined insoluble), humic acid (HA, insoluble at a pH of 1) and fulvic acid (FA, soluble at any pH) (Schafer, 2001). HA can be precipitated at pH<2.0, where as FA remains in solution.

2.5.2 Characterization of Natural Organics

Organic material can originate from various sources. The fraction of organic matter that derives from the biota growing in the water bodies is classified as internal or autochthonous NOM. This source of organic matter is due to the excretion and decay of organisms including bacteria, algae and vascular plants. The external organic matter (allochthonous) enters the water stream from the watershed, and originates from degradation of terrestrial vegetation and soil leaching during runoff (Thurman, 1985).

Chemical characterization of organic matter is also complex. To date, it has not been possible to identify all organic molecules in water. The difficulty of this approach results from the great complexity of the organic matrix, constituted by a mixture of hundreds of simple molecules or hetero-polymers, and the very low concentration of these compounds. Consequently, organic matter characterization is only possible through various fractionation and measurement techniques that give partial information on organic matter levels, and chemical functions or molecules, depending on the methodology used (Amy, 1993).

The characterization of natural organics is important in order to understand treatment behaviour and to compare results to other waters. The main characteristics of natural organics are molecular weight, functional groups, hydrophobicity and charge. Results obtained are often relative, depending on the method used and thus vary greatly, even for identical compounds (Schafer, 2001). A variety of treatment processes can be used to control organic matter in drinking water. Removal of organic matter varies widely, and is generally between 10 and 90% (Volk et al., 2002). The degree of organic carbon removal depends on several parameters such as the quality and quantity of organic materials in the source water, the treatment train design and operational conditions. In general, organic matter levels are reduced after settling, adsorption, granular activated carbon (GAC) filtration or membrane processes. Oxidation processes with ozone or chlorine lead to the formation of biodegradable compounds.

2.5.2.1 Organic Carbon

A sum parameter for organic matter is total organic carbon (TOC) or dissolved organic carbon (DOC). DOC or TOC will not give any information about the different fractions of NOM. DOC/TOC analysis can be problematic at low concentrations (several 100 µg/l), where contamination due to wash water, chemicals, atmosphere, and sample vials can be higher than the value of interest. Different methods of DOC/TOC analysis are available, but only the UV/persulfate oxidation method appears successful for determination of low concentrations (Greenberg et al., 1992; Koprivnjak et al., 1995).

Fractionation of natural organics is required to link characteristics to treatment behaviour. Particulate organic carbon (POC) can be easily separated from dissolved organic matter using a 0.45 µm filter. This operation distinguishes the parameters TOC and DOC by definition. POC is the fraction of the TOC that is retained on a 0.45 µm porosity membrane. DOC is the organic carbon smaller than 0.45 µm in diameter. POC generally represents a minor fraction (below 10%) of the TOC (Thurman, 1985).

Figure 2-8 shows the continuum of organic carbon in natural waters. Filtration removes macroscopic particulate organic carbon, such as zooplankton, algae, bacteria, and detrital organic matter from soil and plants. Viruses and some ultra-small bacteria are the only types of organisms that pass through a filter and enter the dissolved organic fraction.

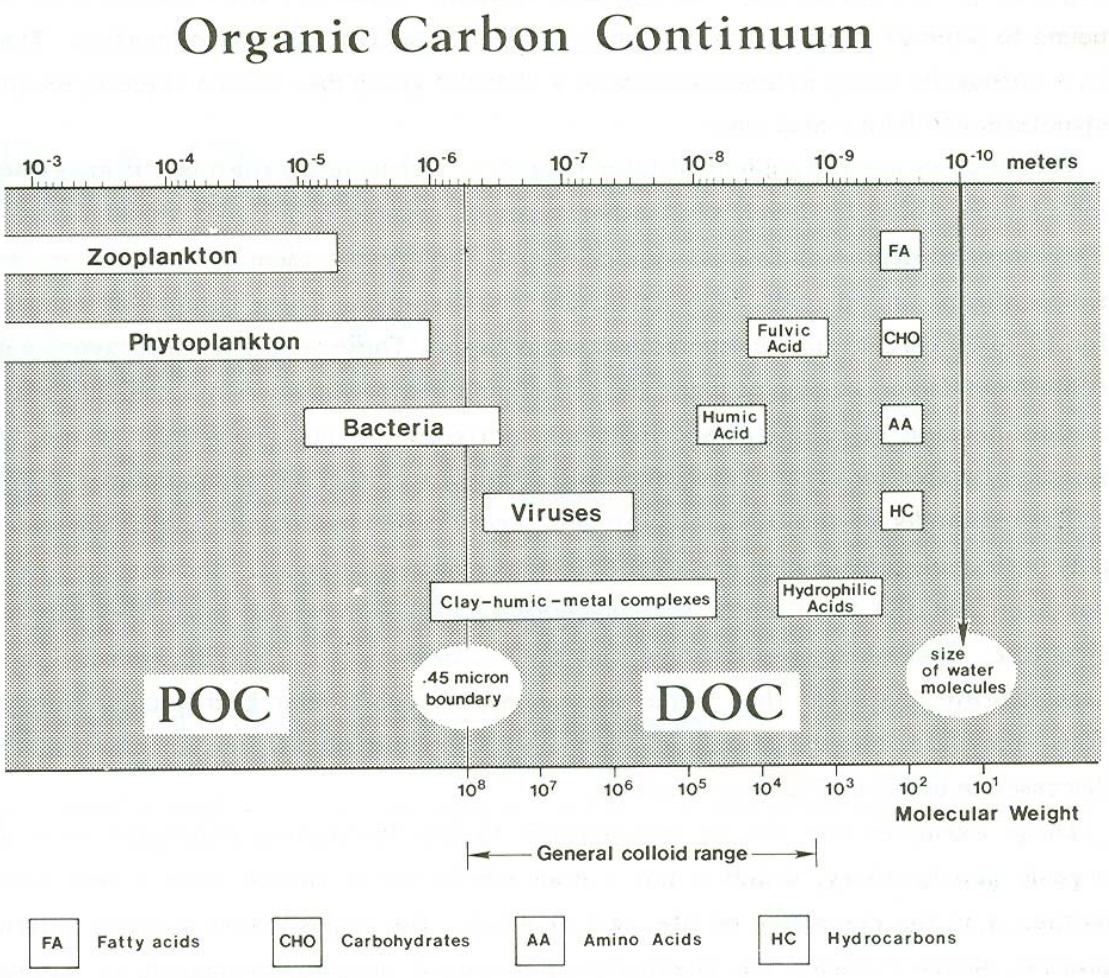


Figure 2-8 Continuum of particulate and dissolved organic carbon in natural waters (FA=fatty acids, CHO=carbohydrates, AA=amino acids, HC=hydrocarbons) *(Source: Thurman, 1985)*

2.5.2.2 UV absorbance

NOM removal in water treatment processes is typically quantified by TOC measurements, which can be time consuming and expensive. Because the double bonds in organic molecules absorb ultraviolet light at 254 nm (UV_{254}), UV absorbance measurements can provide a quick estimate of the organic carbon content of raw or treated water samples. UV absorbance measurements are used for monitoring changes in raw water quality, coagulation performance, and as a surrogate for DOC. The UV/TOC ratio is often used to determine the humic fraction in the organic matter or to determine the aromaticity of a sample.

The concept of Specific UV Absorbance (SUVA) has been developed as an operational indicator of the nature of NOM. SUVA is defined as the UV absorbance of a water sample at a wavelength of 254 nm normalized for dissolved organic carbon (DOC)

concentration. It is a calculated parameter obtained by dividing a sample's ultraviolet absorption at a wavelength of 254 nm (UV_{254}) (in cm^{-1}) by its concentration of dissolved organic carbon (DOC) (in mg/L).

$$SUVA = \frac{UV_{254}(cm^{-1}) \times 100}{DOC(mg/L)} \quad \text{..... (2.1)}$$

Guidelines for the interpretation of SUVA values are presented in Table 2-7.

Although the numerical relationship between UV absorbance and TOC is unique to each raw water, a change in TOC can always be detected as a change in UV absorbance. This makes UV absorbance measurements well suited to monitor changes in NOM concentration.

Table 2-7 Guidelines on the nature of NOM

SUVA value	Composition
< 2	Mostly non-humics, Low hydrophobicity, Low molecular weight
2 - 4	Mixture of aquatic humics and other NOM, Mixture of hydrophobic and hydrophilic NOM, Mixture of molecular weights
>4	Mostly aquatic-humics, High hydrophobicity, High molecular weight

Source: (Edzwald and Tobiason, 1999)

2.5.2.3 Fluorescence

Fluorescence is the phenomenon in which absorption of light of a given wavelength by a fluorescent molecule (fluorophore) is followed by the emission of light at longer wavelengths. The distribution of wavelength-dependent intensity that causes fluorescence is known as the fluorescence excitation spectrum, and the distribution of wavelength-dependent intensity of emitted energy is known as the fluorescence emission spectrum.

Fluorescent organic matter is constituent of river waters. Between 40 to 60 % of natural organic matter is fluorescent (Baker, 2001). This fluorescent material principally comprises proteins and organic acids derived from the decay of plant and animal matter within the catchments. Fluorescence occurs when these molecules, having been excited by a high energy light source that raised the energy levels of the electrons within the molecules, release energy in the form of light.

Fluorescence excitation-emission matrix is used as NOM fingerprinting tool. It is a 3-dimentional spectra showing fluorescence intensity determined by excitation-emission wavelengths. By using the techniques of Fluorescence, protein, fulvic and humic like materials can be identified based upon their characteristic excitation and emission wavelength. Humic-like peaks have higher excitation/emission wavelengths as compared to protein-like peaks.

Proteins contain three aromatic amino acid residues (tryptophan, tyrosine, and phenylalanine) which may contribute to their intrinsic fluorescence. Changes in intrinsic fluorescence can be used to monitor structural changes in a protein. Protein fluorescence is generally excited at 280 nm or at longer wavelengths, usually at 295 nm (Mocz, 1999). Most of the emissions are due to excitation of tryptophan residues, with a few emissions due to tyrosine and phenylalanine. Table 2-8 summarizes the fluorescence characteristics of the three aromatic residues.

Table 2-8 Excitation-emission wavelengths of the three protein aromatic residues

Aromatic residues	Excitations (nm)	Emissions (nm)
Tryptophan	280	348
Tyrosine	274	303
phenylalanine	257	282

Source: (Mocz, 1999)

Baker presented in his paper the fluorescence EEM of a typical river water sample for an excitation wavelengths varying from 250 to 425 nm and emission wavelengths varying from 300 to 500 nm (Baker, 2001) . In his study three fluorescence peaks were identified as described below:-

- Tryptophan fluorescence at 275 nm excitation and 350 nm emission
- Fulvic-like fluorescence at 320 – 340 nm excitation and 410 - 430 nm emission
- Humic-like fluorescence at 370 – 390 nm excitation and 460 - 480 nm emission

2.5.2.4 Size of NOM

Size and molecular weight are important characteristics in water treatment, as diffusion coefficients and removal efficiencies are directly dependent on the size of a solute. A number of methods exist to measure this important parameter and each method has its own limitations (Schafer, 2001). In more recent years, studies have focused on the use of membranes, field flow fractionation (FFF) and chromatographic methods due to their relative ease of use and reproducibility.

High performance size exclusion chromatography (HPSEC) separates NOM constituents according to molecular weight (MW) by a differential permeation process, using a high performance liquid chromatography system with an online UV and DOC detector. This technique is simple and informative.

2.6 Endocrine Disrupting Compounds (EDCs) and their removal

The endocrine system is a set of glands and the hormones they produce, which help guide the development, growth, reproduction, and behaviour of animals and humans. Some hormones are also released from parts of the body that are not glands, such as the stomach, intestines or nerve cells, and act closer to where they are released (IPCS, 2002).

Some chemicals, both natural and man-made, can interfere with endocrine glands and their hormones or where the hormones act - the target tissues. These chemicals are called 'endocrine disruptors' or 'endocrine disrupting chemicals' (EDCs).

The potential presence of EDCs in river water is a topic of increasing interest and the potential transport of EDCs into riverbank filtered water presents a major concern (Ray et al., 2002). EDCs are present in industrial and domestic wastewater, both of which are sources of surface water pollution.

The presence of EDCs in the environment raise concerns because:

- harmful effects have been observed on reproduction, growth and development in certain species of wildlife and
- there are increases in some human reproductive disorders and some cancers which could be related to disturbance of the endocrine system

Although there is no substantial evidence, it is believed that EDCs exposure could be harmful to humans and could be a reason for some of the increases in human disorders such as breast cancer, uterine cancer, testicular cancer, prostate cancer or thyroid cancer. More research is needed to investigate this possibility. Exposure of humans to EDCs can occur via contaminated food or water, and chemicals used in consumer products.

Despite early evidence, the phenomenon of endocrine disruption has only become an overtly topical environmental issue since the early 1990s. The reason it came to the forefront was that studies have revealed potential problems with human male reproductive health, in the form of reduced sperm quality/counts as well as worldwide increase in testicular cancer, with EDCs cited as a possible cause. Evidence was also emerging that certain wildlife were experiencing endocrine disruption to their reproductive systems, with exposure to environmental pollutants cited as the cause (e.g

egg shelling thinning due to pesticides, estrogens and surfactants feminizing fish) (Birkett and Lester, 2003).

Sewage treatment works (STWs) are able to remove some EDCs throughout the treatment process. However, depending on the level of treatment, varying concentrations of EDCs have been identified in sewage effluent and sludge. Consequently wastewater effluent has been shown to contain concentrations of EDCs capable of inducing adverse reactions in biota, which are present in surface waters. Although EDCs may be present in effluent at trace concentrations, adverse effects have been observed in wildlife and may have health implications for humans.

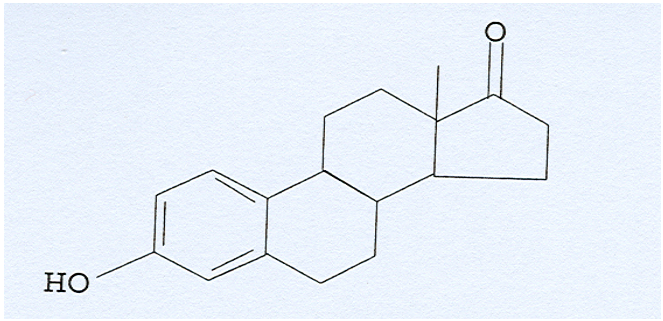
The receiving aquatic environment for effluent discharge can be groundwater or more commonly surface waters. EDCs have been identified as responsible for estrogenic effects observed in fish present in surface waters. The most causative EDCs have been determined as the steroid estrogens, estrone (E1), 17β-estradiol (E2), and ethynlestradiol (EE2). E1 and E2 are naturally occurring; however, EE2 is synthetic compounds from contraceptive sources. These compounds have been investigated and found by researchers (Andersen *et al.*, 2003; Ingerslev *et al.*, 2003) that they occur in wastewater effluent. The presence of these compounds in the aquatic environment has been primarily attributed to their incomplete removal during the sewage treatment process. The fate of EDCs present within the effluent is partly dependent on the type of receiving water as well as the compounds own physicochemical properties. Estrogenic effects are reduced after discharge into receiving waters because of dilution, degradation and sorption processes.

Many EDCs have a high sorption potential and low water solubility and volatility. The water solubility of steroid estrogens range from 0.3 to approximately 13 mg/L with the natural steroid having the highest solubility. The synthetic steroids have the highest octanol-water partitioning coefficients ($\log K_{ow}$). Estrogens are non-volatile, highly lipophilic substances that can be expected to adsorb to solids in environmental matrices. Hence, they can be removed by RBF. Table 2-9 presents the physicochemical properties of steroid estrogens.

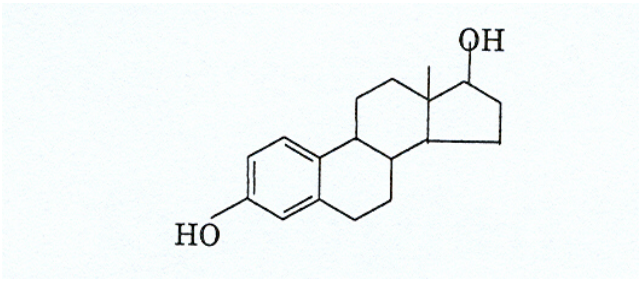
Table 2-9 Physiochemical properties of steroid estrogens.

Estrogens	Molecular wt.	Water solubility (mg/L at 20 ^{o}C)	Log K_{ow}
E1	270.4	13	3.43
E2	272.4	13	3.94
EE2	296.4	4.8	4.15

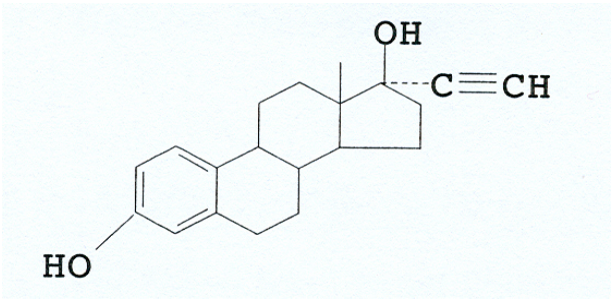
Source: (Ingerslev and Halling-Sørensen, 2003)



a) Estrone (E1)



b) 17β-Estradiol (E2)



c) Ethynlestradiol (EE2)

Figure 2-9 Chemical Structures of Estrogen compounds

2.7 Research Needs

Literature review on RBF system revealed some important topics/issues of interest which needs further study in the future. Some of the issues include:

- Determining appropriate sites for riverbank filtration
- Hydraulic investigation and test pumping.
- Forecasting yield—analytical and modelling tools
- System design methodology
- Investigation of the impact of clogging on the performance of RBF
- Quantifying and predicting riverbed clogging
- Treatment and removal mechanisms
- Sustainable operation issues.

3 MATERIALS AND METHODS

3.1 Introduction

This chapter explains the methods and experimental procedures followed for data collection and analysis in order to attain objectives of the research. The research was carried out in three stages. The first stage was a desk study to review literatures on riverbank filtration. Secondly, data collection was carried out through laboratory based soil column and batch experiments. The last stage involved analysis and interpretation of collected data from the experiments. Each of these stages is elaborated below.

3.2 Desk Study

Desk study (literature review) was one of the main parts of this research methodology. Desk study was mainly focused on the basic concept on RBF, the experience of different countries in the technology/historical background, motivation for increasing interest in RBF systems, processes and mechanisms involved in contaminant removal, factors affecting the design of RBF systems, procedures being used by researchers during laboratory studies and current issues/research areas. Existing researches and published papers that are significant to this work were critically reviewed.

3.3 Experimental Setup

3.3.1 Soil Column Experimental Setup

Laboratory based soil columns, constructed and instrumented according to the schematic diagram shown in Figure 3-1 were used for evaluating the removal of OM fractions from Delft canal water and wastewater secondary effluent. The columns were constructed with uPVC pipe with internal diameter of 100 mm. The set up was made in such a way that there are two columns of each 2.5 m height connected in series. There were two such setups to run two experiments with different influent water quality at the same time. The bottom of each pipe was packed with filter media support of 20 cm thick graded gravel and then filled with silica sand material of size 0.8 to 1.25 mm above the gravel support layer.

The two columns were connected with silicone tubes and 14 sampling points were provided as shown in Figure 3-1. The first five sampling points were placed closely to each other (SP1-SP2=5 cm, SP2-SP3=10 cm, SP3-SP4=10 cm, SP4-SP5=20 cm) in order to investigate the role of biomass/Schmutzdecke layer in the removal of OM fractions. The remaining sampling points were placed every 50 cm interval. In addition, valves to control the hydraulic loading rate under gravity flow and manometers to

control the head losses through the soil column were provided. A backwashing system was also provided in order to clean the filter media with clean tap water whenever the effluent flow rate would be reduced significantly from its initial value as a result of clogging, if any.

3.3.2 Batch Experimental Setup

Batch experimental setups were used to investigate OM removal and characterization of OM for comparison with the result from the soil column. This was carried out under both aerobic and anoxic conditions with three different influents in triplicates: Delft canal water (DCW), canal water mixed with wastewater secondary effluent (DCW+SE) (1:1 ratio) and wastewater secondary effluent alone (SE). The batch experimental setup is shown in Figure 3-3.

Similar batch experimental setups were also deployed to investigate the removal efficiency of RBF system for three EDCs namely 17β-Estradiol (E2), Ethynlestradiol (EE2) and Estrone (E1). A total of 16 batch reactors were used. Eight batch reactors were used to analyse the effect of biodegradation in the removal and the remaining eight to analyse the effect of adsorption only by prohibiting microbial activity by adding Sodium Azide (2 mM NaN_3). The details of the setup are presented in table 3-1.

Table 3-1 Details of various conditions for EDCs measurement

Influent	Redox condition	Intended removal process	No. of reactors used	Remark
1. DCW+SE	Aerobic	Abiotic	2	Ripened sand
	Aerobic	Biotic	2	Ripened sand
	Anoxic	Biotic	2	Ripened sand
	Aerobic	Abiotic	2	No sand (control-1)
	Aerobic	Abiotic	2	Fresh sand (control-2)
2. MQ water	Aerobic	Abiotic	2	Fresh sand (control-3)
3. DCW	Aerobic	Biotic	2	Ripened sand
4. SE	Aerobic	Biotic	2	Ripened sand

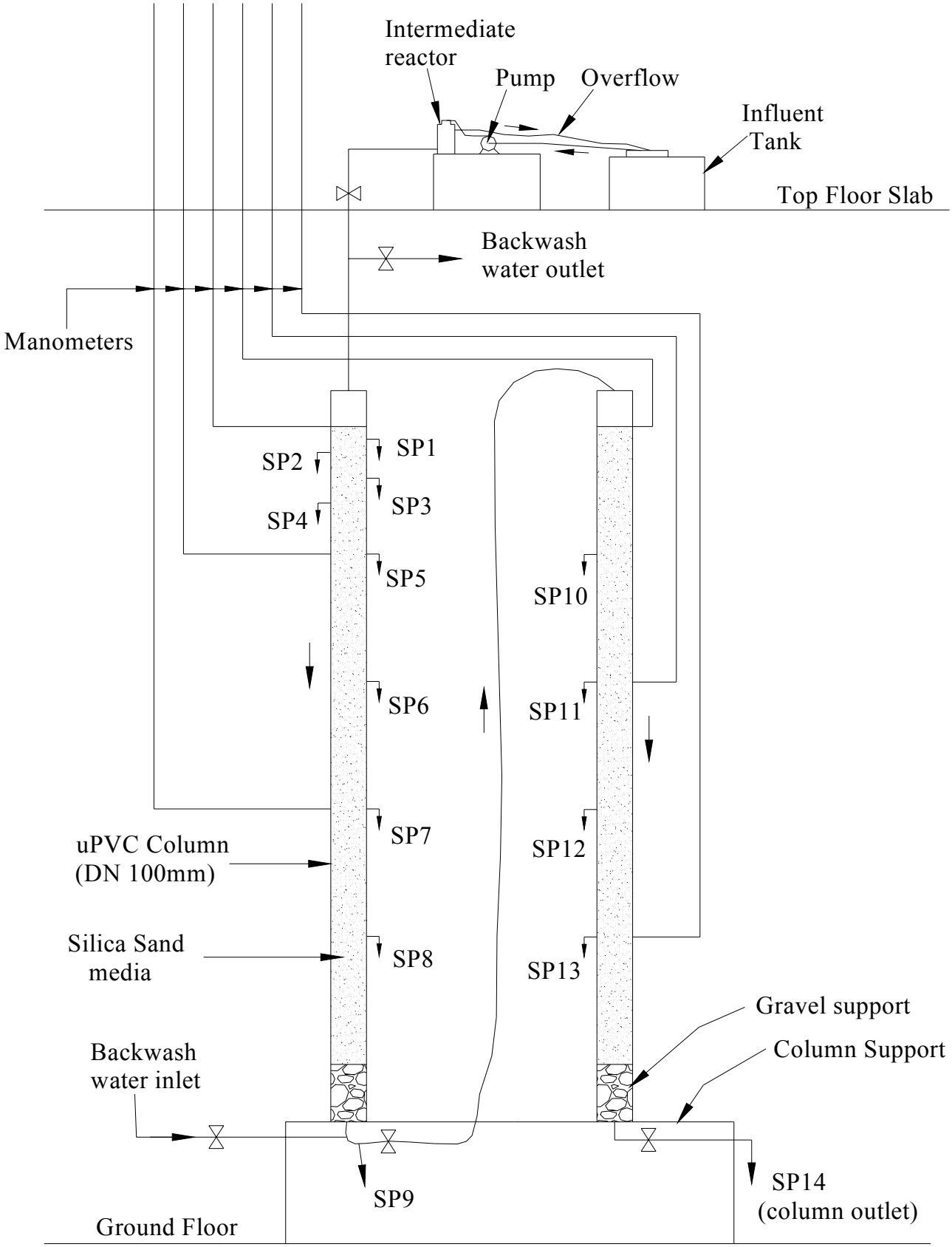


Figure 3-1 Schematic diagram of the soil column experimental setup.

Figure 3-2 Laboratory scale experimental setup of the soil column system

a) Aerobic reactors b) Anoxic reactors

Figure 3-3 Batch experimental setups

3.4 Experimental Process Conditions and Procedures

Delft Canal water and wastewater secondary effluent from Hoek van Holland wastewater treatment plant were used as influent water. The main water quality parameters of these influents were measured and the results are included in chapter 4.1. Experiments were carried out by varying process conditions (oxic, anoxic condition and various loading rates) to evaluate RBF performance as shown in table 3-2 and 3-3.

3.4.1 Process Conditions

a) Applied Influent water quality

In order to determine the effect of influent water quality on organic matter removal during RBF, Delft canal water and wastewater secondary effluent were chosen to be used as a feed to the soil column and batch experiments. Wastewater secondary effluent was applied after it is mixed up with Delft canal water in 1:1 ratio. This was done to investigate the impacts of wastewater discharge in to surface water on the performance of RBF. Application of various influent waters with different levels of quality was expected to give an insight on the level of treatments required after RBF.

The performance of RBF was tested by applying the influent water in the following ways:

i) Batch experiments
- Delft canal water (100%)
- Delft canal water mixed with wastewater secondary effluent (50 % each)
- Wastewater secondary effluent (100%)

ii) Soil column experiments
- Delft canal water (100%)
- Delft canal water mixed with wastewater secondary effluent (50 % each)

b) Aerobic and anoxic conditions

In both soil column and batch experiments, aerobic conditions were maintained by aeration of influent water for aerobic biodegradation process. Under aerobic condition O_2 is the electron acceptor.
Anoxic conditions were established by constantly stripping off O_2 using Nitrogen gas by connecting fine diffusers to N_2 line in the laboratory as shown in Figure 3-3b. For this condition NO_3 is the electron acceptor.

c) Hydraulic loading rate

To investigate the effect of hydraulic loading rate on the removal of OM during RBF, the soil column were operated at a loading rate of 0.625 and 1.25 m/d. These loading rates were attained by valve control at the outlet of the soil column using a measuring cylinder and a stop watch. The EBCT corresponding to a hydraulic loading rate of 0.625 and 1.25 m/d were 8 and 4 days respectively.

d) Filter media

The filter media used for the soil column and batch experiments was silica sand of size 0.8 mm – 1.25 mm. These sizes of sand are in the range of medium sand (0.42 – 2 mm) as per American Society for Testing and Materials (ASTM) particle size classification. Finer sand sizes are avoided to prevent clogging in the soil column.

The total effective depth of the filter bed for one set up is 5 m. The media was first washed with acid and demineralised water before transferring to the soil column in order to remove background organics, if any, present in the sand.

Table 3.2 and 3.3 summarizes the experimental process conditions of the soil column and batch experiments respectively.

Table 3-2 Process conditions for soil-column experiments

Expt. no.	Influent	Hydraulic loading rate	Redox condition
1	Delft canal water	1.25 m/d	Aerobic
2	Delft canal water	0.625 m/d	Aerobic
3	Delft canal water + wastewater secondary effluent (1:1 ratio)	1.25 m/d	Aerobic
4	Delft canal water + wastewater secondary effluent (1:1 ratio)	0.625 m/d	Aerobic

Table 3-3 Process conditions for batch experiments

Expt.	Influent	Redox condition
1	Delft canal water	Aerobic
2	Secondary effluent	Aerobic, Anoxic
3	Delft canal water + wastewater secondary effluent (1:1 ratio)	Aerobic

3.4.2 Soil Column Experimental Procedure

1) Water from the above stated sources were collected, characterized and stored at 4 ^{O}C before application to the soil column. Storage at this temperature was aimed at minimizing biological activities. The collected water samples were characterized to determine the composition and strength of influent to be applied to the soil column system.
2) At the beginning, the filter material in the column was conditioned with the influent water. This biological acclimation of the soil column system was continued until a steady state was reached with respect to DOC removal. For this, the influent water was percolated through the fixed bed for about one and half month in order to form a biofilm of microorganism population.
3) After conditioning (steady state), the influent water was applied to the soil column under different process conditions.
4) Sampling from various sampling points along the soil column.
5) Analysis of various relevant parameters (DOC, TOC, O_2, UVA_{254}, pH, and NO_3) for the samples collected.

3.4.3 Batch Experimental Procedure

1) Sample water collection, characterization, and storage at 4 ^{O}C before application to the batch reactors.

2) Bio-sand preparation. For this, about 3 kg of silica sand (0.8-1.25 mm) was put in a 10-litre container filled with Delft canal water. The water inside the reactor was then continuously stirred and renewed with a new batch of water every 4 days for about a month. Similar arrangements were carried out to prepare bio sand with delft canal water mixed with wastewater secondary effluent.

3) Batch experiment was then conducted for various process conditions shown in table 3-2. For aerobic condition nine 0.5 litre reactors were prepared in triplicate for three different feed waters by transferring 75 g of bio-sand to each reactor. For anoxic condition two reactors (1 litre capacity) were prepared with wastewater secondary effluent by transferring 125 g of bio-sand to each reactor. The reactors were put on a shaker set at a frequency of 100 rpm in a dark room.

4) Analysis of DOC and UVA was carried out by taking samples of influent and effluent every four days over the period of operation of the batch experiments to determine the BDOC component.

3.5 Analytical Methods and Equipments

A brief description of the methods and equipments used to measure parameters of concern for this research work is presented in the following sub sections.

3.5.1 pH, EC and O_2

Measurement of pH was carried out by using METROHM-691 pH meter (Swiss made) which was calibrated prior to the measurement. Samples of about 120 ml volume was collected in a plastic cup from the influent and various sampling points of the soil column and was placed on a magnetic stirrer to ensure uniformity. Then, the meter probe (electrode) was immersed in the sample after rinsing it thoroughly by spouting demineralized water from plastic wash bottle. The stable final reading was then taken.

The electrical conductivity of influent water was measured with WTW cond 330i conductivity meter. The meter probe was inserted in the sample, stirred to ensure uniform mixing and a stable reading obtained was then recorded.

Dissolved oxygen was measured with HACK HQ10 Oxygen meter. The dissolved oxygen of samples from various sampling points of the soil column was measured by connecting syringe at the sampling point. The probe of the oxygen meter was inserted in the syringe and the valve of the sampling point slowly opened. A stable reading obtained was then recorded. This method of oxygen measurement was followed to avoid contact of the sample with air as much as possible.

3.5.2 Ammonia, NH_4-N

Ammonia measurements were carried out by using Dichloroisocyanurate method. Brief descriptions of the analytical methods and procedures are presented as follows:

Equipments used

- Perkin Elmer UV/VIS Spectrophotometer with 1 cm cells (Cuvette)
- Volumetric flasks (50 ml)
- Pipets

Reagents prepared

- **Salicylate reagent:** 130 g of sodiumsalicylate ($NaC_7H_5O_3$) and 130 g of sodiumcitratedihydrat ($Na_3C_6H_5O_7.2H_2O$) were dissolved in about 650 ml deminertalized water in a 1000 ml volumetric flask. 0.970 g of disodiumpentacyano nitrosylferrate (III) ($Na_2Fe(CN)_5NO.2H_2O$) was then added & mixed and the flask filled up to the mark with demi water.

- **Dichloroisocyanurate reagent**: 32.0 g of NaOH was dissolved in 500 ml of demineralized water, cooled to room temperature and 2.00 g of sodiumdichloroisocyanurate ($NaC_3N_3O_3Cl_2$) added. The volume was then made up to 1000 ml and mixed.

- **Stock NH_4Cl:** 3.819 g of anhydrous NH_4Cl was dissolved in demineralized water and diluted to 1000 ml.
  1.00 ml = 1.00 mg N

- **Standard NH_4Cl:** 10 ml of stock solution was diluted to 1000 ml.

Standard preparation

In order to prepare calibration line (NH_4-N vs. Absorbance), the following series of standards were made by diluting the previously prepared standard solutions to 50 ml.

Table 3-4 Series of standards for preparation of calibration line

Volume of standard solution diluted to 50 ml	NH_4-N (mg/ L)
0	0
0.5	0.1
1.0	0.2
2.0	0.4
3.0	0.6
5.0	1.0
7.0	1.4
10.0	2.0

Procedure

a) Filtered samples of about 20 ml were transferred to a 50 ml volumetric flask and diluted to about 40 ml.
b) 4.0 ml of Salicylate reagent was added and mixed
c) 4.0 ml of Dichloroisocyanurate reagent was added and mixed
d) The mixture was then filled up to the mark with demineralized water and mixed
e) Absorbance at 655 nm of both the standard solutions and the samples were determined using a spectrophotometer between 1 and 3 hours
f) Calibration curve was then prepared for the readings of the standard solutions (NH_4-N vs. Absorbance at 655)

g) From the mathematical expression of the calibration line, the NH4-N concentration of the samples was determined for a particular absorbance.

3.5.3 Anions (NO_3-N, SO_4^{2-}, PO_4-P)

Anions were measured using DIONEX, ICS-1000 Ion Chromatography system coupled with ISA-100 automated sample injector shown in Figure 3-4. A filtered sample of about 1 ml was used for the analysis in the Ion Chromatography system. Milli-Q and control sample of known anions concentration were always analysed prior to the real sample during each measurement. The machine needs about 8 minutes to analyse one sample with single injection.

3.5.4 Fluorescence Excitation-Emission Matrix

Sample preparation

Samples were first filtered with 0.45 μm cellulose acetate membrane filter (Whatman) which was pre-rinsed with Milli-Q water and sample water in series. DOC of the samples was then measured using Model 700 total organic carbon analyser (O.I Corporation, USA). Based on the measured DOC level, samples were diluted to about 1 mg/L of DOC with 0.01M KCl solution which was pre-adjusted to a pH of $2.8(\pm 0.1)$ using HCl.

Measurement

A spectrofluorometer was used to measure and record the fluorescence of a sample. The Fluorescence (excitation-emission matrix) of the influent and effluent samples from the soil column and batch reactors were analysed by using FluoroMax-3 spectrofluorometer (HORIBA Jobin Yvon Inc., USA) shown in Figure 3-5. The entire excitation and emission matrix (EEMs) were obtained by measuring the emission spectra in the range of 290 – 530 nm at 2 nm intervals, with an excitation range of 240 to 450 nm at 10 nm intervals. EEMs of each sample were subtracted with an EEM of 0.01 M KCl solution set as a blank EEM. The instrument takes about 15 minutes to analyse one sample.

Figure 3-4 Ion Chromatography system

Figure 3-5 FluoroMax-3 for fluorescence measurement

3.5.5 Dissolved Organic Carbon, DOC

Sample preparation

Samples were first filtered with 0.45 μm cellulose acetate membrane filter using a 30 ml syringe and filter head. However, to avoid leaching of DOC from the filter itself, the filter was washed twice with 30 ml Milli-Q water and then a bit flushed with the sample itself before filtering the samples. The samples were prepared for analysis in an injection vials (glass vials) of 40 ml. volume.

Solutions preparation

- Phosphoric acid (H_3PO_4) solution:- 59 ml of 85 % H_3PO_4 was diluted with milli-Q water to 1000 ml. This solution is used to convert all inorganic carbon in the sample to CO_2.
- Sodium Peroxodisulfate solution ($Na_2S_2O_8$):- 100 g of $Na_2S_2O_8$ was dissolved in milli-Q water and diluted to 1000 ml. This solution is used to oxidize organic constituents in the sample.

Measurement

DOC of the samples was measured using Model 700 total organic carbon analyser (O.I Corporation, USA) shown in Figure 3-6. During each analysis, measurement was done in duplicates and an average was taken as the DOC concentration. In addition, a control sample with known DOC concentration was analysed during each measurement. Before the measurement of samples, three Milli-Q water samples were measured in order to clean the system and a DOC concentration of about 0.05 mg/L would imply that the machine is ready for analysis of the samples. The machine takes 16 minutes to analyse one sample with double injection. The machine was calibrated to measure a DOC concentration between 0.01 and 10 mg/L. Therefore, the samples were diluted to meet this requirement.

3.5.6 Size Exclusion Chromatography, HPSEC- UVA/DOC/Fluorescence

Sample preparation

Samples were first filtered with 0.45 μm cellulose acetate membrane filter in the same way as for DOC analysis. Ionic strength (conductivity) and pH of the sample was adjusted to the same level as the mobile phase before injection (EC $\approx$ 4.9 to 5.1 mS/cm). 4 ml of sample was then injected to the machine: 2 ml being used for flushing the coil (injection loop) and 2 ml for HPSEC-UVA/DOC analysis.

Measurement

The HP-SEC measurement was performed with HPLC (Shimadzu LC600) coupled with a UV-Vis detector (Shimadzu SPD-10Avp) and an on-line DOC detector (modified Ionic Sievers Turbo TOC analyser) as shown in Figure 3-7. The system used a TSK HW-50S column (column size: 2 cm x 25 cm, particle size: 35 μm Toyopearl HW resin) and the flow rate was 1 ml/min. The mobile phase (eluent) was prepared with Milli-Q water buffered with phosphate (0.0024 M NaH_2PO_4 + 0.0016 M Na_2HPO_4, pH 6.8) and 0.025 M Na_2SO_4, producing 0.1 M of an ionic strength. The inorganic carbon is converted to CO_2 and removed through inorganic carbon remover (ICR). The machine needs 2 hour to analyse single sample.

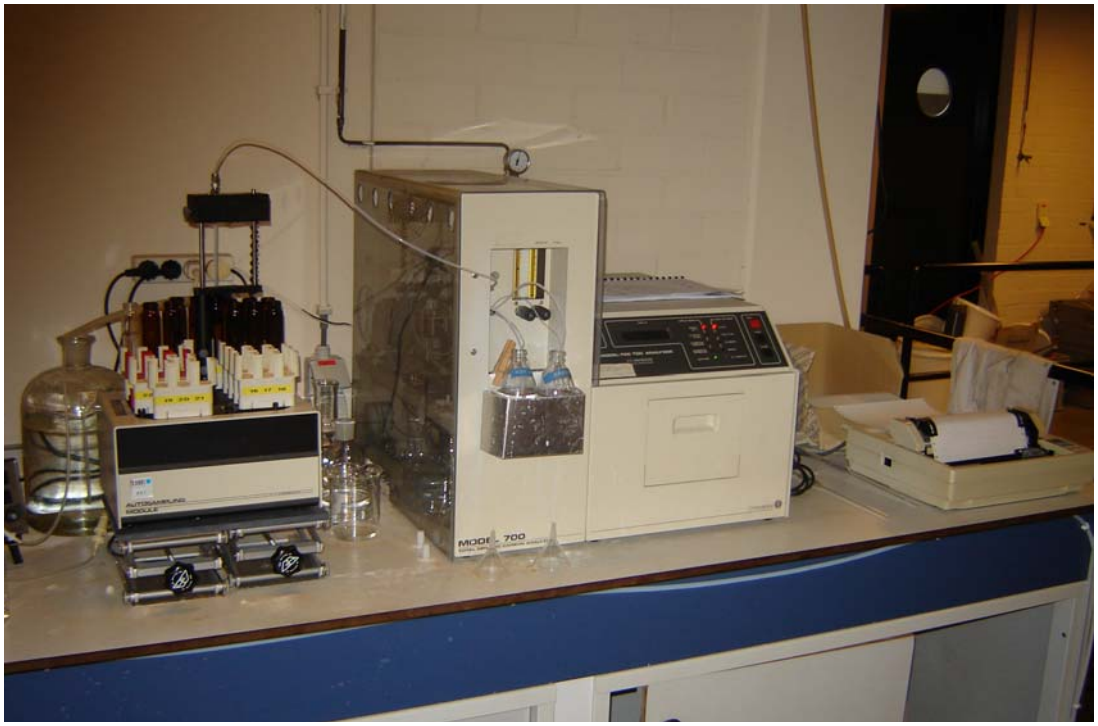


Figure 3-6 Total Organic Carbon Analyser

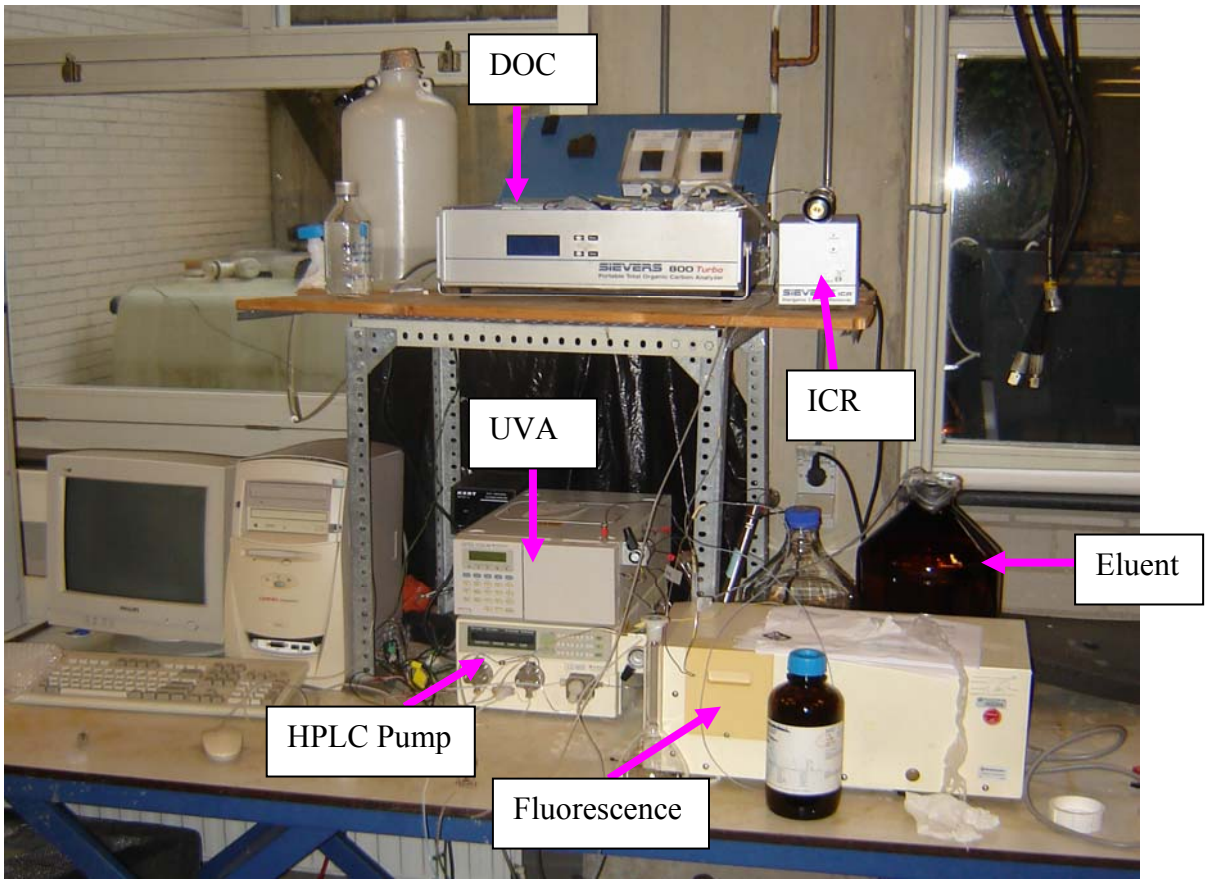


Figure 3-7 HPLC-SEC -DOC/UV Analyser

3.5.7 UV absorbance (UVA_{254})

UV absorbance measurement at a wavelength of 254 nm was carried out by Perkin Elmer UV/VIS Spectrophotometer using 1 cm cell of type QS suitable for wavelength below 300 nm. The samples are first filtered in a similar way as for the DOC measurement. Care has been taken not to have stain on the surface and air bubbles inside of the cell wall, as these affect the measurement. Cuvett was flushed thoroughly with Milli-Q water between samples and was rinsed with each sample before being filled. A spectrophotometer for absorbance measurements of various parameters are shown in Figure 3-8.

Figure 3-8 A Spectrophotometer for absorbance measurements

3.5.8 Endocrine Disrupting Compounds, EDCs

Quantification of estrogenic compounds (E1, E2 and EE2) was carried out by using biological technique known as ELISA (Enzyme-linked immunosorbent assay). Brief descriptions of the analytical method and procedures are presented as follows:

Measuring Principle

E1, E2, and EE2 ELISA test kits specifically detect estrogenic hormone E1, E2, and EE2 respectively. The analysis is based on a competitive reaction where enzyme-labelled standard E1 (E2 or EE2) competes with free E1 (E2 or EE2) in the sample for binding to a specific monoclonal antibody immobilised to the surface of a microplate. The amount of labelled E1 (E2 or EE2) bound to the antibody is determined by addition of a non-coloured substrate which is converted into a coloured product. The colour intensity is measured at 450 nm and is inversely proportional to the amount of E1 (E2 or EE2) in the sample. The assay is calibrated using a standard solution of E1 (E2 or EE2) supplied with the kit.

Equipments used

- Microplate reader
- ELISA kit – it contains coated and uncoated microplate, plate cover, and reagents required for the assay.
- Glass fiber filter and filtering equipment
- Vacuum manifold
- Solid phase extraction cartridge (SPE column)
- micropipettes

Reagents

The following reagents are available in the kit

- Standard E1, E2, and EE2: The solutions are prepared as 10 % MeOH (methanol).

	Standard concentration (ug/L)				
E1	0	0.05	0.3	0.8	5.0
E2	0	0.05	0.15	0.4	1.0
EE2	0	0.05	0.15	0.5	3.0

- Antigen-enzyme conjugate solution
- Wash solution
- Colour solution
- Stop solution

In addition, dichloromethane and hexane were used in the sample preparation step.

Procedure

i) Sample pre-treatment

- Filtration of raw water samples (500 ml) through glass fibre filter (1 um pore diameter).
- Concentration and cleanup (extraction) of filtered samples using solid phase extraction (SPE) technique to a final 1 ml sample volume (figure 3-9).

ii) ELISA test

- 100 ul of conjugate solution and then 100 ul of E1 (E2 or EE2) standards or 100 ul of sample prepared as 10 % methanol solution were transferred into each well of the uncoated microplate.

- Then 100 ul of the mixture prepared in the above step was dispensed into each coated well of the microplate and incubated for 60 minutes at room temperature
- The content of each well of the microplate was then decanted and the wells washed three times with wash solution of 300 ul. The plate was firmly tapped out to remove solutions from the microplate wells.
- 100 ul of colour solution was added to each well of the microplate and incubated for 30 minutes at room temperature. This has changed the solution to blue colour.
- Then 100 ul of stop solution was added to terminate the reaction. This has turned the blue coloured solution to yellow.
- Finally absorbance at 450 nm of both the standard solutions and the samples were determined using a spectrophotometer (microplate reader) with in 15 minutes time.
- Standard calibration curve was then prepared for the readings of the standard solutions
- Sample concentration was determined from the calibration line for a particular absorbance.

Figure 3-9 Sample concentration and cleanup using solid phase extraction (SPE) technique

4 RESULTS AND DISCUSSION

This chapter primarily presents the results obtained after studying the efficiency of RBF system through laboratory based soil column and batch experiments under various process conditions. Organic matter removal and characterization for influent and effluent water samples are presented. In addition, removal of EDCs was investigated in batch reactors and results obtained are discussed.

4.1 Influent Characterization

Two sources of water were selected as influent to the soil column and batch experiments: Delft canal water and wastewater secondary effluent. Canal water was collected from OUDE Delft, on the back side of UNESCO-IHE and wastewater secondary effluent from Hoek Van Holland wastewater treatment plant located in South Holland on the North Sea coast.

Wastewater effluent was mixed with canal water (1:1 ratio) before application to the soil column. This was done to investigate the impact of wastewater effluent on surface water during RBF systems. In many developed countries, the percentage of wastewater effluent in receiving waters can be in the order of 50 %. In periods of low flow when rainfall is low and demand is at its highest, the percentage can be up to 90 % (Birkett and Lester, 2003).

The characteristics of influents applied to the soil column and batch reactors are presented in Table 4-1. Influents were stored in the dark at 4°C immediately after collection. Pre-filtration of the samples were done with 45 um sieve to avoid settling of larger size materials. This prevented the columns from clogging.

Table 4-1 Influent water quality parameters

Parameters	Units	Delft canal water	Secondary effluent
O_2	mg/L	8.5	7.5
pH	-	7.8	7.11
Temperature	^oC	13	11.1
EC	μ S/cm	1236	1150
NH_4-N	mg/L	0.49	< 0.1
NO_3-N	mg/L	3.46	4.79
PO_4-P	mg/L	0.30	1.23
SO_4	mg/L	212	78
DOC	mg/L	18.61 ± 2.02	15.62 ± 2.31
UVA_{254}	cm^{-1}	0.599 ± 0.05	0.418 ± 0.05
SUVA	L/mg-m	3.22 ± 0.16	2.68 ± 0.15

4.2 RBF performance investigation for OM removal through soil column experiment

4.2.1 Soil column ripening process

At the start of the soil column experiment both columns (SC1 and SC2) were fed with Delft canal water mixed with wastewater secondary effluent in equal proportions (1:1). This biological acclimation (ripening) process was continued for more than a month till the soil columns stabilized with respect to DOC removal. During the process, influent and effluent DOC concentrations were continuously monitored. Oxic condition was maintained by continuous aeration of the influent in a small plastic bottle placed next to the main big tank by using a fine bubble diffuser (Figure 3.1). The small intermediate plastic bottle was needed in order to prevent DOC degradation of the influent before entering the column by reducing residence time in the tank. In addition the influent tank was fed daily with the amount of water needed to operate the column; the rest of the influent being stored in the fridge.

Figure 4-1 shows the variation in influent and effluent DOC concentration during the ripening process while Figure 4-2 shows the amount of DOC degradation in percent during ripening process. Figure 4-3 represents a normalized plot of the data which shows the extent of DOC removal during the process. The average influent DOC concentration during the ripening period was 15.71 ± 1.71 and the effluent DOC was 12.53 ± 1.65 and 12.43 ± 1.64 for SC1 and SC2 respectively. On average a DOC removal of about 20 % was obtained for both columns at the end of ripening period.

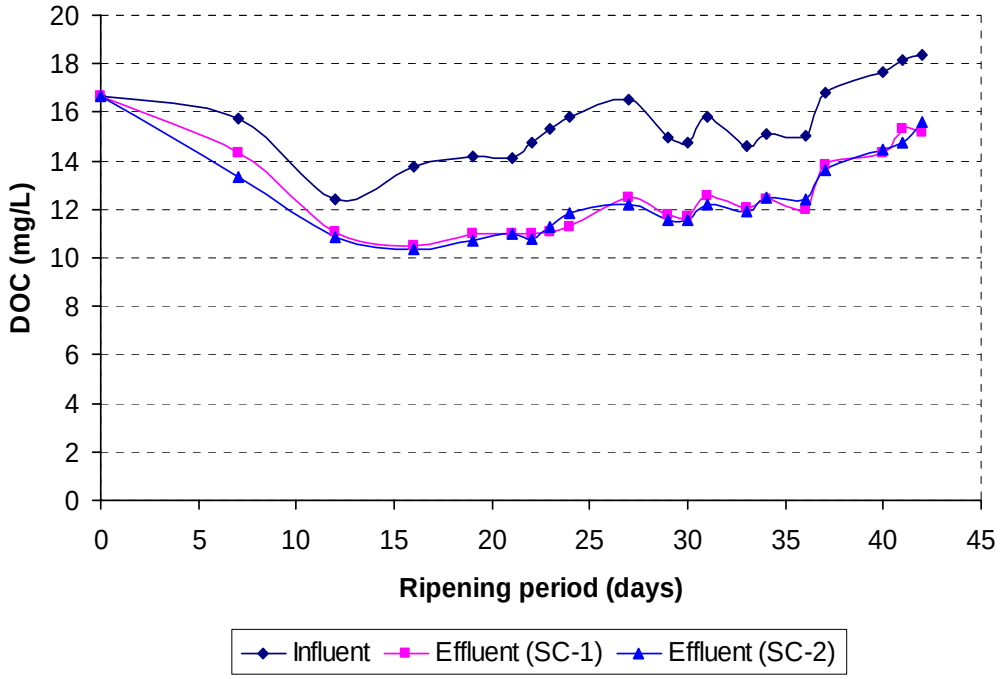


Figure 4-1 Change in DOC concentration of influent and effluent during ripening of the soil columns (Influent: DCW+SE, HLR=1.25 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

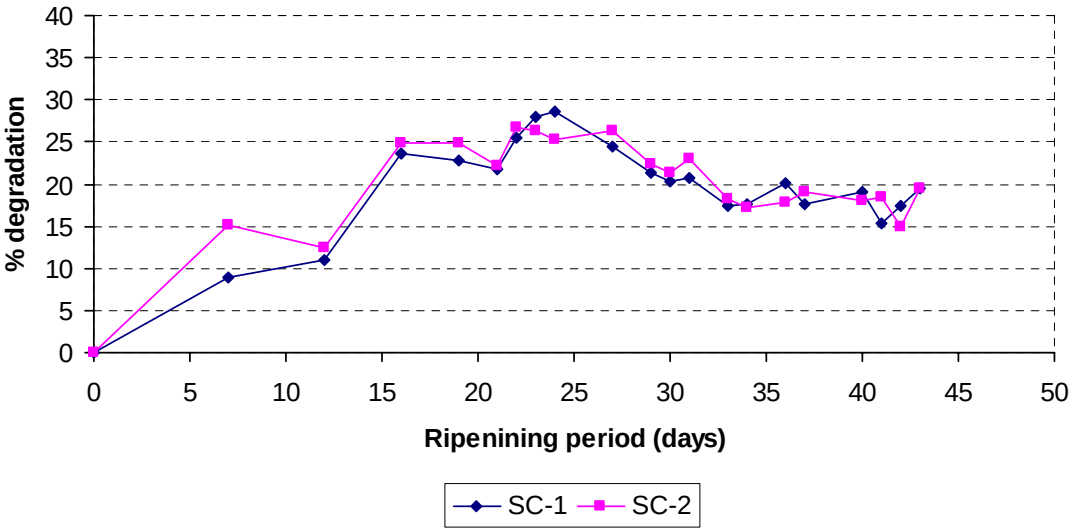


Figure 4-2 Change in DOC degradation in the soil columns during the ripening period (Influent: DCW+SE, HLR=1.25 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

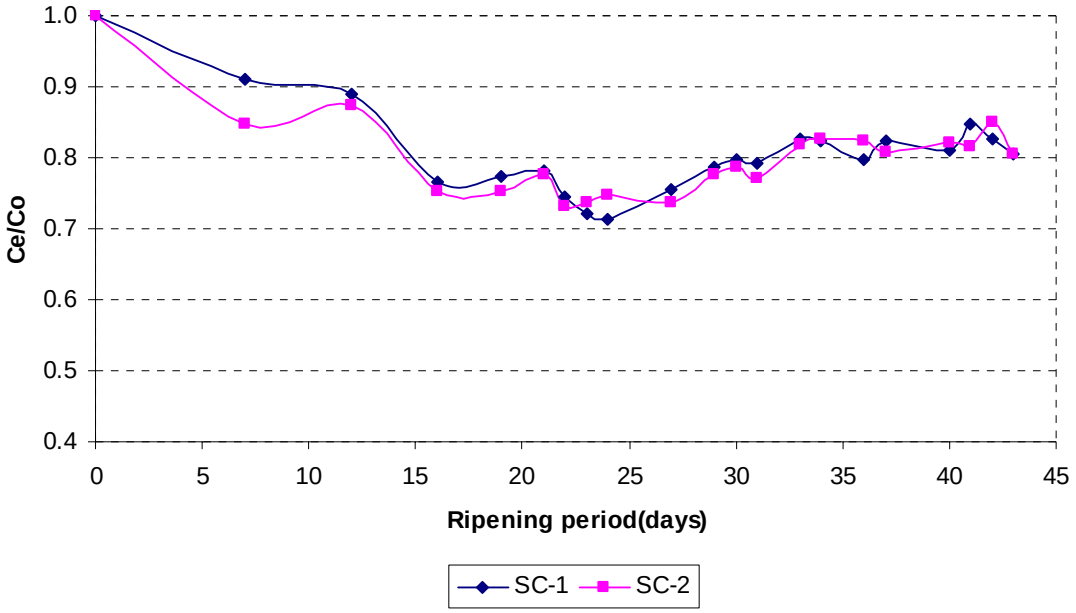


Figure 4-3 DOC removal with time during ripening of soil columns (Influent: DCW+SE, HLR=1.25 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

4.2.2 Soil column experiments with Delft canal water mixed with wastewater secondary effluent (DCW+SE)

After ripening, the soil column was operated at different hydraulic loading rates to investigate its performance under steady state conditions. DOC was measured at various sampling points in the column. Other parameters of interest like pH, dissolved oxygen, nitrate and ammonia were also monitored. The applied HLRs and the corresponding flow rates and EBCTs are shown in Table 4-2.

Table 4-2 Hydraulic loading rates, EBCT and flow rates

HLR (m/d)	EBCT (days)	Actual residence time (days)	Flow rate (L/d)
1.25	4	1.2	9.8
0.625	8	2.4	4.9

4.2.2.1 Performance at hydraulic loading rate of 1.25 m/d

Measurements of DOC and UVA taken under steady state after ripening of the columns with HLR of 1.25 m/d are shown in Figures 4-4 to 4-9. From the profiles it was found that DOC removal in SC1 was about 20 % (from 20.12 mg/L to 16.03 mg/L). Almost the same removal efficiency was also found in SC2 which was running under the same

conditions as SC1. This removal efficiency is specific to conditions under which this experiment was carried out. In an actual RBF system often there will be more DOC reduction due to other processes such as dilution by the ground water system. In addition, the removal efficiency obtained was limited to a maximum travel length of 5 m.

The DOC from wastewater secondary effluent is expected to be composed of more refractory organics which are not easily biodegradable. This is because most of the easily biodegradable organics are removed during various treatment steps before secondary clarifiers.

As can be seen from the DOC profiles, DOC concentrations along the depth in the soil column showed a decreasing trend. However, the extent of removal in the first 50 cm depth was more as compared to the overall removal. The DOC removal in the first 50 cm of SC1 was found to be about 54 % of the total removal. This is attributed to the more biological activity in top layer of the soil column. The biological activity was verified by ATP measurement at various points along the soil column (see section 4.2.3.3).

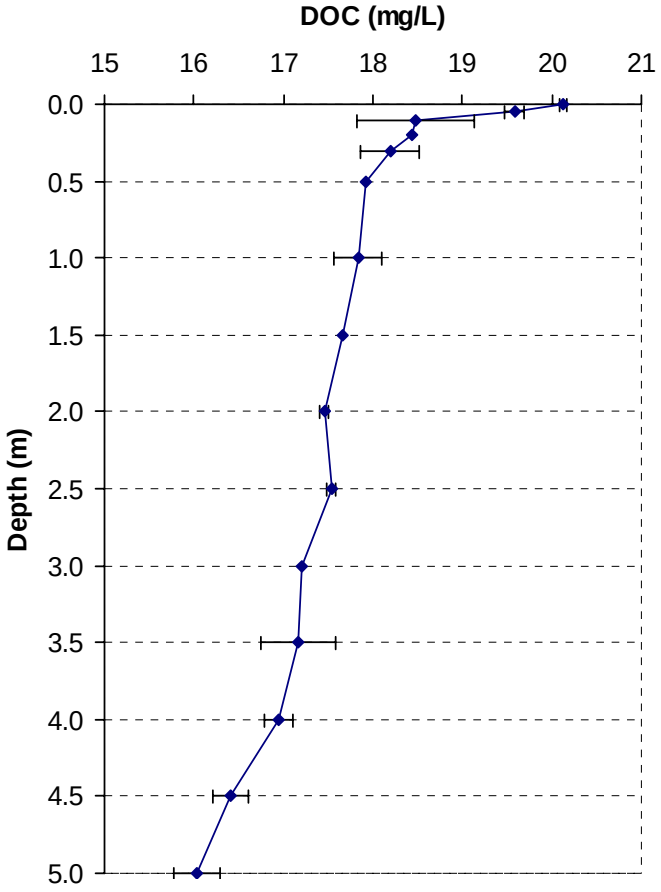


Figure 4-4 DOC profile of SC1 under steady state conditions (Influent: DCW+SE, HLR=1.25 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

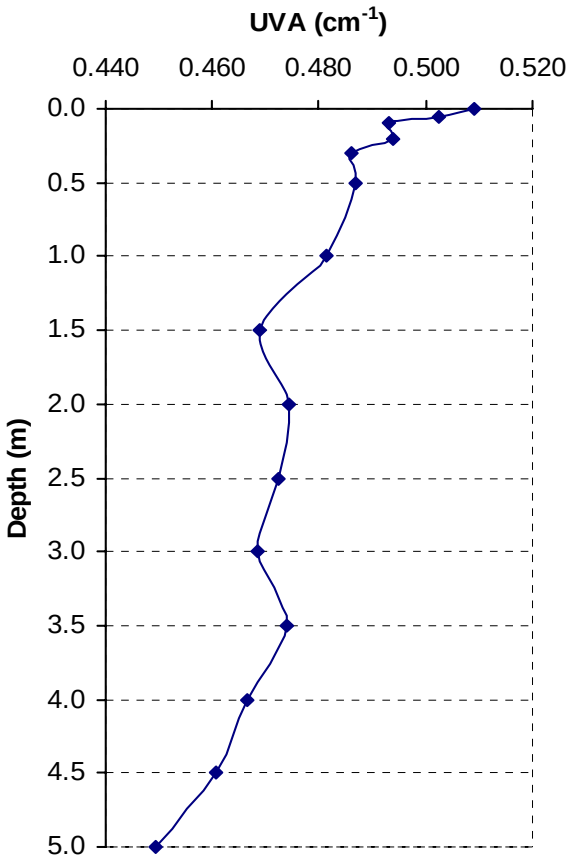


Figure 4-5 UVA profile of SC1 under steady state conditions (Influent: DCW+SE, HLR=1.25 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

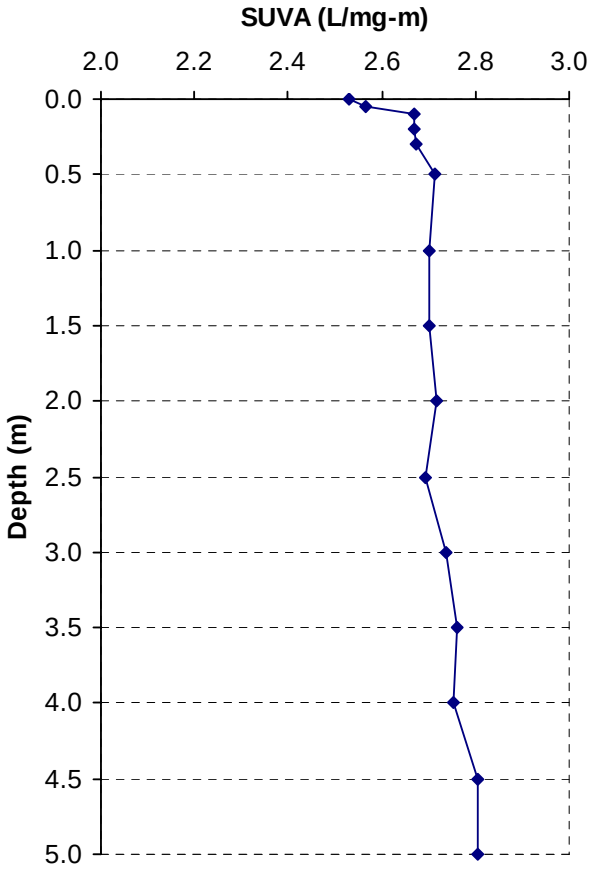


Figure 4-6 SUVA profile of SC1 under steady state conditions (Influent: DCW+SE, HLR=1.25 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

The SUVA value, which has strong relation with the aromatic characteristics of organics, has shown an increasing trend along the depth. The SUVA value increased from 2.51 L/mg-m at the top of the column to 2.81 L/mg-m at the bottom of the column. This is a consequence of the removal of non-humic substances (biopolymers) which resulted in an increase in aromaticity. The effluent has higher SUVA value compared to the influent, suggesting that the effluent contained higher aromatic carbon content.

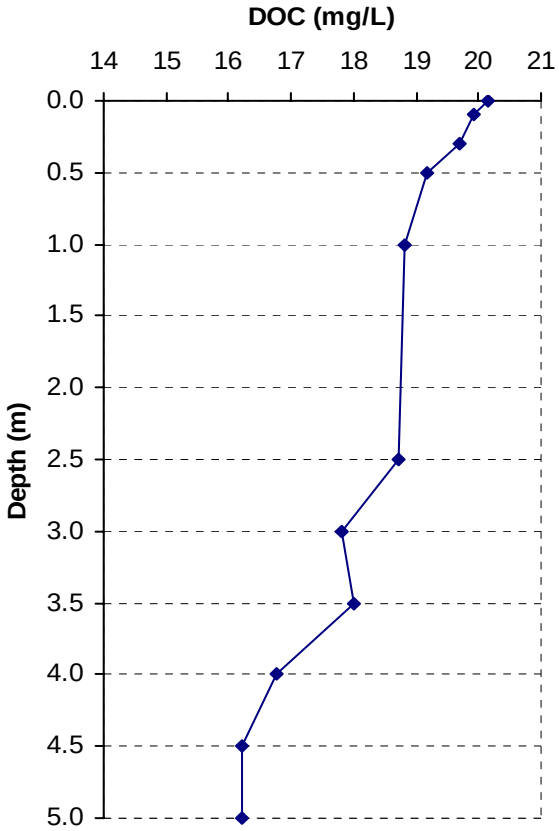


Figure 4-7 DOC profile of SC2 under steady state conditions (Influent: DCW+SE, HLR=1.25 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

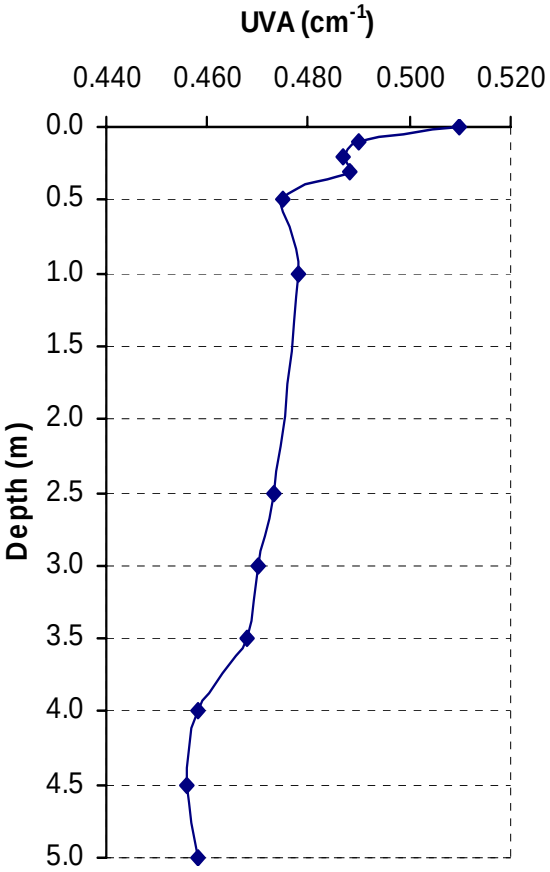


Figure 4-8 UVA profile of SC2 under steady state conditions (Influent: DCW+SE, HLR=1.25 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

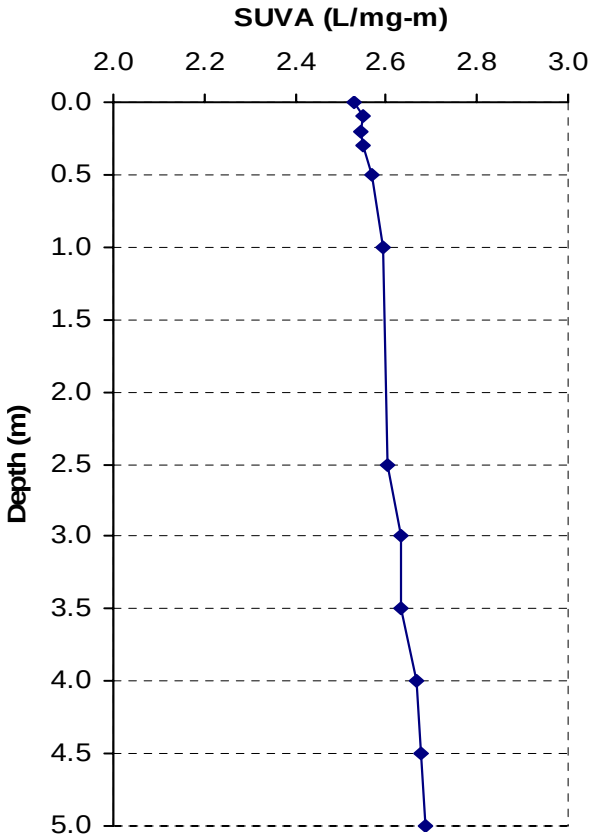


Figure 4-9 SUVA profile of SC2 under steady state conditions (Influent: DCW+SE, HLR=1.25 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

The DOC profile data of the soil columns were used to develop a mathematical model describing DOC removal with time. The DOC present in water could, in general, be divided into three components with respect to biodegradability: (i) easily biodegradable, (ii) slowly biodegradable and (iii) non-biodegradable components. Hence, a three term model incorporating these components was used to explain the DOC removal during RBF as shown in the following equation. Depth (distance) in the soil column was converted to time using the relation with HLR and EBCT.

$$C_t = C_1 e^{-k_1 t} + C_2 e^{-k_2 t} + C_3 \quad \text{..... (4.1)}$$

$$Co = C_1 + C_2 + C_3 \quad \text{..... (4.2)}$$

Where: C_t = DOC concentration at any time t (mg/L)
Co = Initial DOC concentration (mg/L)
C_1 = initial concentration of easily biodegradable DOC (mg/L)
C_2 = initial concentration of slowly biodegradable DOC (mg/L)
C_3 = concentration of non-biodegradable DOC component (mg/L)

k_1, k_2 = rate constants of biodegradation process (day^{-1})
t = time for biodegradation process (days)

Furthermore, the above equation (4.1) can also be written in terms of distance.

$$C_D = C_1 e^{-\lambda_1 D} + C_2 e^{-\lambda_2 D} + C_3 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.3)$$

Where: λ_1, λ_2 = rate constants of biodegradation process with respect to distance (m^{-1})
D = depth of soil column or aquifer (m)

Graphic software, Slide Write Plus, was used to fit the measured data in the above model. The modelled DOC removal kinetics obtained for SC1 with a HLR of 1.25 m/d is shown in Figure 4-10. The kinetic model parameters obtained are presented in Table 4-3. As per this model, the maximum achievable percentage of DOC removal by biodegradation during RBF for the given water quality under the conditions stated above is about 53 %. The corresponding distance to reach this DOC removal efficiency level is about 120 m.

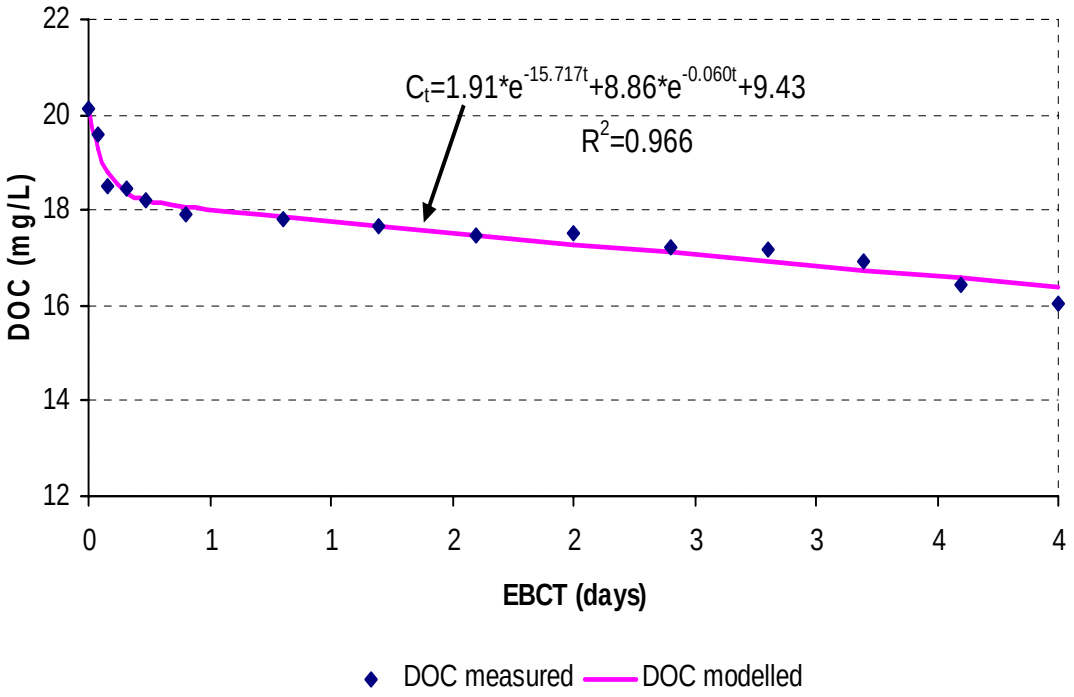


Figure 4-10 Measured and modelled DOC with time for SC1 under steady state (Influent: DCW+SE, HLR=1.25 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

Table 4-3 DOC removal model parameters for SC1 with DCW+SE and HLR=1.25 m/d

Model Parameter	Co	C_1	C_2	C_3	k_1	k_2
Unit	mg/L	mg/L	mg/L	mg/L	day^{-1}	day^{-1}
Value	20.20	1.91	8.86	9.43	15.717	0.060

In addition to the DOC and UVA values, parameters like dissolved oxygen, pH, ammonia, and nitrate were monitored at various sampling points of the soil columns under steady state. Measurements of nitrate in the applied influents showed that, comparatively, there is more nitrate in secondary effluent (4.79 mg/L NO_3-N) than in Delft canal water (3.46 mg/L NO_3-N). However, Delft canal water has more ammonia concentration than secondary effluent. The results of the measurements are shown in Table 4-4.

Table 4-4 Concentration of Nitrate and ammonia in applied influents

Parameter	**DCW**	**DCW+SE**	**SE**
NH_4-N	0.49 mg/L	0.26 mg/L	< 0.1
NO_3-N	3.46 mg/L	4.21 mg/L	4.79 mg/L

Oxygen and pH profiles for a HLR of 1.25 m/d are shown in Figure 4-11 and 4-12 respectively. The oxygen profile for SC1 showed a decrease of oxygen from 8.8 mg/L to 1.7 mg/L. Of the total consumption, about 59 % was consumed within the first 50 cm of the column. This shows that most of the biological activity, especially the biodegradation process, was occurring in top layer of the soil column. Measurement of ammonia in the effluent of SC1 showed that there was no ammonia in the effluent. This is an indication that nitrification process was taking place in the soil column. This process also consumes oxygen. The following reaction describes the nitrification process:

1) Ammonia to Nitrite by Nitrosomonas:

$$55NH_4^+ + 76O_2 + 109HCO_3^- \rightarrow C_5H_7O_2N + 54NO_2^- + 57H_2O + 104H_2CO_3 \quad \text{..... (4.4)}$$

2) Nitrite to Nitrate by Nitrobacter:

$$400NO_2^- + NH_4^+ + 4H_2CO_3 + HCO_3^- + 195O_2 \rightarrow C_5H_7O_2N + 3H_2O + 400\ NO_3^- \quad \text{..... (4.5)}$$

In the above process approximately 4.3 mg O_2 are consumed for every mg of ammonia-nitrogen oxidized to nitrate-nitrogen. Measurement of nitrate in influent and effluent

samples from the soil column (SC1) showed an increase from 3.39 mg/L to 4.39 mg/L. This was due to nitrification process in the soil column.

The pH profile obtained (Figure 4-12) also showed a decreasing trend from influent towards effluent along the soil column. The pH of influent was 8.42 while that of effluent was 7.73. This could possibly be due to production of carbon dioxide during degradation of organics and production of carbonic acid during the nitrification process.

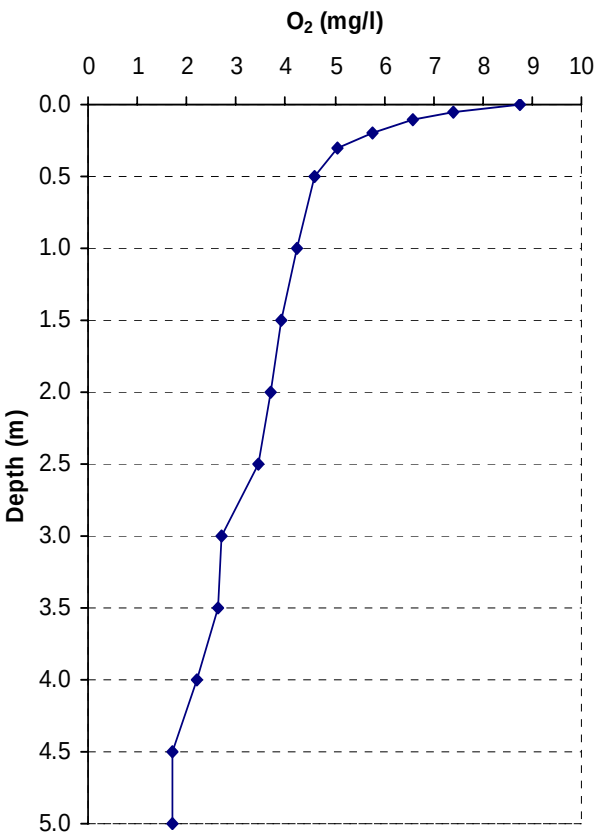


Figure 4-11 DO profile of SC1 under steady state conditions (Influent: DCW+SE, HLR=1.25 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

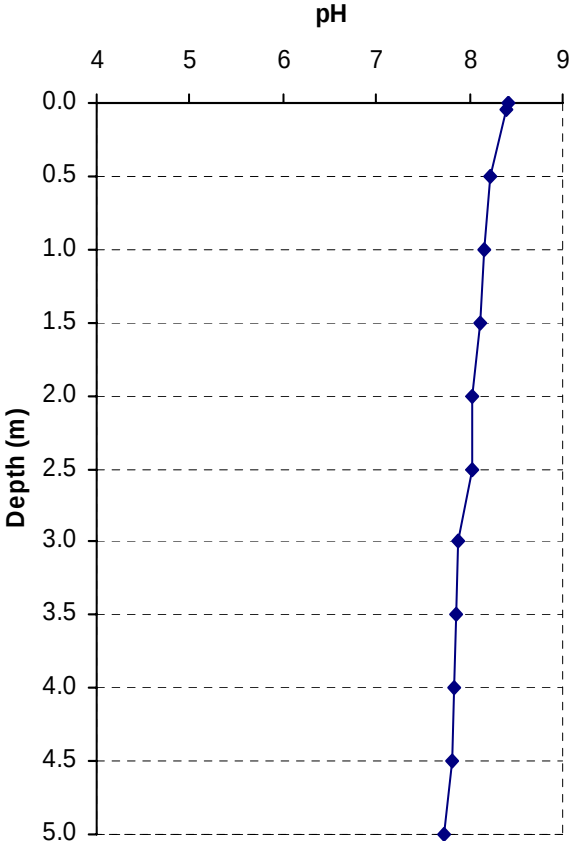


Figure 4-12 pH profile of SC1 under steady state conditions (Influent: DCW+SE, HLR=1.25 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

4.2.2.2 Performance at hydraulic loading rate of 0.625 m/d

After collecting the necessary data at a HLR of 1.25 m/d, the hydraulic loading rate was reduced by half to 0.625 m/d to study the effect of hydraulic loading rate on the performance of SC1. After reducing the HLR to 0.625 m/d an acclimation period was given and parameters like DOC and UVA were monitored until the column was

stabilized with respect to DOC removal. The results of measurement under steady state are shown in Figure 4-13 and 4-14 for DOC and UVA, respectively.

At a HLR of 0.625 m/d, the influent and effluent DOC concentration at steady state was 15.14 mg/L and 12.61 mg/L respectively. The total removal of DOC with a reduced hydraulic loading rate of 0.625 m/d was found to be 17 %. This removal was lower than the one obtained at HLR = 1.25 m/d. The performance was reduced despite the higher residence time with HLR = 0.625 m/d. This could be justified as follows: at lower HLR (0.625 m/d) the BDOC of the influent water might not have been sufficient to feed the already developed biomass with HLR 1.25 m/d. Therefore, with less food (substrate) available for the biomass with a higher HRT, there would obviously be a die off which would increase the effluent DOC. If there had been extra BDOC left (unused) during the run with HLR 1.25 m/d, then with a reduction in HLR (more residence time) the bacteria would have used the remaining BDOC and hence more removal could have been achieved. Another justification for the reduction in performance could be the reduction in the biodegradable fraction of influent due to seasonal variation of the quality of canal water.

For a given water quality, if more residence time than necessary is given for biodegradation of a certain amount of BDOC, then the biomass will be starved for the extra time and their count will be reduced; hence removal efficiency will also be reduced. Therefore, increasing HRT will not always imply an increase in DOC removal.

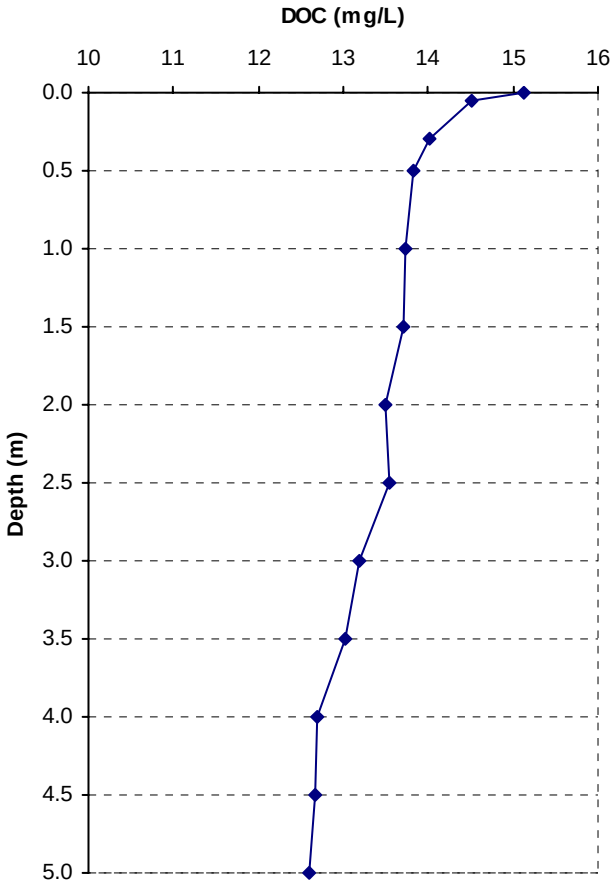


Figure 4-13 DOC profile of SC1 under steady state conditions (Influent: DCW+SE, HLR=0.625 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

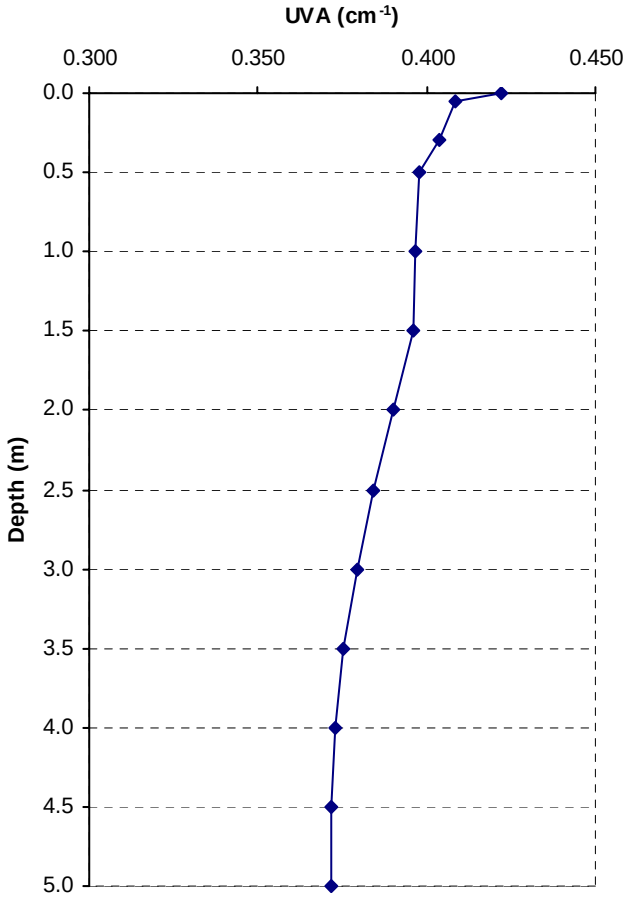


Figure 4-14 UVA profile of SC1 under steady state conditions (Influent: DCW+SE, HLR=0.625 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

As can be seen from Figure 4-13, DOC concentration along the depth in the soil column showed a decreasing trend. However, the extent of removal in the first 50 cm depth is more as compared to the overall removal which was also the case observed for the same column at HLR of 1.25 m/d. The DOC in the first 50 cm depth was decreased from 15.14 mg/L to 13.83 mg/L at a HLR of 0.625 m/d. The DOC removal in the first 50 cm was found to be about 52 % of the total removal compared to 54 % at HLR of 1.25 m/d. This is attributed to the more biological activity in the top layer of the soil column.

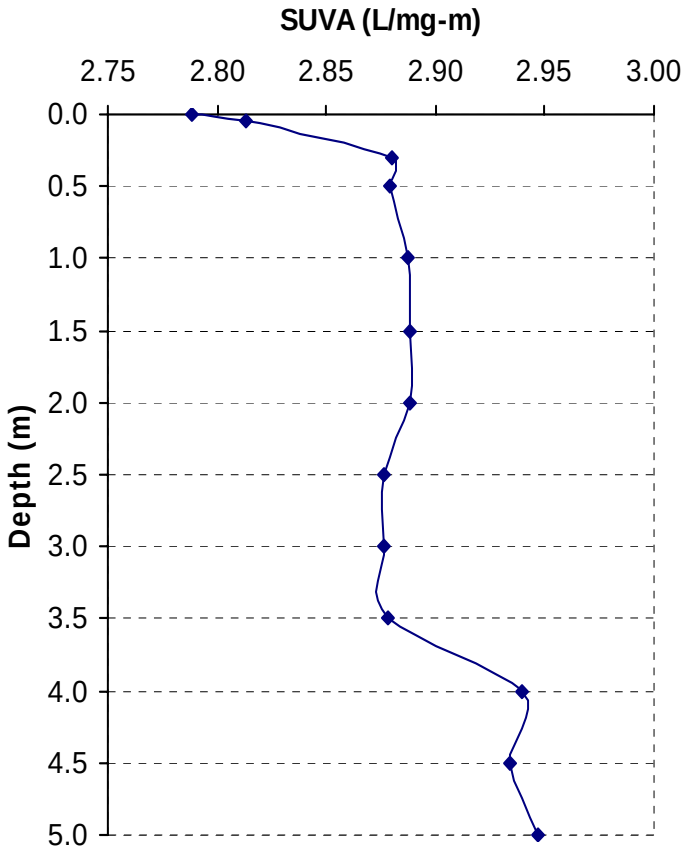


Figure 4-15 SUVA profile of SC1 under steady state conditions (Influent: DCW+SE, HLR=0.625 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

Like was done at a HLR of 1.25 m/d, the DOC profile data of SC1 at a HLR of 0.625 m/d was used to develop a mathematical model describing DOC removal with time. A three term model incorporating easily biodegradable, slowly biodegradable and non-biodegradable components of organic matter was used to explain DOC removal during RBF (the general equation under section 4.2.2.1). Fitting the model with measured data using Slide Write Plus resulted in a DOC removal kinetics shown in Figure 4-16.

The kinetic model parameters obtained are presented in Table 4-5. As per this model, the maximum achievable percentage of DOC removal during RBF for the given water quality under the conditions stated above is about 54 %.

Table 4-5 DOC removal model parameters for SC1 with DCW and HLR = 0.625 m/d

Model Parameter	Co	C_1	C_2	C_3	k_1	k_2
Unit	mg/L	mg/L	mg/L	mg/L	day^{-1}	day^{-1}
Value	15.14	1.02	7.17	6.95	11.28	0.03

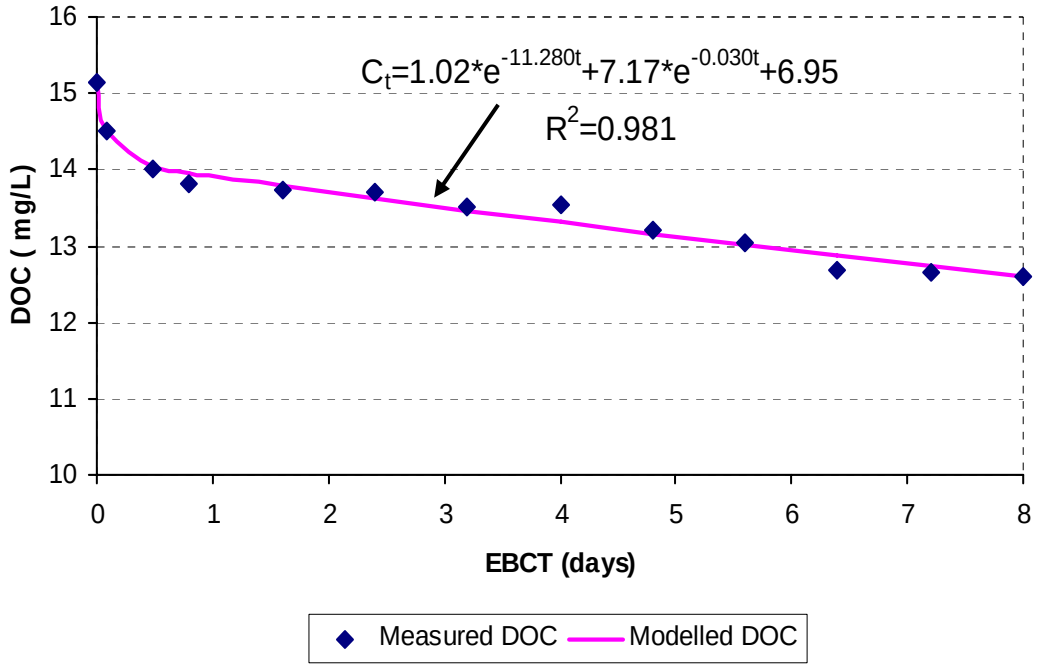


Figure 4-16 Measured and modelled DOC with time for SC1 under steady state (Influent: DCW+SE, HLR=0.625 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

The O_2 and pH profiles for SC1 at a HLR of 0.625 m/d are shown in Figure 4-17 and 4-18 respectively. The oxygen concentration was reduced from 8.9 mg/L to 2.2 mg/L. The overall reduction in oxygen concentration at HLR of 0.625 m/d was found to be about 75 % compared to 81 % for the same column at HLR of 1.25 m/d. As more DOC was removed from the column at HLR of 1.25 m/d, more oxygen was consumed.

Measurements of nitrate in the influent and effluent of SC1 at HLR of 0.625 m/d showed an increment of about 11 % (from 3.81 mg/l to 4.24 mg/L) which was an indication that nitrification process was taking place in the soil column. This process also consumes oxygen. Because of the same reason as explained for SC1 with a HLR of 1.25 m/d, the pH profile obtained for HLR of 0.625 m/d (Figure 4-18) also showed a decreasing trend from the influent towards effluent along the soil column.

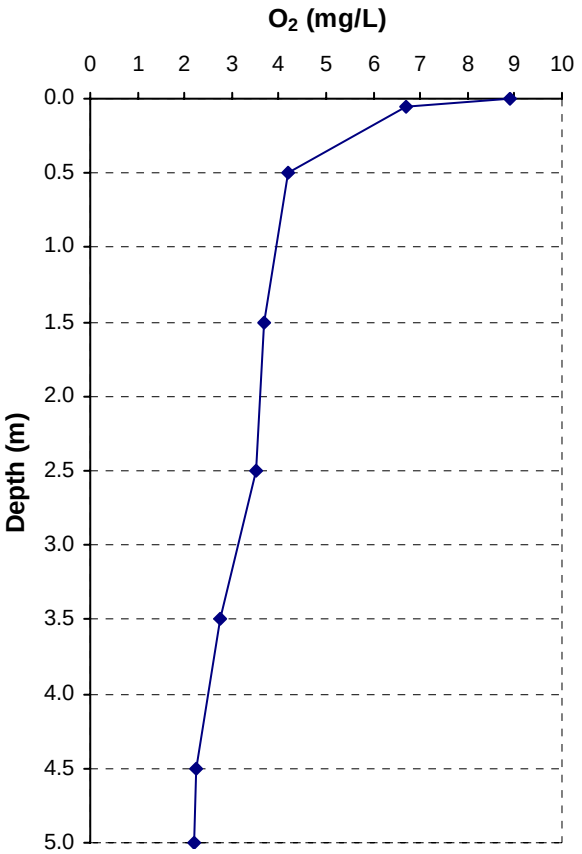


Figure 4-17 DO profile of SC1 under steady state conditions (Influent: DCW+SE, HLR=0.625 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

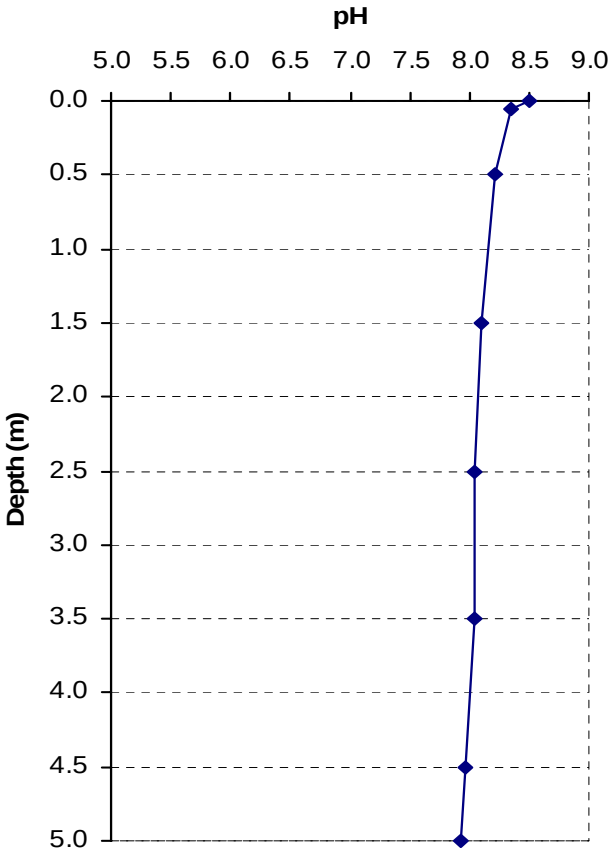


Figure 4-18 pH profile of SC1 under steady state conditions (Influent: DCW+SE, HLR=0.625 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

DOC biodegradation has a strong relation with dissolved oxygen. Oxygen is required for microbes to decompose organic matter efficiently. Using data of DOC and oxygen profiles, a plot of DOC removed against dissolved oxygen consumed was made and a correlation coefficient above 0.9 was found at both hydraulic loading rates (0.625 m/d and 1.25 m/d). Figure 4-19 and 4-20 show correlations between the two parameters. From the slope of the equation it can be seen that 1 mg of O_2 was consumed to remove 0.493 and 0.425 mg of DOC for soil column with HLR 1.25 and 0.625 m/d respectively. The following equation describes the theoretical concept of organic reduction.

$$CH_2O + O_2 \Longrightarrow CO_2 + H_2O \quad \text{..... (4.6)}$$

Theoretically, as the equation shows, 1 mg of O_2 is required to oxidize 0.938 mg of CH_2O into 0.375 mg of carbon as CO_2. Therefore, what was obtained from the experimental correlation was close to the theoretical value.

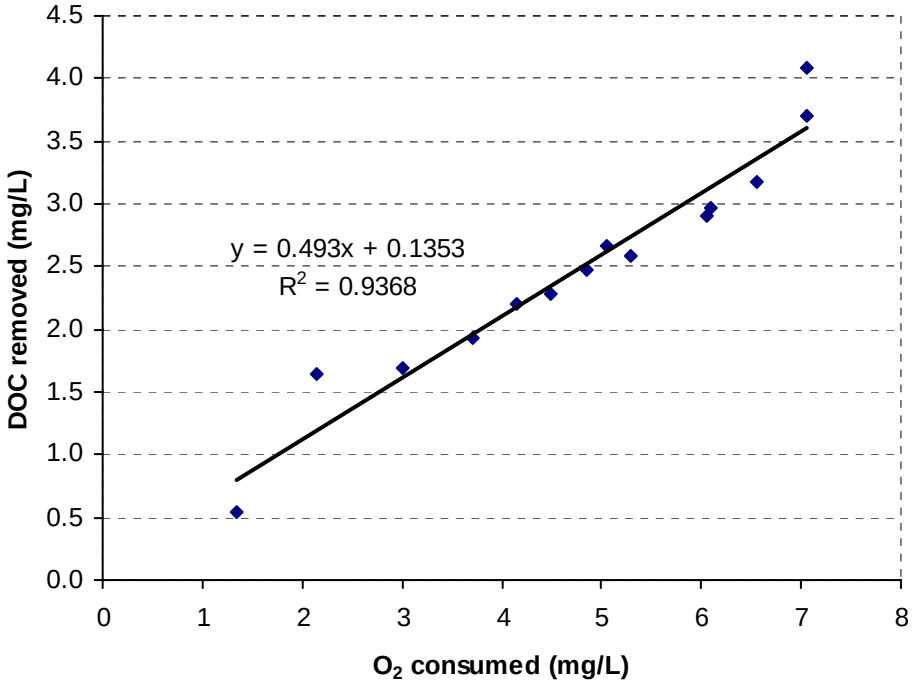


Figure 4-19 Correlation of DOC removal with oxygen consumption for SC1 at steady state (Influent: DCW+SE, HLR=1.25 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

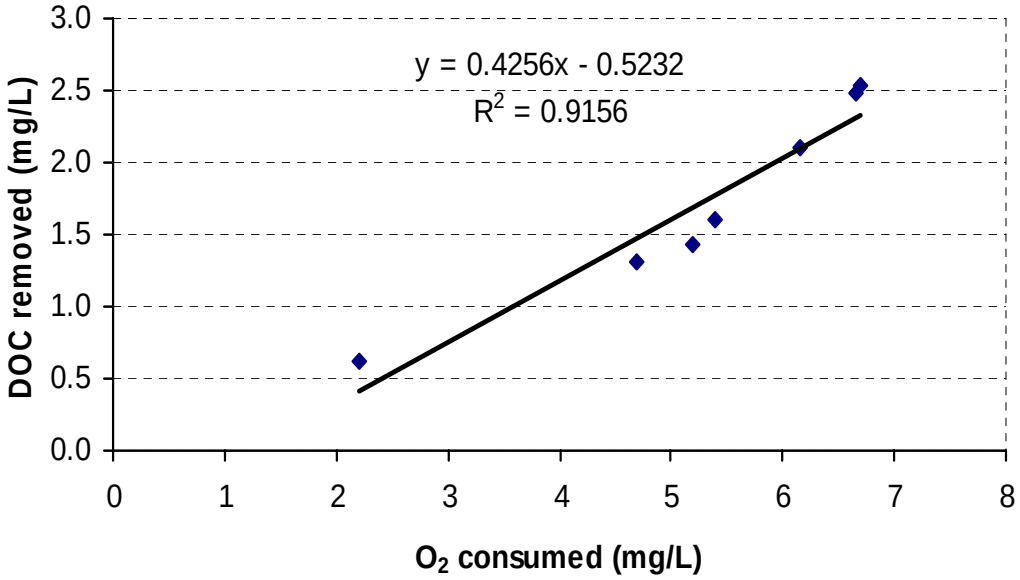


Figure 4-20 Correlation of DOC removal with oxygen consumption for SC1 at steady state (Influent: DCW+SE, HLR=0.625 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

4.2.3 Soil column experiments with Delft Canal Water (DCW)

4.2.3.1 Ripening process

As described under section 4-2-1, at the beginning of the experiment both columns (SC1 and SC2) were operated with a mixture of Delft canal water and wastewater secondary effluent in a 1:1 ratio. However, after taking measurements of various parameters at a steady state, the influent for SC2 was changed to Delft canal water. Biological acclimation with Delft canal water at HLR of 1.25 m/d was continued until the DOC removal was stabilized. During the process, influent and effluent DOC concentrations were continuously monitored. Oxic condition was maintained by continuous aeration of the influent in a small plastic bottle placed next to the main influent tank by using a fine bubble diffuser.

Figure 4-21 shows the variation in influent and effluent DOC concentration during the ripening process while Figure 4-22 represents a normalized plot of the data which shows the extent of DOC removal during the process. As can be seen from these figures, a steady state was reached after a week of introducing DCW as a feed. However, the ripening process was continued for about 22 days. The average influent DOC concentration during the ripening period was 19.76 ± 1.74 and the effluent DOC was 17.22 ± 1.29. On average a DOC removal of about 13 % was obtained. Though Delft canal water has a higher DOC, the removal efficiency was lower than that obtained for the mixture (DCW+SE) (20 %). The result indicated that Delft canal water has less BDOC than the wastewater secondary effluent.

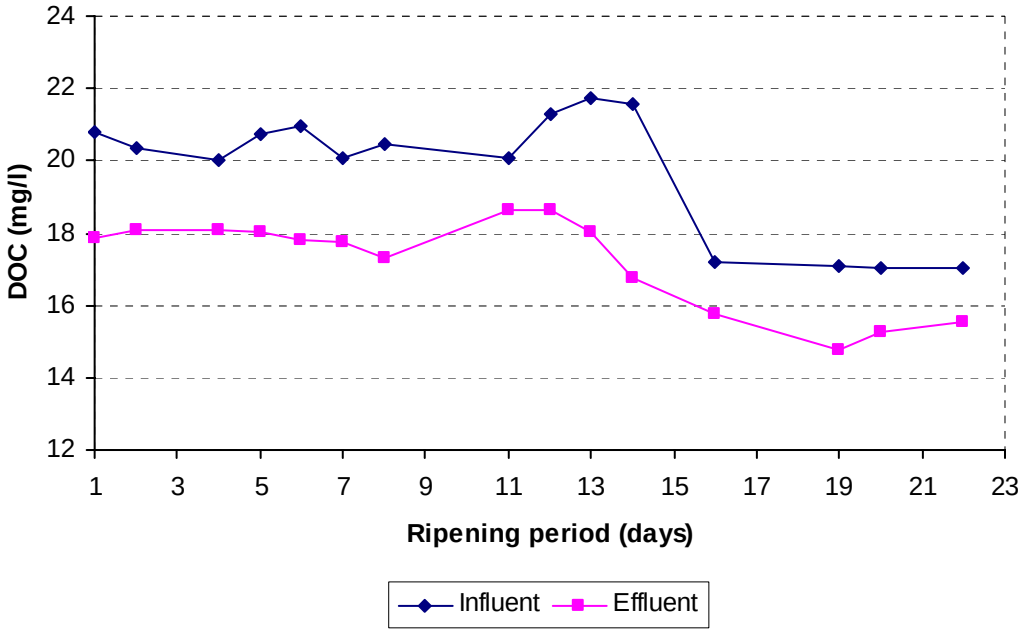


Figure 4-21 Change in DOC concentration of influent and effluent during ripening of SC2 (Influent: DCW, HLR=1.25 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

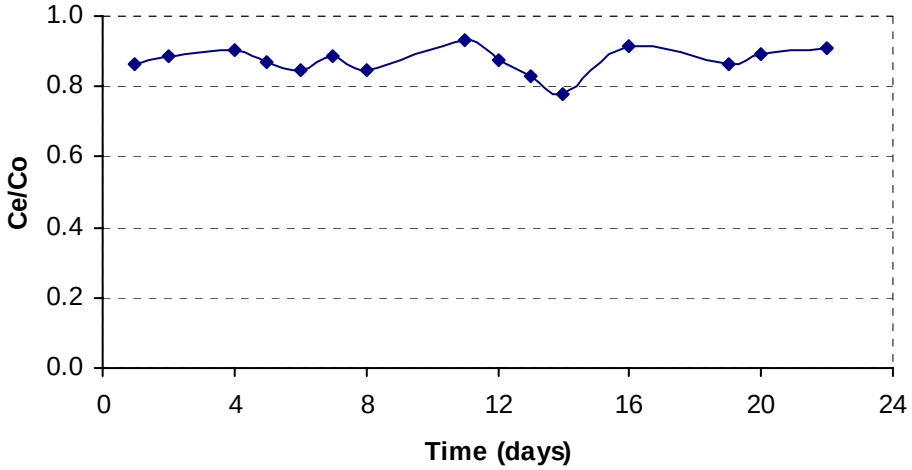


Figure 4-22 DOC removal with time during ripening of SC2 (Influent: DCW, HLR=1.25 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

4.2.3.2 Performance at hydraulic loading rate of 1.25 m/d

Measurements of DOC and UVA taken under steady state after ripening of the column at a HLR of 1.25 m/d are shown in Figures 4-23 and 4-24 respectively. From Figure 4-23, it was found that the influent and effluent DOC of SC2 fed with DCW at a HLR of 1.25 m/d were 19.24 mg/L and 16.75 mg/L, respectively, which resulted in a DOC removal of about 13 %. As explained earlier, this removal efficiency obtained was limited to a maximum depth of 5 m.

In comparison with SC1 with the same HLR, SC2 has less removal efficiency. This is due to the low BDOC in DCW as compared to SE. As can be seen from Figure 4-23, DOC removal along the depth in the soil column showed a decreasing trend. However, the extent of removal in the first 50 cm depth was more as compared to the overall removal. The DOC removal in the first 50 cm of SC2 was found to be about 58 % of the total removal. This is attributed to the more biological activity in top layer of the soil column.

The UVA values showed a decreasing trend from inlet towards the outlet of the soil column with a significant decrease in the first 50 cm ($\approx$40 %) due to the higher removal of non-humic substances in the top layer of the soil column increasing the aromatic characteristics of organics.

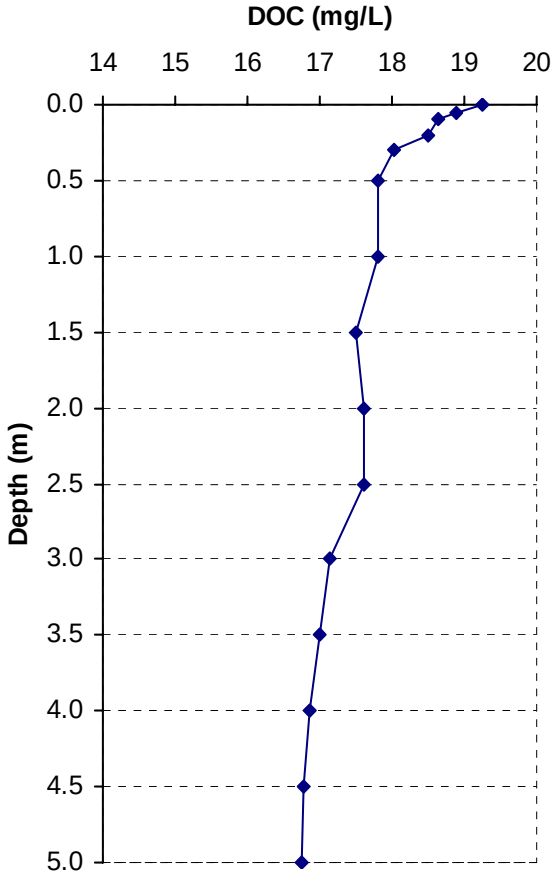


Figure 4-23 DOC profile of SC2 under steady state conditions (Influent: DCW, HLR=1.25 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

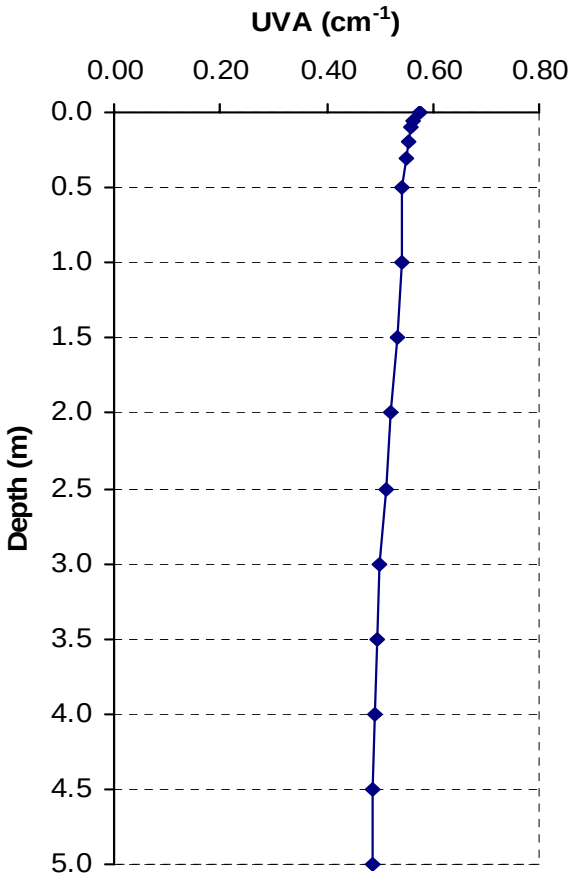


Figure 4-24 UVA profile of SC2 under steady state conditions (Influent: DCW, HLR=1.25 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

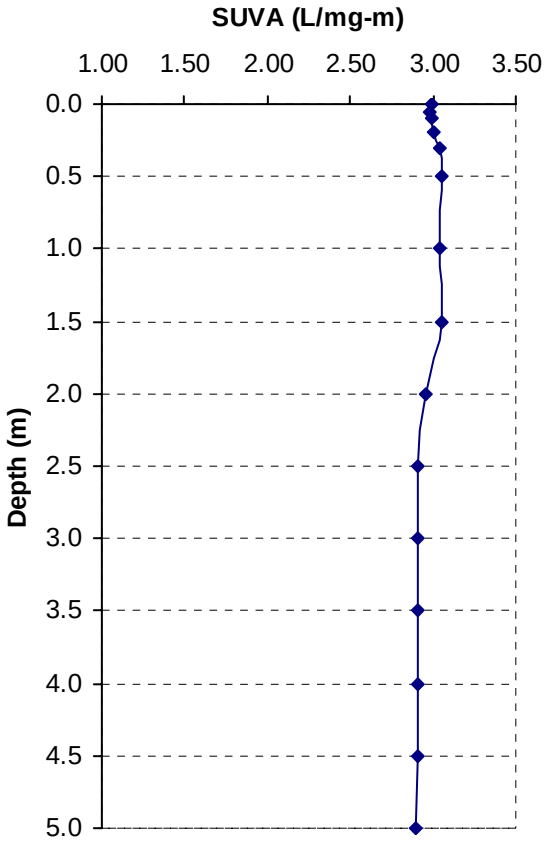


Figure 4-25 SUVA profile of SC2 under steady state conditions (Influent: DCW, HLR=1.25 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

Like was done for SC1, the DOC profile data of SC2 was used to develop a mathematical model describing DOC removal with time. A three term model incorporating easily biodegradable, slowly biodegradable and non-biodegradable components of organic matter was used to explain DOC removal during RBF (the general equation under section 4.2.2.1). Fitting the model with measured data using Slide Write Plus resulted in a DOC removal kinetics shown in Figure 4-26.

The kinetic model parameters obtained are presented in Table 4-6. As per this model, the maximum achievable percentage of DOC removal during RBF for the given water quality under the conditions stated above is about 44 %. The corresponding distance to reach this DOC removal efficiency is about 140 m.

Table 4-6 DOC removal model parameters for SC2 with DCW and HLR=1.25 m/d

Model Parameter	Co	C_1	C_2	C_3	k_1	k_2
Unit	mg/L	mg/L	mg/L	mg/L	day^{-1}	day^{-1}
Value	19.24	1.21	7.26	10.77	7.750	0.051

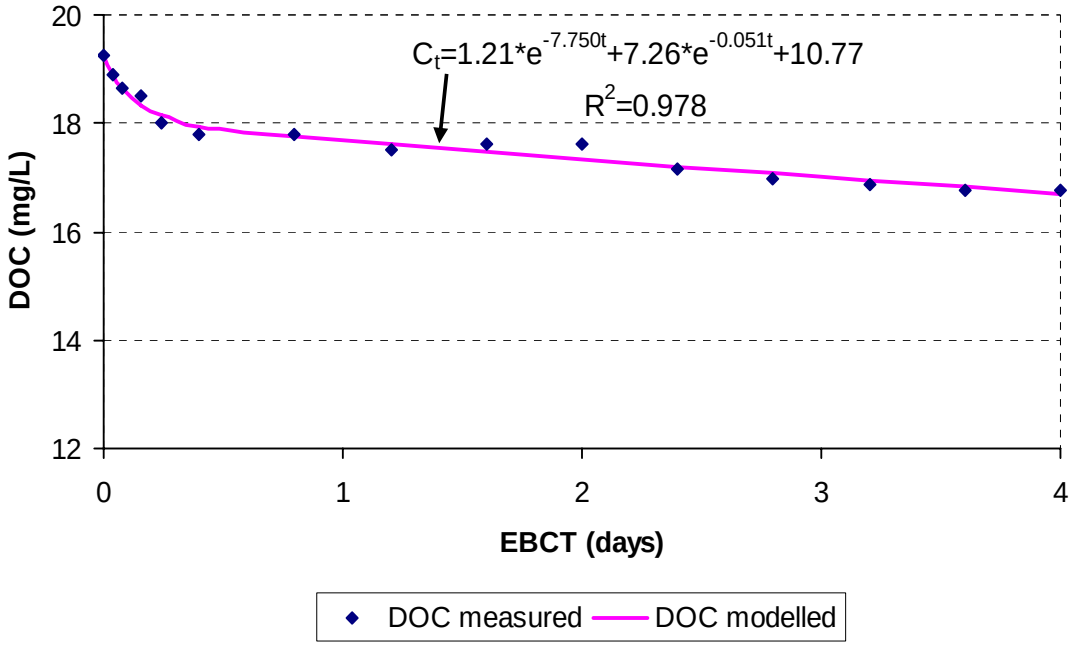


Figure 4-26 Measured and modelled DOC with time for SC2 under steady state (Influent: DCW, HLR=1.25 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

In the same way as done for SC1, parameters like dissolved oxygen, pH, ammonia, and nitrate were monitored at various sampling points of SC2 under steady state. Oxygen and pH profiles for soil column with HLR of 1.25 m/d are shown in Figure 4-27 and 4-28 respectively. The oxygen profile has shown a decrease from 9.0 mg/L to 1.8 mg/L. Of the total consumption, about 61 % of oxygen was consumed within the first 50 cm of the column. This shows that most of the biological activities especially biodegradation process occurs on top layer of the soil column.

The pH profile obtained (Figure 4-28) also showed a decreasing trend from the influent towards the effluent along the soil column. As described in previous section, this could possibly be due to production of carbon dioxide during degradation of organics and production of carbonic acid during nitrification process.

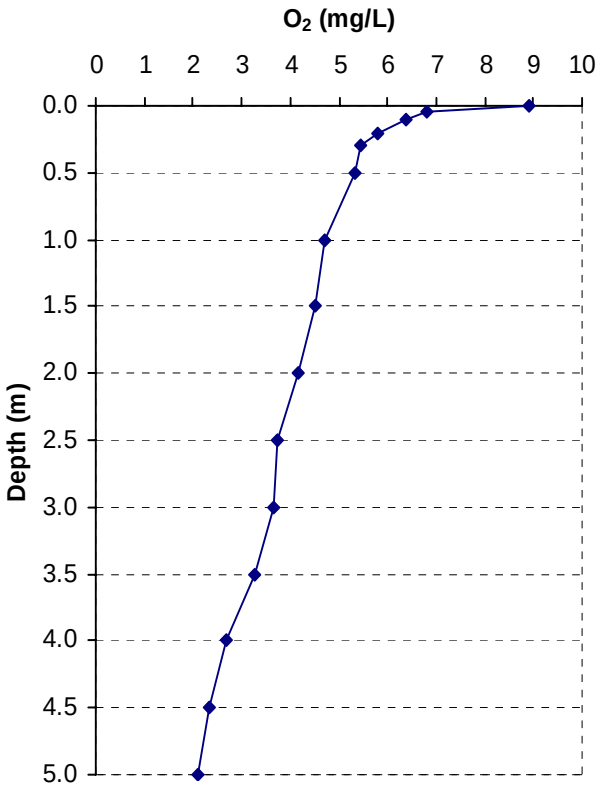


Figure 4-27 DO profile of SC2 under steady state conditions (Influent: DCW, HLR=1.25 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

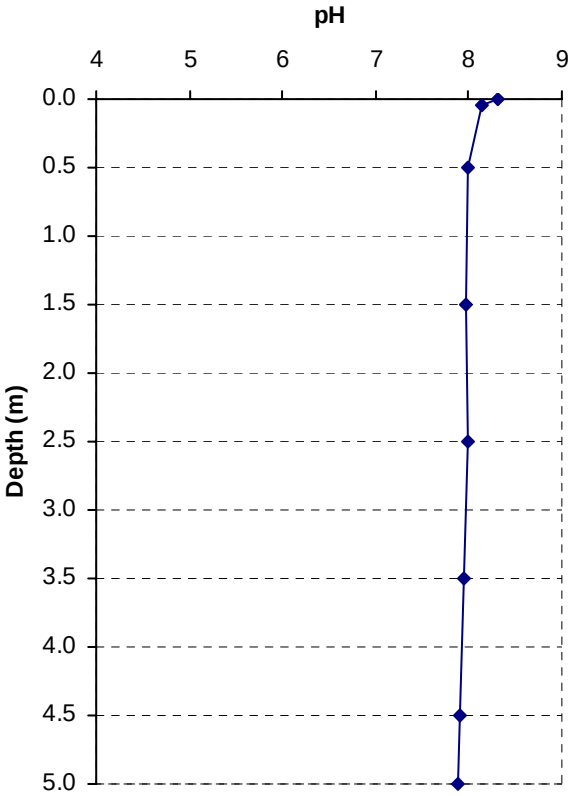


Figure 4-28 pH profile of SC2 under steady state conditions (Influent: DCW, HLR=1.25 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

4.2.3.3 Performance at hydraulic loading rate of 0.625 m/d

Similar to the case for SC1, hydraulic loading rate for SC2 was reduced by half after collecting relevant data at a HLR of 1.25 m/d. After reducing the HLR to 0.625 m/d an acclimation period was given and parameters like DOC and UVA were monitored until the column was stabilized with respect to DOC removal. The results of measurement under steady state are shown in Figure 4-29 and 4-30 for DOC and UVA respectively.

The total reduction in DOC with a reduced hydraulic loading rate of 0.625 m/d was found to be 10 % (from 17.39 mg/L to 15.62 mg/L). This removal is lower than the one obtained at a HLR = 1.25 m/d (13 %). The same reasoning as for SC1 applies for SC2 for the decrease in performance.

As can be seen from Figure 4-29, DOC concentration along the depth in the soil column showed a decreasing trend. However, the extent of removal in the first 50 cm depth is more as compared to the overall removal which was also the case observed for the same column at a HLR of 1.25 m/d. The DOC in the first 50 cm depth was decreased from

17.39 mg/L to 16.42 mg/L at a HLR of 0.625 m/d. The DOC removal in the first 50 cm was found to be about 55 % of the total removal compared to 58 % at a HLR of 1.25 m/d. This is attributed to the more biological activity in top layer of the soil column.

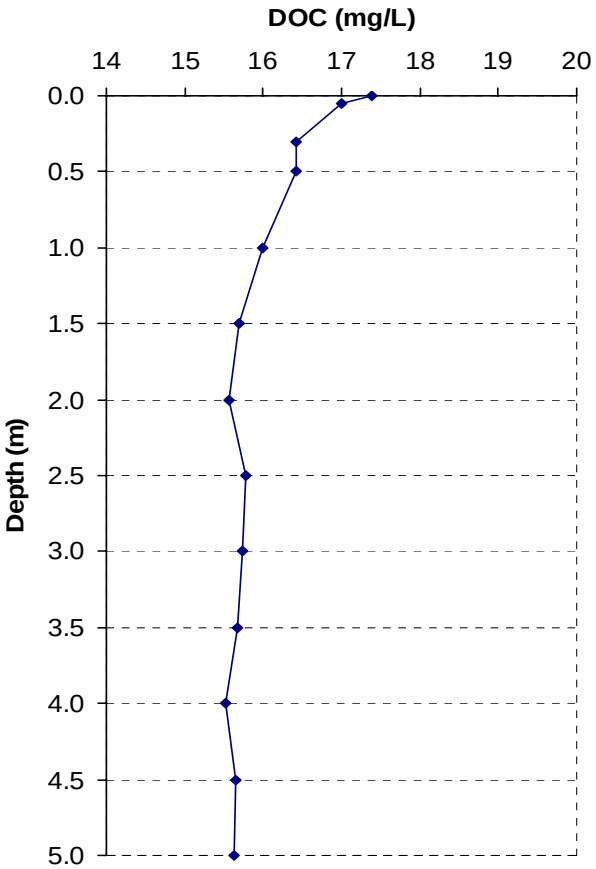


Figure 4-29 DOC profile of SC2 under steady state conditions (Influent: DCW, HLR=0.625 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

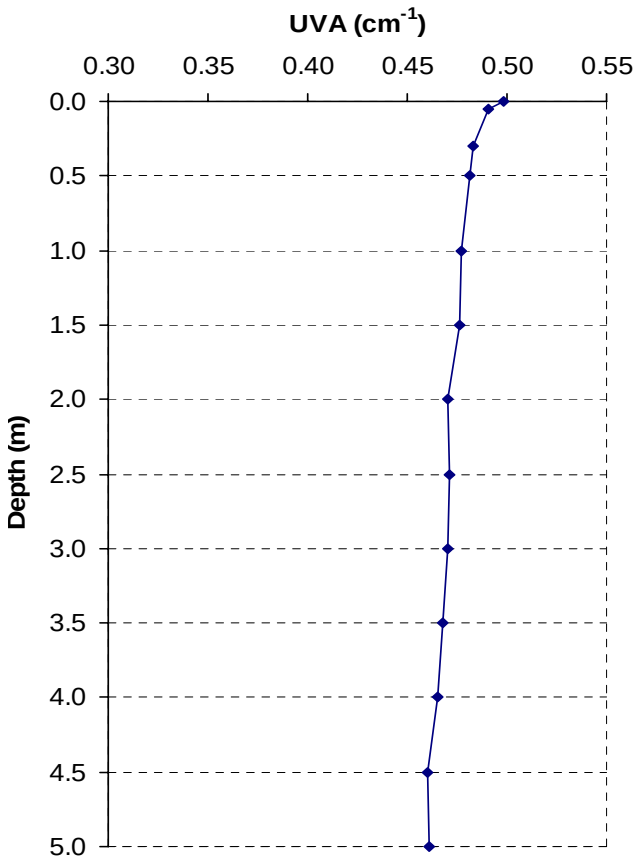


Figure 4-30 UVA profile of SC2 under steady state conditions (Influent: DCW, HLR=0.625 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

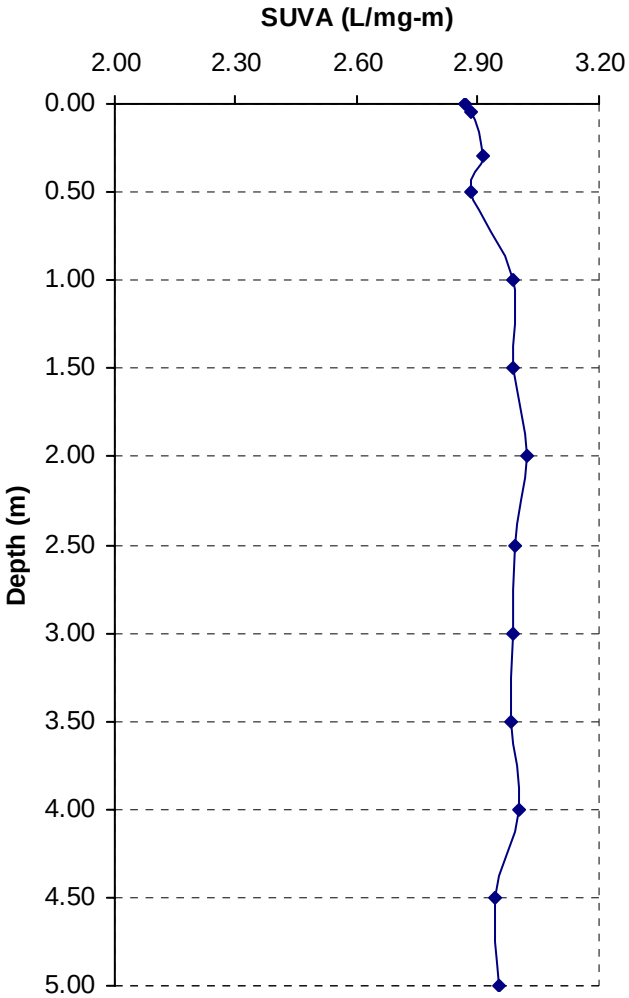


Figure 4-31 SUVA profile of SC2 under steady state conditions (Influent: DCW, HLR=0.625 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

Figure 4-32 shows a three term mathematical model describing DOC removal with time for SC2 at a HLR of 0.625 m/d. The kinetic model parameters obtained are presented in Table 4-7. As per this model, the maximum achievable percentage of DOC removal during RBF for the given water quality under the conditions stated above is about 19 % as compared to 44 % for the same column at a HLR of 1.25 m/d.

Table 4-7 DOC removal model parameters for SC2 with DCW and HLR=0.625 m/d

Model Parameter	Co	C_1	C_2	C_3	k_1	k_2
Unit	mg/L	mg/L	mg/L	mg/L	day^{-1}	day^{-1}
Value	17.27	1.54	1.70	14.03	1.248	0.009

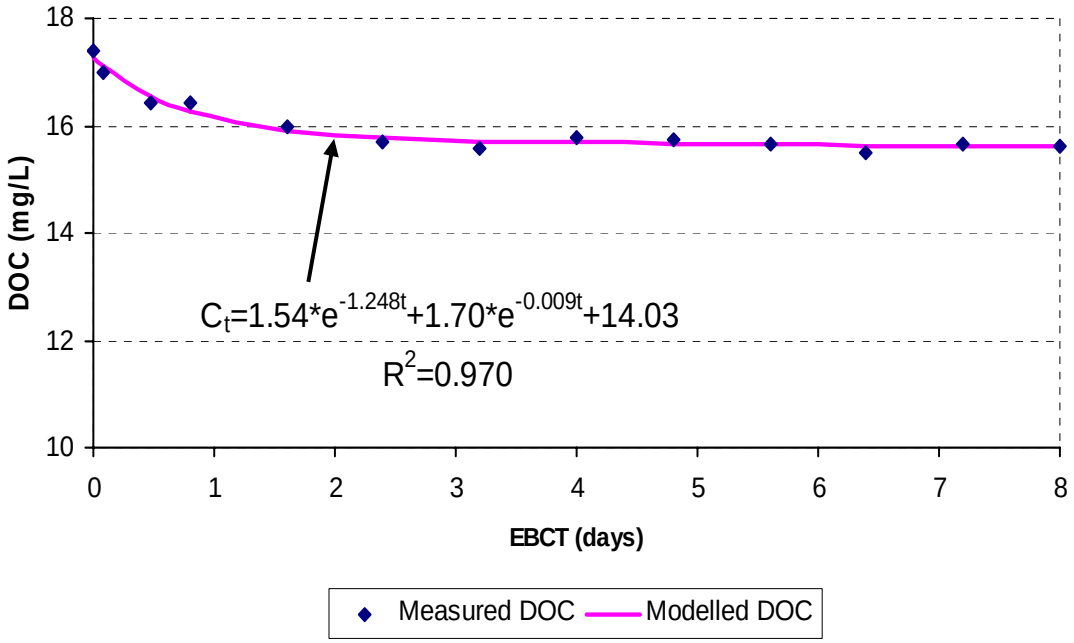


Figure 4-32 Measured and modelled DOC with time for SC2 under steady state (Influent: DCW+SE, HLR=0.625 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

The O_2 and pH profiles for SC2 at a HLR of 0.625 m/d are shown in Figure 4-33 and 4-34 respectively. The overall reduction in oxygen concentration was found to be about 64 % (from 8.80 mg/L to 3.15 mg/L) as compared to 76 % for the same column at HLR of 1.25 m/d. As more DOC was removed from the column with HLR of 1.25 m/d, more oxygen was consumed.

Measurement of nitrate in influent and effluent of SC2 at HLR of 0.625 m/d showed an increment of about 5 % (from 3.92 mg/l to 4.11 mg/L) which was an indication that nitrification process was taking place. However, this increment was less compared to SC1 at the same hydraulic loading rate despite the relatively higher ammonia concentration in the influent (DCW) of SC2. Similar trend (result) was obtained for soil column at HLR of 1.25 m/d. This could be due to the variation in the type of nitrifying bacteria in DCW and SE.

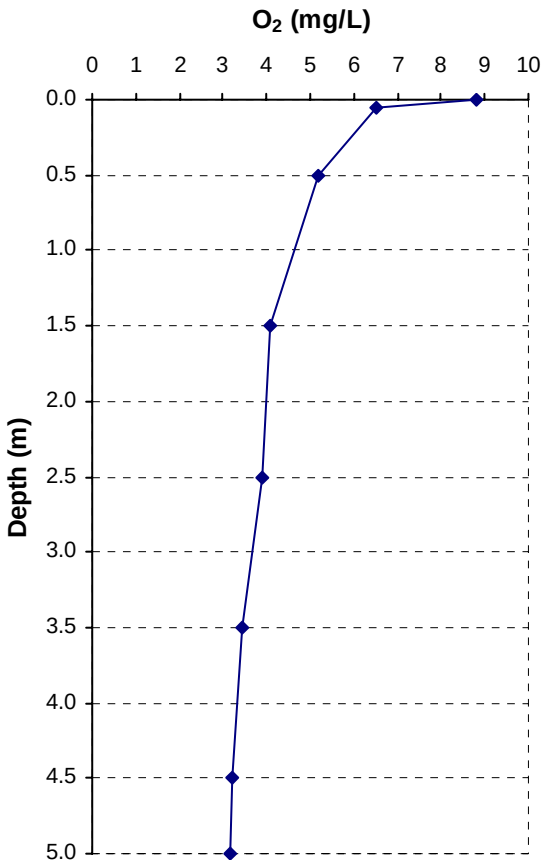


Figure 4-33 DO profile of SC2 under steady state conditions (Influent: DCW, HLR=0.625 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

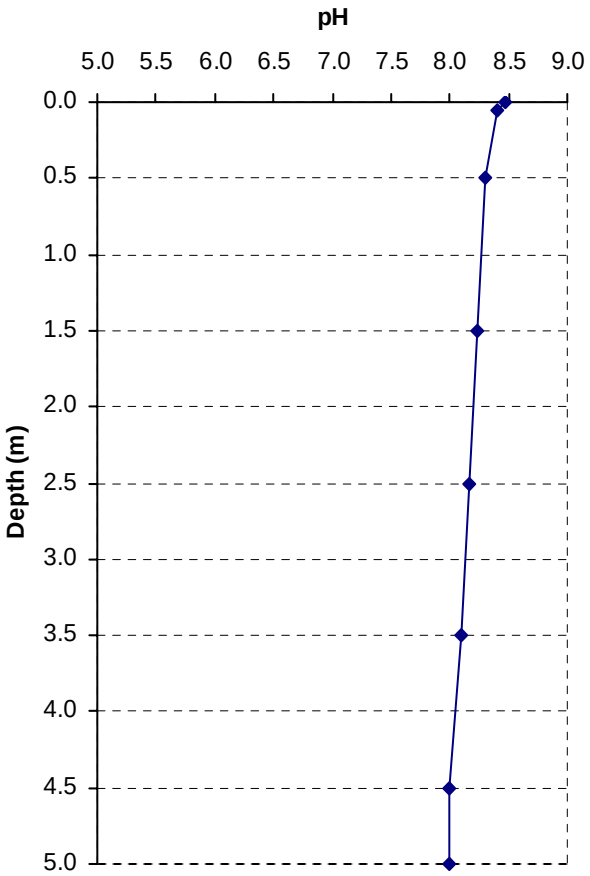


Figure 4-34 pH profile of SC2 under steady state conditions (Influent: DCW, HLR=0.625 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

A correlation was made between oxygen and DOC for soil column operated with DCW at hydraulic loading rates 0.625 m/d and 1.25 m/d. Using the data of DOC and oxygen profiles, a plot of DOC removed against dissolved oxygen consumed was made and a correlation coefficient of above 0.9 was found at both hydraulic loading rates. Figure 4-35 and 4-36 show correlations between the two parameters. From the slope of the equation it can be seen that 1 mg of O_2 is consumed to remove 0.458 and 0.423 mg of DOC from column at HLR 1.25 and 0.625 m/d respectively, which is comparable with the theoretical carbon removal (0.375 mg) (see section 4-2-2-3 for theoretical concept).

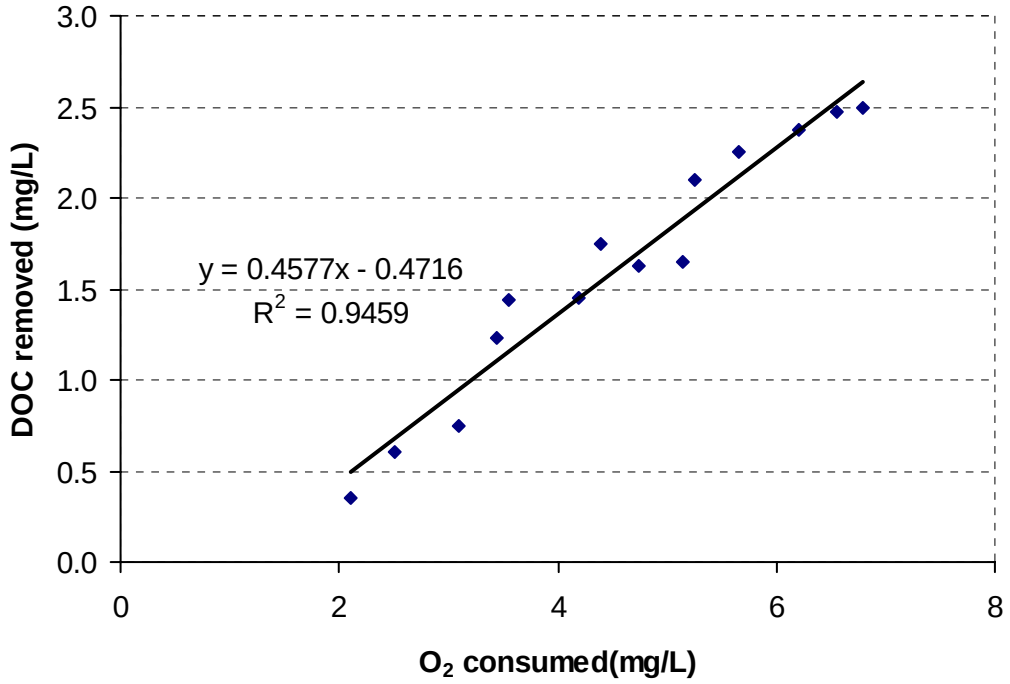


Figure 4-35 Correlation of DOC removal with oxygen consumption for SC2 under steady state (Influent: DCW, HLR=1.25 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

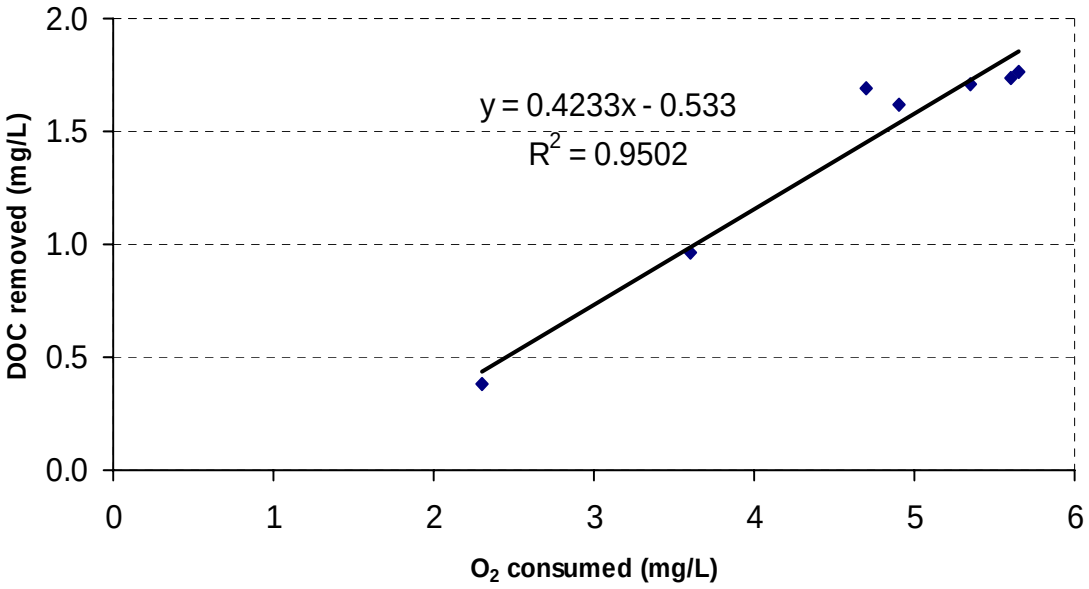


Figure 4-36 Correlation of DOC removal with oxygen consumption for SC2 under steady state (Influent: DCW, HLR=0.625 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

Biomass measurements were also carried out for both SC1 and SC2 at various sampling points of the columns. This measurement was done at HLR of 0.625 m/d for both columns. A total of 14 samples, 7 from each column, were taken for analysis. From the

seven samples four samples were taken from the first 50 cm depth where most of the biological activity was expected. Samples were sent to Haarlem lab (North Holland) for analysis. ATP was used for measuring biomass in the columns. It is a better way of measuring biomass as compared to other conventional methods such as plate count method or volatile suspended solid (VSS) method. ATP method measures total active biomass.

The results of ATP measurements for two soil columns SC1 and SC2 together with DOC and oxygen are shown in Figure 4-37 and 4-38 respectively. As can be seen from the graph the trends of ATP are pretty much similar to that of DOC and O_2. ATP measurement in the top part of the soil column showed a higher concentration (88,181 pg ATP/gm of sand) from SC1 (DCW+SE) as compared to SC2 (DCW) (78,021 pg ATP/gm of sand); the difference being about 10,160 pg ATP per gram of dry sand. This was also an indication that SE has more BDOC than DCW. The ATP at the bottom of SC1 and SC2 was found to be 557 pg ATP/gm of sand and 252 pg ATP/gm of sand, respectively.

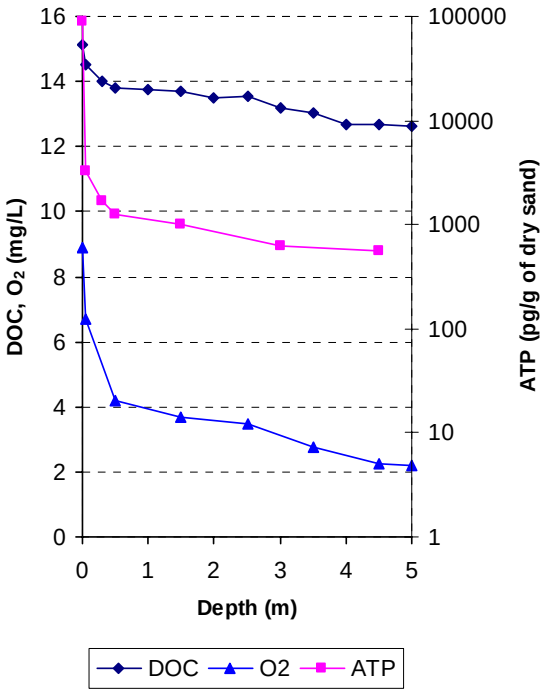


Figure 4-37 ATP profile of SC1 together with DOC and O_2 (Influent: DCW+SE, HLR=0.625 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

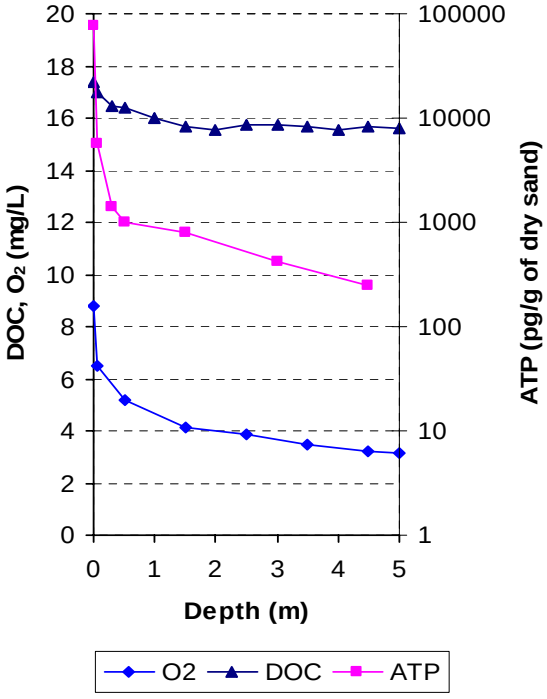


Figure 4-38 ATP profile of SC2 together with DOC and O_2 (Influent: DCW, HLR=0.625 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

A correlation was made between ATP and DOC for the two soil columns SC1 and SC2. Using the data of DOC and ATP profiles, a plot of DOC removed against ATP measured was made and a correlation coefficient of about 0.9 was found for both columns. Figure 4-39 and 4-40 show correlations between the two parameters for SC1 and SC2 respectively. From the slopes of the equations it can be seen that more biomass (almost twice) is required to get a reduction in DOC of 1 mg/L from SC2 as compared to SC1.

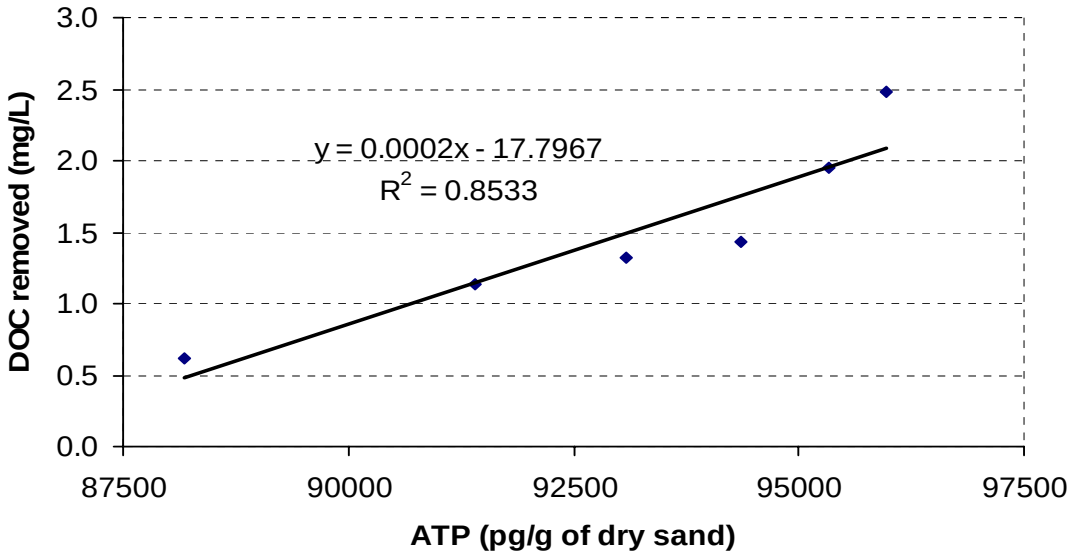


Figure 4-39 Correlation of DOC removal with ATP for SC1 under steady state (Influent: DCW+SE, HLR=0.625 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

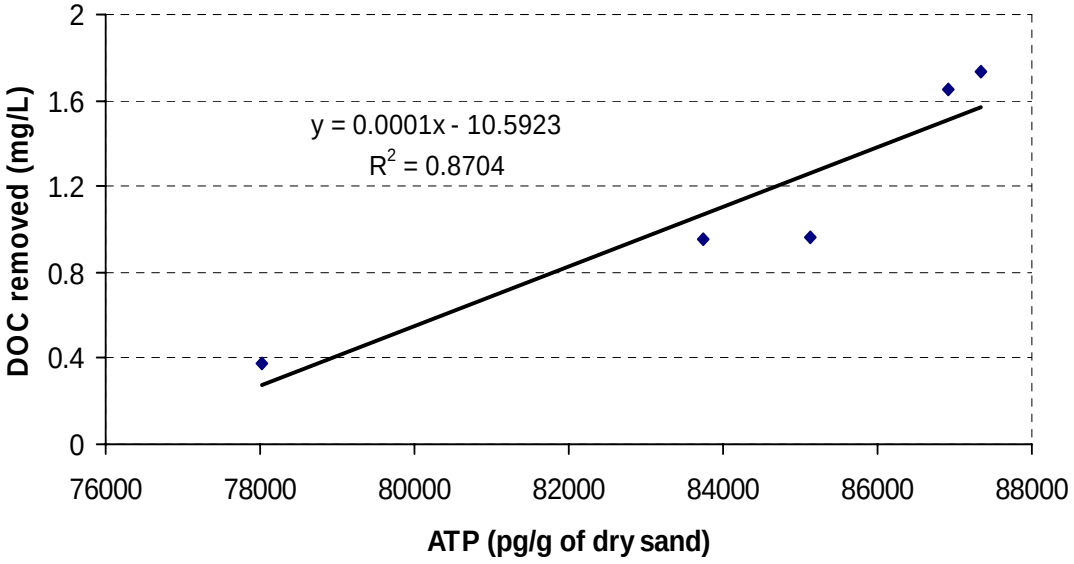


Figure 4-40 Correlation of DOC removal with ATP for SC2 under steady state (Influent: DCW, HLR=0.625 m/d, Column depth= 5 m, media size 0.8 – 1.25 mm, aerobic condition)

4.3 Batch studies for organic matter removal

Batch experimental setups in triplicate were deployed to study organic matter removal and to compare with results from the soil column. This was done under both aerobic and anoxic conditions with three different influents: Delft canal water (DCW), canal water mixed with secondary effluent (1:1 ratio) (DCW+SE) and secondary effluent (SE).

The batch reactors were acclimated for more than two months. During the process the feed to the batch was changed every four days and influent & effluent DOC concentration was continuously monitored. The average influent and effluent DOC concentration during ripening period for different applied influents are shown in Table 4-8. As can be seen from the table DCW has a higher average value of DOC, UVA and SUVA as compared to other samples. However, despite a higher initial DOC, its increase in SUVA is low which depicts the low BDOC content of DCW. Though SE has more than two fold increment in SUVA value, its effluent SUVA is less than that of DCW. This shows the more humic nature of DCW. The general trend of the data shown in Table 4-8 is in conformity with the corresponding result from soil column experiment.

Table 4-8 Average influent and effluent DOC, UVA and SUVA values of batch reactors during ripening period

Applied Influent	DOC (mg/L)		UVA (cm^{-1})		SUVA (L/mg-m)		Increase in SUVA (%)
	Influent	Effluent	Influent	Effluent	Influent	Effluent	
DCW	18.61 ± 2.02	16.45 ± 1.55	0.599 ± 0.05	0.559 ± 0.05	3.22	3.40	5.6
DCW+SE	17.27 ± 1.13	14.62 ± 1.36	0.509 ± 0.02	0.474 ± 0.03	2.95	3.24	9.8
SE	15.62 ± 2.31	12.81 ± 2.26	0.418 ± 0.05	0.386 ± 0.05	2.68	3.01	12.3

Table 4-9 shows the removal efficiency of batch reactors at the end of ripening period. As can be seen from the table at the end of ripening period a DOC removal of about 19, 21, and 22 percent were obtained in batch reactors with DCW, DCW+SE and SE respectively.

Table 4-9 Removal efficiency of batch reactors at the end of ripening period under aerobic condition

Applied Influent	Measured DOC (mg/L)		DOC removal (%)
	Influent	Effluent	
DCW	20.92	16.86	19
DCW+SE	17.13	13.49	21
SE	12.37	9.62	22

The results of investigation of batch reactors with respect to DOC, UVA, nitrate and ammonia under aerobic and anoxic conditions after steady state are presented in the following subsections.

4.3.1 Experiments under aerobic condition

Nine batch reactors were used to investigate organic matter removal under aerobic conditions. Three different influents in triplicate were monitored over a period of more than two months until DOC values are more or less stabilized. After biological acclimation of these reactors, measurement of DOC and UVA were carried out at short time interval for four days and the results are presented in Figure 4-41 and 4-42. The influent DOC concentration for reactors fed with DCW, DCW+SE and SE were 19.45 mg/L, 18.26 mg/L and 17.48 mg/L, respectively, while the corresponding effluent DOC concentration were 15.5 mg/L, 13.82 mg/L and 13.09 mg/L. This resulted in DOC removal of 20 %, 24 % and 25 % for reactors fed with DCW, DCW+SE and SE, respectively.

The analysis of batch experiment made by sampling at short time intervals for four days without changing the feed showed comparable result with the one reached at the end of the ripening period (Table 4-10). The small variation might have occurred due to the daily reduction (during sampling) of the volume of water in the reactors.

Table 4-10 DOC degradation during batch experiment under aerobic condition

Influent	**% DOC Degradation**	
	At the end of ripening	**At the end of 4 days measurement after ripening**
DCW	19	20
DCW+SE	21	24
SE	22	25

Figure 4-41 and 4-42 show a higher reduction of DOC at the beginning (the first one day) of the experiment. Comparatively more reduction was shown for SE in the first one day. As explained before, this is due to the presence of more BDOC (non humics) in SE than other samples. In addition, Figure 4-42 depicts a faster reaction rate and more removal in the batch reactor fed with SE.

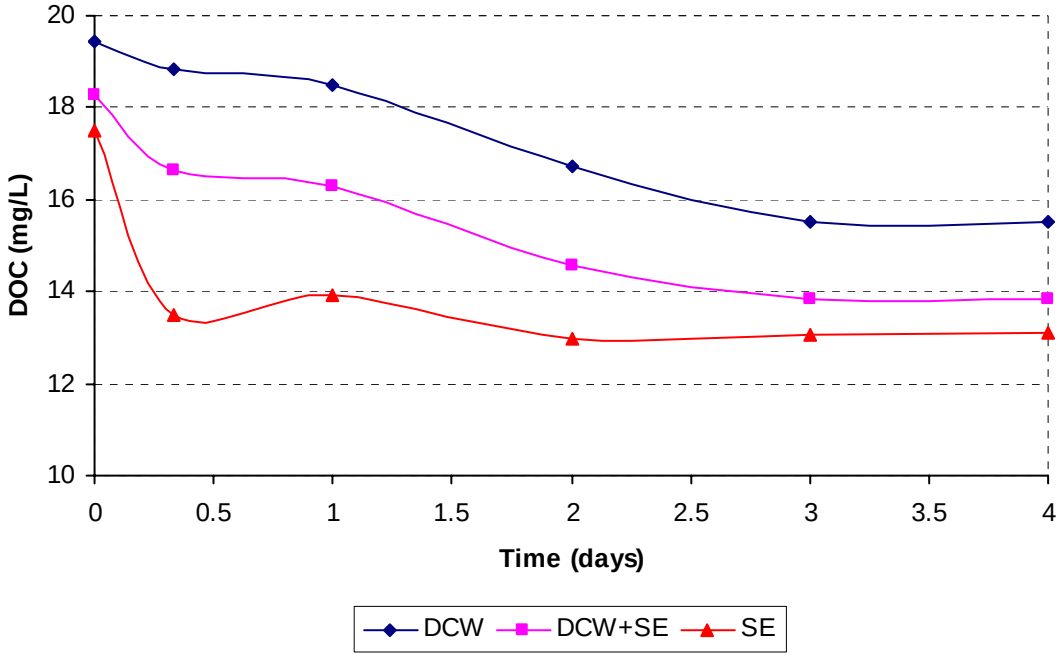


Figure 4-41 Change in DOC degradation with time during batch experiments under steady state condition (Influent: as shown in the legend, media size 0.8 – 1.25 mm, aerobic condition)

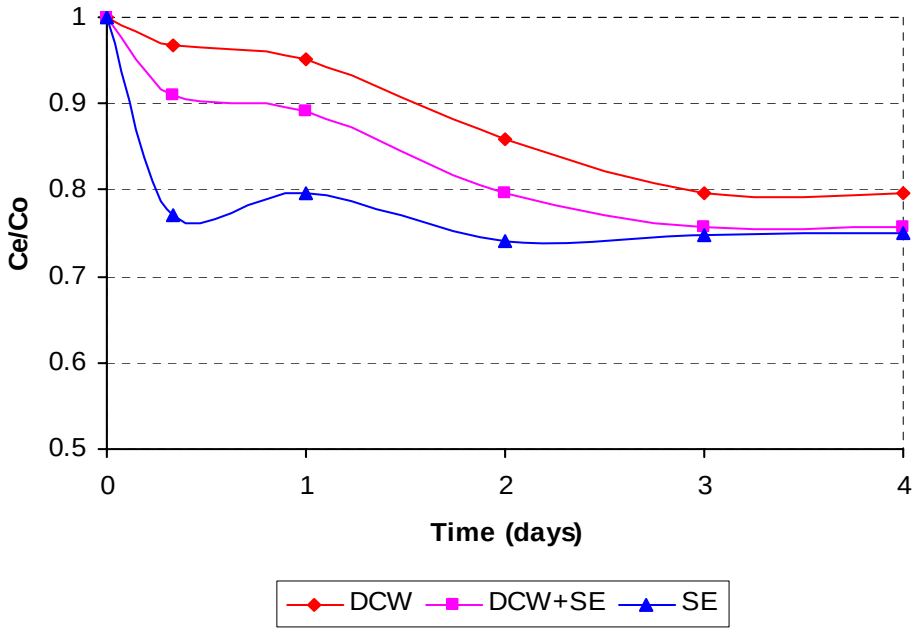


Figure 4-42 DOC removal with time during batch experiments under steady state condition (Influent: as shown in the legend, media size 0.8 – 1.25 mm, aerobic condition)

Figure 4-43 shows a three term mathematical model describing DOC removal with time for the batch reactors with three different feed waters. The kinetic model parameters obtained are presented in Table 4-11. As per these models, the maximum achievable percentage of DOC removal during RBF with DCW, DCW mixed with SE and SE are about 34, 26 and 27 % respectively. The predicted models resulted in lower maximum achievable DOC removal efficiencies for all batch reactors as compared to the model predicted for soil columns at a HLR of 1.25 m/d.

Table 4-11 DOC removal model parameters for batch reactors with different influents

Model Parameter		Co	C_1	C_2	C_3	k_1	k_2
Unit		mg/L	mg/L	mg/L	mg/L	day^{-1}	day^{-1}
Influent	**DCW**	19.54	1.78	4.87	12.89	0.261	0.261
	DCW+SE	18.04	2.07	2.67	13.30	0.625	0.621
	SE	17.48	3.71	1.08	12.69	204.033	0.314

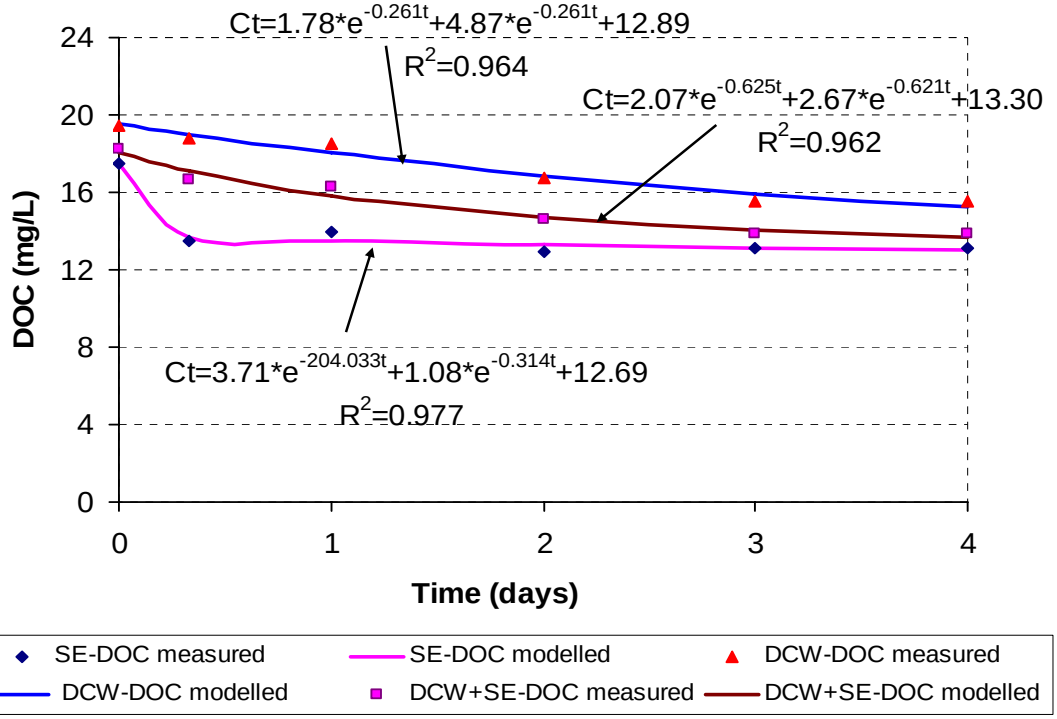


Figure 4-43 Measured and modelled DOC with time for batch reactors under steady state with different feed water (Influent: as shown in the legend, media size 0.8 – 1.25 mm, aerobic condition)

In addition to DOC and UVA, measurement of ammonia and nitrate was carried out in batch reactors under aerobic conditions. The measurement showed nitrification was occurring though the available ammonia was small. Table 4-12 presents the results of

the measurement. It can be seen that the increase in NO_3-N for DCW was less as compared to that of SE, though its ammonia concentration was more than four fold. The variation in the type of nitrifying bacteria in the source water could be the possible reason for slow nitrification process in DCW and relatively better nitrification in SE sample. A similar result was obtained from the soil column experiment.

Table 4-12 Nitrate in influent and effluent of batch reactors under aerobic condition

	NH_4-N (mg/l)	NO_3-N (mg/L)		Increment in NO_3-N (%)
		Influent	Effluent	
DCW	0.49	3.46	4.15	20
SE	0.1	4.79	5.97	25

Comparison of DOC removals was made for the batch reactor with the soil column at HLR of 1.25 m/d under aerobic conditions. The performance of batch reactors with respect to DOC removal was found to be better than soil column. The comparison was made for HRT of 4 days in both cases. The results obtained and discussed in previous sections are summarised in Table 4-13.

Table 4-13 Comparison of batch reactors and soil column for DOC removal at HRT=4 days

Influent	% DOC degradation	
	Batch reactor	Soil column (HLR=1.25 m/d)
DCW	20	13
DCW+SE	24	20

The better performance for the batch reactor was attributed to the higher surface loading of sample water per gram of sand. The soil column contained approximately 75 kg of sand which was exposed to 40 litre of water for four days. Batch reactors, however, contained 75 g of sand and were exposed to 300 ml of water for the same four days. This yields a higher surface loading of 4 ml sample per gram sand for batch reactor versus 0.5 ml/g sand for soil column. This could have resulted in a lower bio-degradation in the soil column.

In general, under comparable conditions, soil batch reactors are used to obtain an idea and information about the effluent quality that would be obtained with a column system.

4.3.2 Experiments under anoxic condition

In order to make a comparison of organic matter removal between batch reactors under aerobic and anoxic condition, four batch reactors (1 litre capacity) fed with SE were prepared, two of them being aerobic and the other two anoxic. After biological acclimation of these reactors measurement of DOC was carried out at five days interval for fifteen days with out changing influent water.

Figure 4-44 shows DOC removal with time under steady state conditions. In fifteen days the DOC concentration in aerobic reactor was reduced from 15.0 mg/L to 10.76 mg/L while in anoxic reactors it was reduced from 15.65 mg/L to 13.81 mg/L. This corresponds to a DOC removal of 28 % for aerobic reactor as compared to 12 % for anoxic ones. In the first five days, the DOC concentration was reduced to 11.47 mg/L and 15.23 mg/L in aerobic and anoxic reactors, respectively. This corresponds to a DOC removal of 24 % for aerobic reactor and 3 % for anoxic ones. As can be seen from the graph the rate of removal until the first sampling was very high for aerobic conditions as compared to anoxic conditions in which case the slope is very flat. The result also showed that anoxic decomposition of organics was a very slow process compared to the aerobic process. However, it also showed that some DOC removal is feasible also under anoxic conditions that might occur during RBF.

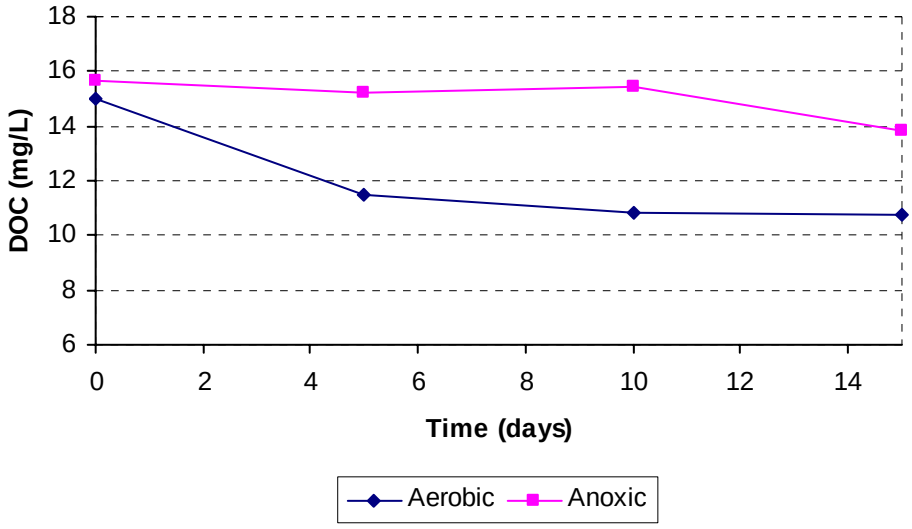


Figure 4-44 DOC removal with time during batch experiments under steady state condition (Influent: SE, media size 0.8 – 1.25 mm)

4.4 Batch studies for EDCs removal

4.4.1 Measurement of EDCs in influents and validation tests

Before studying removal of EDCs (E1, E2 and EE2) in batch reactors, ELISA validation tests were carried out making use of DCW and SE samples with and without spiking E1, E2 and EE2. This was done to measure concentrations of E1, E2 and EE2 in the samples and also to look at their recovery. In order to accomplish this task, sample pre-treatment for ELISA was carried out by a solid phase extraction (SPE) technique using 500 ml of each sample. The results of the tests are shown in Table 4-14.

Table 4-14 Results of ELISA validation test

sample	Estrogens	spiked (ng/L)	ELISA (ng/L)	Recovery (%)
DCW	E1	0	46.3	
		40	83.3	97
	E2	0	1.4	
		2	3	88
	EE2	0	3.5	
		1.2	8.9	108
SE	E1	0	33.7	
		40	69.3	94
	E2	0	3	
		4	6	86
	EE2	0	5.2	
		1.2	6.1	95

From the ELISA test it was found that concentration of E1 is more in DCW as compared to SE sample. However, E2 and EE2 are more abundant in the SE sample.

As per the results shown in Table 4-11, all ELISA tests have shown good recoveries (86 – 108 %) as compared to result obtained by previous study. A study made on similar estrogens compounds reported recoveries ranging from 45 to 95 % (Mansell *et al.*, 2004).

4.4.2 Investigation of EDCs removal in batch reactors

Batch reactors were deployed with various influents under different redox conditions to simulate processes occurring during RBF and to study EDCs (steroid estrogens) removal during water percolation through porous media. The different arrangements of batch reactors for this study are presented under section 3.3.2, Table 3-1.

Adsorption and biodegradation are the twowhy responsible removal mechanisms for EDCs during the RBF process. Compounds that are being removed primarily via adsorption have the potential to remobilize (Birkett and Lester, 2003). If the compounds are being degraded, then they may be transformed to a non- estrogenic form and no longer be capable of causing endocrine disruption.

Estrogens (E1, E2 and EE2) with a concentration of 100 ng/L were spiked in all reactors except control-3 (MQ with fresh sand). Sodium azide was also added at 130 mg/L concentration to all abiotic reactors in order to stop microbial activity. After doing this, samples were taken on day 0 and day 5 and analysed for initial and residual EDCs concentrations. The results are shown in Table 4-15 and 4-16.

Table 4-15 shows ELISA recovery rates for the three steroid estrogens compound under various conditions. A relatively better recovery rates was found for E2 and EE2. No estrogen was added in control-3 (MQ with fresh sand). Accordingly, the results of the measurements both in influent and effluents showed that there was no E1, E2 and EE2 in this reactor.

The results of removal of EDCs in batch reactors under various conditions are shown in Table 4-16. The removal of EDCs under different conditions ranges from 47 to 98 percent. Biotic (aerobic) reactors showed better performance than abiotic (aerobic) and biotic (anoxic) reactors. The removal efficiencies in biotic aerobic reactors with DCW mixed with SE were 96, 93 and 79 % for E1, E2 and EE2, respectively, while the corresponding removal under abiotic (aerobic) condition were 79, 84 and 65 %. This shows that about 17, 9 and 14 % of E1, E2 and EE2 were removed by the biodegradation process only. However, in abiotic reactors, though sodium azide was added, the ATP measurement showed that there was biomass activity. Therefore, removal by the biodegradation process is likely to be higher. The ATP measurement showed 961 and 2614 pg ATP/g of sand in abiotic and biotic reactors respectively. In general, the results showed that adsorption was the primary mechanism of removal for E1, E2 and EE2. The result also showed that removal efficiency under biotic aerobic conditions was more by 24, 25 and 32 % for E1, E2 and EE2, respectively, as compared to biotic anoxic condition.

An attempt was also made to quantify the amount of E1, E2 and EE2 that can be removed by adsorption using a linear sorption model of the form given in equation 4.7. In using this equation, data on TOC of biomass per gram of sand was taken from previous MSc study made by Katukiza (2006). He found a minimum and maximum of 35 and 58 mg respectively of biomass TOC per gram of sand from his soil column study. The calculation made for S using this range of data showed that the sand in the batch reactors have excess capacity to adsorb E1, E2 and EE2. Therefore, as per this model, all E1, E2 and EE2 can be 100 % removed from the influents by adsorption. However,

the experimental results showed that there were also removals by biodegradation. This could be possible because if an EDC is adsorbed, it may still be slowly biodegradable. The detail calculation sheet is attached in the appendix.

$$S = K_d * C \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.7)$$

where S = mass sorbed per mass of sorbent (mg/kg)
K_d = partition or distribution coefficient
C = concentration in water at equilibrium (mg/L)

Kd represents the ratio of the mass concentration of a contaminant sorbed to soil to its concentration in the surrounding water and is given by:

$$K_d = K_{OC} * f_{OC} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.8)$$

$$K_{OC} = 0.63 K_{OW} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.9)$$

where f_{OC} = organic carbon fraction of the sand
K_{OC} = organic carbon partition coefficient of the contaminant
K_{OW} = octanol-water partition coefficient of the contaminant

Table 4-15 ELISA recovery rates during batch experiments

Sample	Conditions	Expected influent concentration with a spike of 100 ng/L			Measured influent concentration after spiking (ng/L)			Recovery (%)		
		E1	E2	EE2	E1	E2	EE2	E1	E2	EE2
DCW+SE	Abiotic (aerobic)	140	102.2	104.4	63.2	82.5	84.7	45	81	81
	Biotic (aerobic)	140	102.2	104.4	79.1	98.5	97.8	57	96	94
	Biotic (anoxic)	140	102.2	104.4	83.0	96.9	66.8	59	95	64
	Control-1*	140	102.2	104.4	88.5	101.7	96.0	63	100	92
	Control-2*	140	102.2	104.4	86.0	85.2	76.4	61	83	73
Milli-Q	Control-3*	0	0	0	0	0	0	-	-	-
DCW	Biotic (aerobic)	146.3	101.4	103.5	139.5	119.3	112.2	95	118	108
SE	Biotic (aerobic)	133.7	103.0	105.2	109.9	113.1	70.6	82	110	67

* Details of these controls are presented under section 3.3.2, Table 3-1

Table 4-16 Results of EDCs removal in batch reactors under various conditions

Sample	Conditions	Measured influent concentration (ng/L)			Measured effluent concentration (ng/L)			Removal (%)		
		E1	E2	EE2	E1	E2	EE2	E1	E2	EE2
DCW+SE	Abiotic (aerobic)	63.2	82.5	84.7	13.3	13.6	29.7	79	84	65
	Biotic (aerobic)	79.1	98.5	97.8	3.0	7.3	20.1	96	93	79
	Biotic (anoxic)	83.0	96.9	66.8	22.9	30.8	35.7	72	68	47
	Control-1 (no sand)	88.5	101.7	96.0	96.3	34.5	24.0	-9	66	-
	Control-2 (fresh sand)	86.0	85.2	76.4	80.0	34.1	37.4	7	60	51
Milli-Q	Control-3 (fresh sand)	0	0	0	0	0	0	0	0	0
DCW	Biotic (aerobic)	139.5	119.3	112.2	2.2	6.2	15.6	98	95	86
SE	Biotic (aerobic)	109.9	113.1	70.6	2.0	5.9	12.2	98	95	83

Figure 4-45 shows E2 removal versus soil microbial activity determined by ATP. The data used in the figure was collected from all batch reactors with different influent. The higher microbial activity in sands enhanced removal of selected estrogen compounds. Figure 4-46 also shows dissolved organic carbon (DOC) reduction versus E2 removal and the removal of E2 increased with an increased reduction of DOC. Observed DOC reduction is believed to be by biodegradation which is affected by sand microbial activity. This showed the correlation between DOC reduction and E2 removal which verified the biodegradation of estrogen compounds. An attempt was also made to fit similar curves for E1 and EE2 as in the Figures 4-40 and 4-41, however, the data points did not show similar trend. The transformation of E2 to E1 could possibly have affected the results of E1 to get curves with similar trend.

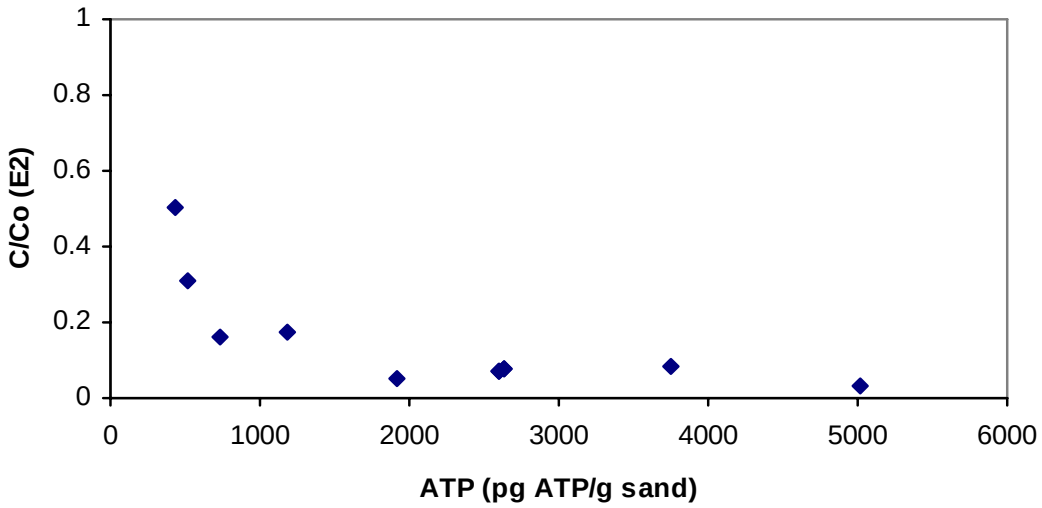


Figure 4-45 E2 removal versus biomass activity in batch reactors under different conditions (influents)

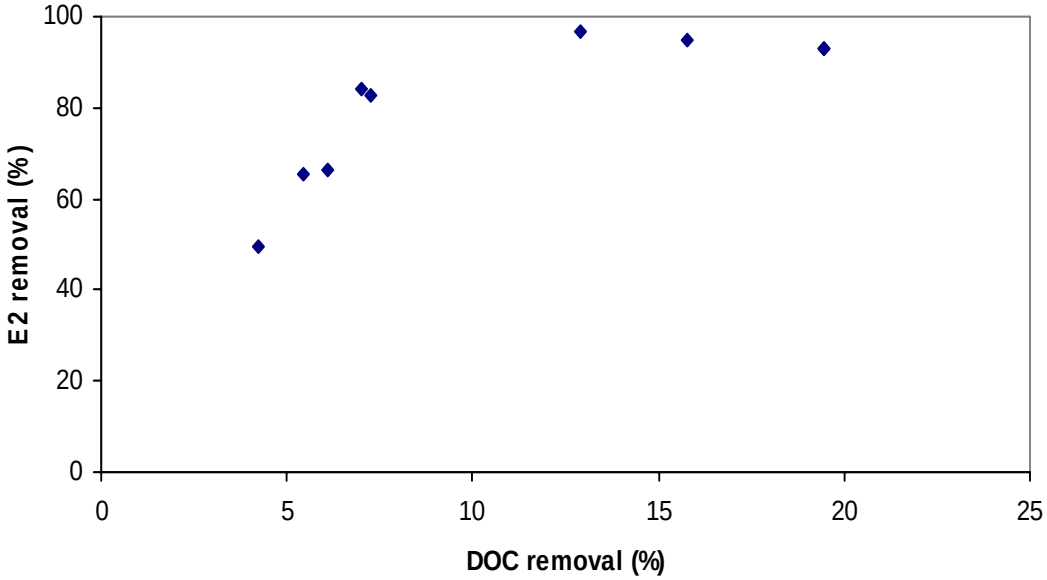


Figure 4-46 E2 removal versus DOC reduction in batch reactors under different conditions (influents)

In the batch experiment without media (control 1), the effluent concentration of E1 was found to be higher than the initial concentration. The feed water, secondary effluent mixed with canal water (1:1 ratio), contains microorganisms which were capable of transformation of E2 to E1 partly; however, the oxidation rate of E1 to E3 (estriol) was limited due the low microbial concentration. ATP measurements were taken in the influent of control-1 reactor just before the addition of estrogen compounds and it was 130 ng/liter. It is comparably lower than that of biotic reactors containing acclimated sands. The study done by Jűrgens showed that microorganisms in water samples from an English river were capable of transforming E2 to E1 with half-lives of 0.2-9 days when incubated at 20 °C (Jurgens *et al.*, 2002). In this study, there was limitation of oxidation of E1 to a less estrogenic compound. EE2 which has the highest sorption coefficient in selected estrogen compounds was mainly removed from the aqueous phase by adsorption onto associated particles in feed water and subsequent biodegradation.

In control 2 (fresh sand), E1 and E2 showed 7 and 60 % removal, respectively, and this may be due to low bioactivity in fresh sands or free TOC contents on sand (bioadsorption) which reflected the accumulation of E1 in aqueous phase. The presence of dissolved organic carbon in feed water amended with secondary effluent and Delft canal water may have competed with estrogen compounds for binding sites onto fresh sand. Also, adsorption capacity coefficient value is strongly correlated to the organic content of the sorbent. Thus, fresh sand treated under 550 °C heat chamber which results in no organic matter remained on the sand appeared to be a weak absorbent for estrogens than acclimated sand used in this study. In this batch experiment, the result also showed that due to low microbial activity E2 was only partially reduced and the

loss of E2 was accompanied by a corresponding accumulation of E1 as shown in control 1.

The removal of estrogen compounds under anoxic conditions showed the effect of redox conditions in removing selected estrogen compounds. In anoxic conditions, the removal efficiencies of E1, E2 and EE2 showed 72, 68 and 47 % respectively. During anoxic condition, removal efficiencies by biodegradation of selected estrogen compounds were lowered because the rate of anoxic biodegradation of phenolic organic compounds occurs at a much slower rate than the aerobic route, so adsorption is the dominant removal mechanism of these estrogen compounds in an anoxic environment. Similar results were shown by Czajka and Londry that the fate of EE2 under anoxic condition is dominated by sorption rather than biodegradation, and E2 was only partially reduced (Czajka and Londry, 2006). In this study, EE2 was more limited by the absence of oxygen. The fate of the estrogen compounds using different electron acceptors such as iron and sulfate was not investigated. Nitrate was only initially added to feed water as a source of elector acceptor in order to maintain anoxic conditions throughout the experiment period.

In aerobic batch experiments, three batch reactors which were acclimated for more than three months with a different source of feed water were used to determine whether different environments or microbial groups may affect biodegradation of estrogens: ((i) Delft canal water, (ii) Secondary effluent, (iii) Delft canal water with secondary effluent). A study done by Layton et al. showed that microbial group in municipal WWTPs have shown a much better biodegradation capacity than that in industrial WWTPs (Layton *et al.*, 2000). In this study, all three batch reactors showed similar removal efficiencies on selected estrogen compounds. All acclimated sands have ATP concentration with 2000-2500 pg ATP/g of dry sand. Thus, the microbial activity played a more limiting factor in the biodegradation removal of selected estrogen compounds than the diversity of microbial group or environments.

4.5 Organic matter characterization

Characterization of organic matter is not an easy task. To date, it has not been possible to identify all organic component molecules in water. The difficulty results from the great complexity of the organic matrix, constituted by a mixture of hundreds of simple molecules and the very low concentration of these compounds. Consequently, organic matter characterization is only possible through various fractionation and measurement techniques that give partial information on organic matter levels, and chemical functions or molecules, depending on the methodology used.

Characterization of organic matter was carried out for DCW, DCW mixed with SE and SE samples by measuring DOC, UVA, fluorescence and HPSEC-UVA/DOC/Fluorescence. The results are presented in the following sub sections.

4.5.1 DOC

Dissolved organic carbon (DOC) is the most commonly used parameter to quantify organic matter. The presence of organic matter (OM) strongly impacts drinking water treatment, water quality, and water behavior during distribution. DOC concentrations were determined continuously in a batch reactors and soil column experiments simulating RBF system. The results of the average DOC values for various samples studied are shown in Table 4-17 and 4-18.

Table 4-17 Average DOC values in batch reactors

Sample	Influent	Effluent
	DOC	DOC
DCW	18.61 ± 2.02	16.45 ± 1.55
DCW+SE*	17.27 ± 1.13	14.62 ± 1.36
SE	15.62 ± 2.31	12.81 ± 2.26

* The mix is in a 1:1 ratio

Table 4-18 Average DOC values in soil column experiment (HLR=1.25 m/d)

column	Sample	Influent	Effluent
		DOC	DOC
SC1	DCW+SE*	15.71 ± 1.71	12.53 ± 1.65
SC2	DCW+SE*	15.71 ± 1.71	12.43 ± 1.64
	DCW	19.76 ± 1.74	17.22 ± 1.29

* The mix is in a 1:1 ratio

From the results, it was found that Delft canal water (DCW) has more DOC than the secondary effluent (SE) from Hoek Van Holland treatment plant. However, under the same conditions, the biodegradability of DCW organic matter was less than that of SE. The BDOC levels in different influents of the soil column experiments under different HLR were estimated from the DOC removal kinetic curves modelled in previous sub-sections and are presented in Table 4-19.

Table 4-19 Estimates of BDOC levels in different influents of the soil column experiments

Influents	BDOC level (mg/L)	
	HLR = 1.25 m/d	HLR = 0.625 m/d
DCW	8.47	3.24
DCW+SE	10.77	8.19

4.5.2 UV absorbance

UV absorbance (UVA_{254}) in a natural water sample generally increases as OM concentration increases. Valuable information about the character and size of OM can be obtained through the use of UVA. The specific UV value (SUVA) is used to describe this information.

The average SUVA value for DCW, DCW+SE, and SE were calculated using the relation described in chapter 2, sub section 2.5.2.2. It was found that the influent and effluent UV absorbance values of Delft canal water were higher than that of the wastewater secondary effluent. The same was true for SUVA values. This was an indication that the OM in DCW was more aromatic than SE.

The SUVA values for all samples were found to be in the range of 2 to 4, which is an indication for a mixture of high and low molecular weight, humic and non humic, hydrophobic and hydrophilic OM in the samples (refer Table 2.8, chapter 2). However, comparatively, DCW (both influent and effluent) was found to have higher SUVA value than that of other samples, indicating a more humic and hydrophobic nature of OM in DCW.

Table 4-20 and 4-21 present the average UV absorbance and SUVA values of various samples used in batch and soil column experiments respectively.

Table 4-20 Average UV absorbance and SUVA values of samples in batch experiments under aerobic conditions

Sample	Influent			Effluent		
	DOC (mg/L)	UVA (cm^{-1})	SUVA (L/mg-m)	DOC (mg/L)	UVA (cm^{-1})	SUVA (L/mg-m)
DCW	18.61	0.599	3.22	16.45	0.559	3.40
DCW+SE	17.27	0.509	2.95	14.62	0.474	3.24
SE	15.62	0.418	2.68	12.81	0.386	3.01

Table 4-21 Average UV absorbance and SUVA values of samples in soil column experiments under aerobic conditions

column	Sample	Influent			Effluent		
		DOC (mg/L)	UVA (cm^{-1})	SUVA (L/mg-m)	DOC (mg/L)	UVA (cm^{-1})	SUVA (L/mg-m)
SC1	DCW+SE	15.71	0.488	3.11	12.53	0.403	3.22
SC2	DCW+SE	15.71	0.488	3.11	12.43	0.399	3.21

4.5.3 Fluorescence

In most river systems DOM predominantly comprises humic substances, with smaller amounts of carbohydrates and aminoacids; with most carbohydrates and aminoacids being humic bound. Between 40 % and 60 % of DOM is fluorescent; this fluorescent material principally comprises proteins and organic acids (Baker and Lamont-Black, 2001).

Fluorescent DOM exhibits discrete intensity peaks at known wavelengths. Fluorescence intensities predominantly depend on DOM concentration. Other factors like pH, and metal-ion interactions also affect fluorescence intensity.

Water samples were collected from the influent and effluent of batch reactors and soil columns under various process conditions and analysed for fluorescence EEM. The results of the analysis are presented in Figures 4-47 to 4-51. Contour lines represent the distribution of fluorescence intensity at different excitation-emission wavelength pairs. Two EEM peaks were identified in both influent and effluent of all the three different samples analyzed: DCW, DCW+SE and SE. In the figures, peak X is located at excitation wavelength ranging from 320 to 330 nm and emission wavelength from 432 to 440 nm. Peak Y is located at excitation wavelength of around 250 nm and emission wavelength ranging from 442 to 446 nm. These pairs of wavelengths are indication for the presence of humic substances (fulvic like peak). Humic like peaks appear at higher excitation/emission wavelengths and protien like peaks at lower excitation /emission wavelengths. In all the samples analysed, no protein like peak was observed, which usually appears in the excitation range from 250 to 280 nm and emission range from 280 to 350 nm. This could be due to the very small concentration of this material in the source water used for this study.

For most of the analyses, changes in location of peaks between influent and effluent samples was not observed. However, changes (reductions) in intensity were observed for all samples. These changes are due to the reduction in fulvic like material from the influent samples. It was also observed that the percent reductions in intensity between

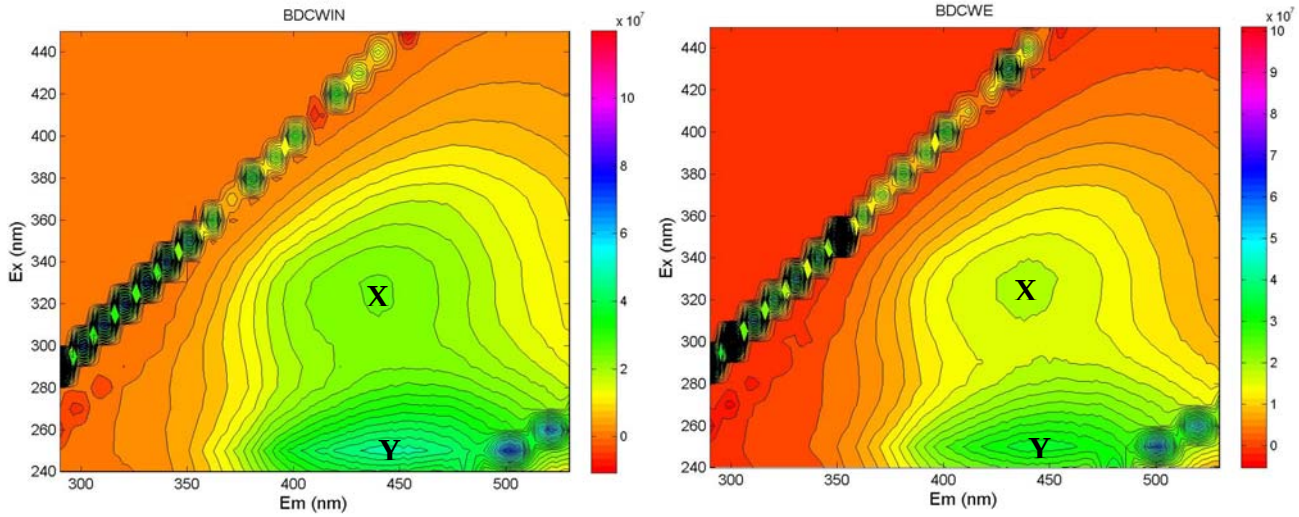
influent and effluent samples are almost the same for both peaks X and Y. A summary of fluorescence EEM of all samples is presented in table 4-23 and 4-24.

Fluorescence wave length difference was observed between DCW and SE samples. These differences could be interpreted as derived from DOM of different ages, origin and therefore different extent of decomposition (Baker and Lamont-Black, 2001).

An attempt was made to use a quantifiable parameter like fluorescence ratio to assess different sources of DOC. A fluorescence ratio (FR) of emission intensities at 450 to 500 nm at an excitation of 370 nm was found to be suggestive of either terrestrial-based (i.e., allochthonous) or algae- and bacteria-based (i.e., autochthonous) origins for the DOC (Donahue *et al.*, 1998; McKnight *et al.*, 2001). A high FR value (>1.8) was correlated with DOC having algae- or bacteria-based sources. Low FR values (<1.5) were more indicative of DOC derived from a plant- or soil-based origin. Table 4-22 presents the FR values for DCW and SE influent samples. The results of the analysis in the table suggested that fluorophors in DCW and SE samples were derived from soils and/or plants. However, it is known that the SE sample was obtained from the effluent of a biological (i.e., bacteria) wastewater treatment plant. Hence, the inferred source based upon FR value was inconsistent with the known origin of the sample. The reason for this not to happen could be the high efficiency of the treatment plant in removing the easily biodegradable organics leaving only refractory organics. This was consistent with the result from fluorescence measurement which didn't show any protein like materials.

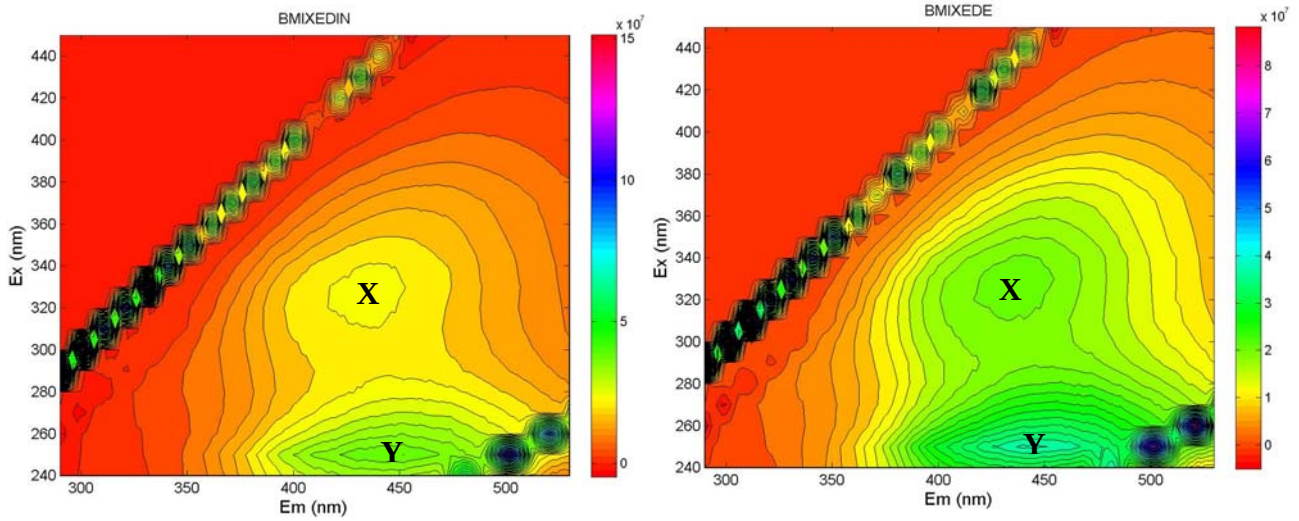
Table 4-22 Fluorescence ratio (FR) calculation

Sample	Fluorescence intensity		FR
	Ex=370 nm, Em=450 nm	Ex=370 nm, Em=500 nm	
DCW	$1.7x10^7$	$1.4x10^7$	1.2
SE	$1.5x10^7$	$1.1x10^7$	1.4



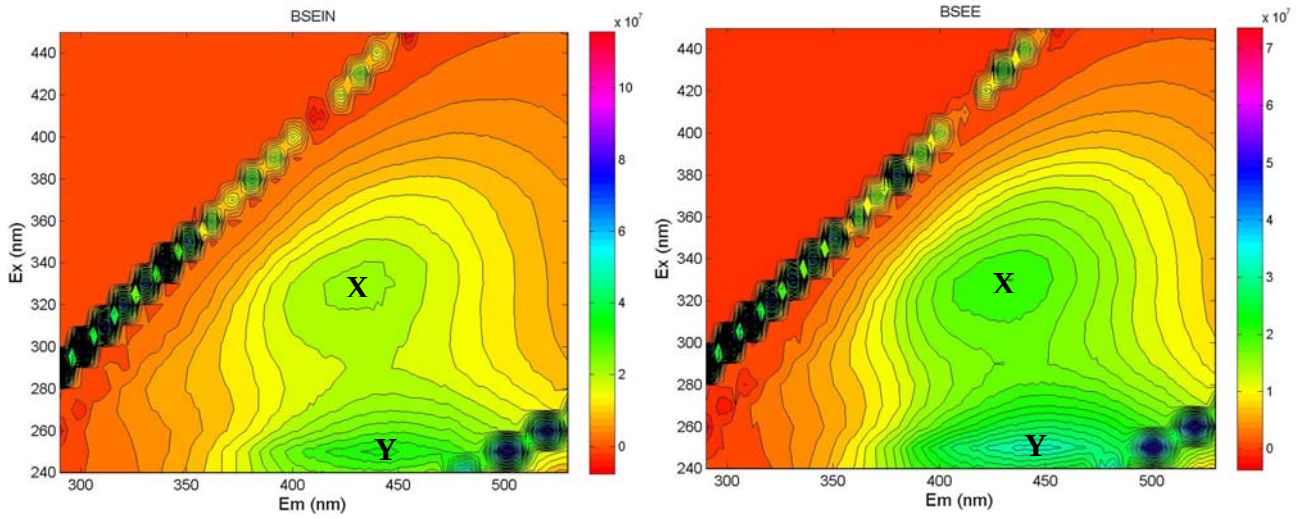
a) Influent b) Effluent

Figure 4-47 Fluorescence EEM for DCW in batch reactor under aerobic condition



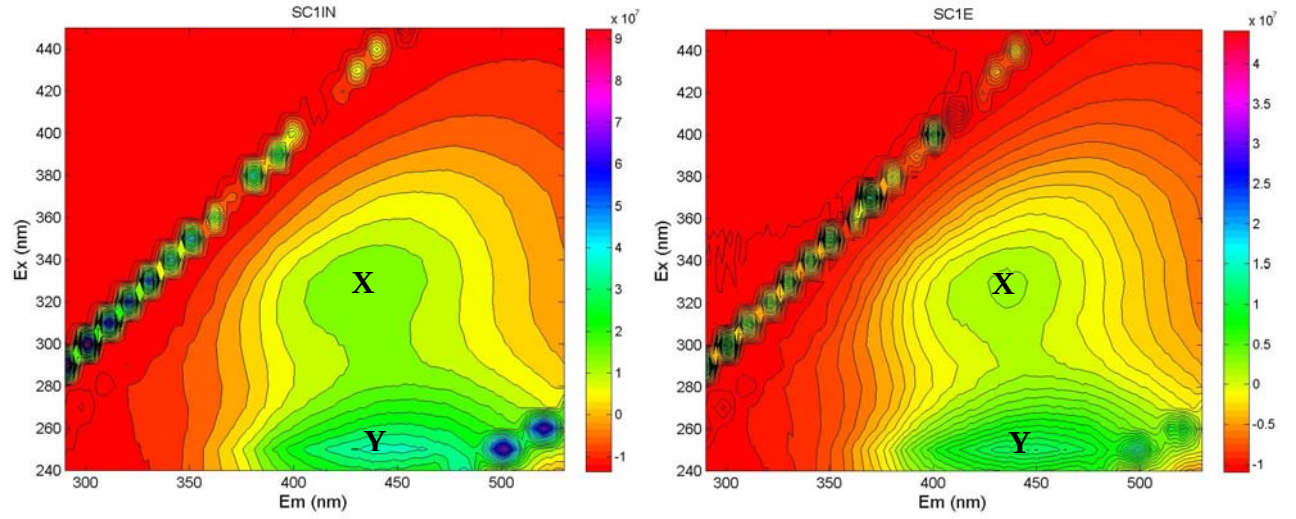
a) Influent b) Effluent

Figure 4-48 Fluorescence EEM for DCW mixed with SE in batch reactor under aerobic condition



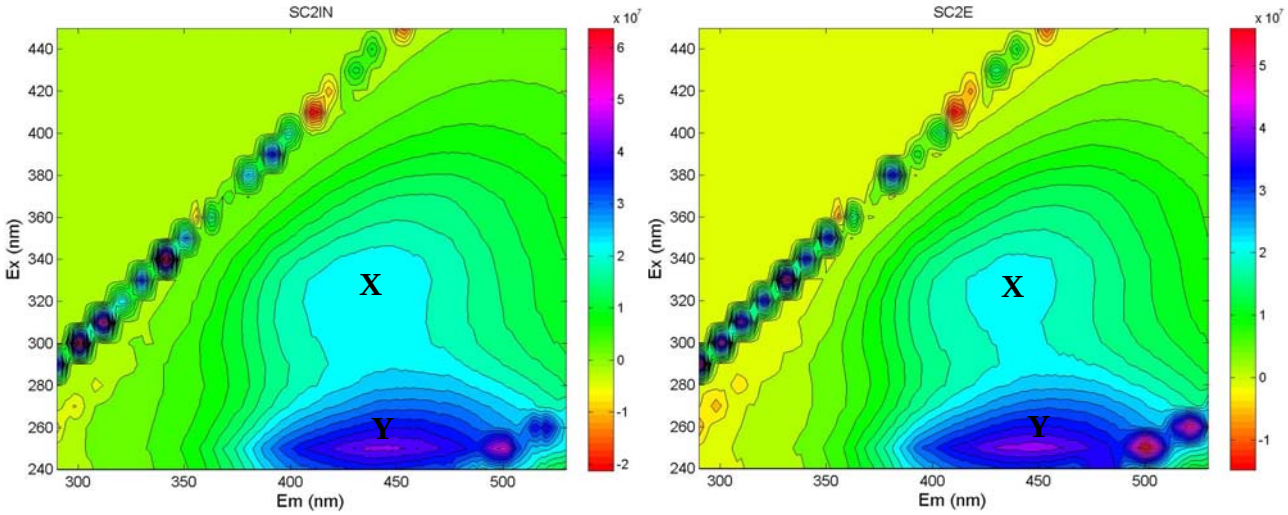
a) Influent b) Effluent

Figure 4-49 Fluorescence EEM for SE in batch reactor under aerobic condition



a) Influent b) Effluent

Figure 4-50 Fluorescence EEM for DCW+SE in soil column 1 (SC-1), HLR=1.25 m/d



a) Influent b) Effluent

Figure 4-51 Fluorescence EEM for DCW in soil column 2 (SC-2), HLR=1.25 m/d

Table 4-23 Summary of Fluorescence EEM analysis results for samples from batch reactors under aerobic conditions

Sample		Peak X			Peak Y			Reduction in Intensity (%)	
		Ex. (nm)	Em. (nm)	Intensity	Ex. (nm)	Em. (nm)	Intensity	Peak X	Peak Y
DCW	Influent	325	440	$2.63x10^7$	250	446	$4.80x10^7$	29	28
	Effluent	325	440	$1.86x10^7$	250	446	$3.48x10^7$		
DCW+SE	Influent	325	436	$2.44x10^7$	250	446	$4.17x10^7$	9	8
	Effluent	325	436	$2.22x10^7$	250	444	$3.84x10^7$		
SE	Influent	330	432	$2.28x10^7$	250	442	$3.51x10^7$	8	7
	Effluent	330	432	$2.10x10^7$	250	444	$3.26x10^7$		

Table 4-24 Summary of Fluorescence EEM analysis results for samples from soil column experiment under aerobic conditions

Sample		Peak X			Peak Y			Reduction in Intensity (%)	
		Ex. (nm)	Em. (nm)	Intensity	Ex. (nm)	Em. (nm)	Intensity	Peak X	Peak Y
SC-1 (DCW+SE)	Influent	325	436	$2.79x10^7$	250	446	$4.80x10^7$	13	12
	Effluent	325	436	$2.44x10^7$	250	446	$4.24x10^7$		
SC-2 (DCW)	Influent	325	438	$2.39x10^7$	250	442	$4.47x10^7$	9	8
	Effluent	325	438	$2.18x10^7$	250	446	$4.12x10^7$		

4.5.4 HPSEC-UVA/DOC/Fluorescence

In order to obtain useful information on molecular weight distribution of OM fractions, four samples, two influent and two effluent samples from SC1 and SC2 at HLR of 0.625 m/d, were sent to Haarlem lab (North Holland) for LC-OCD analysis and the result of the analysis is presented in Figure 4-52. Four peaks appeared that are characteristics of organic carbon: (i) biopolymers (high molecular weight polysaccharides), (ii) humic substance like material, (iii) building blocks of humic substances, and (iv) low molecular weight acids. The chromatograms depict a very low response to biopolymers, both to DOC and UVA detection in the influent samples. It also showed an almost complete removal of OM in the biopolymer fraction. In the other three fractions, as such no changes in the peaks were seen between influent and effluent samples of both SC1 and SC2.

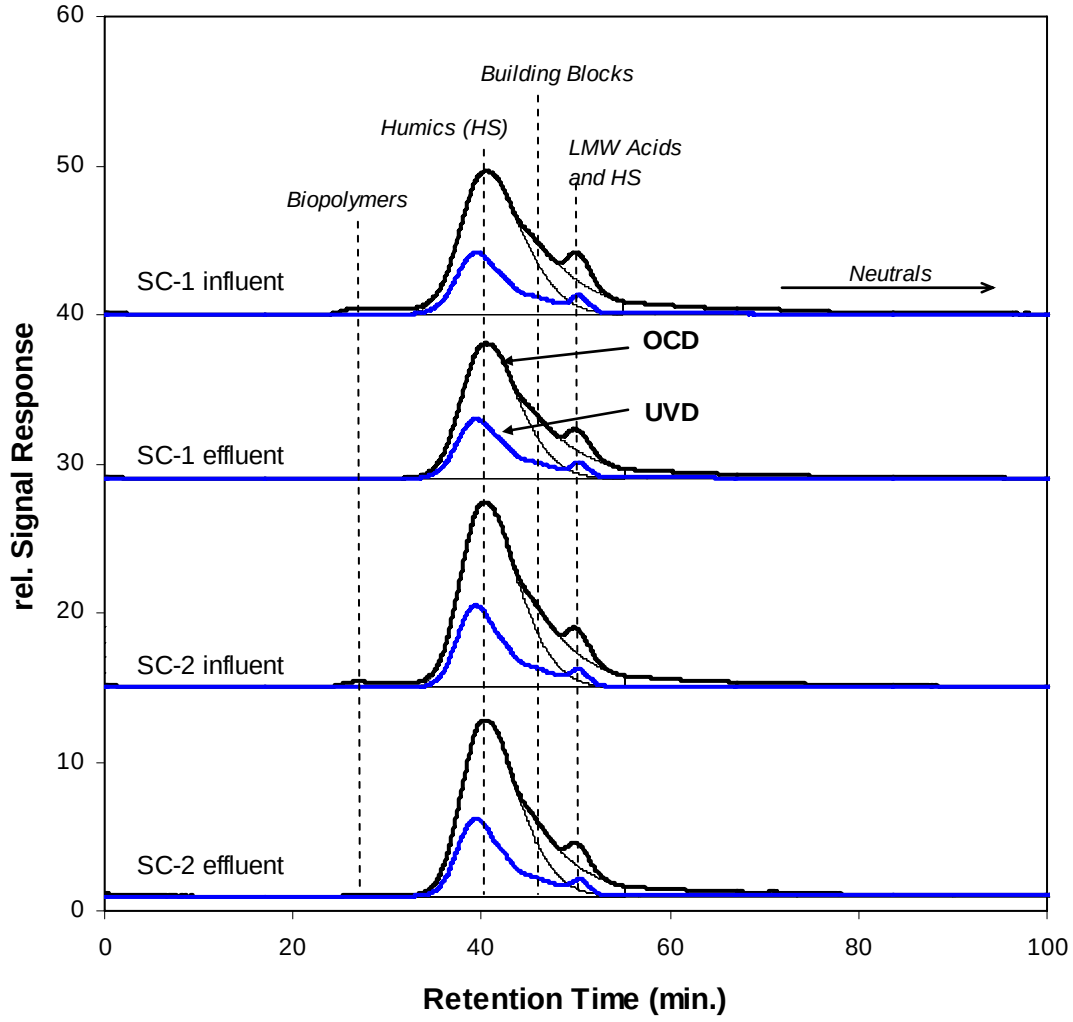


Figure 4-52 Size exclusion chromatograms of water samples from soil columns at HLR = 0.625 m/d

Using the HPSEC-UVA/DOC/Fluorescence machine of the IHE lab, measurements were carried out for UV_{210}, UV_{254}, and fluorescence at a specific excitation-emission wavelength (Ex=250 nm, Em=446 nm). This pair of wavelengths was one of the peaks obtained in EEM analysis under section 4.5.3. The results of the analysis (chromatograms) are presented in Figure 4-53 and 4-54. From these figures some changes (reduction) in UVA and fluorescence between the influent and effluent samples could be observed.

It was also attempted to investigate the presence of protein like material in the samples by applying a specific excitation-emission wavelengths (Ex=280, Em=350). However, no peak was detected as in fluorescence EEM analysis.

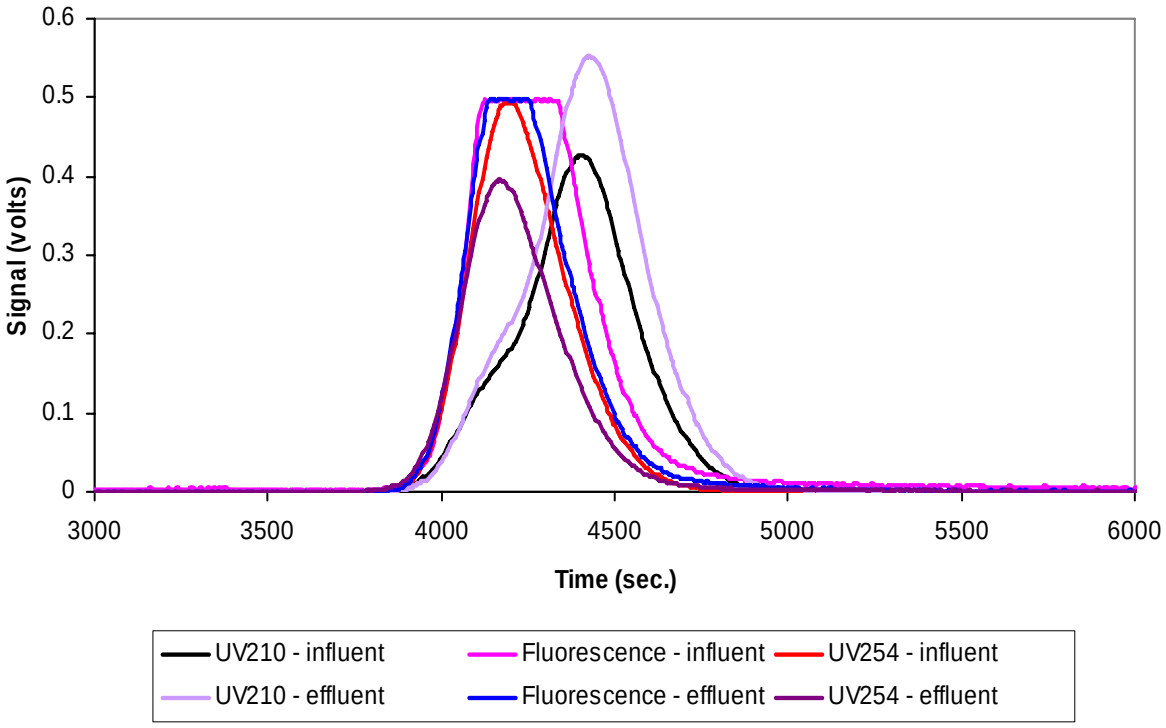


Figure 4-53 Size exclusion chromatograms of water samples from SC1 at HLR = 1.25 m/d

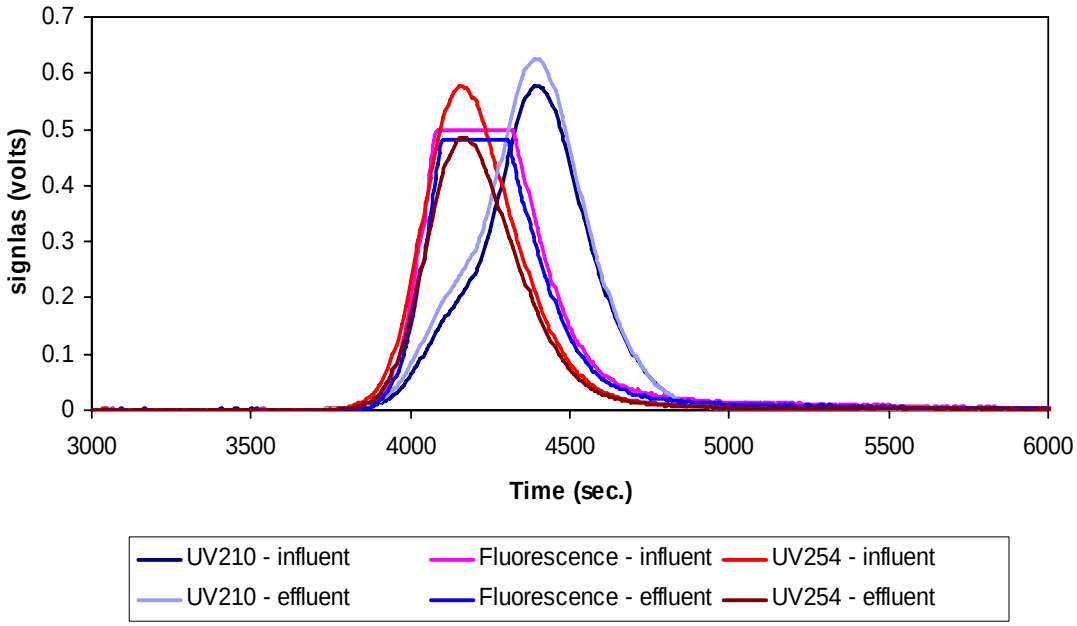


Figure 4-54 Size exclusion chromatograms of water samples from SC2 at HLR = 1.25 m/d

4.6 Practical implications of the study

The results obtained from this study on OM characterization, DOC and EDCs removal during RBF could have many practical implications and applications, some of which are mentioned as follows:-

- The experimental result obtained from this study showed that RBF could be used as a potential pre-treatment method with regard to the attenuation of OM and EDCs from wastewater impacted sources. A maximum achievable DOC removal efficiency of 53 % was obtained from an experiment simulating surface water 50 % impacted by wastewater secondary effluent. This removal efficiency was obtained from a source with most of its DOC characterized as non biodegradable. Better performance can be achieved if sources having better water quality are used.

- Regarding the removal of EDCs, the study found that RBF can remove estrogen compounds from 47 to 98 % depending upon background water quality and process conditions applied (aerobic/anoxic, biotic/abiotic). Hence RBF can be used as viable treatment method for removal of estrogen compounds (E1, E2, and EE2) from wastewater impacted surface water sources.

- DOC removal during RBF is highly dependent on the quality of the source water. In addition, the operating conditions like HLR, aquifer material and the redox conditions are also important. Therefore, this type of study could help to identify suitable water sources which require minimum investment cost in terms of DOC and EDCs removal during RBF.

- Detailed information on organic matter removal by RBF systems subjected to different process and hydrogeological conditions is essential for rational design of RBF systems and to predict degree of purification provided by RBF at various sites. Therefore, as this study was focused on characterization of OM and removal of DOC and EDCs (E1, E2 and EE2) during RBF under different process conditions, the data obtained can be used as an input for rational design and modelling of RBF systems.

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

- DCW was found to have more DOC (18.61 ± 2.02 mg/L) than SE from Hoek Van Holland wastewater treatment plant (15.62 ± 2.31 mg/L). However, DCW has less biodegradable DOC than SE.

- Under steady state condition, influent DOC concentration was reduced from 20.12 mg/L to 16.03 mg/L and from 15.14 mg/L to 12.61 mg/L in SC1 fed with DCW mixed with SE at HLR of 1.25 m/d and 0.625 m/d respectively, resulting in corresponding DOC removal efficiencies of 20 and 17 %. However, in SC2 fed with DCW the reduction was from 19.24 mg/L to 16.75 mg/L and 17.39 mg/L to 15.62 mg/L at a HLR of 1.25 m/d and 0.625 m/d respectively, resulting in corresponding DOC removal efficiencies of 13 and 10 %.

- DCW was found to be more aromatic than SE. Relatively DCW has higher SUVA value (3.22 L/mg-m) as compared to SE (2.68 L/mg-m).

- SUVA values of both DCW and SE indicated the presence of a mixture of high and low molecular weight, humic and non humic, and hydrophobic and hydrophilic NOM. However, relatively DCW has more humic and hydrophobic organic matter (NOM).

- The soil column study showed that more than 50 % of DOC and O_2 were consumed in the top 50 cm layer of the column. This was due to biological activity which was verified by ATP measurement.

- Good correlation of DOC removal with O_2 and biomass development was also observed in the soil columns.

- The fluorescence analysis of both DCW and SE revealed the presence of humic like materials only. No protein like material was observed.

- Results of size exclusion chromatography depicted four peaks that are characteristics of organic carbon: biopolymers, humic substance like material, building blocks of humic substances, and low molecular weight acids.

- Almost complete removal of high molecular weight polysaccharides was observed from the size exclusion chromatogram for both SC1 and SC2 at HLR of 0.625 m/d.

- For a given water quality, if more residence time than necessary is given for biodegradation of the available BDOC, then the biomass will be starved for the extra time and their count will be reduced; hence removal efficiency will also be reduced. Therefore, increasing the HRT will not always imply an increase in DOC removal.

- All samples (DCW, DCW+SE, SE) were characterized by two dominant EEM peaks located near an excitation wavelength 250 – 330 nm and emission wavelength 432 – 446 nm, which is an indication for the presence of humic OM.

- Measurement of EDCs in Delft canal water sample showed concentrations of 46.3 ng/L, 1.4 ng/L and 3.5 ng/L of E1, E2 and EE2 respectively; whereas wastewater secondary effluent from Hoek Van Holland was found to contain E1, E2 and EE2 at concentrations 33.7 ng/L, 3 ng/L and 5.2 ng/L.

- Simulation of RBF system in batch reactors study showed that steroid estrogenic hormones (E1, E2, and EE2) could be efficiently removed from water sources impacted by wastewater effluents.

- The study showed that bioadsorption is the primary mechanism of removal for the three EDCs (E1, E2, and EE2). The overall removal from DCW mixed with SE under aerobic condition was 96, 93 and 79 % for E1, E2 and EE2 respectively.

- Preconditions for the use of bankfiltrated water as raw water are both a good quality of the respective river water and a subsoil passage which guarantees efficient and lasting removal of suspended matter, microorganisms and organic micropollutants.

5.2 Recommendations

- Detailed OM characterization study should be done by taking samples over a long period of time to take in to account the variation in water quality due to seasonal variations.

- EDCs removal during RBF should be further investigated by conducting soil column experiments.

- Study of DOC removal in soil column under anoxic condition should be carried out.

- As the concentration of sodium azide added (130 mg/L) did not inactivate all the biomass in batch reactors, more investigation on EDCs removal under abiotic condition is required for proper differentiation between bio-degradation, bio-sorption and adsorption mechanisms for EDCs removal.

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APPENDICES

Appendix A - Measurement of DOC

A1 - DOC values during ripening of soil columns with DCW + SE
A2 - DOC values in Soil columns (DCW + SE) under steady state
A3 - DOC values during ripening of soil column 2 (SC2) with DCW
A4 - DOC values in SC2 (DCW) under steady state
A5 - Measurement of DOC in batch reactors during ripening
A6 - Measurement of DOC in batch reactors at steady state under aerobic condition
A7 - Measurement of DOC in batch reactors at steady state under anoxic condition

Appendix B - Measurement of UV absorbance (UVA)

B1 - UVA measurements during ripening of soil columns with DCW + SE
B2 - UVA measurements in soil columns at steady state (DCW +SE, DCW)
B3 - UVA measurements in batch reactors during ripening
B4 - UVA measurements in batch reactors at steady state under aerobic condition

Appendix C - Measurement of O_2 and pH

C1 - Concentration of dissolved oxygen in soil columns at steady state condition under different hydraulic loading rate
C2 - pH values in soil columns at steady state

Appendix D - Measurement of Ammonia (NH_4-N)

Appendix E - Measurement of EDCs

Appendix A - Measurement of DOC

A1 – DOC values during ripening of the Soil columns (Influent: DCW + SE, HLR: 1.25 m/d)

Date	DOC (mg/L)		
	Influent	Effluent	
		SC-1	SC-2
9/27/2006	16.65	-	-
10/4/2006	15.73	14.32	13.34
10/9/2006	12.40	11.03	10.84
10/13/2006	13.73	10.50	10.32
10/16/2006	14.21	10.98	10.69
10/18/2006	14.10	11.02	10.96
10/19/2006	14.76	10.98	10.80
10/20/2006	15.33	11.04	11.28
10/21/2006	15.83	11.29	11.83
10/24/2006	16.55	12.49	12.21
10/26/2006	14.94	11.76	11.58
10/27/2006	14.72	11.73	11.58
10/28/2006	15.84	12.55	12.20
10/30/2006	14.58	12.03	11.93
10/31/2006	15.09	12.44	12.48
11/2/2006	15.05	12.02	12.38
11/3/2006	16.79	13.85	13.59
11/6/2006	17.69	14.32	14.50
11/7/2006	18.13	15.34	14.79
11/8/2006	18.37	15.19	15.63
11/9/2006	19.50	15.69	15.70

A2 – DOC values in Soil columns at steady state (Influent: DCW+SE, HLR: 1.25 m/d)

A2-1 - Soil Column 1(SC1)

Applied Influent - Delft Canal Water mixed with wastewater secondary effluent (DCW+SE)
Hydraulic loading rate - 1.25 m/d

Sampling Points	Column depth (m)	DOC (mg/L)		Average DOC (mg/L)
		11/15/2006	11/22/2006	
SC-IN	0.00	20.15	20.09	20.12
SP1	0.05	19.66	19.50	19.58
SP2	0.10	18.94	18.02	18.48
SP3	0.20	-	18.43	18.43
SP4	0.30	18.42	17.96	18.19
SP5	0.50	-	17.92	17.92
SP6	1.00	18.02	17.65	17.83
SP7	1.50	-	17.66	17.66
SP8	2.00	17.42	17.50	17.46
SP9	2.50	17.58	17.50	17.54
SP10	3.00	-	17.21	17.21
SP11	3.50	17.46	16.86	17.16
SP12	4.00	17.06	16.84	16.95
SP13	4.50	16.55	16.27	16.41
SP14	5.00	16.22	15.84	16.03

A2-2 - Soil Column 2 (SC2)

Applied Influent - Delft Canal Water mixed with wastewater secondary effluent (DCW+SE)
Hydraulic loading rate - 1.25 m/d

Sampling Points	Column depth (m)	DOC (mg/L)		Average DOC (mg/L)
		11/13/2006	11/14/2006	
SC-IN	0.00	20.15	20.15	20.15
SP2	0.10	19.92	18.55	19.23
SP3	0.20	18.87	19.38	19.12
SP4	0.30	19.69	18.58	19.13

Sampling Points	Column depth (m)	DOC (mg/L)		Average DOC (mg/L)
		11/13/2006	11/14/2006	
SP5	0.50	19.17	17.80	18.48
SP6	1.00	18.83	18.01	18.42
SP9	2.50	18.74	17.58	18.16
SP10	3.00	17.82	17.89	17.86
SP11	3.50	18.02	17.56	17.79
SP12	4.00	16.76	17.60	17.18
SP13	4.50	16.22	17.88	17.05
SP14	5.00	16.22	17.88	17.05

A2-3 - Soil Column 1 (SC1)

Applied Influent - Delft Canal Water mixed with wastewater secondary effluent (DCW+SE)

Hydraulic loading rate - 0.625 m/d

Sampling Points	Column depth (m)	DOC (mg/L)		Average DOC (mg/L)
		1/29/2007	1/30/2007	
SC-IN	0.00	15.20	15.07	15.14
SP1	0.05	14.55	14.49	14.52
SP4	0.30	13.97	14.05	14.01
SP5	0.50	13.84	13.81	13.83
SP6	1.00	13.68	13.78	13.73
SP7	1.50	13.65	13.77	13.71
SP8	2.00	13.32	13.68	13.50
SP9	2.50	13.50	13.59	13.55
SP10	3.00	13.05	13.34	13.20
SP11	3.50	12.97	13.09	13.03
SP12	4.00	12.62	12.76	12.69
SP13	4.50	12.68	12.64	12.66
SP14	5.00	12.65	12.56	12.61

A3 – DOC values during ripening of Soil column 2 (SC2)

Applied Influent - Delft Canal Water (DCW)
Hydraulic loading rate - 1.25 m/d

Date	DOC (mg/L)	
	Influent	Effluent
11/17/2006	20.77	17.89
11/18/2006	20.35	18.06
11/20/2006	20.04	18.08
11/21/2006	20.73	18.05
11/22/2006	20.96	17.80
11/23/2006	20.05	17.77
11/24/2006	20.47	17.33
11/27/2006	20.07	18.65
11/28/2006	21.26	18.66
11/29/2006	21.76	18.03
11/30/2006	21.55	16.76
12/2/2006	17.21	15.76
12/5/2006	17.08	14.75
12/6/2006	17.05	15.25
12/8/2006	17.05	15.52

A4 - DOC values in SC2 at steady state

A4-1 Applied Influent - Delft Canal Water (DCW)
Hydraulic loading rate - 1.25 m/d

Sampling Points	Column depth (m)	DOC (mg/L)		Average DOC (mg/L)
		12/15/2006	12/18/2006	
SC-IN	0.00	19.33	19.15	19.24
SP1	0.05	19.10	18.69	18.90
SP2	0.10	18.74	18.55	18.64
SP3	0.20	18.49	18.52	18.50
SP4	0.30	18.17	17.87	18.02
SP5	0.50	17.86	17.75	17.80
SP6	1.00	17.83	17.76	17.80

Sampling Points	Column depth (m)	DOC (mg/L)		Average DOC (mg/L)
		12/15/2006	12/18/2006	
SP7	1.50	17.71	17.29	17.50
SP8	2.00	17.70	17.55	17.62
SP9	2.50	17.46	17.74	17.60
SP10	3.00	17.04	17.25	17.15
SP11	3.50	17.00	16.99	16.99
SP12	4.00	16.75	17.00	16.87
SP13	4.50	16.70	16.85	16.78
SP14	5.00	16.70	16.80	16.75

A4-2 Applied Influent - Delft Canal Water (DCW)
Hydraulic loading rate - 0.625 m/d

Sampling Points	Column depth (m)	DOC (mg/L)		Average DOC (mg/L)
		1/29/2007	1/30/2007	
SC-IN	0.00	17.42	17.35	17.39
SP1	0.05	17.01	17.00	17.00
SP4	0.30	16.47	16.38	16.43
SP5	0.50	16.46	16.39	16.42
SP6	1.00	16.00	15.98	15.99
SP7	1.50	15.71	15.67	15.69
SP8	2.00	15.51	15.63	15.57
SP9	2.50	15.80	15.74	15.77
SP10	3.00	15.89	15.58	15.74
SP11	3.50	15.75	15.60	15.68
SP12	4.00	15.46	15.57	15.51
SP13	4.50	15.75	15.54	15.65
SP14	5.00	15.68	15.56	15.62

A5 - Measurement of DOC in batch reactors during ripening

a) Applied Influent - Delft Canal Water (DCW)

Date		DOC (mg/L)						Average DOC (mg/L)	
		Reactor 1		Reactor 2		Reactor 3			
Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
9/5/2006	9/9/2006	15.54	15.00	15.06	14.23	15.64	14.75	15.42	14.66
9/9/2006	9/13/2006	17.13	16.28	17.77	16.49	17.73	16.47	17.54	16.41
9/13/2006	9/18/2006	19.99	18.61	19.90	18.46	20.30	18.45	20.06	18.51
9/18/2006	9/22/2006	20.43	18.84	20.83	18.17	20.62	18.22	20.63	18.41
10/2/2006	10/9/2006	17.40	14.92	17.05	15.04	17.32	14.86	17.26	14.94
10/13/2006	10/18/2006	17.84	15.56	16.42	15.12	17.22	13.64	17.16	14.77
10/18/2006	10/24/2006	19.87	16.96	20.12	17.31	19.70	16.95	19.90	17.07
10/24/2006	10/28/2006	20.84	17.08	21.06	16.90	20.87	16.59	20.92	16.86

b) Applied Influent - Delft Canal Water mixed with wastewater secondary effluent (DCW+SE) (1:1)

Date		DOC (mg/L)						Average DOC (mg/L)	
		Reactor 1		Reactor 2		Reactor 3			
Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
9/5/2006	9/9/2006	16.22	15.02	17.06	14.64	16.75	15.13	16.68	14.93
9/9/2006	9/13/2006	17.76	15.53	18.23	15.58	18.62	16.35	18.20	15.82
9/13/2006	9/18/2006	18.46	15.98	18.71	16.41	18.38	16.57	18.52	16.32
9/18/2006	9/22/2006	18.75	16.47	18.85	15.63	18.60	16.17	18.73	16.09
10/2/2006	10/9/2006	16.57	13.83	16.86	13.62	16.53	13.75	16.65	13.74
10/13/2006	10/18/2006	15.19	12.86	15.73	12.53	15.36	12.73	15.43	12.71
10/18/2006	10/24/2006	16.23	14.05	16.93	13.70	17.35	13.89	16.83	13.88
10/24/2006	10/28/2006	17.30	13.44	17.04	13.50	17.04	13.51	17.13	13.49

c) Applied Influent - Wastewater secondary effluent (SE)

Date		DOC (mg/L)						Average DOC (mg/L)	
		Reactor 1		Reactor 2		Reactor 3			
Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
9/5/2006	9/9/2006	17.22	15.24	17.32	15.51	17.61	15.16	17.39	15.30
9/9/2006	9/13/2006	17.71	15.18	18.77	14.55	18.35	15.02	18.27	14.92
9/13/2006	9/18/2006	17.80	14.65	18.64	14.65	16.73	14.65	17.72	14.65
9/18/2006	9/22/2006	16.92	13.92	16.81	13.53	16.67	13.93	16.80	13.79
10/2/2006	10/9/2006	15.79	12.90	16.00	13.80	15.65	12.83	15.81	13.18
10/13/2006	10/18/2006	13.05	10.56	13.10	10.50	13.52	10.67	13.23	10.58
10/18/2006	10/24/2006	13.09	10.29	13.54	10.64	13.46	10.50	13.36	10.48
10/24/2006	10/28/2006	12.57	9.94	12.15	9.52	12.40	9.41	12.37	9.62

A6 - Measurement of DOC in batch reactors at steady state under aerobic condition

a) Applied Influent - Delft canal water (DCW)

Days	Date	DOC (mg/L)			Average DOC (mg/L)
		Reactor 1	Reactor 2	Reactor 3	
0	12/18/2006	19.21	19.40	19.76	19.45
0.5	12/18/2006	18.99	18.41	19.10	18.83
1	12/19/2006	18.18	18.50	18.85	18.51
2	12/20/2006	18.63	12.67	18.84	16.71
3	12/21/2006	13.57	17.92	15.01	15.50
4	12/22/2006	13.57	17.92	15.01	15.50

b) Applied Influent - Delft canal water mixed with wastewater secondary effluent (DCW+SE) (1:1)

Days	Date	DOC (mg/L)			Average DOC (mg/L)
		Reactor 1	Reactor 2	Reactor 3	
0	12/18/2006	17.92	18.45	18.42	18.26
0.5	12/18/2006	15.94	16.96	17.00	16.63
1	12/19/2006	13.79	17.48	17.60	16.29
2	12/20/2006	16.02	14.41	13.25	14.56
3	12/21/2006	13.82	16.62	15.87	13.82
4	12/22/2006	15.62	15.50	15.67	13.82

c) Applied Influent - Wastewater secondary effluent (SE)

Days	Date	DOC (mg/L)			Average DOC (mg/L)
		Reactor 1	Reactor 2	Reactor 3	
0	12/18/2006	17.69	17.16	17.59	17.48
0.5	12/18/2006	11.44	15.04	13.93	13.47
1	12/19/2006	12.09	14.98	14.72	13.93
2	12/20/2006	11.02	13.96	11.95	12.95
3	12/21/2006	13.11	13.07	13.04	13.08
4	12/22/2006	13.04	12.99	13.24	13.09

A7 - Measurement of DOC in batch reactors at steady state under anoxic condition

Applied Influent - Wastewater secondary effluent (SE)

Days	Date	Aerobic condition DOC (mg/L)		Average DOC (mg/L)	Anoxic condition DOC (mg/L)		Average DOC (mg/L)
		Reactor 1	Reactor 2		Reactor 1	Reactor 2	
0	19/02/2007	14.77	15.23	15.00	15.49	15.81	15.65
5	23/02/2007	11.33	11.61	11.47	14.62	15.84	15.23
10	28/02/2007	10.89	10.74	10.82	15.37	15.45	15.41
15	05/03/2007	10.68	10.84	10.76	13.77	13.86	13.81

Appendix B - Measurement of UV absorbance (UVA)

B1 - UVA measurements during ripening of the Soil columns

Applied Influent - Delft Canal Water mixed with wastewater secondary effluent (DCW+SE)
Hydraulic loading rate - 1.25 m/d

Date	UVA (cm^{-1})		
	Influent	Effluent	
		SC-1	SC-2
10/16/2006	0.417	0.329	0.324
10/18/2006	0.414	0.326	0.338
10/19/2006	0.422	0.330	0.333
10/20/2006	0.455	0.336	0.352
10/21/2006	0.486	0.361	0.357
10/24/2006	0.510	0.389	0.391
10/26/2006	0.516	0.406	0.397
10/27/2006	0.518	0.440	0.434
10/28/2006	0.512	0.440	0.434
10/30/2006	0.495	0.425	0.419
10/31/2006	0.503	0.435	0.433
11/2/2006	0.501	0.427	0.425
11/3/2006	0.489	0.426	0.419
11/6/2006	0.524	0.447	0.424
11/7/2006	0.512	0.441	0.434
11/8/2006	0.515	0.442	0.436
11/9/2006	0.512	0.446	0.440

B2 - UVA measurements in Soil columns at steady state

B2-1 - Soil Column 1(SC1)

Applied Influent - Delft Canal Water mixed with wastewater secondary effluent (DCW+SE)

a) Hydraulic loading rate - 1.25 m/d

Sampling Points	Column depth (m)	UVA (cm^{-1})		Average UVA (cm^{-1})
		11/15/2006	11/22/2006	
SC-IN	0.00	0.512	0.506	0.509
SP1	0.05	0.501	0.504	0.503
SP2	0.10	0.498	0.488	0.493
SP3	0.20	0.496	0.492	0.494
SP4	0.30	0.489	0.483	0.486
SP5	0.50	0.488	0.486	0.487
SP6	1.00	0.482	0.481	0.482
SP7	1.50	0.461	0.477	0.469
SP8	2.00	0.474	0.475	0.475
SP9	2.50	0.474	0.471	0.473
SP10	3.00	0.466	0.471	0.469
SP11	3.50	0.475	0.473	0.474
SP12	4.00	0.465	0.468	0.467
SP13	4.50	0.453	0.468	0.461
SP14	5.00	0.449	0.450	0.450

b) Hydraulic loading rate - 0.625 m/d

Sampling Points	Column depth (m)	UVA (cm-1)		Average UVA (cm-1)
		1/29/2007	1/30/2007	
SC-IN	0.00	0.423	0.421	0.422
SP1	0.05	0.411	0.406	0.409
SP4	0.30	0.407	0.400	0.404
SP5	0.50	0.398	0.398	0.398
SP6	1.00	0.395	0.398	0.397
SP7	1.50	0.393	0.399	0.396
SP8	2.00	0.382	0.398	0.390
SP9	2.50	0.383	0.385	0.384
SP10	3.00	0.380	0.379	0.380

Sampling Points	Column depth (m)	UVA (cm-1)		Average UVA (cm-1)
		1/29/2007	1/30/2007	
SP11	3.50	0.379	0.371	0.375
SP12	4.00	0.377	0.369	0.373
SP13	4.50	0.378	0.365	0.372
SP14	5.00	0.375	0.368	0.372

B2-2 - Soil Column 2 (SC2)

Applied Influent - Delft Canal Water mixed with wastewater secondary effluent (DCW+SE)

Hydraulic loading rate - 1.25 m/d

Sampling Points	Column depth (m)	UVA (cm^{-1})
		11/13/2006
SC-IN	0.00	0.510
SP2	0.10	0.490
SP3	0.20	0.487
SP4	0.30	0.488
SP5	0.50	0.475
SP6	1.00	0.478
SP9	2.50	0.473
SP10	3.00	0.470
SP11	3.50	0.468
SP12	4.00	0.458
SP13	4.50	0.456
SP14	5.00	0.458

B2-3 - Soil Column 2 (SC2)

Applied Influent - Delft Canal Water (DCW)

a) Hydraulic loading rate - 1.25 m/d

Sampling Points	Column depth (m)	UVA (cm^{-1})		Average UVA (cm^{-1})
		12/15/2006	12/18/2006	
SC-IN	0.00	0.575	0.579	0.577
SP1	0.05	0.572	0.556	0.564
SP2	0.10	0.562	0.554	0.558
SP3	0.20	0.557	0.556	0.557
SP4	0.30	0.549	0.549	0.549
SP5	0.50	0.533	0.553	0.543
SP6	1.00	0.531	0.552	0.542
SP7	1.50	0.520	0.548	0.534
SP8	2.00	0.507	0.537	0.522
SP9	2.50	0.499	0.523	0.511
SP10	3.00	0.489	0.508	0.499
SP11	3.50	0.486	0.501	0.494
SP12	4.00	0.483	0.497	0.490
SP13	4.50	0.481	0.495	0.488
SP14	5.00	0.479	0.491	0.485

b) Hydraulic loading rate - 0.625 m/d

Sampling Points	Column depth (m)	UVA (cm^{-1})		Average UVA (cm^{-1})
		1/29/2007	1/30/2007	
SC-IN	0.00	0.499	0.498	0.499
SP1	0.05	0.490	0.491	0.491
SP4	0.30	0.485	0.481	0.483
SP5	0.50	0.482	0.481	0.482
SP6	1.00	0.476	0.479	0.478
SP7	1.50	0.475	0.477	0.476
SP8	2.00	0.469	0.472	0.471
SP9	2.50	0.471	0.472	0.472
SP10	3.00	0.471	0.469	0.470
SP11	3.50	0.470	0.465	0.468
SP12	4.00	0.464	0.467	0.466
SP13	4.50	0.460	0.461	0.461
SP14	5.00	0.459	0.463	0.461

B3 - UVA measurements in batch reactors during ripening

a) Applied Influent - Delft Canal Water (DCW)

Date	Batch reactor (BR)	UVA (cm^{-1})		Average UVA (cm^{-1})		Standard deviation	
		Influent	Effluent	Influent	Effluent	Influent	Effluent
10/13/2006	BR1	0.541	0.500	0.544	0.495	0.003	0.006
	BR2	0.546	0.498				
	BR3	0.544	0.488				
10/18/2006	BR1	0.639	0.573	0.625	0.567	0.012	0.006
	BR2	0.618	0.567				
	BR3	0.617	0.562				
10/24/2006	BR1	0.649	0.612	0.653	0.614	0.004	0.003
	BR2	0.656	0.617				
	BR3	0.653	0.613				
10/28/2006	BR1	0.659	0.623	0.659	0.623	0.001	0.001
	BR2	0.659	0.624				
	BR3	0.660	0.622				
10/1/2006	BR1	0.602	0.561	0.592	0.562	0.009	0.001
	BR2	0.587	0.563				
	BR3	0.586	0.562				
11/6/2006	BR1	0.557	0.520	0.558	0.526	0.002	0.005
	BR2	0.557	0.528				
	BR3	0.561	0.529				
11/10/2006	BR1	0.557	0.520	0.560	0.526	0.004	0.005
	BR2	0.565	0.528				
	BR3	0.558	0.529				

b) Applied Influent - Delft Canal Water mixed with wastewater secondary effluent (DCW+SE) (1:1)

Date	Batch reactor (BR)	UVA (cm^{-1})		Average UVA (cm^{-1})		Standard deviation	
		Influent	Effluent	Influent	Effluent	Influent	Effluent
10/13/2006	BR1	0.455	0.418	0.459	0.411	0.004	0.010
	BR2	0.463	0.400				
	BR3	0.459	0.415				
10/18/2006	BR1	0.500	0.457	0.506	0.454	0.006	0.005
	BR2	0.507	0.449				
	BR3	0.511	0.457				
10/24/2006	BR1	0.521	0.498	0.522	0.497	0.002	0.001
	BR2	0.522	0.496				
	BR3	0.524	0.497				
10/28/2006	BR1	0.522	0.495	0.525	0.493	0.003	0.002
	BR2	0.528	0.493				
	BR3	0.526	0.491				
10/1/2006	BR1	0.530	0.496	0.531	0.499	0.001	0.003
	BR2	0.532	0.501				
	BR3	0.531	0.499				
11/6/2006	BR1	0.505	0.481	0.506	0.482	0.001	0.003
	BR2	0.506	0.485				
	BR3	0.506	0.479				
11/10/2006	BR1	0.515	0.481	0.513	0.482	0.002	0.003
	BR2	0.512	0.485				
	BR3	0.512	0.479				

c) Applied Influent - Wastewater secondary effluent (SE)

Date	Batch reactor (BR)	UVA (cm^{-1})		Average UVA (cm^{-1})		Standard deviation	
		Influent	Effluent	Influent	Effluent	Influent	Effluent
10/13/2006	BR1	0.381	0.353	0.377	0.352	0.005	0.003
	BR2	0.379	0.349				
	BR3	0.372	0.354				
10/18/2006	BR1	0.379	0.346	0.384	0.347	0.005	0.004
	BR2	0.386	0.352				
	BR3	0.388	0.344				
10/24/2006	BR1	0.370	0.350	0.371	0.350	0.002	0.001
	BR2	0.369	0.351				
	BR3	0.373	0.350				
10/28/2006	BR1	0.372	0.347	0.372	0.348	0.002	0.001
	BR2	0.370	0.347				
	BR3	0.374	0.349				
10/1/2006	BR1	0.466	0.432	0.467	0.430	0.002	0.002
	BR2	0.469	0.430				
	BR3	0.465	0.429				
11/6/2006	BR1	0.476	0.437	0.478	0.437	0.002	0.001
	BR2	0.478	0.438				
	BR3	0.480	0.436				
11/10/2006	BR1	0.478	0.437	0.477	0.437	0.001	0.001
	BR2	0.476	0.438				
	BR3	0.477	0.436				

B4 - UVA measurements in batch reactors at steady state under aerobic condition

a) Applied Influent - Delft Canal Water (DCW)

Days	Batch reactor (BR)	UVA (cm^{-1})	Average UVA (cm^{-1})	Standard deviation
0	BR1	0.548	0.571	0.020
	BR2	0.583		
	BR3	0.581		
0.5	BR1	0.576	0.573	0.008
	BR2	0.564		
	BR3	0.578		
1	BR1	0.553	0.565	0.011
	BR2	0.57		
	BR3	0.573		
2	BR1	0.550	0.560	0.009
	BR2	0.566		
	BR3	0.565		
3	BR1	0.553	0.557	0.004
	BR2	0.560		
	BR3	0.557		
4	BR1	0.549	0.555	0.005
	BR2	0.559		
	BR3	0.556		

b) Applied Influent - Delft Canal Water mixed with wastewater secondary effluent (DCW+SE) (1:1)

Days	Batch reactor (BR)	UVA (cm^{-1})	Average UVA (cm^{-1})	Standard deviation
0	BR1	0.484	0.488	0.003
	BR2	0.489		
	BR3	0.49		
0.5	BR1	0.469	0.484	0.013
	BR2	0.49		
	BR3	0.492		
1	BR1	0.47	0.476	0.005

Days	Batch reactor (BR)	UVA (cm^{-1})	Average UVA (cm^{-1})	Standard deviation
	BR2	0.478		
	BR3	0.48		
2	BR1	0.466	0.470	0.004
	BR2	0.472		
	BR3	0.473		
3	BR1	0.461	0.460	0.005
	BR2	0.465		
	BR3	0.455		
4	BR1	0.451	0.460	0.008
	BR2	0.464		
	BR3	0.465		

c) Applied Influent - Wastewater secondary effluent (SE)

Days	Batch reactor (BR)	UVA (cm^{-1})	Average UVA (cm^{-1})	Standard deviation
0	BR1	0.4	0.401	0.001
	BR2	0.4		
	BR3	0.402		
0.5	BR1	0.386	0.395	0.008
	BR2	0.399		
	BR3	0.401		
1	BR1	0.378	0.385	0.006
	BR2	0.388		
	BR3	0.39		
2	BR1	0.370	0.378	0.007
	BR2	0.381		
	BR3	0.382		
3	BR1	0.377	0.375	0.006
	BR2	0.368		
	BR3	0.380		
4	BR1	0.366	0.373	0.007
	BR2	0.375		
	BR3	0.379		

Appendix C - Measurement of O_2 and pH

C1 - Concentration of dissolved oxygen for soil column at steady state condition under different hydraulic loading rates

i) Applied Influent: Delft canal water mixed with secondary effluent and HLR: 1.25 m/d

Sampling Points	Column depth (m)	SC1		Average O_2 (mg/L)	SC2		Average O_2 (mg/L)
		12/1/2006	12/2/2006		12/4/2006	12/5/2006	
SC-IN	0.00	8.7	8.8	8.8	9.0	8.9	9.0
SP1	0.05	7.4	7.4	7.4	7.4	7.5	7.5
SP2	0.10	6.7	6.5	6.6	6.7	6.6	6.7
SP3	0.20	5.8	5.7	5.8	5.8	5.1	5.5
SP4	0.30	5.0	5.1	5.1	5.0	4.6	4.8
SP5	0.50	4.6	4.6	4.6	4.6	4.5	4.6
SP6	1.00	4.3	4.2	4.3	4.3	3.9	4.1
SP7	1.50	3.8	4.0	3.9	3.8	3.4	3.6
SP8	2.00	3.7	3.7	3.7	3.7	3.4	3.6
SP9	2.50	3.5	3.4	3.5	3.5	3.1	3.3
SP10	3.00	2.8	2.6	2.7	2.8	2.8	2.8
SP11	3.50	2.6	2.7	2.7	2.6	2.5	2.6
SP12	4.00	2.1	2.3	2.2	2.1	2.2	2.2
SP13	4.50	1.8	1.6	1.7	1.8	1.8	1.8
SP14	5.00	1.8	1.6	1.7	1.8	1.8	1.8

ii) Applied Influent: Delft canal water and HLR: 1.25 m/d

Sampling Points	Column depth (m)	SC2		Average O_2 (mg/L)
		12/20/2006	12/21/2006	
SC-IN	0.00	8.9	8.9	8.9
SP1	0.05	6.8	6.8	6.8
SP2	0.10	6.3	6.5	6.4
SP3	0.20	5.7	5.9	5.8
SP4	0.30	5.4	5.5	5.5
SP5	0.50	5.2	5.5	5.4
SP6	1.00	4.8	4.6	4.7
SP7	1.50	4.5	4.5	4.5
SP8	2.00	4.1	4.2	4.2
SP9	2.50	3.8	3.7	3.8
SP10	3.00	3.6	3.7	3.7

Sampling Points	Column depth (m)	SC2		Average O_2 (mg/L)
		12/20/2006	12/21/2006	
SP11	3.50	3.3	3.2	3.3
SP12	4.00	2.8	2.6	2.7
SP13	4.50	2.4	2.3	2.4
SP14	5.00	2.2	2.0	2.1

iii) Applied Influent: Delft canal water mixed with secondary effluent and HLR: 0.625 m/d

Sampling Points	Column depth (m)	SC1		Average O_2 (mg/L)
		1/30/2007	1/31/2007	
SC-IN	0.00	8.90	8.9	8.90
SP1	0.05	6.80	6.6	6.70
SP5	0.50	4.20	4.2	4.20
SP7	1.50	3.60	3.8	3.70
SP9	2.50	3.50	3.5	3.50
SP11	3.50	2.70	2.8	2.75
SP13	4.50	2.20	2.3	2.25
SP14	5.00	2.10	2.3	2.20

iv) Applied Influent: Delft canal water and HLR: 0.625 m/d

Sampling Points	Column depth (m)	SC2		Average O_2 (mg/L)
		1/30/2007	1/31/2007	
SC-IN	0.00	8.8	8.8	8.80
SP1	0.05	6.4	6.6	6.50
SP5	0.50	5.3	5.1	5.20
SP7	1.50	4.3	3.9	4.10
SP9	2.50	4.0	3.8	3.90
SP11	3.50	3.6	3.3	3.45
SP13	4.50	3.3	3.1	3.20
SP14	5.00	3.2	3.1	3.15

C2 - pH values for soil column at steady state

i) Hydraulic loading rate = 1.25 m/d

Sampling Points	Column depth (m)	pH values	
		SC1 (12/6/2006)	SC2 (12/21/2006)
SC-IN	0.00	8.42	8.31
SP1	0.05	8.40	8.15
SP5	0.50	8.22	7.99
SP7	1.50	8.11	7.98
SP9	2.50	8.04	7.99
SP11	3.50	7.86	7.94
SP13	4.50	7.82	7.90
SP14	5.00	7.73	7.89

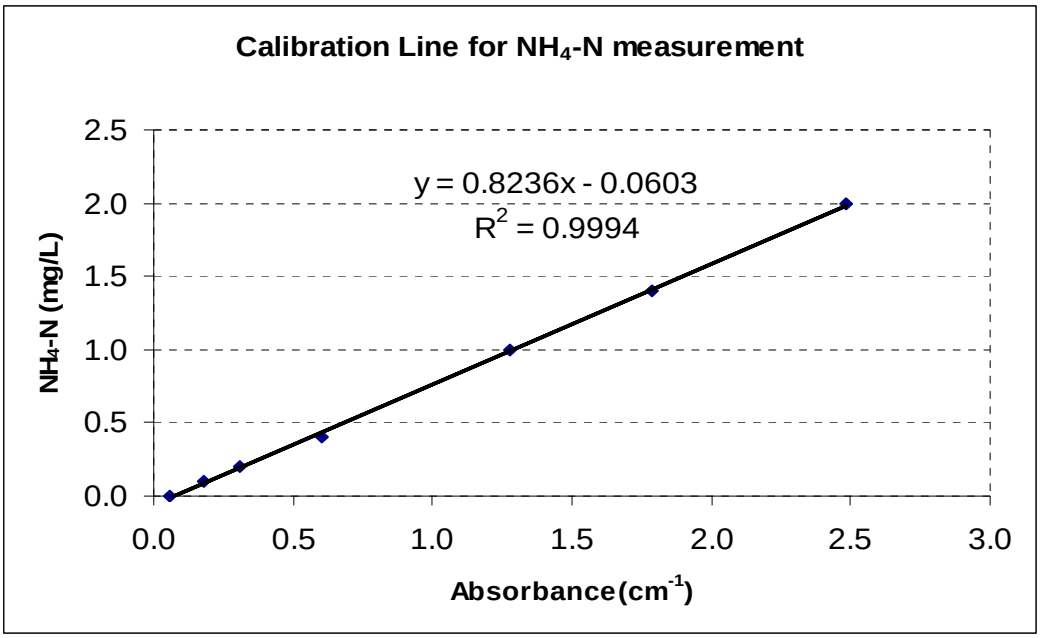
ii) Hydraulic loading rate = 0.625 m/d

Sampling Points	Column depth (m)	pH values	
		SC1 (1/30/2007)	SC2 (1/30/2007)
SC-IN	0.00	8.50	8.47
SP1	0.05	8.35	8.40
SP5	0.50	8.22	8.31
SP7	1.50	8.11	8.24
SP9	2.50	8.05	8.17
SP11	3.50	8.05	8.09
SP13	4.50	7.96	8.00
SP14	5.00	7.92	8.00

Appendix D - Measurement of Ammonia (NH_4-N)

Series of standards for preparation of calibration line
Concentration of standards = 10 mg/L

Volume of standards diluted to 50ml	NH_4-N (mg/L)	Absorbance at 655 nm
0	0.0	0.058
0.5	0.1	0.183
1	0.2	0.306
2	0.4	0.603
3	0.6	0.919
5	1.0	1.280
7	1.4	1.790
10	2.0	2.485



Concentration of ammonia in applied influents

Influent	Absorbance		NH_4-N (mg/L)		Avg. NH_4-N (mg/L)
	1	2	1	2	
DCW	0.314	0.304	0.496	0.475	0.485
DCW+SE	0.198	0.198	0.257	0.257	0.257
SE	0.076	0.087	0.006	0.028	< 0.1

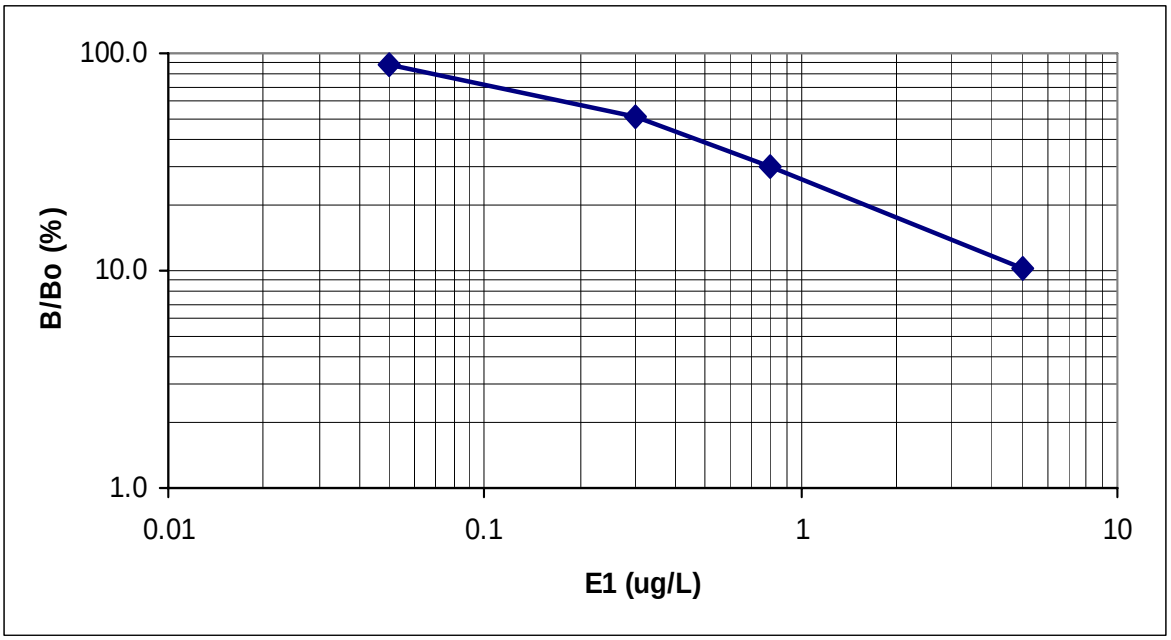
Appendix E - Measurement of EDCs

Calibration line for ELISA measurement

i) E1 ELISA

E1 (ug/L)	Absorbance at 450	Avg. Absorbance	B/Bo*
0	1.135	1.071	100
	1.007		
0.05	0.933	0.9395	87.7
	0.946		
0.3	0.541	0.541	50.5
	0.541		
0.8	0.33	0.3245	30.3
	0.319		
5	0.111	0.109	10.2
	0.107		

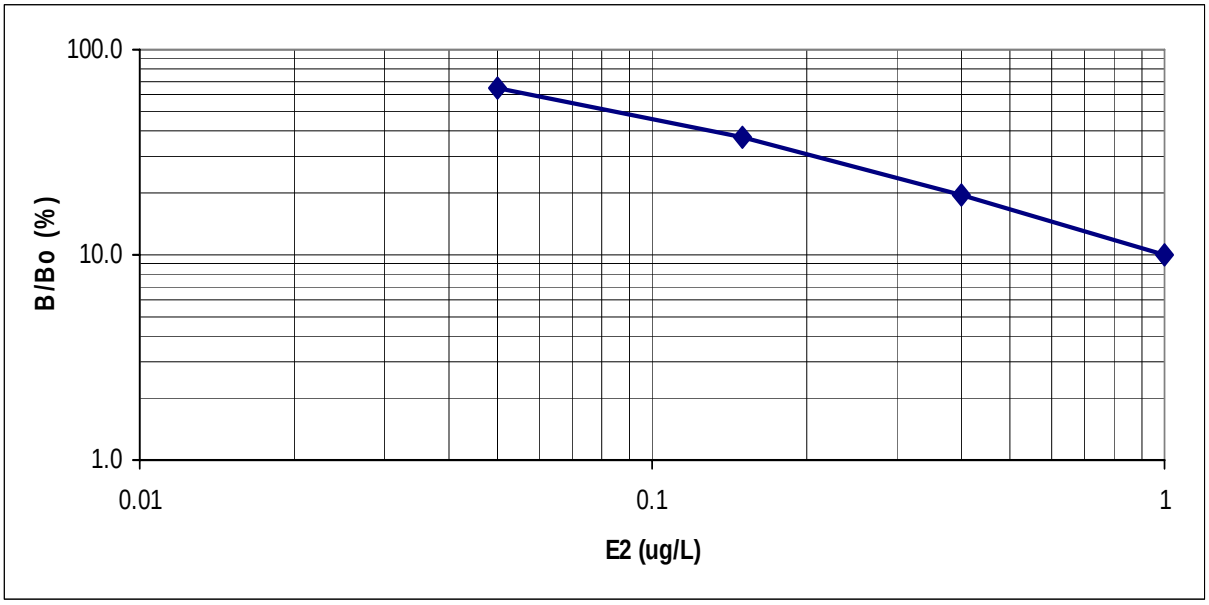
* B/Bo = standard E1 absorbance/absorbance at E1=0 ug/L



ii) E2 ELISA

E2 (ug/L)	Absorbance at 450	Avg. Absorbance	B/Bo*
0	1.459	1.387	100
	1.315		
0.05	0.905	0.8935	64.4
	0.882		
0.15	0.543	0.5125	37.0
	0.482		
0.4	0.267	0.27	19.5
	0.273		
1	0.148	0.1395	10.1
	0.131		

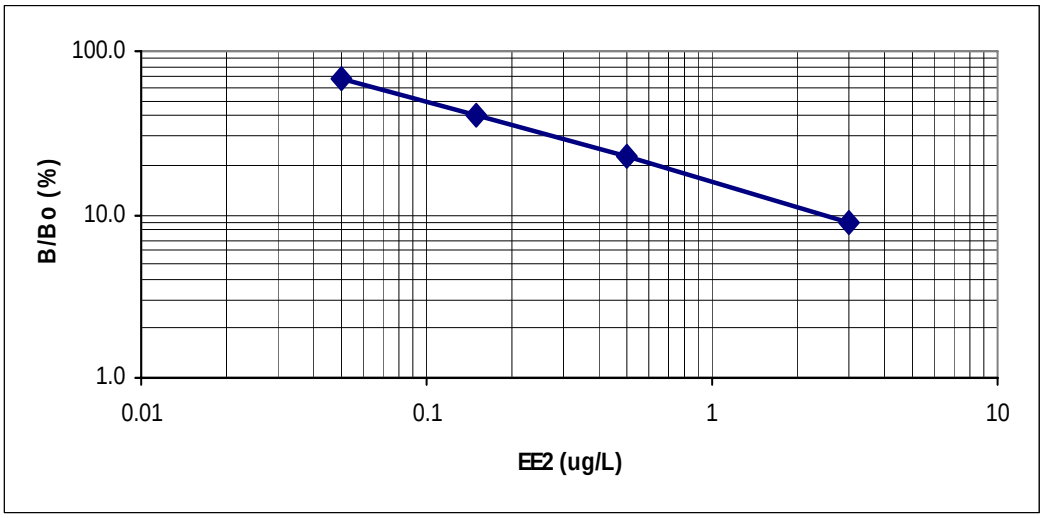
* B/Bo = standard E2 absorbance/absorbance at E2=0 ug/L



iii) EE2 ELISA

EE2 (ug/L)	Absorbance at 450	Avg. Absorbance	B/Bo*
0	1.223	1.173	100
	1.123		
0.05	0.83	0.792	67.5
	0.754		
0.15	0.495	0.4795	40.9
	0.464		
0.5	0.252	0.2665	22.7
	0.281		
3	0.112	0.1035	8.8
	0.095		

* B/Bo = standard EE2 absorbance/absorbance at EE2=0 ug/L



Calculation of adsorption capacity of sands in batch reactor for E1, E2 and EE2 by using linear sorption model

$S = K_d * C$

$K_d = K_{OC} * f_{OC}$

$K_{OC} = 0.63 K_{OW}$

where S = mass sorbed per mass of sorbent (mg/kg)

K_d = partition or distribution coefficient

C = concentration in water at equilibrium (mg/L)

f_{OC} = organic carbon fraction of the sand

K_{OC} = organic carbon partition coefficient of the contaminant

K_{OW} = octanol-water partition coefficient of the contaminant

- Assuming 35 - 58 mg TOC of biomass/gm of sand, => foc = 0.03 - 0.06
- Sample Volume = 400 ml
- Mass of sand in the batch reactor = 75 gm

	Co(ng/L)	Cf(ng/L)	logKow	Koc	Kd		S (mg/Kg)		that can be sorbed (mg)		sorbate (mg)
					foc=0.03	foc=0.06	foc=0.03	foc=0.06	foc=0.03	foc=0.06	
E1	140	13.3	3.43	1696	51	102	0.00068	0.00135	5.07E-05	0.000101	0.000056
E2	102.2	13.6	3.94	5487	165	329	0.00224	0.00448	1.68E-04	0.000336	0.000041
EE2	104.4	29.7	4.15	8899	267	534	0.00793	0.01586	5.95E-04	0.001189	0.000042