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Study of Pilot-scale Filtration at Minneapolis Water Works

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Extract:

Minneapolis Water Works (MWW) in Minnesota, United States, has experienced occasional taste and odor episodes with their river water source. This thesis investigates the potential benefits of installing granular activated carbon (GAC) filters at MWW, replacing existing anthracite medium filters and eliminating the need for powdered activated carbon as taste and odor protection. Pilot scale filters of GAC and anthracite media have been studied and batch reactor tests have been performed – projecting the potential filtration and sorption capacity of GAC filters at MWW.

Key words:

1. Water-treatment process
2. Granular activated carbon (GAC)
3. Pilot-scale filtration
4. Sorption capacity

Preface

During this thesis I have completed the experimental work at the University of Minnesota (UMN). The research topic was drinking water filtration and sorption of compounds causing taste and odor at the Minneapolis Water Works (MWW). My involvement in this particular research is a result of a growing collaboration between the departments of environmental engineering at the Norwegian University of Science and Technology (NTNU) and the UMN. I was encouraged by my supervisors to choose this project, not only because of the well established academic ambience in Minnesota, but also, as a stay abroad could be a valuable experience in itself. Working with the UMN and the MWW was interesting – being able to experience a part of water and wastewater engineering in a foreign country and being provided with knowledge and advice by several skilled professionals.

I would like to thank my supervisors, Associate Professor Cynthia Hallé and Professor Stein Wold Østerhus at the Department of Hydraulic and Environmental Engineering, NTNU, for their helpful and constructive guidance. I also direct great thanks to my supervisor in Minnesota, Professor Raymond Hozalski at the department of Civil Engineering, UMN. In addition to always offering great academic help and advice, I appreciate that he showed care in my social well-being while being in Minnesota, also inviting me to his house and serving great food.

Furthermore, among other supportive people at the Department of Civil Engineering at the UMN, I would like to thank master student Jacqueline Strait, who has been my closest collaborator throughout the project – giving me the introduction and guidance to laboratory work and being a reliable coworker in all other aspects of the project. Also, I would like to express my appreciation to Professors Paige Novak and Timothy LaPara for giving me access to their laboratories. I dedicate extra gratitude to Professor Novak and her family for the great hospitality and food I experienced when I was invited to their house. Finally, from the UMN, I would like to thank PhD Student Youchul Jeon for help in laboratory work.

Last, but not least, I would like to thank the staff at Fridley Softening Plant at MWW for touring me on their treatment facilities and for cooperating with me in my research. My gratitude goes especially to Water Quality Manager George Kraynick and Chemist/Bacteriologist Christopher Rydell for excellent answers to my questions whenever they arose.

Nils Darre Seip,
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Abstract

Minneapolis Water Works (MWW) in Minnesota, United States, represents one of many water utilities with taste and odor (T&O) problems. The Minneapolis drinking water has had "earthy" and "musty" T&O, due to a seasonal occurrence of geosmin in the river water source. The current measure against geosmin and other T&O compounds at MWW, is the use of powdered activated carbon (PAC), occasionally combined with oxidation by potassium permanganate. There are reasons to believe that installing granular activated carbon (GAC) filters, replacing existing anthracite medium filters and eliminating the need for PAC, will improve the protection against T&O. With a goal of investigating potential benefits of GAC filters versus the current treatment scheme, MWW and the University of Minnesota established a research project, in which this report is a contribution. Pilot-scale filtration and a batch experiment were done in relation to this report, to study removal performance of two different GAC products and one anthracite product with respect to different water quality parameters. Differences between GAC and anthracite media were reflected in sorption related removal data; pilot-scale filtration during 120 operation days proved a better removal of natural organic matter, specific ultraviolet absorption and geosmin in GAC filters compared to anthracite filters. With an empty bed contact time of 12.7 minutes (equal to the full-scale MWW), GAC filters removed an average of 100% of the DOC at operation day 16. At operation days 52 and 120, the average DOC removal rates in the GAC filters were 53% and 32% respectively. The data from this research suggests that the DOC breakthrough will be slow and gradual. Geosmin removal rates in the GAC filters were consistently sufficient, assuring that the effluent concentrations of geosmin stayed below 1.89 ng/L, based on 35 effluent concentration measurements with influent concentrations up to 47.70 ng/L. Batch reactor tests suggested that geosmin will be adsorbed onto Calgon GAC and Norit GAC in accordance with linear and Langmuir isotherm models. Based on the results of this study, GAC filtration seems desirable to MWW, adding needed sorption capacity – hence better removing T&O compounds. No significant distinction with regard to performance was found between Calgon and Norit GAC products.

Sammendrag (Abstract in Norwegian)

Minneapolis Water Works (MWW) i Minnesota representerer en av flere amerikanske drikkevannsetater som opplever smaks- og luktproblematikk. Blant annet har en "jord-aktig" og "muggen" smak og lukt tidvis preget vannet, grunnet en sesongbetont forekomst av geosmin i råvannskilden – Mississippielven. Det nåværende tiltaket mot geosmin og andre smaks- og luktforbindelser ved MWW er dosering av pulverisert aktivert karbon (PAC), av og til kombinert med oksidering fra kaliumpermanganat. Det er grunnlag for å tro at en installasjon av filter med granulært aktivert karbon (GAC), på bekostning av eksisterende antrasittbaserte filter, vil fjerne smak og lukt mer effektivt fra vannet. Det vil dessuten fjerne behovet for den nåværene PAC-doseringen. Med mål om å studere potensielle fordeler ved GAC-filter versus det eksisterende filtreringssystem opprettet MWW og The University of Minnesota et forskningsprosjekt, hvilket denne oppgaven er et bidrag til. Et pilotfiltreringsanlegg og et batch-reaktor-eksperiment har lagt grunnlaget for denne studien, som ser på renseeffekter med hensyn til ulike vannkvalitetsparametere for to ulike GAC-produkt, samt en type antrasitt. Forskjellene mellom GAC og antrasitt som filtermedium har blitt observert i renseeffekter som knyttes til sorpsjon. Med en "empty bed contact time" på 12.7 minutter (tilsvarende fullskala-anlegget ved MWW) fjernet GAC-filterne gjennomsnittlig 100% løst organisk karbon (DOC) etter 16 dager i drift. Ved dag nummer 52 og 120 i drift var gjennomsnittlig DOC-fjerning henholdsvis 53% og 32%. Denne studien viser med andre ord en gradvis og langsom nedgang i sorpsjonskapasiteten til GAC. Geosmin i utløpene fra GAC-filterne ble aldri målt over 1.89 ng/L; det ble målt 35 uløpskonsentrasjoner, og innløpskonsentrasjonen varierte fra 0 til 47.70 ng/L. Batch-reaktor-eksperimenter viser at GAC-medium fra produsentene Calgon og Norit begge kan uttrykkes gjennom lineære og Langmuir- sorsjonsisotermer. Basert på resultatene fra denne studien synes GAC-filtrering fordelaktig for MWW, med en forventet økt sorpsjonskapasitet – og dermed en bedre fjerning av lukt og smak. Ingen signifikante forskjeller ble funnet mellon GAC fra produsentene Calgon og Norit.

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List of Acronyms

DOC	Dissolved Organic Carbon
GAC	Granular Activated Carbon
GC/MS	Gas Chromatography / Mass Spectroscopy
HSPME	Headspace Solid-Phase Micro-Extraction
MIB-2	2-methylisoborneol
MWW	Minneapolis Water Works
ND	Not Detected
NOM	Natural Organic Matter
PAC	Powdered Activated Carbon
SD	Standard Deviation
SUVA	Specific Ultraviolet Absorption
T&O	Taste and Odor
TOC	Total Organic Carbon

1. Introduction

Access to fresh water and water quality varies between communities, and few water sources provide water pure enough to be consumed directly. Water is treated to remove chemical and biological contaminants, suspended solids, and gases. A key aspect of water treatment and supply is maintaining hygienically safe water. Nevertheless, consumers also have aesthetic wants for their tap water. Examples of aesthetic water qualities include hardness, temperature, color, taste, and odor. Taste and odor (T&O) represent an important concern for water consumers. Hence, utilities with T&O issues spend between 4.5% and 9.2% of their budgets addressing these problems (Suffet et al., 1996).

The largest North American survey of water utilities regarding T&O issues, Suffet, Corado et al. (1996), revealed that 43% of utilities surveyed had experienced a T&O event lasting longer than a week. A wide range of T&O characteristics were reported, including earthy, chlorinous, grassy, swampy, septic, sulfide, fishy, medicinal, and chemical. Among plausible causes for T&O problems we find plankton, synthetic organics, decaying vegetation, bacteria, disinfection byproducts, and the disinfectant itself (Suffet et al., 1996). Different measures exist for removing T&O from water. Based on the target compound, physical, chemical, or biological processes can be applied (Hargesheimer and Watson, 1996) (Wilkinson, 2012).

Minneapolis Water Works (MWW) represents one of many American water suppliers that must dedicate significant attention to T&O problems because of a year-round problem with taste and odor from their surface water source, the Mississippi river. One of the main challenges at MWW is the seasonal presence of geosmin, an organic compound that gives the water unpleasant taste and odor at very low concentrations (5 ng/L) (Sam, 2012). Based on other studies and experience, there are reasons to believe that the geosmin removal (and the T&O removal in general) can be improved at MWW by modifying the current treatment process (Wilkinson, 2012, Rydell and Kraynick, 2013). The proposed plan is to stop the current addition of powdered activated carbon (PAC) combined with a conventional filtration using dual medial filter with anthracite and sand and to replace the anthracite by granular activated carbon (GAC) in a conventional filtration process. The projected modification is intending to increase sorption capacity, and hereby removal of T&O compounds. To study the performance of GAC filters, MWW and the University of Minnesota initiated a shared research project. This thesis will compare the current treatment process versus the proposed water treatment at MWW.

First, in chapter 2, the detailed research goals and objectives will be presented. Essentially, the topic of study is GAC filtration and sorption performance. In chapter 3, background information for the research is provided – with a thorough presentation of the water treatment plant at MWW and a review of the challenges with respect to T&O. Chapter 4 contains a review of relevant literature, describing the concepts of filtration and sorption, and addressing important water quality parameters for this research. Geosmin and organic carbon constitute vital parameters in this thesis. Research materials and methods are described in chapter 5, including a description of the pilot-scale filtration plant and the operating conditions. Operational conditions at the pilot plant affect the performance of the plant, and have been given great emphasis when interpreting research results. In chapter 6, research results are presented and discussed. After a brief overview in section 6.1, GAC sorption of organic carbon, ultraviolet absorbtion and geosmin is discussed in light of the pilot-scale filters data. In the final sections 6.6-6.8, filters performance regarding ammonium, nitrates, particles and turbidity. Finally, in chapter 7, the major findings of this research are summarized, and corresponding conclusions are drawn.

2. Research Goals and Objectives

The main objective of this thesis is to study how GAC filters perform at MWW with respect to removal of organic carbon, ultraviolet absorption and geosmin – and consequently obtaining an understanding of GAC sorption capacity at MWW. Additionally, a description of GAC filter removal of ammonium, nitrite, nitrate, particles and turbidity is an affirmed goal. Within the study of GAC, a comparison of two different products, Calgon-F400 and Norit F-400 should be obtained. Last but not least, a comparison between GAC and anthracite based filters should be established with a discussion on potential future benefits with GAC filtration at MWW.

3. Background

3.1 Taste and Odor Issues in Minneapolis

T&O events have led to customer dissatisfaction in Minneapolis for years. Figure 1 shows the number of monthly registered customer complaints regarding T&O at MWW, from November 2007 to November 2013. The general trend is that T&O complaints occur more frequently during late spring, summer, and early fall. Most notable, however, are perhaps the two tallest columns, counting 81 and 98 registered complaints, in July 2008 and March 2010 respectively. In July 2008, 79 complaints were received within a period of six days – 72 of which described the T&O as either "musty" or "swampy/lake". In March 2010, 93 complaints were received within a period of 10 days – 79 complaints this time characterized the T&O as "fishy".

Among the various registered complaints, "musty", "earthy", "swamp/lake" and "fishy" are highly represented. Earthy, musty T&O is a common problem for surface water utilities, and is typically caused by geosmin or 2-methylisoborneol (MIB-2) (Choi et al., 2010). Geosmin and MIB-2 are organic compounds mainly produced by blue-green algae (cyanobacteria) (Chang et al., 2007) and are described more carefully in section 4.4.3. In this report, geosmin is the T&O compound given most attention.

Fishy tasting and smelling water can be caused by numerous compounds, but are generally produced by algae, and a blossom will typically occur in spring – a description that corresponds well with the T&O event of Minneapolis in March 2010 (Figure 1). In addition to the major event in March 2010, smaller events of complaints about fishy T&O have occurred every year from 2007 to 2013.
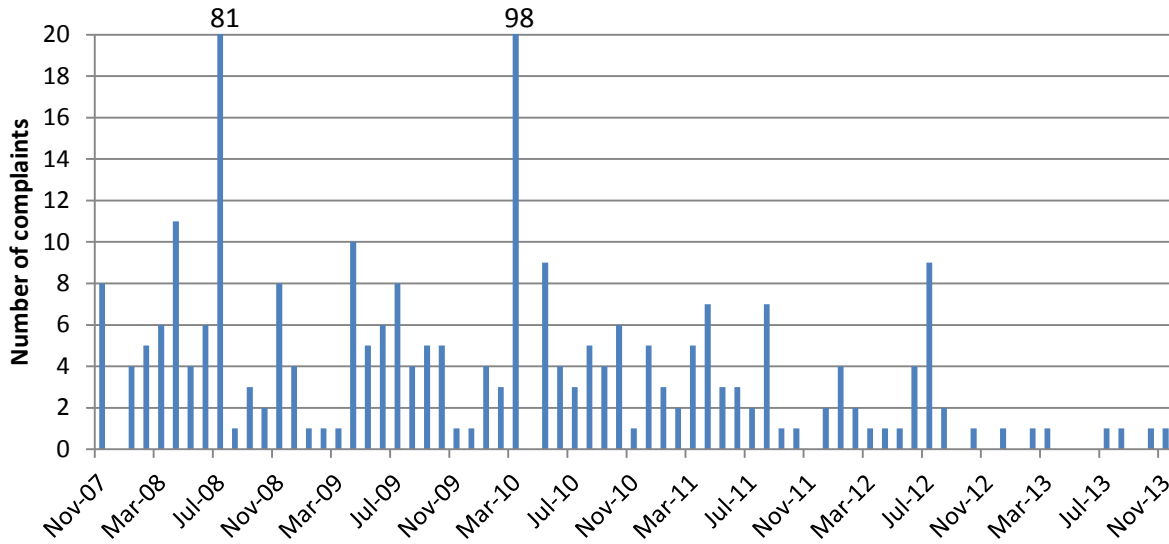
Figure 1: Registered complaints at MWW from November 2007 to November 2013

Figure 1 shows that in 2013, notably fewer customer complaints were received compared to previous years. The geosmin concentrations in the treated water were, accordingly, kept below the T&O threshold of 5 ng/L (Figure 2). MIB-2 concentrations in the treated water during the same period were also below the threshold for detection – measuring a maximum concentration of 3.3 ng/L (T&O threshold for MIB-2 is 15-18 ng/L).

Figure 2 shows the influent and effluent concentrations of geosmin at MWW from the end of 2012 throughout the year of 2013. Despite the low effluent concentrations, the raw water carried concentrations that occasionally well exceeded the human T&O threshold. Thus, MWW maintained sufficient removal rates of geosmin in 2013. Successful removal seemed to be valid for MIB-2 and other T&O compounds. The sufficient removal rates of 2013 are explained by a new management with a stricter policy regarding the use of T&O measures. The current T&O measures at MWW consist in application of potassium permanganate for oxidation and powdered activated carbon (PAC) for sorption (further explained in section 3.3.1). The new policy requires application of PAC, not only when needed, but continuously throughout the whole year. Addition of potassium permanganate is also being done more frequently – whenever the slightest odor is detected in the river water.
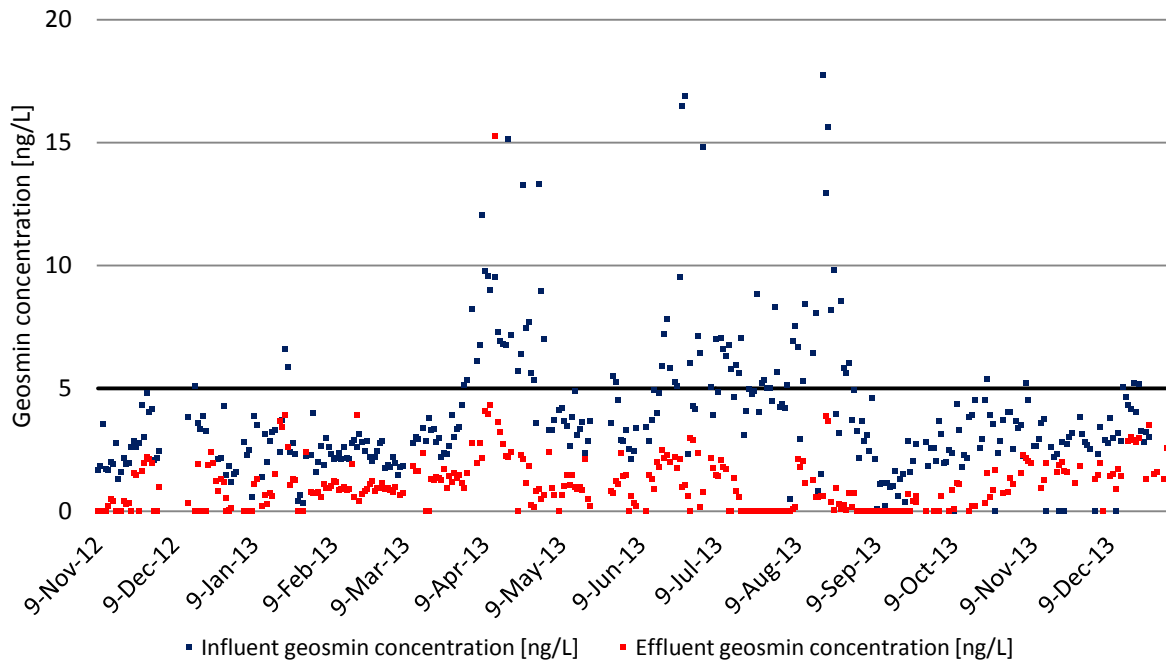
Figure 2: Geosmin concentrations at MWW treatment plant. The human T&O threshold is about 5 ng/L.

Improvements were obtained in 2013. Nevertheless – earthy/musty/swampy/fishy water remains one of MWW's constant threats. The current T&O removal processes seem to be efficient, but are costly, both in economical terms and the need of high alert from the staff.

3.2 Introduction of Minneapolis Water Works

MWW provides potable water for about half a million people plus different institutions and industries, and has a daily water production of 212 000 m³. MWW is located in Minnesota, U.S. and is surrounded by a typical continental climate. Summers are warm and humid, while winters are cold and snowy. The shifting seasons, combined with the use of a surface water source, ensure that MWW are fed with raw water of fluctuating quality over the course of one year. The varying conditions can be illustrated by the average temperatures of July and January, which are 23.2 °C and -9.1 °C, respectively (ClimateSations, 2014). Figure 3 shows the location of Minneapolis, at the west bank of the Mississippi river, and also indicates (with the red pointer) how the raw water intake of MWW is located north and upstream of the city. In the lower right of the picture, we can see the city center of St. Paul. The municipality of St. Paul also uses Mississippi water to supply their citizens. River water is led to the treatment plant in St. Paul through a system of lakes.
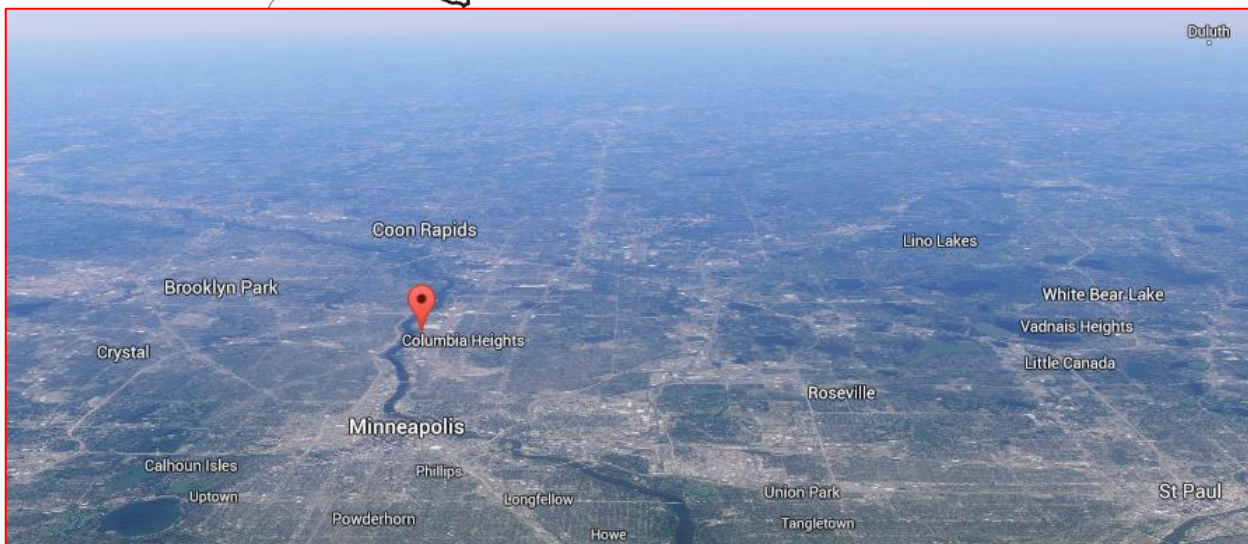
Figure 3: Location of the raw water intake of Minneapolis Water Works. (GoogleMaps, 2014)

3.3 Minneapolis Water Works – Existing Water Treatment and Future Plans

MWW has a dual treatment scheme – consisting of one granular media filtration plant and a parallel membrane ultrafiltration (UF) plant. As shown in the schematic of Figure 4, the pre-treatment is located at *Fridley Softening Plant* before the water is sent into two parallels, systems, at *Fridley Filter Plant* and Columbia *Heights Filter Plant*, respectively. During normal operation condition, 67% of the stream passes through the granular media filtration and 33% through the membrane filters. Nevertheless, both parallel systems are capable of covering the full water demand alone. These parallel systems increase safety and enable MWW to shut one down for maintenance purposes. Moreover, the utility operators can choose between two processes based on the characteristics of the influent water. (Rydell and Kraynick, 2013)

Pre-treatment consists of coagulation with aluminum- or ferric sulfate and slaked lime addition for increased alkalinity. CO_2 is then added for pH control before the water is sent to either granular media filtration or membrane filtration. The granular filtration process (framed red in Figure 4) is based on a conventional filtration concept with anthracite based trimedia filters (anthracite with sand and gravel). Ferric chloride is used as flocculant and chlorine gas and ammonia are added in order to disinfect with both chlorine and chloramines. Granular media filtration processes are reviewed in section 4.1. The UF plant has a capacity of 265 ML/d and was the largest of its kind in North America when commissioned in 2007. The UF plant provide MWW with additional protection against chlorine-tolerant organisms such as Cryptosporidium (Pressdee et al., 2005).

Fridley Softening Plant (FSP)

Raw water

P.S. #5 - low

Mixing Chambers (4)

Solids recirculation

Spaulding precipitators (softening cones,12)

To Dewatering

P.S. #4

Recarbonation chambers (2)

Softened Water Basin (75 Mgal)

Basin bypass (Seasonally)

Columbia Heights Filter Plant (CHFP)

P.S. #6

Mixing Chambers (2 – different sizes)

Coagulation/ Sedimentation (6)

Backwash recycle (May be routed to head of softening when basin is bypassed)

Granular Media Filters (24)
No longer in service

Columbia Heights Membrane Plant (CHMP)

CHMP Feed Pumps

Ultrafiltration Units (40)

Fridley Filter Plant (FFP)

Mixing Chambers (4)

Coagulation/ Sedimentation (4)

Granular Media Filters (20)

P.S. #2
P.S. #3

Backwash recycle

Clearwells 16 MG each

P.S. #5 - High

As needed

Distribution

P.S. #9

Clearwells

10 MG

P.S. #8

45 MG

Hilltop Reservoirs

Gravity from Hilltop to distribution

P.S. #7 & North High

Distribution

Pump Stations

Minneapolis Water Works Treatment Plant Schematic

(February 2013)

a T&O Treatment Additives

Potassium Permanganate (KMnO4) added during taste and odor episodes at either
  a. Raw Water or d. "Post"
Powdered Activated Carbon (PAC) added in any combination of locations:
  b. "Pre", c. "Mid", or d. "Post"
  e. Is option if KMnO4 added to d.

n Chemical Addition Points:

1. Alum (Al2(SO4)3) or Ferric sulfate (Fe2(SO4)3)
2. Lime (slaked, Ca(OH)2), alternate to [1] for coagulant addition.
3. Carbon dioxide addition.
4. Chlorine (Cl2), Ferric Chloride (FeCl3),
5. Ammonia (NH3)
6. Fluoride as H2SiF6, additional FeCl3 if needed
7. Ammonia, Ortho-Polyphosphate, alternate to [6] for
8. Fluoride
9. Chlorine, Ammonia
10. Fluoride as H2SiF6, Ortho-Polyphosphate

Figure 4: MWW treatment schematic. The granular filtration process is shown in the red frame.

3.3.1 Treatment of Taste and Odor at Minneapolis Water Works

Currently, MWW disposes a standby system which can be activated when T&O compounds are detected in the raw water. The system involves addition of potassium permanganate for oxidation of T&O-causing compounds – followed by addition of PAC for T&O removal through sorption. As already mentioned, PAC is currently added. As discussed in section 4.2.2, the use of PAC has some disadvantages compared to other T&O measures – one being the potential high costs when used extensively. Hence, it was suggested to replace the existing anthracite filter media with GAC, adding sorption capability and replacing the PAC as sorbent. The proposed substitute will clearly change the granular media filtration step (colored red in Figure 4) and hopefully increase T&O removal.

4. Literature Review

In this chapter the theoretical basis for the study is reviewed. The first section describes the unit process of filtration, and discusses the uses of different filter media. In the second part, the important phenomenon of sorption is reviewed, including a comparison of powdered and granular activated carbon as sorbents. In the third and final section, GAC filtration with biological geosmin removal is discussed.

4.1 Filtration in drinking water treatment

Filtration is in this report referring to granular media filtration. Typically, in the context of water purification, other forms of filtration are more specifically labeled (e.g. membrane filtration).

The purpose of drinking water filtration is the separation of solids from water, by interposing a medium, such as sand or GAC, through which the water can pass. Flocs and other impurities are retained in the medium, while the water passes through. A typical process treatment train for surface water is shown in Figure 5. This process is based on "conventional" filtration (meaning that there is coagulation, flocculation and a primary particle separation step prior to filtration). Figure 5 reflects the process at MWW, where sedimentation is used as the primary particle separation step. Alternatively, water can be filtered directly after coagulation and flocculation. This is known as "direct" filtration and is mostly used for low turbidity waters. Another option, "in-line" filtration, involves filtration without flocculation and sedimentation, making coagulant addition the only pre-treatment. Filtration and coagulation then occurs simultaneously in the filter. MWW is using a surface water source, which typically leads to conventional filtration as the desired process; direct and in-line filtration fits with more stable raw waters with consistently low turbidity and color (Au and LeChevallier, 2004).
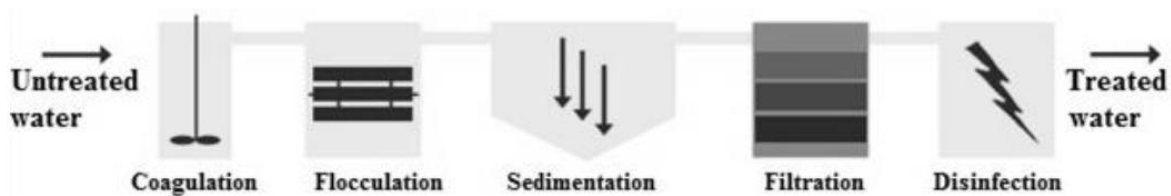

Figure 5: Treatment train for a conventional filtration process

Empty bed contact time (EBCT) is a key design parameter for effective filter-sorber beds (Kim, et al., 1997). EBCT is calculated by dividing empty bed volume by flowrate through the granular media. Thus, increasing the bed volume or reducing the flow rate through the filter will result in longer EBCT. The EBCT is an important parameter in GAC filters design, as it affects the sorption capacity development. Higher EBCT values can delay breakthrough and reduce the GAC replacement/regeneration frequency. Typical EBCTs for water treatment applications range between 5 to 30 minutes. (Crittenden and Harza, 2005)

4.1.1 Filtration Mechanisms

Separation of substances from water can be achieved by numerous mechanisms within the filters, depending on the media type and operation conditions. Particles larger than the filter bed pores will remain on the bed, a mechanism often referred to as straining. If filter grains are small, filter bed pores are small – leading to frequent clogging when the influent has a high particle concentration. This mechanism occurs mainly in slow filters, as rapid filtration processes remove larger particles (iron or aluminum flocs) in the preceding removal process of sedimentation or flotation. In rapid filtration the particle removal normally occurs inside the filter bed. The clogging then spreads over the whole filter bed height. As seen in Figure 6, suspended and colloidal particles have different ways of being transported to the filter media. (TU-Delft, 2013)
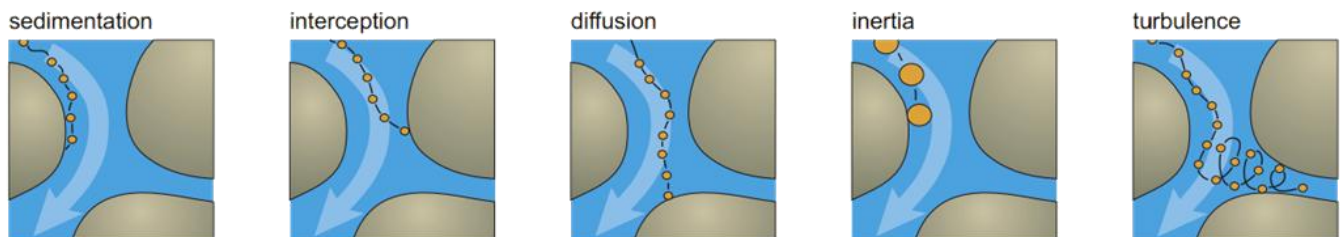
Figure 6: Ways of particle transportation within a filter medium (TU-Delft, 2013)

The particle will typically follow the pathway of the flowing water through the filter. The pore structure of the filter bed will however make the water pathway complex and irregular. If the pathway gets curved, heavy particles are subjected to attach to the medium due to inertia. When the water flow approaches a filter grain, particles can become intercepted. Heavier particles are often attached to the filter through sedimentation, whereas particles of smaller mass can be captured due to diffusion. In parts of the filter turbulent flow can occur, and particles might get transported to the media grains. (Crittenden and Harza, 2005)

Consequently, suspended and colloidal particles may be attached to the filter grains when exposed to each other. Van der Waals forces give an attracting effect between grain and particle. Electrostatic forces can lead to both attraction and repulsion, depending on the particle charge. As suspended colloidal particles normally have a negative charge, particles are destabilized by coagulation. Destabilization makes particles floc more easily but can help the filtration as well – as e.g. sand filters, potentially repulsing colloidal particles of negative charge. (TU-Delft, 2013)

Chemical and biological mechanisms can also be present in the filter bed. Among possible biological mechanisms in the filters we find bacterial oxidation of manganese and decomposition of methane, ammonium (described in section 4.4.5) and biodegradable organic matter. Decomposition of methane in the filter results in an uninhibited bacteria growth of bacteria leading to rapid clogging. Consequently, any methane must be removed prior to filtration. (TU-Delft, 2013)

4.1.2 Filter Media

There is a variety of granular filter media products available. There are different standard ways of expressing the main characteristics of filter media. The "effective size" represents the size of a sieve opening which permits 10 percent of media particles (by weight) to pass. "Uniformity coefficient" indicates the sieve opening that will just pass 60 percent (by weight) of a representative sample of the media, divided by effective size. The "apparent density" describes the media weight per apparent volume, giving a reflection of porosity. The "iodine number" expresses the amount of iodine adsorbed by one gram of carbon at equilibrium with a 0.02N iodine concentration filtrate (Crittenden and Harza, 2005). Typical filter media are addressed with typical characteristic values in Table 1.

Table 1: Typical filter media characteristics (Crittenden and Harza, 2005) (Ratnayaka et al., 2009)

Type	Apparent Density [g/ml]	Iodine Number [mg/g]	Effective Size [mm]	Uniformity Coefficient (max.)
Sand	~2.65	-	0.4-0.8	1.3-1.7
Anthracite	~0.73	-	0.8-2.0	1.3-1.7
GAC	0.4-0.6	600-1200	0.8-2.0	1.3-2.4

In this section, three main categories of filter media are described: Sand, Anthracite and GAC. On top of different media products, there are also different ways of arranging a granular media filter. The filter can be arranged as a "monomedium" (e.g. silica sand), a "dual media" (e.g. anthracite coal and sand) and a "trimedia"/"multimedia" (e.g. coal, sand and gravel). (Au and LeChevallier, 2004). Hence section 3.3, the filters used in the MWW pilot plant are trimedia types, having a layer of sand and gravel underneath the main media.

Silica sand is the most common filter medium used in drinking water treatment. Sand filters with low flow rate per unit of surface (typically 0.04-0.40 m/hr) are known as "slow sand filters". Slow sand filtration is the original way of filtering in water treatment, and is based solely on the formation of a biologically active layer on the filter bed top. Although slow sand filters are still in use in some European cities, "rapid filters" (typically 0.4-3.1 m/hr) of sand or other granular media have been the typical filter process choice in the United States for decades (Droste, 1997). As opposed to slow sand filters, where removal occurs in the upper layers, rapid filters are designed to remove solids throughout the whole filter depth. The higher hydraulic loads, faster creating head loss, and the deeper penetration of particles lead to the need of backwashing as rejuvenation method. After backwashing heavier grains tends to settle first, sorting the filter bed with tiny voids on top and gradually larger voids downwards in the filter bed. This grading is undesired as the finest grains on top will contribute to rapid clogging and little use of lower filter layers. Hence, it is important with more uniform grain sizes in a rapid sand filter than in slow sand filters (Droste, 1997).

Due to its filtration properties anthracite coal is extensively used in water filtration. Anthracite consists of durable coal particles that come in various sizes and hardness levels. Anthracite has shown to stand longer filter runs than equivalent sand filters. With a unique density anthracite can easily be combined with other media in a multi-media filter. (GEWater, 2012)

Activated carbon is a highly porous material made from carbon rich materials like wood, lignite or coal. The carbon is "activated" by reagglomeration. Essentially, this prepares the carbon to withstand abrasion of repeated backwashing, hydraulic transport and reactivation for reuse. It also makes the carbon like a molecular sponge – ensuring that pores of different sizes are present, ready to adsorb contaminants of different molecular weights. As mentioned in section 4.2.1, adsorption occurs in the inner spaces of a porous media like GAC. Backwashing alone will not remove the molecules absorbed into the pores. The point at which the GAC has used all its absorption capacity, the media can be regenerated – a process which is typically handled by the manufacturer. (CalgonCarbon, 2012b)

GAC typically has a total surface area of 500 m^2 per gram, giving high sorption ability. Hence, GAC filters have the ability to remove particles through filtration and organic compounds through sorption. Typical GAC filters are configured as shown in Figure 7 and Figure 8. Post filtration adsorption places the GAC filter after a conventional filtration process. Filtration and adsorption simply introduces the GAC in the filter of a conventional filtration train (EPA, 2014).
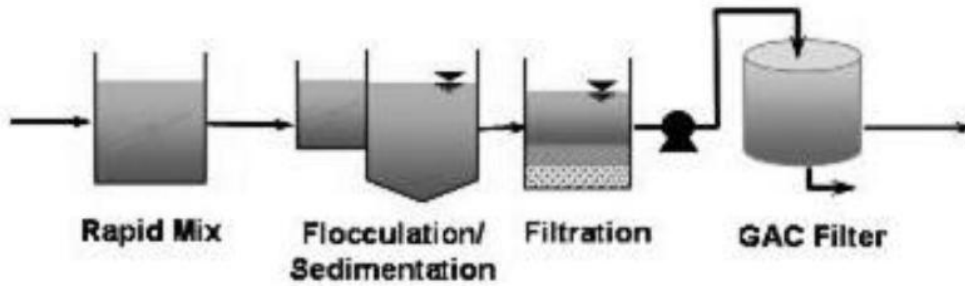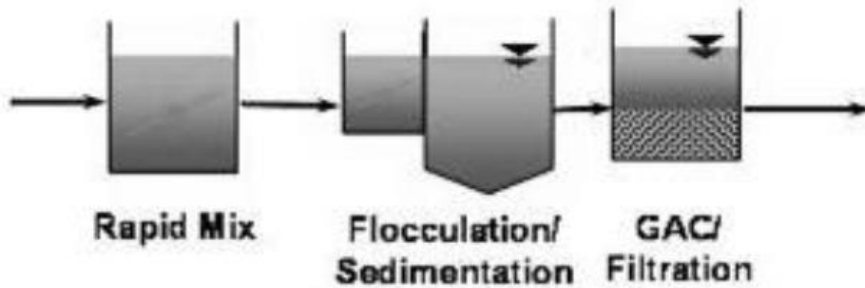

Figure 7: Post filtration adsorption (EPA, 2014)

Figure 8: Simultaneous adsorption and filtration (EPA, 2014)

4.2 Sorption

Sorption is an important physical-chemical process in certain filter media types. The driving force of sorption is the concentration gradient between the bulk solution and the sorbent surface. Hence, a sorbate can be both adsorbed and desorbed by the media filter. In the case of a porous filter media, the sorbate can be further transferred into the media pores, once adsorbed to the surface. The internal transport of sorbates in a media grain (e.g. GAC) is a result of either surface diffusion along internal surfaces or pore diffusion through water in the pores. (Scharf et al., 2010)

4.2.1 Sorption Isotherms

Sorption capacity at a given background temperature and given conditions can be described by an isotherm. The Freundlich and Langmuir isotherms are the common ones used, alongside the linear isotherm model. The linear model is described through equation 1.

$$q_e = k\,C_e \qquad (1)$$

Where q_e is absorbent phase concentration (ng geosmin/mg GAC)

k is the linear adsorption capacity parameter (L/mg)

C_e is the liquid phase geosmin concentration (ng/L)

Freundlich's model is an empirically developed sorption model for media such as activated carbon, and is shown in equation 2.

$$q_e = k\,C_e^{1/n} \qquad (2)$$

Where q_e is absorbent phase concentration (ng geosmin/mg GAC)

k is Freundlich adsorption capacity parameter (L/mg)

C_e is Liquid phase geosmin concentration (ng/L)

$1/n$ is Freundlich adsorption capacity parameter

The Langmuir isotherm assumes constant free energy of all adsorption sites and a reversible dynamic. Langmuir's isotherm described sorption through equation 3.

$$q_e = \frac{Q_M \, b \, C_e}{1 + b \, C_e}$$

(3)

Where q_e is adsorbent phase concentration (ng geosmin/mg GAC)

Q_M is maximum adsorbent phase concentration of adsorbate (ng geosmin/mg GAC)

b   is Langmuir adsorption constant

C_e is equilibrium concentration of adsorbate in solution (ng/L)

(Benjamin and Benjamin, 2001)

4.2.2 Sorption by Acitvated Carbon

Powdered activated carbon (PAC) is essentially the same product as the granular version (GAC), only crushed into finer powder granules with diameters of between 0.15 and 0.25 mm. The GAC grain diameter is typically about 1.2 – 1.6 mm. Both GAC and PAC have the same porosity, but PAC has more surface area per gram and will hence reach equilibrium with the sorbate concentration faster than GAC will. GAC however, with larger grains, is often used in a packed filter bed, whereas PAC is usually applied by rapid mixing and removed during sedimentation (Scharf et al., 2010). This leads to two different reactor situations for the two types of activated carbon – PAC is applied in a completely mixed reactor (CMR) system and GAC filters resembles a plug flow reactor (PFR) (Figure 9 and Figure 10).

As equation 4 and 5 imply, the PAC seeks equilibrium with the effluent sorbate concentration, whereas GAC searches equilibrium with the influent sorbate concentration. Hence, PAC will have a lower equilibrium concentration (ng sorbate/mg carbon) compared to GAC – requiring more carbon for removing the same mass of sorbate (Scharf et al., 2010). Note that equations 4 and 5 assume a first order reaction.

The advantages are that PAC can be used only when needed, and is applicable to existing plants, potentially being a cheap alternative (Newcombe and Cook, 2002). With a price of $650/ton however, PAC could become expensive. Prolonged use might result in significant costs, emphasized by the difficulties of dosing it correctly. Dosing at higher levels than needed leads to unnecessary high for the utility, and conversely, under-dosing results in consumer complaints (Newcombe and Cook, 2002). Furthermore, PAC gives an extra load to solids handling systems, sedimentation systems, and sludge management operations (Scharf et al., 2010).

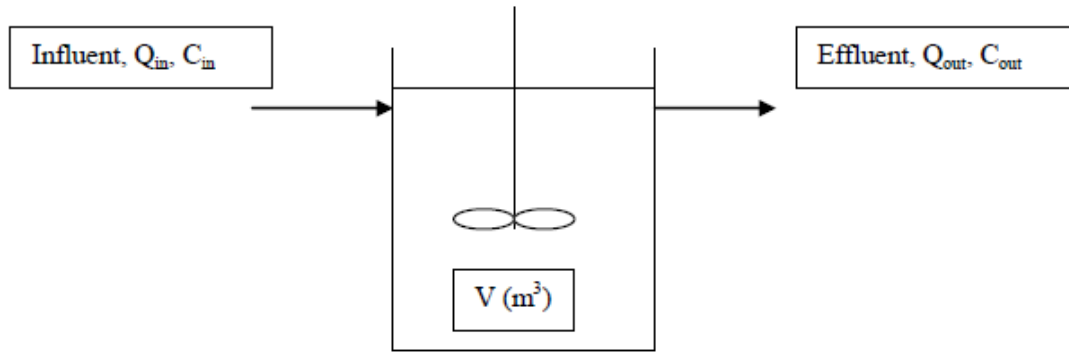**Figure 9: Completely Mixed Reactor (CMR)**

$$C_{out} = \frac{C_{in}}{1 + k\tau}$$
(4)

Where C   is the contaminant concentration

k   is reaction constant

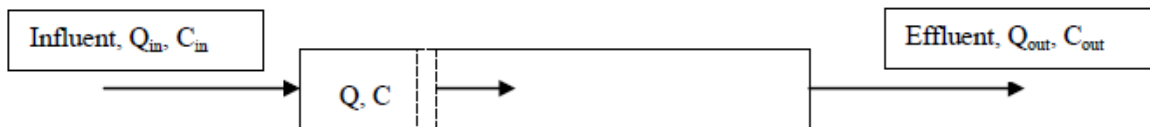τ is filter residence time

Figure 10: Plug Flow Reactor (PFR)

$$C_{out} = C_{in}e^{-k\tau}$$
(5)

Where C   is contaminant concentration

k   is reaction constant

τ is filter residence time

(Droste, 1997)

4.2.3 Geosmin Sorption

A study shows that geosmin concentrations of 66 ng/L were decreased to below the detection threshold with doses up to 10 mg/L of PAC (Scharf et al., 2010). One hour contact time is typically required for the sorption to reach equilibrium (Newcombe and Cook, 2002). In T&O episodes with geosmin levels exceeding 66 ng/L however, the use of PAC gets more undesirable due to the high does needed. As mentioned in the previous section, GAC in a filter bed process allows a more efficient use of activated carbon, hence, needing less carbon in a T&O situation of high geosmin concentrations (Herzing, et al., 1977).

Geosmin sorption to activated carbon also depends on pH, natural organic matter (NOM) concentration, temperature and alkalinity. NOM gives other sorbates competition over the adsorption spaces. Sorption of geosmin is however only slightly affected by NOM concentration, whereas sorption of MIB-2 is strongly inhibited by NOM. (Newcombe and Cook, 2002)

The type and production of activated carbon will also affect the geosmin absorbing properties (Bruce et al., 2002). According to Bruce, et al., 2002 coal-based activated carbon normally serves better sorptive abilities in comparison to wood- or lignite- based activated carbon. Anticipated geosmin removal at a particular water treatment plant must however be determined taking the particular background conditions into consideration. The initial step will typically consist in developing batch isotherms to determine the most suitable activated carbon for the exact sorbate (geosmin, in this case) and the exact water being treated (Randtke and Snoeyink, 1983).

4.3 Geosmin Removal in Biofilters

Research and experiences with high relevance to MWW have been obtained at St. Paul Regional Water Services, which are treating surface water descending from the same Mississippi water as MWW are using. (Wilkinson, 2012) The location of St. Paul can be seen in Figure 3. A pilot-scale GAC filtration study was done, and a switch from anthracite to GAC filtration was implemented successfully.

An interesting finding in this study was that the useful life of the full-scale GAC filters exceeded the prognosis of both batch tests and other software models. The main hypothesized explanation for this was that geosmin was degraded by certain microorganisms residing in the filter, relieving the GAC sorption. A pilot-scale column system of GAC filters was fed with 100 ng/L of geosmin, resulting in the development of a geosmin-degrading biofilm after 40 days. The geosmin-degrading organisms proved to be robust by resuming geosmin degradation after 6 weeks without any fed geosmin. The study also showed that GAC type did not have importance for biomass levels or geosmin removal. (Wilkinson, 2012)

Biological filtration has been practiced ever since water was started filtered, playing a central part in e.g. slow sand filtration. But the conscious use of filter mediums (anthracite or GAC) to support microbial biomass is something of more recent; biologically active GAC filters have been used since the 1970s. Biological activity was embraced initially because it exceeded the filter bed life, needing less frequent regeneration or replacement. Nowadays, biofiltration is often targeted to remove a specific compound such as e.g. geosmin. Removal of TOC was generally between 5-15% in the biologically active GAC filters, with slightly higher removal efficiencies in the warmer months of May through September. (Wilkinson, 2012)

4.4 Relevant Water Quality Parameters

Taste and odor can become an issue in drinking water through multiple sources. However, geosmin, MIB-2 and numerous other taste and odor compounds are classified as organic chemicals naturally present in water bodies. NOM is used to describe this diverse matrix of water constituents. In addition to causing potential tastes and odors, NOM is related to a yellowish coloring in water. On top of the aesthetic concerns, NOM can form carcinogenic disinfection byproducts when reacting with chlorine. NOM is most commonly measured as total organic carbon (TOC), but can also be expressed through other parameters – sometimes specific fractions of TOC or the absorption of ultraviolet radiation can be of interest. These bulk parameters are often more practical to measure, rather than each individual compound separately. (Crittenden and Harza, 2005)

4.4.1 Organic Carbon

TOC is a measure of all carbon atoms covalently tied in an organic molecule of a water sample. As TOC is a sum measurement it will not detect any specific organic contamination. It will nevertheless detect the presence of all organic compounds, in which any organic contaminants are included. In surface waters, typical TOC concentrations range from 1 to 20 mg/L. Dissolved organic carbon (DOC) represents the part of TOC dissolved in the water. In this report DOC is accurately defined as the TOC with a smaller size than 0.45 µm. Typical DOC concentrations are of 80-90% of TOC. (Crittenden and Harza, 2005)

A common way of determining TOC is to measure both Total Carbon (TC) and Inorganic Carbon (IC). TOC is then found through subtracting the IC from TC. Other typical measurements of TOC include removal of the IC prior to measurement, through purging the acidified sample with carbon-free air, then measuring the carbon remaining. This variant is known as non-purgeable organic carbon (sometimes abbreviated NPOC). (EPA, 2005)

4.4.2 Ultraviolet Absorption

Specific ultraviolet absorption (SUVA) is a relationship between the UV absorbance at 254 nm wavelength (UV_{254}) and the DOC concentration of a water sample (Equation 6). Water samples are filtered before injected into a spectrophotometer for absorption measurement at 254 nm UV. Although both DOC and UV_{254} reflect NOM content, the ratio between the two can vary with different water bodies and throughout different seasons. SUVA determines the disinfection by-product formation potential, and has often been put in correlation to the hydrophobic share of NOM. Thus, SUVA can provide information concerning changes in NOM composition. SUVA is reported in units of L/mg · m. (EPA, 2005)

$$SUVA = \frac{UV_{254}}{DOC}$$

(6)

Color in drinking water is also measured as absorption through spectrophotometers, typically using 410 nm UV light (NSA, 2002).

4.4.3 Geosmin

Intuitively, "geosmin" is derived by the Greek words for earth "ge" and odor "osme". Geosmin, Trans-1,10-dimethyl-trans-9-decalol, is a metabolite of actinomycetes, cyanobacteria and some other microorganisms, and is typically produced in northern climates. Geosmin production peaks in the summer season (Zaitlin and Watson, 2006). Chemically, it is described as a bicyclic alcohol, with the formula $C_{12}H_{22}O$; the geosmin molecule has two saturated 6-carbon rings with two methyl groups and one hydroxyl group (Chang et al., 2007).
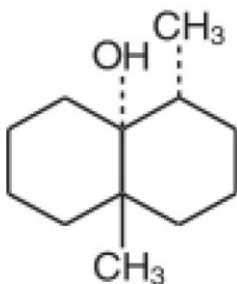

Figure 11: Molecular structure of geosmin.

Geosmin can be detected by humans at low concentration, with an odor threshold concentration, typically ranging from 4 to 10 ng/L. Removal of geosmin from water can be done through physical, chemical or biological treatment (Scharf et al., 2010). However, the common unit operations of coagulation, sedimentation, and filtration are often insufficient at lowering geosmin concentrations below the T&O threshold (Bruce et al., 2002).

4.4.4 Particles and Turbidity

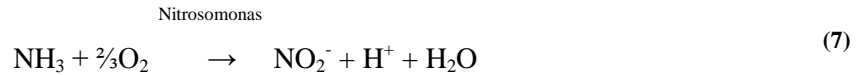"Finely divided solids of greater size than molecules", typically fall within the definition of particles, and include a great variety of organic (e.g. DNA and polysaccharides) and inorganic (e.g. clays and silts) water constituents. Particle content represents a relevant water property in both hygienic and aesthetic terms. Two main reasons for removing particles are the potential negative impact on water treatment processes and the potential health threat of pathogenic particles. Particles are often, have a relatively large surface area compared to their small mass, and serve a potential adsorption sink for toxins like heavy metals and chlorinated hydrocarbons. Furthermore, natural organic matter can be absorbed onto particles, potentially disturbing disinfection. The natural sources of particles in water include weathering of soil, chemical precipitation, atmospheric deposition and biologic activity by algae, bacteria and other higher microorganisms. Anthropogenic activities like industry and agriculture can also affect the particle situation in a water source.(Crittenden and Harza, 2005).

Turbidity is a measurement that addresses the cloudiness of water, and is a result of scattering and absorption of light by suspended solids. Turbidity is measured in nephelometric turbidity units (NTU) and is defined as "an expression of the optical property that causes light to be scattered and absorbed rather than transmitted with no change in direction or flux level through the sample" (Rice et al., 2012). U.S. regulations set a requirement of a maximum of 0.3 NTU in 95% of the monthly filtered water samples. Most utilities therefore set their treatment goal to 0.1 NTU. Although turbidity is widely used as the parameter describing particle concentration, turbidity measurements cannot be mutually related to any other quantifiable particle presentation. (Crittenden and Harza, 2005)

Particle removal is done through sedimentation or flotation and through various types of filtration. A typical treatment scheme includes preceding coagulation and flocculation. Coagulants aid in destabilizing colloids so that particles can grow together during flocculation. Quantification and analysis of particulate matter in waters can be done through gravimetric techniques, particle size counting and microscopic observation. (Crittenden and Harza, 2005)

4.4.5 Ammonium, Nitrate and Nitrite

Nitrogen is present in natural waters in the main forms of ammonia gas (NH_3), ammonium (NH_4), nitrate (NO_3^-) and nitrite (NO_2^-). Transformation between these forms is thoroughly related to biologic activity, as nitrogen is a vital nutrient for vegetation and living organisms (Rice et al., 2012). The changeover in state from ammonia to nitrate is known as nitrification. Nitrification requires oxygen and two separate genera of bacteria (respectively Nitrosomonas and Nitrobacter) as indicated in equations 7 and 8.

$$NH_3 + \tfrac{2}{3}O_2 \quad \xrightarrow{\text{Nitrosomonas}} \quad NO_2^- + H^+ + H_2O \tag{7}$$

$$NO_2^- + \tfrac{1}{2}O_2 \quad \xrightarrow{\text{Nitrobacter}} \quad NO_3^- \tag{8}$$

Total reaction: $\quad NH_3 + 2O_2 \quad \rightarrow \quad NO_3^- + H^+ + H_2O$ (9)

(Droste, 1997)

Nitrification is also temperature dependent as the oxygen uptake of water is reduced with a reduction in temperature. Moreover Nitrosomonas and Nitrobacter will grow slower with reduced temperature, as they both grow optimally around 20-30°C (AWWA, 2006).

Among several applications, nitrate is widely used in inorganic fertilizers. Nitrates are also present in vegetation, as they are a key nutrient for plants. Another natural source of nitrates is the endogenous production in mammals. Nitrates can thus appear in surface waters and ground waters from agricultural activity, septic tanks and more. (Crittenden and Harza, 2005)

5. Materials and Methods

In this study, samples have been collected at a pilot-scale filtration set-up. The pilot-scale filtration plant is described in section 5.1, and the operational history and conditions are reviewed in section 5.2. Water sample collection and storage methods are presented in section 5.3. Thereafter, the different analysis instruments and methods are reviewed, and ultimately the procedure of doing a sorption isotherm batch test is explained.

5.1 Pilot-scale Filtration Plant

As the main action of the research project, a pilot-scale filtration plant was constructed at the MWW Fridley Softening Plant. The pilot-scale plant was designed as shown in Figure 12. The red framing of Figure 12 underlines the fact that the pilot plant is taking water from the recarbonation tank effluent and mimicking the replacement at Fridley Filter Plant which is displayed in a red frame in Figure 4. The pilot plant consists of eight parallel filter columns, which include three different filter types; three columns have GAC produced by Calgon, two columns have GAC produced by Norit and three columns have the anthracite filter media currently in use at the full-scale plant. The filter columns are all trimedia filters, having two additional layers consisting of sand and gravel.
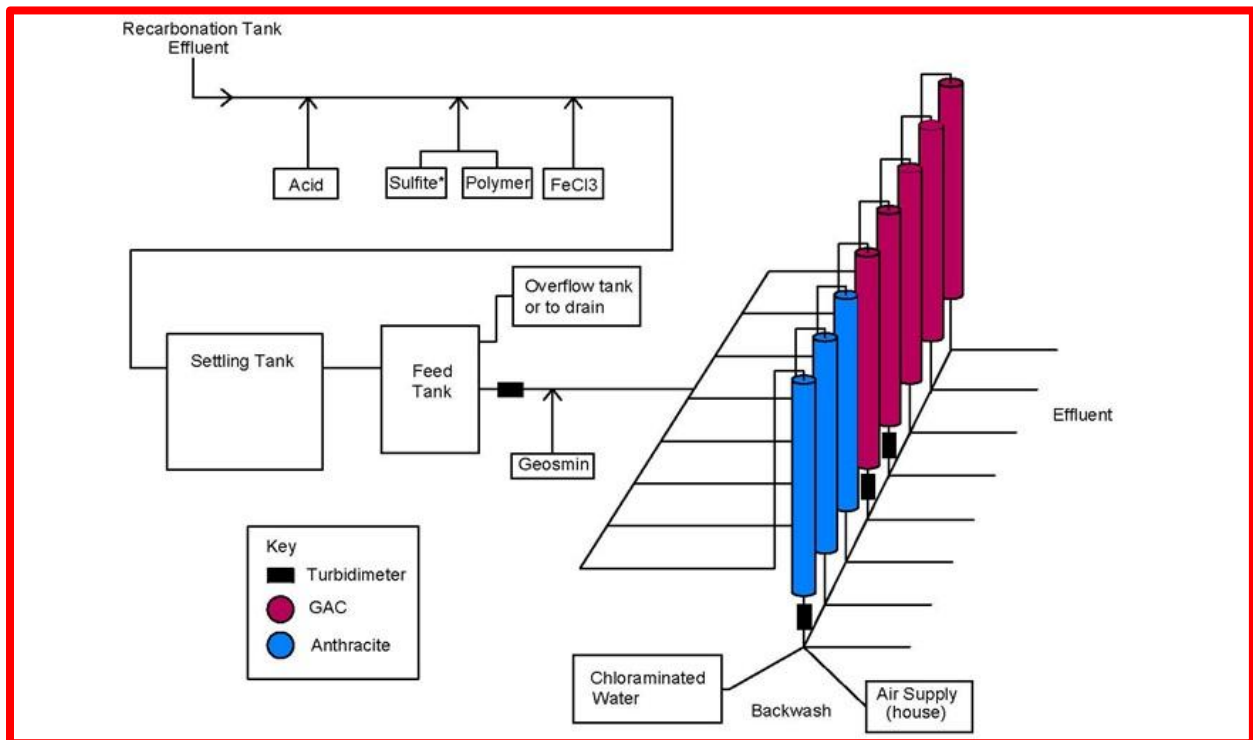

Figure 12: Schematic of the granular filtration pilot-plant. *Sulfite is only added in the rare cases of chlorination prior to filtration.

After the water is taken from the recarbonation tank effluent, hydrochloric acid (HCl) is added to lower the pH from around 10 to 8.0-8.5. In certain cases, the operators can decide to chlorinate the water both before and after recarbonation, meaning that chlorinated water could be fed to pilot plant and the filters – which is not desired, as high chlorine levels could kill the biological flora in the filters. The biological activity in the GAC filters is an important object of study for the UMN in this research project. Hence, sulfite will be added to dechlorinate the water, if needed. Just as for the full-scale filtration plant, ferric chloride is added as flocculant. After the sedimentation step, the pilot plant has a "Feed Tank". The purpose of the feed tank is to ensure steady hydraulic conditions for 8 small pumps lifting water into each of the filter column. Backwashing of the filters is done every 4 days, and consists of 5 minutes of air scour followed by 10 minutes of chloraminated tap water. The operation parameters of the pilot-scale filters are quantified in Table 2. The loading rate of 2.44 m/hour (58.7 $m^3/ m^2 \cdot$day) corresponds to the same loading rate per area as for the full-scale plant (1 gallon per minute per square feet).

Table 2: Pilot plant operation parameters

Parameter	Value
Empty Bed Contact Time [min]	12.7
Flow Rate [m/hour]	2.44
Time of Backwash Air Scour [min]	5
Backwash Air Scour Rate [$m^3/ hour \cdot m^2$]	71.5
Time of Backwash Water [min]	10
Backwash Water Flow Rate [m/hour]	41.4 / 24.2 (GAC / Anthracite)
Time Between Backwashes [days]	4

The filter columns all have an inner diameter of 95.25 mm (3.75 inches). The filters are vertically built up as shown in Table 3. Table 4 displays the characteristics of the two types of GAC used in this pilot plant: Calgon F-400 and Norit F-400

Table 3: Filter media depth distribution

Column	Media	Depth [mm]
1, 4 and 5	Anthracite	457
	Sand	254
	Gravel	102
2, 3, 6, 7 and 8	GAC	508
	Sand	305
	Gravel	102

Table 4: Physical characteristics of GAC (CalgonCarbon, 2012a) (Norit, 2013)

Granular Activated Carbon Characteristics							
Type	Apparent Density [g/mL]	Iodine Number [mg/g]	Effective Size [mm]	Uniformity Coefficient (max.)	US Mesh		
					USS	Oversize [%]	Undersize [%]
Calgon f-400	0.49	1000	0.55-0.75	1.9	12 x 40	5	4
Norit f-400	0.49	1000	0.7	1.6	12 x 40	5	4

Figure 13: Picture of the filter columns of the pilot-scale filtration plant of MWW.

5.2 Pilot Plant Operation and Conditions

Commissioning of the pilot filters was on October 25th. 2013, but due to different problems, one month was necessary to achieve stable operational conditions. The filters were continuously run from November 25th.

Figure 14 has an overview of pilot plant operation days and the corresponding temperature in the raw river water. It shows that the pilot plant filters have been running almost entirely with raw water of about 1.1 °C.
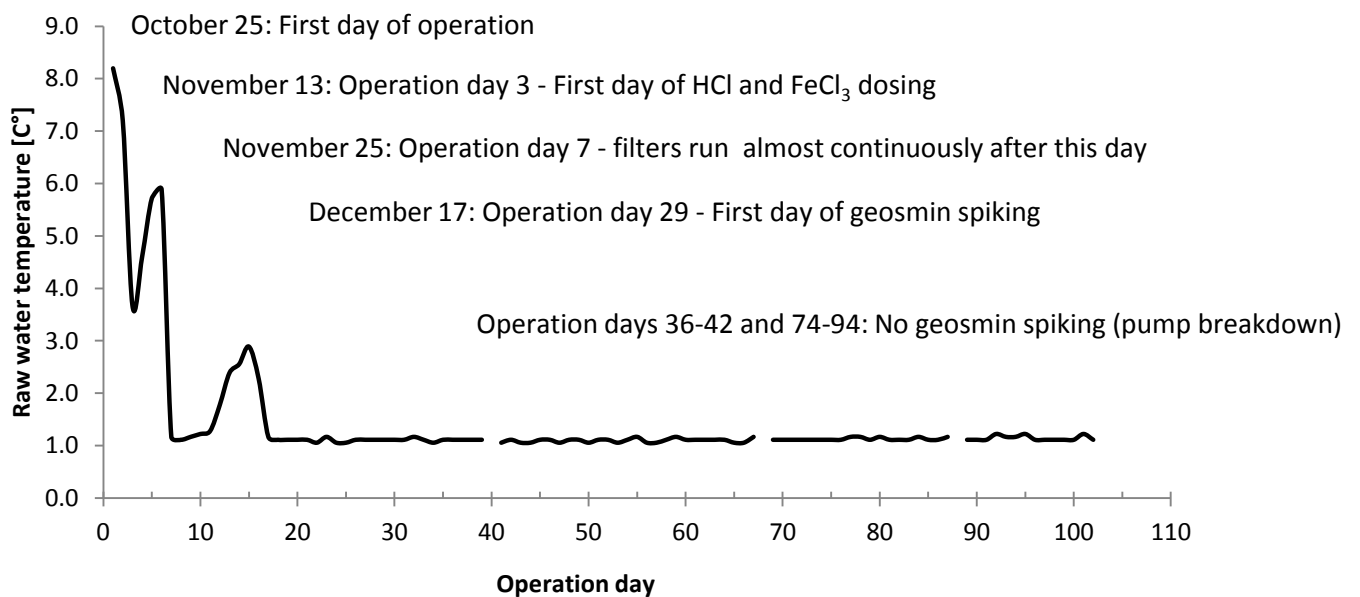

Figure 14: Raw water temperatures as a function of pilot plant operation days

November had 20 days without operation due to problems with the feed from the recarbonation tank of the full-scale plant and the need for replacing a pump that stopped working. This demonstrates one of many practical challenges related to the start-up of a new pilot plant.

Figure 14, moreover, reveals that the addition of chemicals has not been steady for each day of operation. Furthermore, the correct dosing of HCl and $FeCl_3$ was not achieved before the end of November, and the correct dosing of geosmin was still not under control by the end of February. These difficulties are related to the challenges with pumping a small volume accurately into a water flow.

5.3 Sample collection and storage

This study has been done by repeating the following routine:

- Collecting and storing/preserving samples from the nine sample points in the pilot plant (one at the filter columns influent and one at each of the eight filter effluents).
- Analyzing the samples with respect to different water quality parameters.

Water samples tested for nitrate should be collected in glass or polyethylene containers (EPA, 2012). Hence, 80 ml glass bottles were used to collecting samples. These samples were used both for particle and nitrate/nitrite analysis. The sampling bottles were always prepared by cleaning with dishwashing detergent and tap water before afterwards rinsing three times over with deionized water. When collecting samples for TOC analysis, specifically designated glass vials were used. The vials were prepared due to a standardized protocol: washed, rinsed with deionized water, air dried and finally *baked* (put in 550°C oven for six hours).

Samples were withdrawn from the nine designated sample ports, always after flushing the sample port for ten seconds in order to empty any old water. Figure 15 shows sample point of one of the GAC Norit filter columns, which represents the appearance of all nine sample ports.

Figure 15: Sample port at the filter column effluent (marked with a white ring)

Samples were placed in a refrigerator at 4°C immediately after collection and kept refrigerated until time of analysis. A mobile cooler was always brought to the Pilot on the time of sampling. In order to preserve the TOC/DOC samples, three to four drops of 6 M phosphoric acid were added. The addition of acid to TOC/DOC samples decreases pH and hereby stops the microorganisms from metabolizing organic matter present in the sample (Wallace, 2003). The TOC/DOC samples were stored in the refrigerator for up to 7 days prior to analysis.

5.4 Analytical Methods

If not otherwise noted, the water used is "MilliQ" water of "type 1" (deionized and filtered through a 0.2 μm membrane to meet standard laboratory requirements).

5.4.1 Organic Carbon

TOC and DOC concentration was analyzed by the *TOC Analyzer Sievers 900*. The same procedure was followed for both TOC and DOC analysis, with one exception – The samples were filtered through 0.45 μm prior to DOC analysis, in order to remove any suspended organic carbon.

The TOC Analyzer allows unattended operation. It calculates and auto-applies the appropriate reagent flow rate for any sample. The only user intervention needed, is sparging the sample for 5 minutes with nitrogen gas prior to analysis, inserting the sample vial in the TOC Analyzer and pressing start on the instrument touch screen. The nitrogen gas is introduced to convert any inorganic carbon to CO_2. In the case of this research, we are thus measuring non-purgeable organic carbon. In the TOC Analyzer, UV radiation and addition of persulfate leads to oxidation of the organic carbon present in the sample. To measure the CO_2 produced from the organic carbon, the instrument uses membrane conductometric detection technology. A gas-permeable membrane selectively passes only the CO_2 generated from the oxidation. The operating range of the TOC Analyzer is between 0.03 ng/L and 50 mg/L. (GEWater, 2014a) (GEWater, 2014b)

5.4.2 Ultraviolet Absorbance

UV absorbance was measured through spectrophotometry. The instrument, Beckman DU 530, requires five minutes of warming up after power is switched on, and a reading of a blank sample (Milli-Q water), before the samples can be injected. The absorbance is read instantly, so several samples can be read in a matter of few minutes. (GMI, 2014)

5.4.3 Geosmin

The common way to measure geosmin concentrations is through headspace solid phase micro extraction (HSPME) followed by gas chromatography/mass spectrometry (GC/MS):
A sample is transferred to a vial with sufficient extra space to generate headspace. Salt is thereafter added to the vial to increase the portioning of geosmin into the generated headspace. The vial is then heated, mixed by shaking, and a solid phase micro extraction (SPME) fiber is inserted in the headspace for a set amount of time. The fiber is then placed directly into a heated gas chromatograph, where the geosmin is desorbed from the SPME fiber. The gas chromatograph (GC) is temperature-programmed to separate the geosmin, which are ultimately detected with a mass spectrometer (MS).

Geosmin concentrations were quantified through the use of HSPME and GC/MS. The analysis was executed by the staff at MWW, Fridely Softening Plant. The procedure was done in agreement with standard operating protocol "SM6040D". The instrument used for HSPME and GC/MS analysis was a Shimadzu Analytical Instruments GC/MS QP2010 SE equipped with a HPSME autosampler.

5.4.4 Ammonium

Measurement of ammonia concentration in waters can be done through different technologies. A traditional way of measuring ammonium is by the Nessler method – based on the yellow to brown color produced by the chemical reaction between the Nessler reagent and ammonia. The Nessler's reagent is an aqueous solution consisting of HgI_2, KI and NaOH. The color is absorbed over a wide range of wavelengths ($\lambda= 400-500$ nm). Ammonia concentration can thus be determined by colorimetric analysis after addition of Nessler reagent. Colorimetric analysis is typically based on the Beer-Lambert law, which states that there is a linear relationship between absorbance and concentration of an absorber of electromagnetic radiation.

Ammonium concentrations were determined by colorimetric analysis after addition of Nessler reagent. Before addition of Nessler's reagent it was desired to remove calcium, iron, magnesium and sulfide, as they can potentially cause disruptive cloudiness. Removal of the unwelcomed compounds was accomplished by addition of $ZnSO_4$. Precipitate formed by the $ZnSO_4$ was removed both mechanically and chemically (by applying the chelating agent EDTA) before addition of Nessler's reagent. The sample was buffered at pH 10.5 to decrease hydrolysis of cyanates and organic nitrogen compounds. After adding the Nessler's reagent to the sample, the sample was mixed by shaking and left incubated for 20 to 30 minutes before colorimetric measurement.

The colorimetric measurement was executed by the Beckman DU® 530 UV-vis spectrophotometer which is presented in section 5.4.2. The sample absorbance was measured at the wavelength of 420 nm. The ammonia concentration was determined based on a standard curve which was re-established for each session of analysis. A stock solution of ammonia is made by dissolving powdered NH_4Cl in water. The stock solution (100 mg/L) was diluted with water into standard solutions of 0, 0.5, 1, 2, 3 and 5 mg/L. The absorbance measured of the standard solutions formed the standard curve (Appendix D).

5.4.5 Nitrite and Nitrate

Nitrite and Nitrate concentrations can be determined by Ion Chromatography. Ion chromatography can be used to detect a wide range of ions and polar molecules; the principle is based on the different levels of attraction from different ionic species to an ion-exchanger resin. Sample solutions run through a pressurized chromatographic resin where ions are absorbed. The ion extraction liquid (eluent), pass through the resin and the absorbed ions begin to separate from the resin. The different retention times of different ions will then reveal the ionic concentrations in the sample. (Haddad and Jackson, 1990)

The instrument used to determine concentrations of nitrite and nitrate ions was the "Metrohm 766 IC Sample Processor". Supported by the software "IC Net 2.3", it allowed unattended operation once all samples were injected. Plastic vials were cleaned through two rounds of Alconox® detergent application and three rinses of distilled water before being used to carry the water samples into the Metrohm instrument.

5.4.6 Particles and Turbidity

For particle counting and size distribution, the analytical method of using Multisizer™ 3 COULTER COUNTER® was applied. Figure 16 shows the Coulter Principle.

The water sample is diluted with a weak electrolyte solution (ISOTON II) before injection into the Multisizer. The particle suspension is drawn through a tiny aperture, separating two electrodes with an electric current flowing between them. The difference in electric potential over the aperture creates a "sensing zone". When particles pass through this "sensing zone", they immediately increase the resistance of the aperture by replacing their own volume of electrolyte. The change in electric resistance generates a pulse that is digitally processed. This pulse is directly proportional to the volume of the particle according to the Coulter Principle. These pulses eventually produce a size distribution which is displayed both in particle volume and correspondingly in particle size (μm). The particle size is the diameter of a sphere of equivalent volume to the particle. In order to measure the total concentration of particles in the sample, a

metering device draws a known volume of the suspension through the aperture. The number of pulses can then establish the overall particle content. (BeckmanCoulter, 2014)
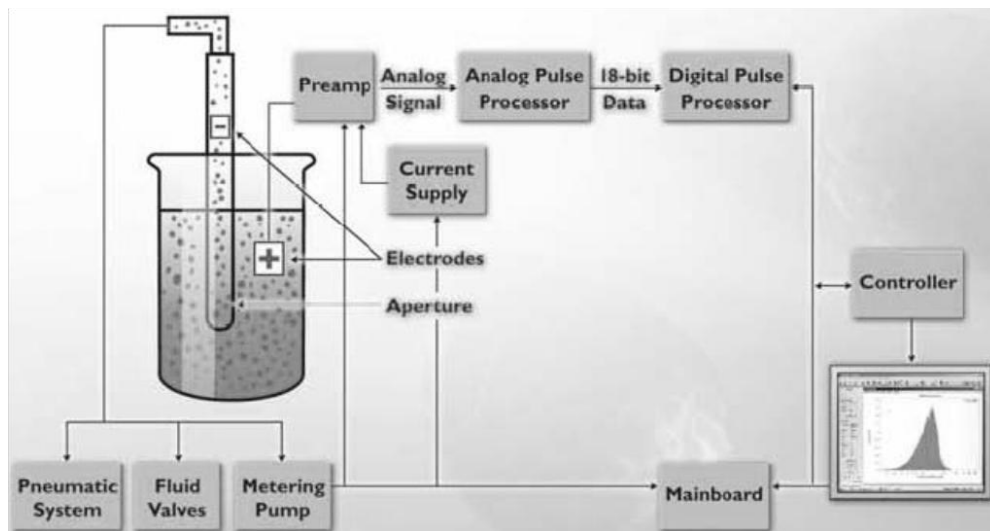

Figure 16: Principle of the Coulter Multisizer (BeckmanCoulter, 2014)

Through this technique, one obtains the number of particles, the volume and the size distribution in one measurement, within a size range of 1.3 μm to 11.5 μm. The analysis still leaves out information that sometimes is of interest, e.g. particle color, shape and composition. As this is a sensitive instrument, steady and standardized conditions are important for achieving an ideal performance. The main measure to ensure steady instrument performance was the control analysis of standard blank samples between the real samples.

The filters influent and column 1, 2 and 3 were additionally equipped with Hach® 1720E turbidimeters, measuring turbidity automatically every 15 minutes.

Turbidity measurements have been used extensively for a long time, whereas particle counters have been gaining more popularity in later years. The obvious benefit of using particle counters over turbidity meters is that particle counters provide information about the size of the particles, in addition to indicating the number of particles. This is often viewed as the more interesting parameter, as particle size is decisive for particle transport and settling. (O'Halloran et al., 2010)

5.5 Sorption Isotherm Batch Test

A Batch reactor test was carried out to study geosmin sorption for two different GAC products (Calgon F-400 and Norit F-400). The very same procedure was performed on both GAC media and is described in this section. Firstly, virgin GAC was crushed and sieved as shown below, only leaving granules smaller than 0.15 mm left (contributing to faster reaching sorption equilibrium).
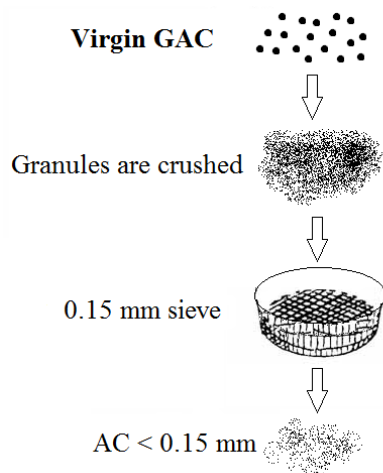

Figure 17: GAC was crushed and sieved

Secondly, five different masses of the activated carbon were measured; the aperture was a *Mettler Toledo AL* weight, with sensitivity down to 1 mg (MettlerToledo, 2007). The activated carbon was weighed in (pre-autoclaved) 1.5 ml containers, which were capped immediately after weighing (Figure 18). Thereafter, the containers were filled with distilled water and shaken to moist the carbon. The five different masses of moisten carbon were at this point introduced into each their glass flask (serving as the batch reactor). Distilled water was filled into the 1.5 ml containers and introduced into the flasks two more times, to ensure that all carbon was transferred from the container to the batch.

Figure 18: Mass of activated carbon and distilled water in 1.5 ml container

The batches were 1 liter glass flasks, sealed with polyurethane caps. Flasks were pre-combusted through 6 hours in 550°C and caps were prepared by a one hour bath in hydrogen peroxide at 70°C, followed by a double rinse with deionized water.

The water used in the batch test was geosmin spiked filter influent water. Water was collected from the pilot-scale filter influent at December 9th 2013 in order for the batch test results to reflect a relevant water quality for MWW. The water was filtered through a 1.2μm *Whatman GF/F* glassfiber filter prior to entering a 12 liter glass tank. This was done to remove a majority of organic distractions, potentially stealing sorption capacity from the geosmin. The 12 liter of filtered water was then dosed with geosmin, and now stored the water that was used for all batches in this research. To further ensure a uniform distribution of geosmin in the 12 liter tank, the water was mixed with a magnetic static mixer for ten minutes. Finally, the geosmin spiked water was introduced to the flasks, where the moist mix of water and activated carbon was already present. The flasks were filled up to the very top and capped immediately to prevent any geosmin from escaping.
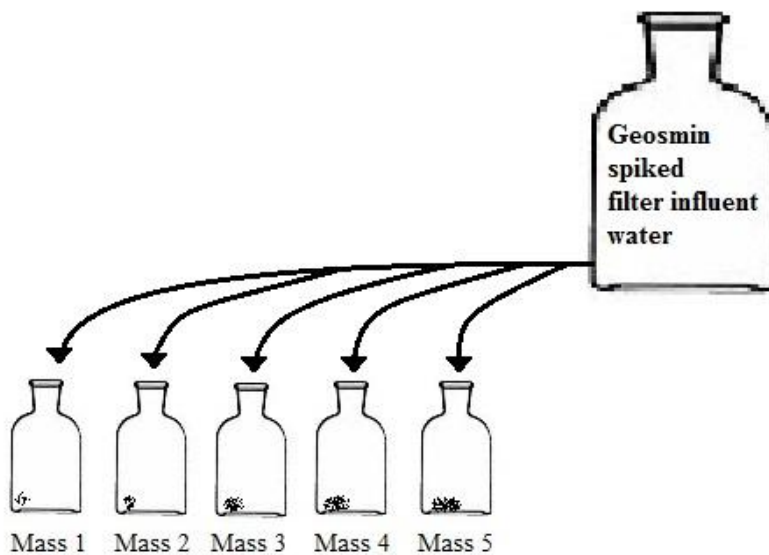

Figure 19: The same geosmin spiked influent water was fed to all batches

The flasks were weighed both dry and when completely filled, in order to accurately estimate the water content and thereby the carbon dosage in mg/L. The flasks were finally placed on a shaker table at 22°C as shown in Figure 20. Staying on this table, the batches were kept in constant rotation with a rate of 100 revolutions per minute, through 60 hours. Based on similar experiments, it was reasonable to assume that sorption equilibrium was going to be reached by this time period. (Scharf et al., 2010).

Figure 20: Bathces placed on shaking table at 22 °C

After 60 hours of reactor time, samples of 10 ml were taken from each batch reactor. Each sample was passed through 0.2 µm filters to ensure that activated carbon was removed, and brought to GC/MS analysis.

A total run of 11 batches were conducted: 5 batches of Calgon GAC medium, 5 batches of Norit GAC medium and 1 control batch (without any carbon).

6. Results and Discussion

This report is based on results from the first three months of steady filter operation. The sampling and data collection will continue for at least 3 more months (March-May 2014) and possibly for longer. Thus, the results presented in this report, represent a start-up period of pilot-scale filters in winter conditions. As discussed in section 4.1, filter performance is influenced by flow rate and EBCT. Filter performance results of this study are based on the pilot plant surface loading rate of 2.44 meters per hour reflecting the rate of the full-scale plant. The EBCT is 12.7 minutes.

6.1 Raw water quality

Hence the pilot plant conditions described in section 5.2, the first 100 operation days of the pilot-scale filtration plant took place during winter – with an average raw water temperature of 1.47 °C. More characteristics of the raw water and the pilot plant influent water are presented in Table 5.

Table 5: Summary of measured quality parameters. Presented with ± standard deviation and number of data points (n)

Water Quality Parameter	Raw water	Pilot plant influent
Temperature [°C]	1.47 ±1.22 (n=99)	-
pH	7.83 ±0.24 (n=98)	8-8.5*
TOC [mg/L]	-	4.00 ±0.22 (n=16)
DOC [mg/L]	-	3.65 ±0.21 (n=12)
UV_{254} [cm^{-1}]	0.180 ±0.034 (n=97)	-
SUVA [L / mg · m]	-	1.58 ±0.27 (n=12)
Geosmin [ng/L]		11.36 ±16.37 (n=7)
Ammonium [mg/L]	0.08 ±0.034 (n=94)	ND** (n=12)
Nitrite [mg/L]	-	ND (n=8)
Nitrate [mg/L]	-	0.83 ±0.18 (n=8)
Turbidity [NTU]	2.40 ±2.26 (n=100)	2.71 ±2.92 (n=9735)

*pH in filter influent is not measured. pH is here assumed to be within the targeted 8-8.5.
**Two influent ammonium values were measured above detection limit and can be seen in Appendix A.

6.2 Organic Carbon Removal

The influent concentration of TOC was consistently measured around 4 mg/L. The average influent TOC concentration was 4.00 mg/L with a standard deviation of 0.22 mg/L (n = 16) whereas the average influent DOC concentration amounted an average of 92.6% of the TOC (corresponding to 3.70 mg/L) with a standard deviation of 10.2% (n = 12). The influent TOC concentrations are plotted with corresponding filter effluent concentrations in Figure 21 as a function of filter running time and accumulated volume of treated water. In Figure 22, the ratio between average filter effluent concentrations and filter influent concentration (C/C_0) is shown with the same horizontal time and volume axis as in Figure 21. GAC filters performed well with respect to organic carbon removal in the first two weeks of operation, with TOC removal rates of about 100% ($C/C_0 = 0$) . Between operation day 14 and 28, different GAC columns measured very different TOC removal efficiencies, ranging from 100% to - 72%. In the data from operation day 43 to 120, the measured removals in the GAC columns are more uniform again, spanning from a high 81% to a low 20% removal. The anthracite filters removed TOC on an average rate of 0.00% with a standard deviation of 14.7% (n = 48). The absence of TOC removal in the anthracite filters are shown in Figure 21 and Figure 22 – anthracite effluent concentrations are mostly equal to the filters influent concentrations, and correspondingly C/C_0 values lies steadily around 1.
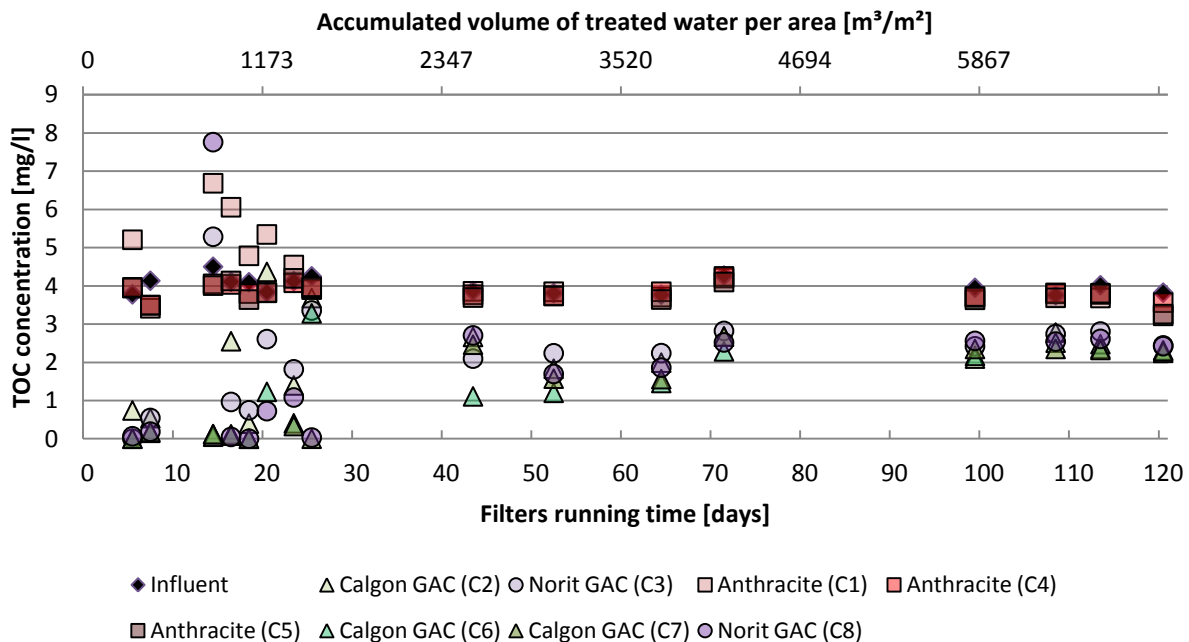

Figure 21: TOC concentrations in filter effluents as a function of filters running time and accumulated volume of treated water
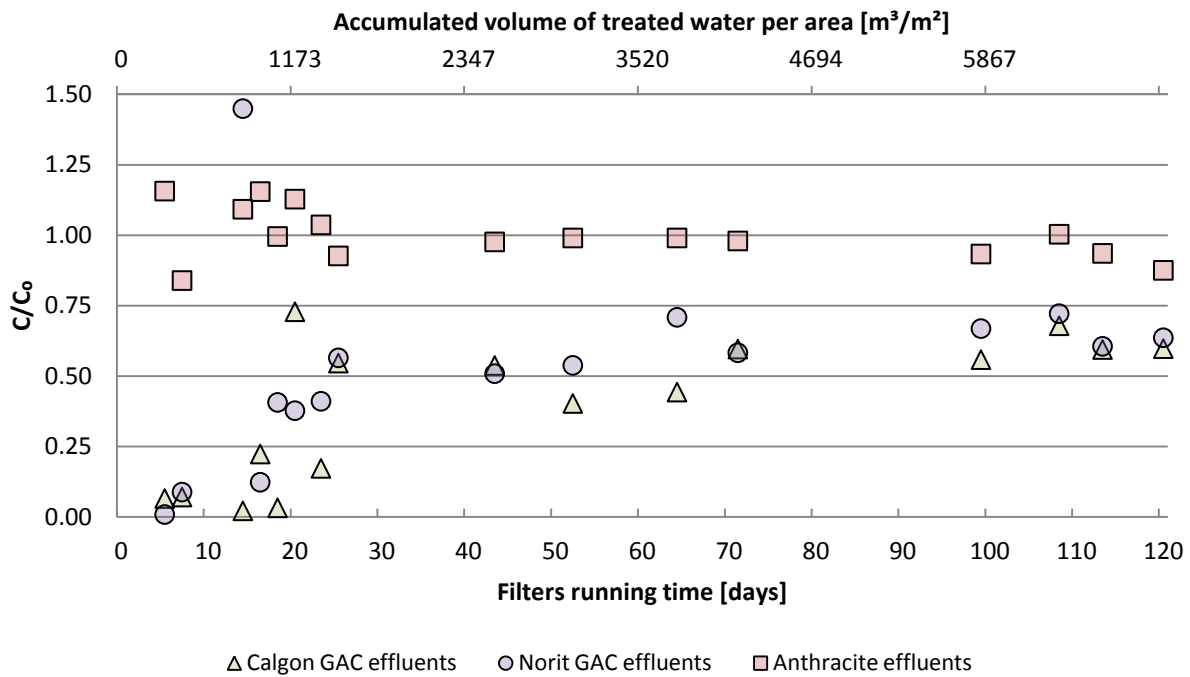
Figure 22: Ratio between mean effluent and influent TOC concentration (C_{avg}/C_0) as a function of filters running time and accumulated volume of treated water

Because the anthracite filters did not remove TOC in the first 120 operation days, it is fair to believe most TOC is removed through adsorption in the GAC filters. This assumption is enforced by the fact that influent TOC and DOC levels were generally the same – suggesting that virtually all organic carbon was dissolved in the water entering the filters. The general trend for the GAC filter columns is a slight decrease in TOC removal rates over time, which also proposes that sorption is the mechanism removing the organic carbon. The gradual reduction in organic carbon removal is expected, as sorption capacity in GAC media gets lower when more and more sorption sites in the carbon grains get occupied with time.

DOC levels are shown in Figure 23 and average rates of DOC removal (on the form C_{avg}/C_0) are given in Figure 24, drawing the same general picture as the TOC concentrations did – with GAC media gradually removing less and anthracite media not removing any organic carbon. The anthracite filters removed DOC on an average rate of -0.17% with a standard deviation of 8.8% (n = 28). There is, however, one notable difference in the DOC versus the TOC data; in the period between day 14 and 28, DOC values are all measured below 1 mg/L except one odd measurement (7.22 mg/L) in a Norit GAC filter column. Hence, the gradual decrease in removal seems more evident in the DOC data than in the TOC data.
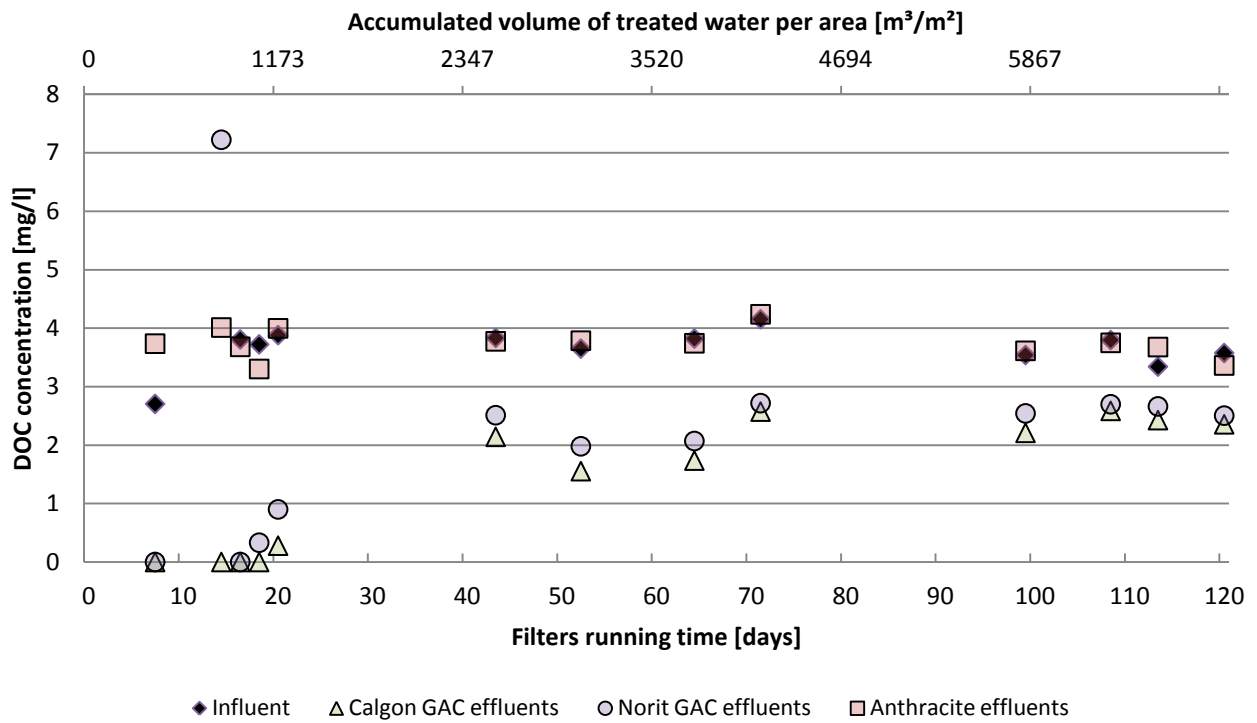
Figure 23: DOC concentrations in filter effluents as a function of filters running time and accumulated volume of treated water
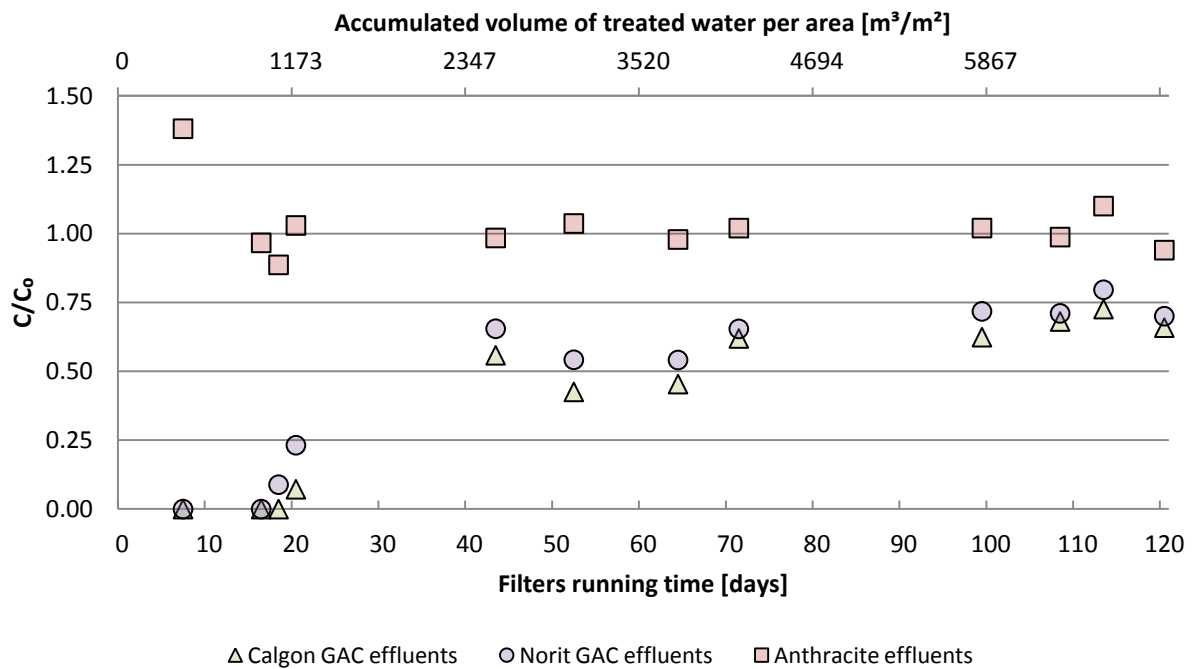

Figure 24: Ratio between mean effluent and influent DOC concentration (C_{avg}/C_0) as a function of filters running time and accumulated volume of treated water

The highly variable TOC measurements in the period between day 14 and 28 stands out from the measurements in the rest of the operation days, and also represent the main difference between TOC and DOC data. Notably lower levels of DOC than TOC suggests that notably more suspended organic carbon were present in some filter effluents during this period. One day (operation day 14) had extreme measured TOC and DOC concentrations for the Norit GAC, well exceeding the influent concentration. No obvious explanation was found to these high values, other than a hypothetical instrumental error or a contamination of the sample.

Virtually no difference is seen between Calgon and Norit produced GAC, if we consider the one extreme Norit data point as an error.

A similar study (Orlandini et al., 1994) spiked pilot-scale GAC filters influent with an average concentration of 2.1 mg/L DOC. The influent used was river water that had been pretreated with coagulation, flocculation and sedimentation. With an EBCT of 7 minutes, the removal efficiency of DOC was reduced to 50% after 17 days and 25% after 60 days. At an EBCT of 20 minutes, the removal efficiency of DOC was reduced to 50% after 63 days and 25% after 160 days. In comparison to the results of Orlandini et al., the pilot plant at MWW had DOC removal reduced to 50% after around 65 operation days, and at operation day 120, DOC removal is still around 31%, with EBCT at 12.7 minutes.
One should be cautious when comparing DOC sorption of different waters of different water characteristics. However, what Orlandini et al. shows, is a graph of the same shape increasing shape of the C/C_0 value over time, indicating that the DOC sorption breakthrough curve from the MWW pilot plant is not at all unique. Moreover, it is evident that increasing the EBCT will delay the DOC breakthrough.

6.3 Specific Ultraviolet Absorption Removal

12 specific ultraviolet absorption measurements are available (starting at operation day 7) and at 7 values for the filter effluents (starting at day 52). Figure 25 shows the SUVA data with filter influent values ranging from 1.3 to 2.3 L/ mg·m. Both types of GAC media seem to reduce SUVA numbers with filter effluent values between 0. 83 and 1.15 L/ mg·m, removing an average of 29.9% (SD = 10.2%, n = 35). Specific ultraviolet absorbance values gets higher with lower DOC concentrations, which means that the GAC filters, in this case, removes UV_{254} absorbance at a higher rate than the DOC. The anthracite filter effluents remove an average of 5.5% of the SUVA (SD = 11.6%, n = 21). The findings of section 6.2 pointed towards no DOC removal in the anthracite filters. Nor is there any significant removal of UV_{254} absorbance in the pilot-scale anthracite filters.

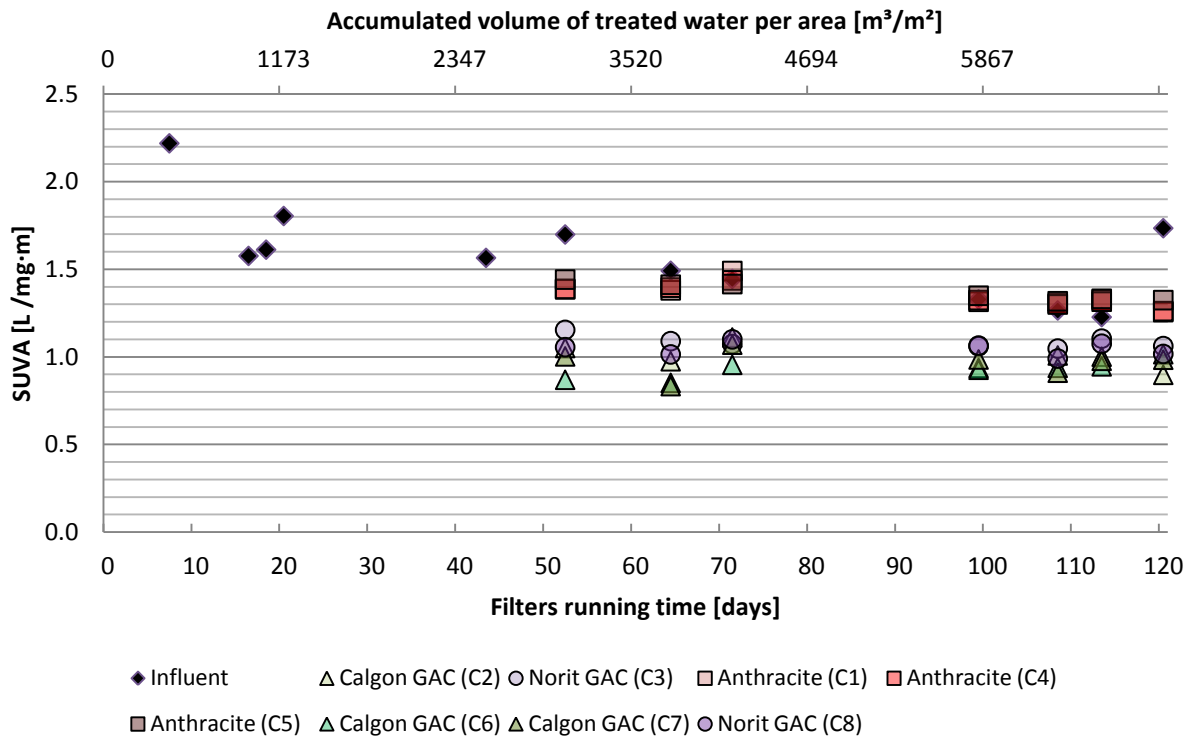The data collected demonstrate how sorption in GAC gives higher SUVA removal than in an anthracite medium.

Figure 25: SUVA values as a function of filter running time and accumulated volume of treated water

6.4 Geosmin Removal

Geosmin was added into the filter influent and the targeted spiked influent concentration was 100 ng/L. However, during the first influent geosmin concentration measurements, values significantly lower than 100 ng/L were measured. Figure 26 displays the first 7 sets of geosmin measurements. In the first three data sets, the geosmin concentration of the anthracite filters lies around the target influent concentration of 100 ng/L. If we assume that the anthracite filters did not remove any geosmin, the actual influent concentration could be close to the target. With this suspicion, an additional static mixer was installed after January, prior to the influent sample port – which will provide proper mixing. Note that the last four sets of data was sampled in times of geosmin pump complications – that probably explain why measurements were lower than at the three first data sets.
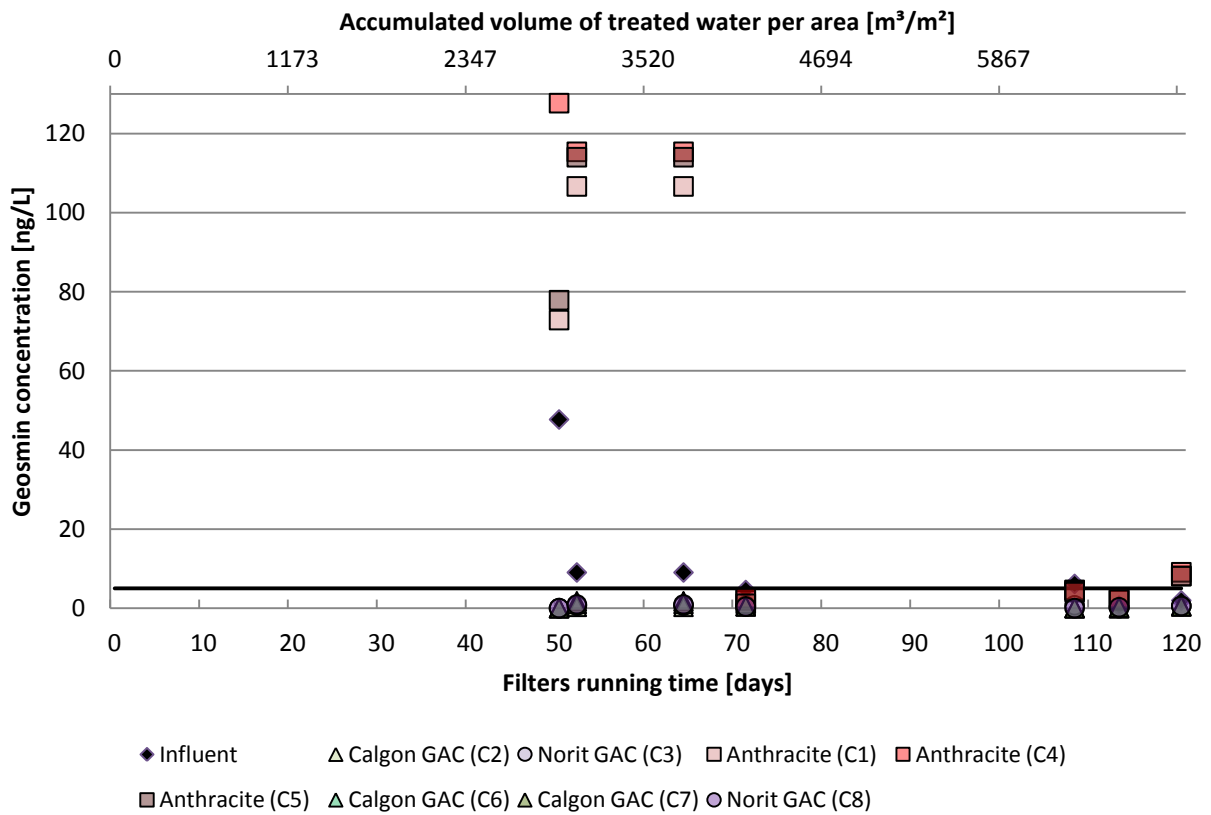

Figure 26: Measured geosmin concentrations at given operation day and with corresponding accumulated volume of treated water.

Figure 26 does not provide enough data points to draw any conclusions about geosmin removal. Regardless, the few data points seem to emphasize the great sorption capacity of GAC compared to anthracite. Geosmin levels in the GAC filter effluents were measured from 0 to 1.89 ng/L, and no clear difference between the Calgon GAC (columns 2, 6 and 7) and the Norit Calgon (columns 3 and 8) was seen. Geosmin concentrations from influent and GAC filters only are provided in Figure 27.
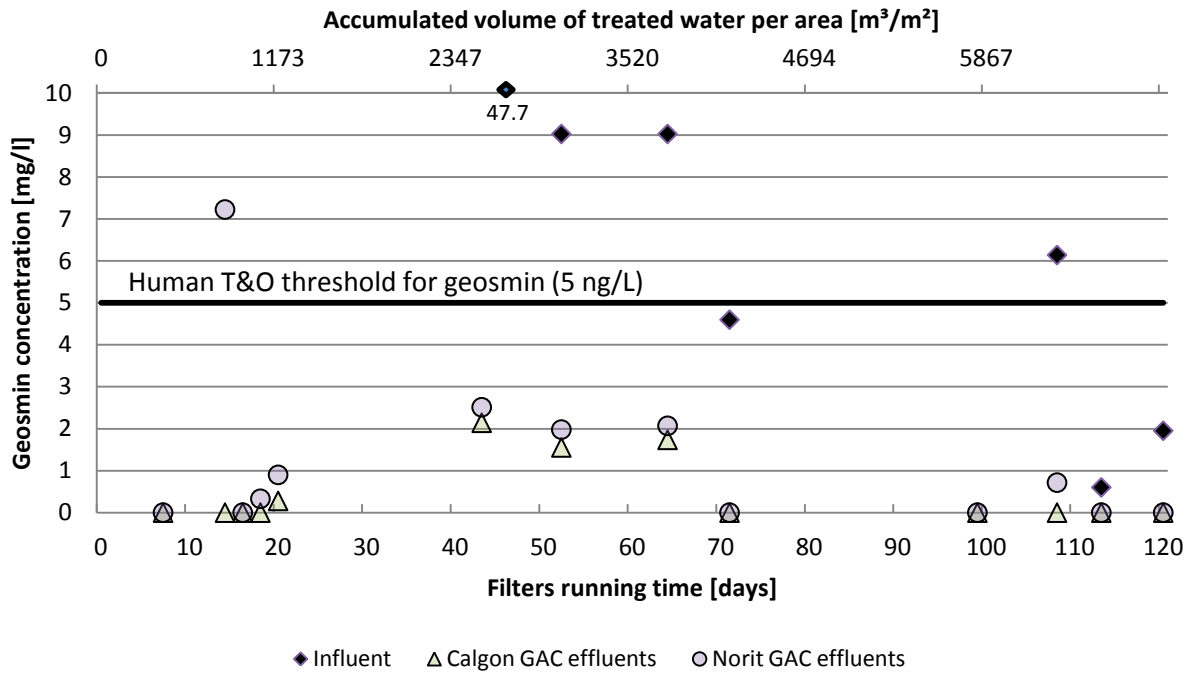

Figure 27: Geosmin concentrations in filters influent and in GAC filter effluents

6.5 Geosmin Sorption Isotherms

Five batches of Calgon GAC, five batches containing Norit GAC and one empty batch (control batch) were fed the very same initial filter influent water spiked with geosmin. The initial geosmin concentration is assumed to be equal to the equilibrium concentration of the control batch (122.65 ng/L). The batches were incubated and kept in motion for 60 hours at 22 °C, assuming that equilibrium concentrations were achieved. A linear isotherm model presentation of the batch results is provided in Figure 28.
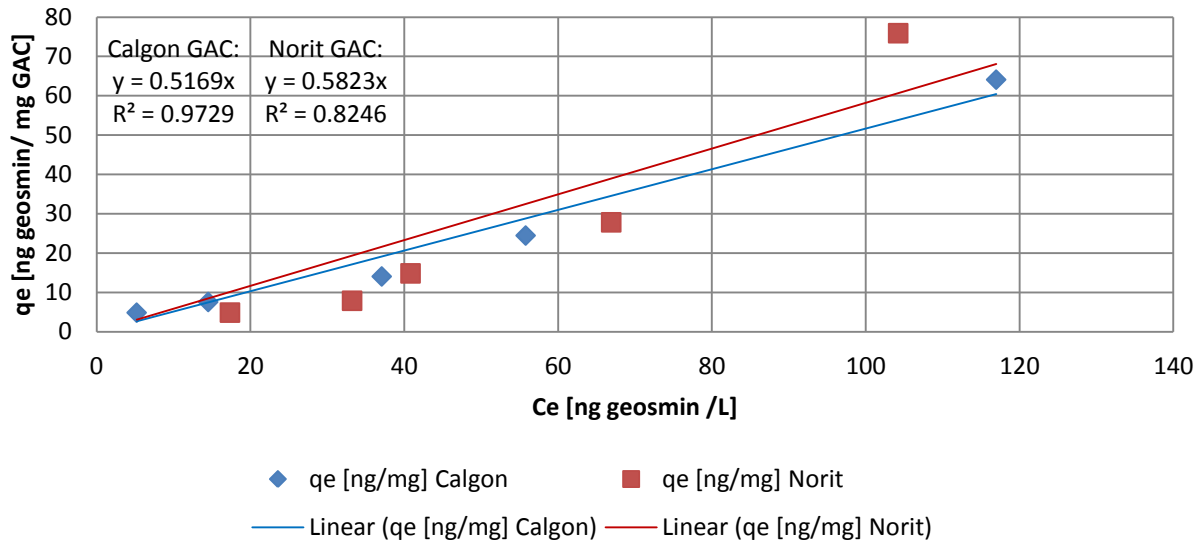
Figure 28: A linear isotherm fit, with qe (adsorption at equilibrium) plotted as a function of Ce (the equilibrium concentration of geosmin).

The results show that a greater amount of geosmin is removed with a greater dosage of activated carbon. The linear isotherm provides a good match with the Calgon GAC ($R^2 = 0.973$), and less good with the Norit GAC ($R^2 = 0.825$). The Freundlich isotherm model gives a good fit for both Calgon and Norit GAC properties ($R^2 = 0.938$ and $R^2 = 0.959$, respectively). The results did not suit the Langmuir model very well with both R^2 values below 0.805. Both Freundlich and Langmuir model fits are shown in Figure 29 and Figure 30, respectively. The best fit equations are collected in Table 6.
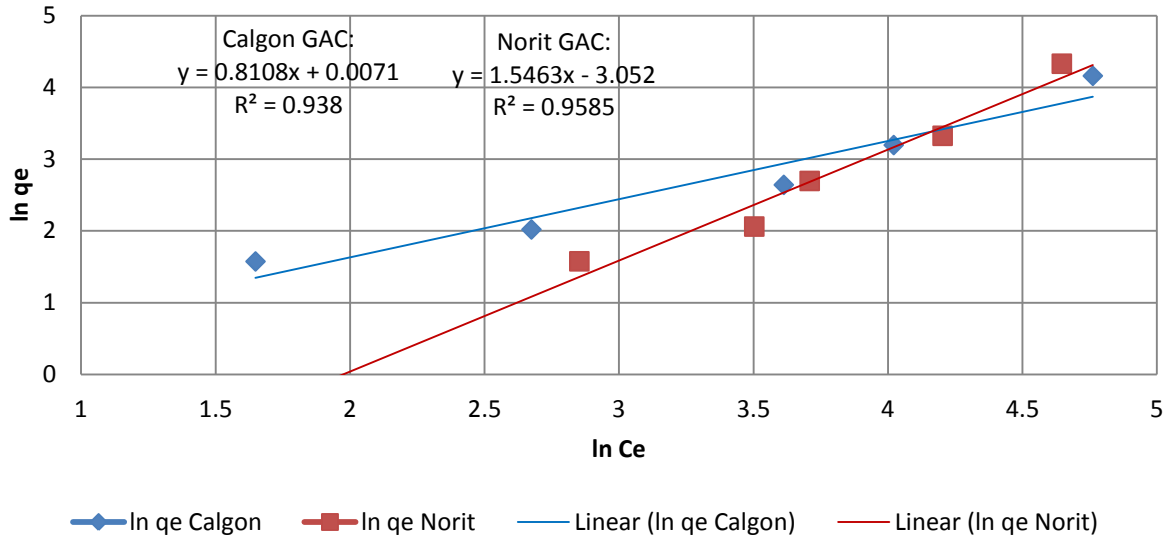
Figure 29: Freundlich isotherms based on batch sorption tests of Calgon and Norit GAC.
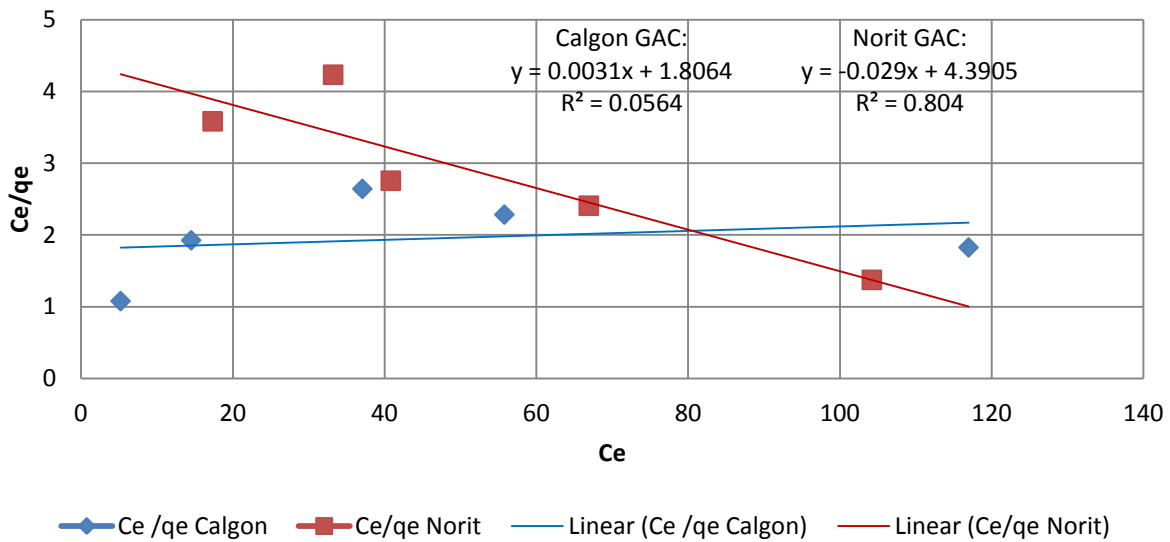

Figure 30: Langmuir isotherms based on batch sorption tests of Calgon and Norit GAC. The fit is poor compared to Freundlich.

Table 6: Freundlich and Linear equations from best fits of batch sorption tests.

Carbon type	Freundlich Isotherm Data			Linear Isotherm Data	
	k [L/mg]	N	R^2	k [L/mg]	R^2
Calgon F-400	1.01	1.23	0.938	0.517	0.973
Norit F-400	0.05	0.65	0.959	0.582	0.825

There is an extra uncertainty to the results of the batches of high carbon dosage. If the mass of carbon in a batch of low carbon dose is measured off by 0.5 mg, the error will be relatively greater than for high carbon dose batches, making the sorption differ correspondingly more. This could for example be the explanation of why the lowest dose Norit batch has notably better sorption than the lowest dose Calgon batch, while the rest of the batches seem to have a uniform sorption performance.

A better fit with the Freundlich isotherm model compared to the Langmuir model can possibly have occurred because the Freundlich model is empirically developed based on sorbents just like GAC. Freundlich is not empirically developed, and is based on both on reversible equilibrium between species. Although both adsorption and desorption probably occurred during the batch test, the net sorption was all adsorption. The batches of this research represent a CMR model, whereas the projected GAC filters at MWW will function similar to a PFR model. Hence equations 4 and 5 from part 4.2.2, the sorption equilibrium concentration are expressed differently. The isotherms obtained in this report might describe sorption of PAC addition as that is more related to CMR. An adapted version might describe the sorption of the GAC filter PFR model precisely.

Important to note, is the fact that these results are derived from water in the pilot plant filters influent December 11th 2013. This water was then passed through 1.2µm glassfiber filters. The results are hence only valid for this specific raw water, at this specific temperature, at this specific pH and so on. However, the results are aimed to reflect the situation at MWW.

6.6 Ammonium, Nitrate and Nitrite concentrations

Almost all influent and effluent ammonium concentrations were measured below the detection limit of 0.5 mg/L. There has seemingly been little ammonium in the sampling period, and no removal rates or other further observations seem to could be extracted from the data. For detailed ammonium data, see Appendix A.

Nitrite was not detected in any of the water samples taken.

Nitrate concentrations were generally found to be in the range from 0.5-1 mg/L, both in influent and effluent water. Two higher values around 1.5 mg/L were measured in one of the GAC filter columns in early December 2013. This column effluent has, since then, been giving values around the rest of the columns, and there does not seem to be a clear explanation for these values. The coinciding influent and effluent concentrations, suggest no nitrate removal in the anthracite and GAC filter beds.
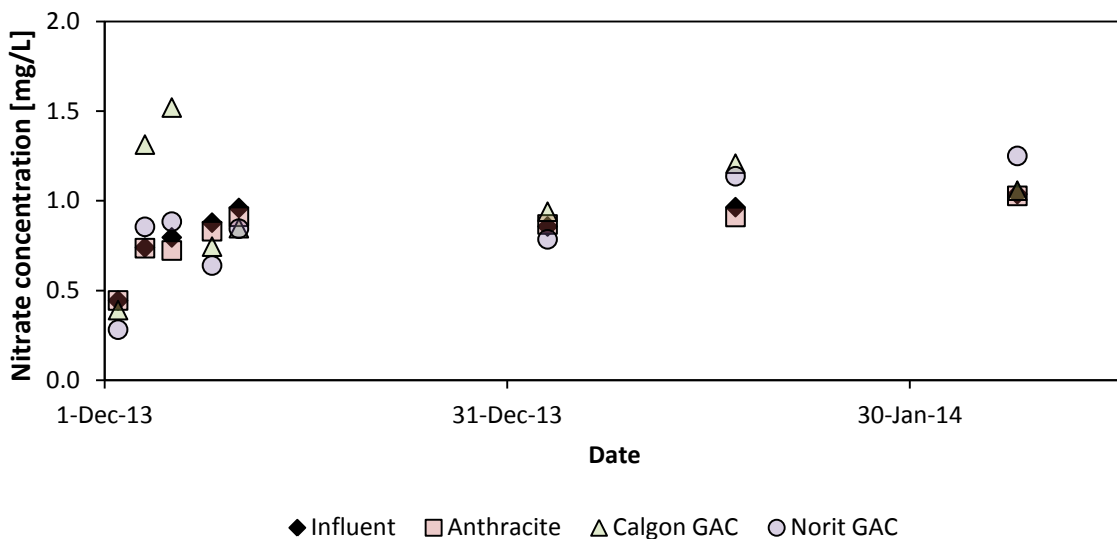

Figure 31: Nitrate concentrations (mean values form the values of Anthracite (3 columns), Calgon GAC (3 columns) and Norit GAC (2 columns).

At a filter start-up phase biological activity is assumed to be absent or negligible. When the filters later become biologically active, nitrifying bacteria can influence the balance between nitrogen species– by e.g. degradation of ammonia to nitrite and nitrate. Studies of the filter media microbial composition might then provide further information – identifying the organisms responsible for the nitrification.

6.7 Particle count and distribution

Particle count numbers can be found in Appendix D. Measurements from 2013 generally show about 10 times higher counts than in 2014. No obvious reason for this clear gap was found, and measurements from 2013 are assumedly giving artificially high counts. The reason for this is not known, but might be related to some flaw in the procedure of sampling or the operation of the particle counter in extraction of the 2013 data. Because of the mentioned gap, no trends are observed in the particle count data over time. For this reason, particle count data analysis is suggested to be resumed at a later stage, when more data is provided, and will not be given comprehensive attention in this report.

With the individual particle counts, the Multisizer[TM]3 instrument also presents the particle size distribution of the counted particles. Figure 32 shows such a distribution, presenting particle data from operation day 45 (January 3rd). The distribution only represents one instant, but anyhow it suggests that particles are removed with similar rates in Calgon GAC, Norit GAC and anthracite. A similar distribution for both GAC and anthracite filter effluents implies that sorption is not contributing to removal of particles with diameters greater than 1.3 µm. Figure 32 shows that the filters remove particles of all sizes (within the detection range of 1.3 to 11.4 µm), and how smaller particles are more numerous than bigger particles.
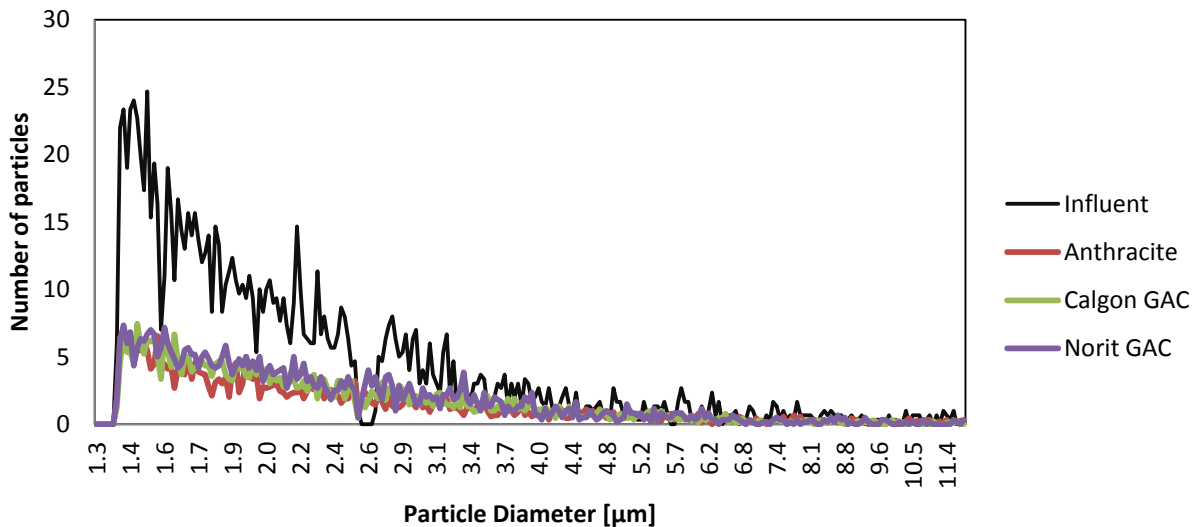

Figure 32: Particle size distribution from operation day 45 (January 3rd 2014)

6.8 Turbidity

Turbidity was measured at various levels in the influent throughout the first 120 operation days of the pilot-scale filters. Figure 33 shows the turbidity over the first 4 months of filter operation. Notable in the influent data, there are two periods of turbidity consistently below 1 NTU (days 8-22 and days 46 to 69), and tree periods (days 0-8, days 22-46 and days 88-120) of significantly higher measured influent turbidity to pilot plant. River water often has highly fluctuating turbidity, making the two periods with constant turbidity below 1 NTU questionable as reflections of the reality. The filter influent has been preceded by coagulation, flocculation and sedimentation throughout both the low and the higher inflow turbidity periods.
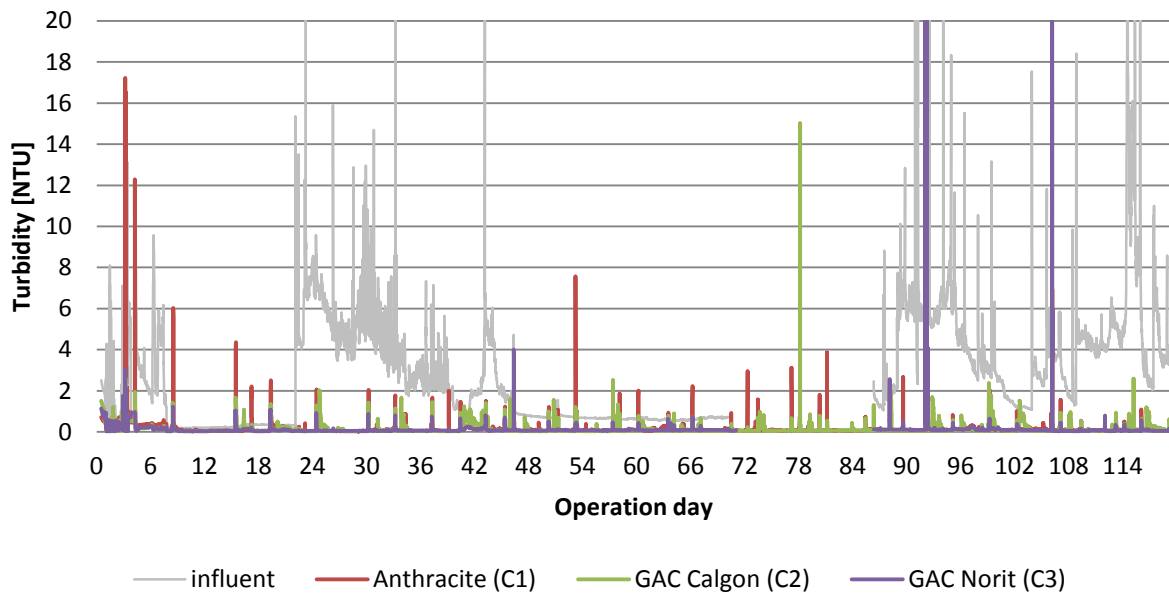

Figure 33: Turbidity data from the 119 first pilot-scale filtration plant. (Note that data from the influent and from the Norit GAC filter is missing between operation days 69 to 85)

Despite two periods of peculiarly low values in the influent turbidimeter, the filter effluents show consistent turbidity throughout the first 120 operation day. Average effluent turbidities are in the same exact range with 0.14, 0.15 and 0.14 for Anthracite, Calgon GAC and Norit GAC , respectively. There are several protruding turbidity peaks in the filter effluent data (Figure 33), seemingly related to the first moments after backwash, when the filter bed has just resettled.

The backwash related peaks in turbidity are demonstrated by Figure 34 – which gives a representative picture of the turbidity measurements around the time of filter backwash. Normally a water utility will send the first filtered water after a backwash to waste. Both GAC filters need a little less than one hour of ripening time, recovering turbidity levels below the critical 0.3 NTU, whereas the anthracite filter used one hour exactly. In order to fulfill the requirement from American regulations, of 95% of monthly turbidity samples below 0.3 NTU, it is recommendable to send filtered water to waste for at least one hour after backwash based on the results of this study.
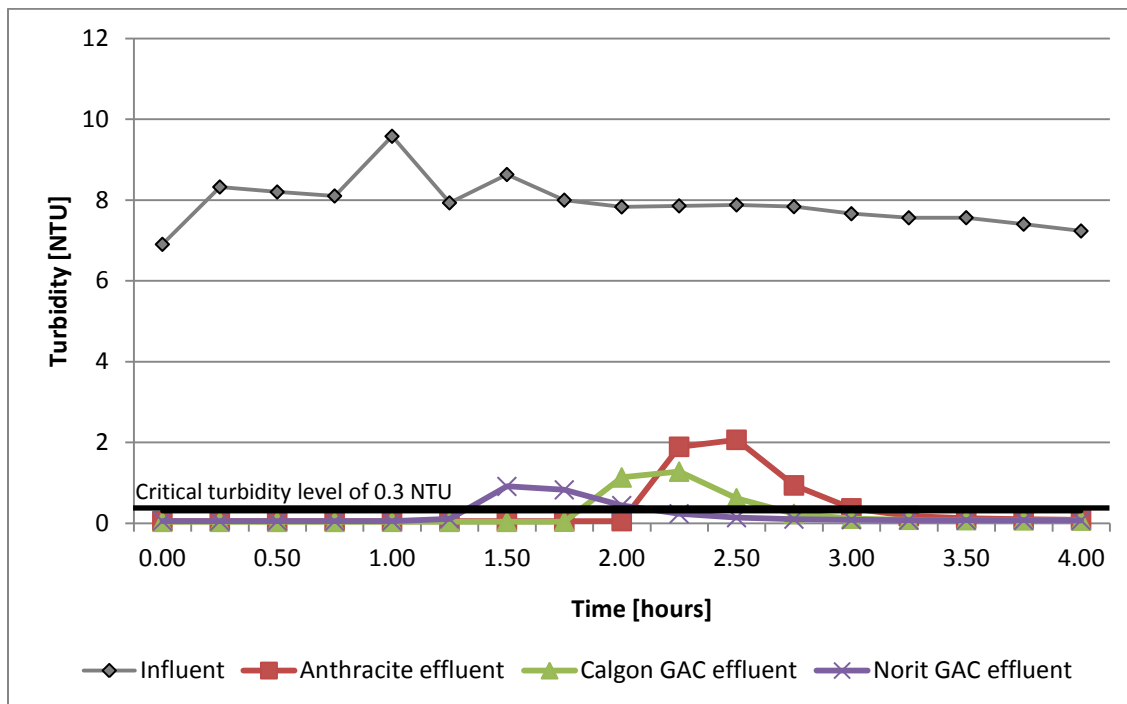

Figure 34: Turbidty measurements at MWW pilot plant through 4 hours in the afternoon of December 11th 2013. The elevated turbidity levels in the effluents coincide with the moments after backwash.

7. Summary and Conclusions

Water aesthetics represent an important concern for water suppliers in many parts of the world. In Minnesota, United States, and throughout other northern climates, geosmin and certain other organic compounds pose seasonal threats to taste and odor in surface waters. Traditional water treatment by sedimentation, coagulation, flocculation, and filtration is often insufficient with respect to organic matter removal. One way of improving the removal organic water contamination is through sorption, which can be preceded by oxidation – in turn to make the organics more biodegradable and more available to adsorption. Activated carbon is widely used as sorbent, and is applied either as PAC or GAC. In this report, pilot-scale filter beds of different media are studied in order to address the potential benefits of using GAC sorption/filtration instead PAC sorption combined with anthracite filtration. In addition to studying data from the first 120 operation days of the pilot filtration plant, a batch reactor test was carried out to investigate the sorptive characteristics of two activated carbon products with respect to geosmin.

Removal of organic matter was evident in the GAC filter media and absent in the anthracite medium from organic carbon data. The study showed a gradual decrease in removal of dissolved organic carbon in the run of 120 filter operation days. At operation day 16, the GAC filters removed an average 100% of the DOC. At operation days 52 and 120 the average DOC removal by the GAC filters, were 53% and 32% respectively. TOC data coincided with the DOC data, suggesting that the organic carbon was mainly dissolved during the period of this study. A reduction in organic carbon removal was expected, as GAC filter media looses sorption capacity as water passes through. The gradual reduction found in this report, represents the expected sorption capacity development for the specific influent water used in this study.

Geosmin removal in the pilot-scale GAC filters was observed, with consistent effluent concentrations below the human detection threshold of 5 ng/L. Nevertheless, due to a modest number of data points, apparent problems of spiking the correct amount into the filter influent and some negative removal rates in the anthracite filters, it is difficult to draw further conclusions. The sorption isotherms, obtained from a batch reactor experiment, provide characteristics of the geosmin removing capability of virgin activated carbon media. The isotherms were established based on water from the filtration influent at Minneapolis Water Works in December 2013, and are aimed to reflect sorption in projected GAC filters in this water utility. The sorption batch data fitted best with linear and Langmuir isotherm models, for both activated carbon products that were included in the experiment.

With respect to other water quality parameters that were given attention, GAC performed equally well or better than anthracite filters. Ammonium and nitrate were measured in low concentrations in both filter influents, while nitrite never was detected in the sample data of this report. No difference between GAC and anthracite filters was found with respect to turbidity and particle removal.

The installation of GAC medium filters, replacing previous anthracite at the St. Paul Regional Water Services, helped reduce T&O episodes; emphasized with the results of this study, it suggests that T&O problems at MWW can be reduced. GAC filters from both manufacturers Calgon and Norit look to function as supposed, and performance does not differ significantly between the two. Based on this study, the type of GAC for the new filters at Fridley Filtration Plant at MWW should be chosen based on what is economically beneficial.

The research project in Minneapolis is still progressing and the MWW pilot filtration plant is kept in operation, at least until the summer of 2014. A prolonged timeline of data will be obtained, which should be carefully considered, as it will draw a longer term picture of the filters performance. An important aspect of the future studies of the pilot-scale GAC filters, will be the biological degradation of geosmin, as a biofilm is expected to be established after the first 3-4 months of filter operation. The filter start-up period relevant for this report, spanned from late October to March, covering the winter season. The filter performance during summer months could be valuable, as it is the peak season of geosmin occurrence.

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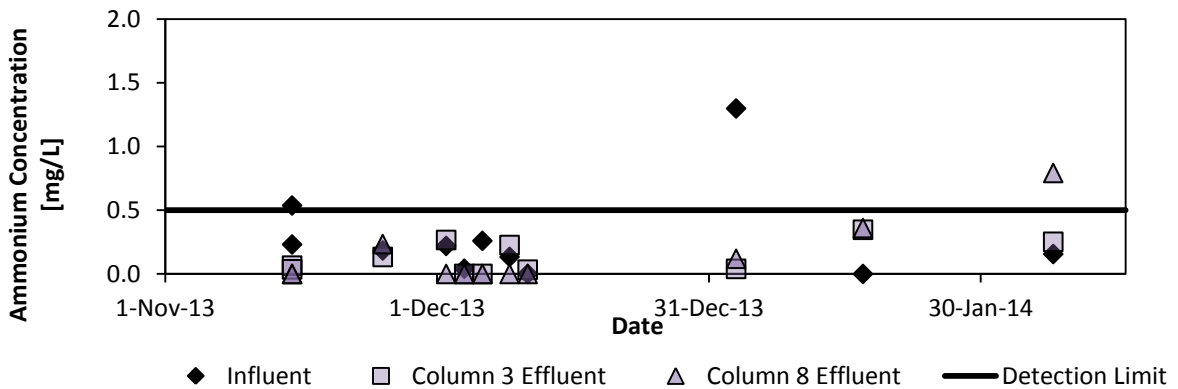
Appendix A: Ammonium Data
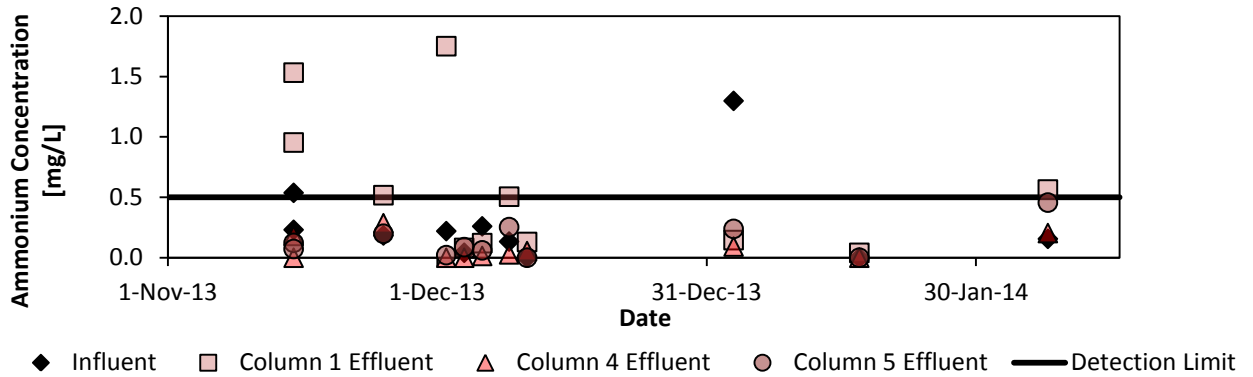
Ammonium concentrations in anthracite filter effluents
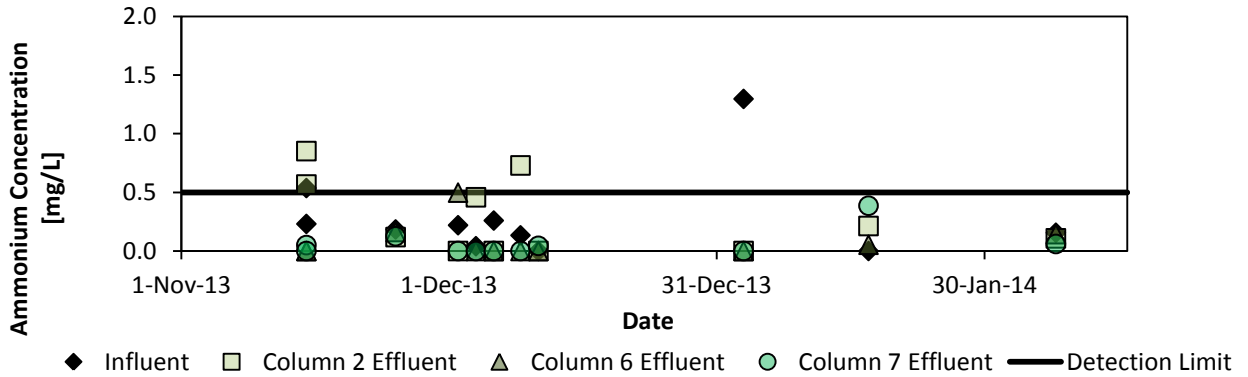
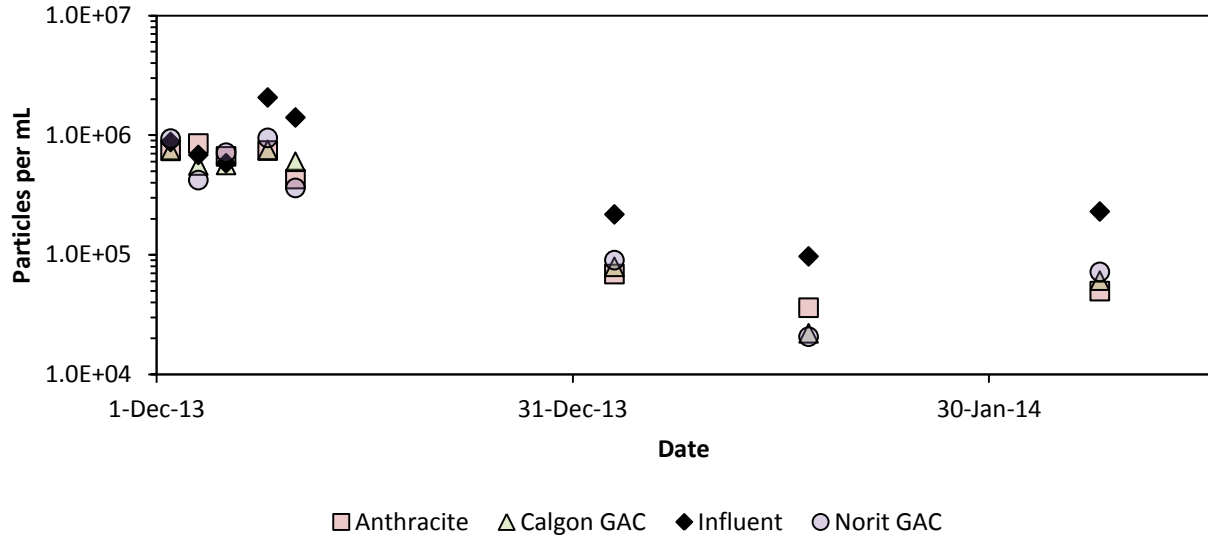Ammonium concentrations in Calgon GAC filter effluents

Ammonium concentrations in Norit filter effluents

Appendix B: Nitrate Data

Nitrate concentrations in anthracite filter effluents

Nitrate concentrations in Calgon GAC filter effluents

Nitrate concentrations in Norit GAC filter effluents
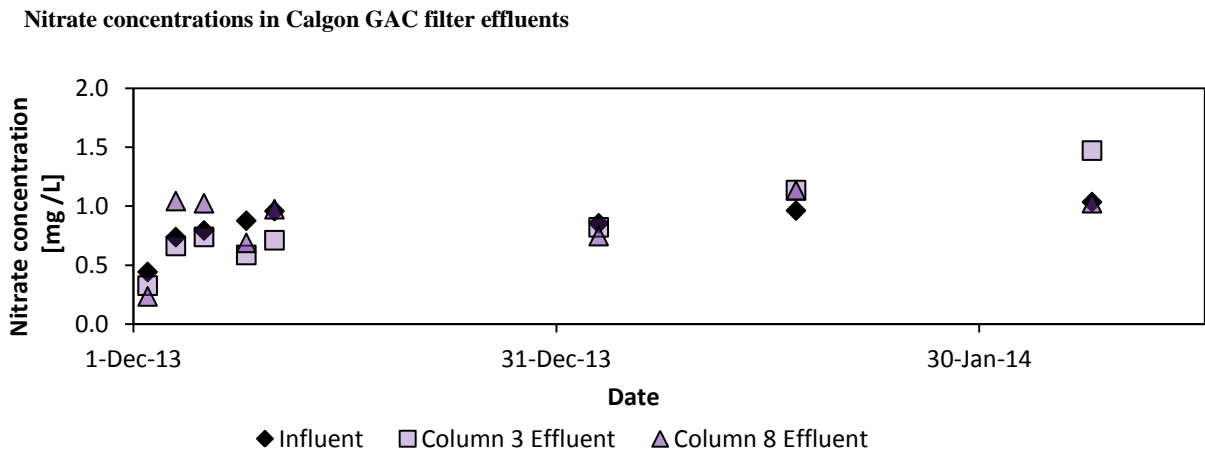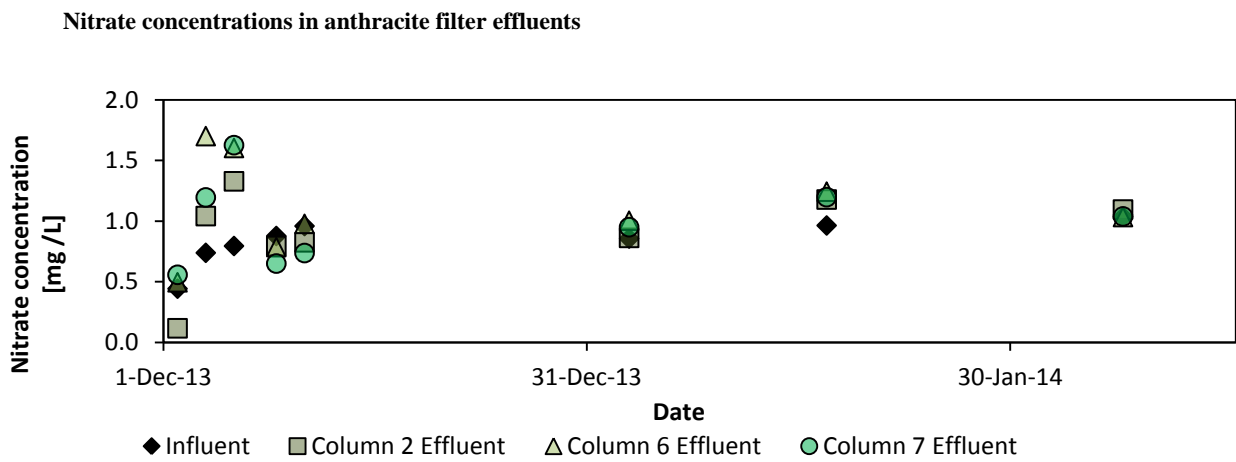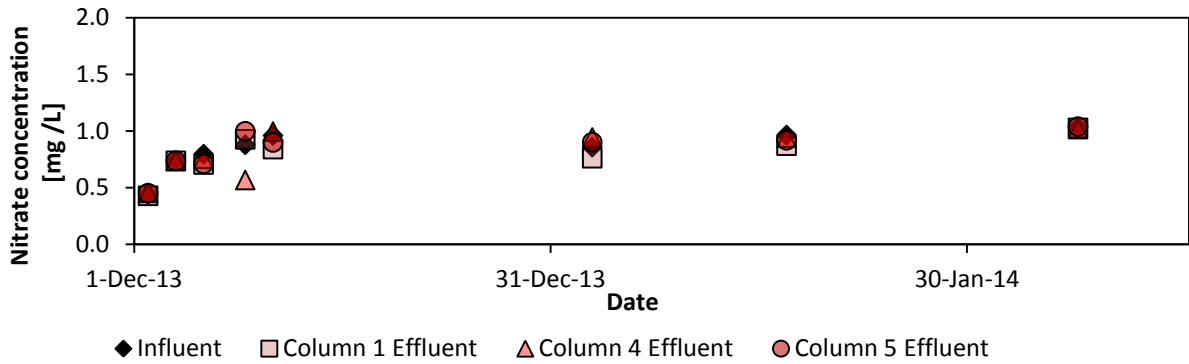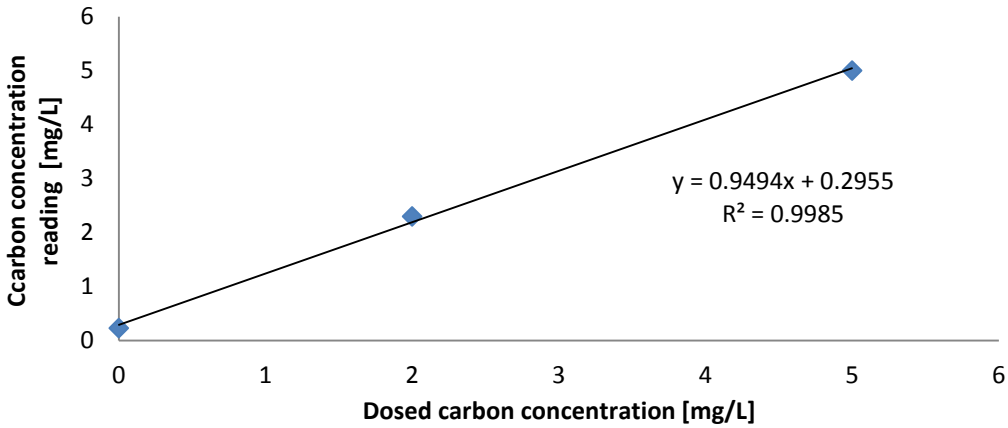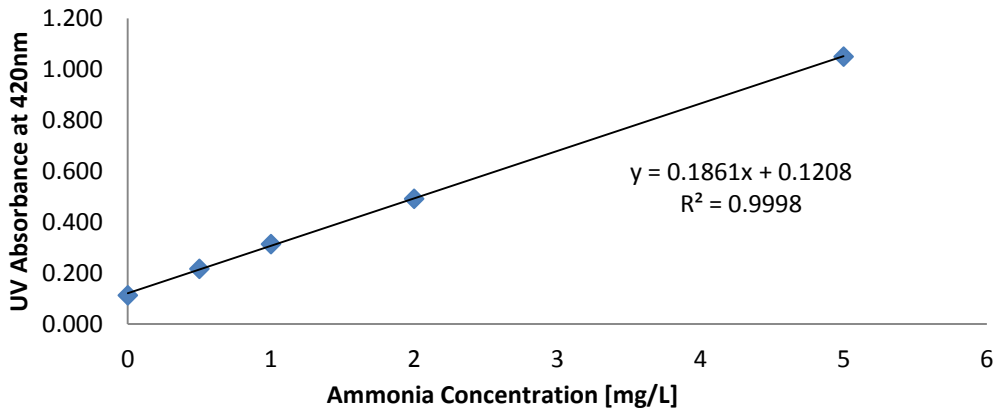
Appendix C: Particle Count Data

Particle count data. Note that the vertical axis has a logarithmic scale. Hence, particle counts from 2013 are in a range of 10 times higher than values of 2014.
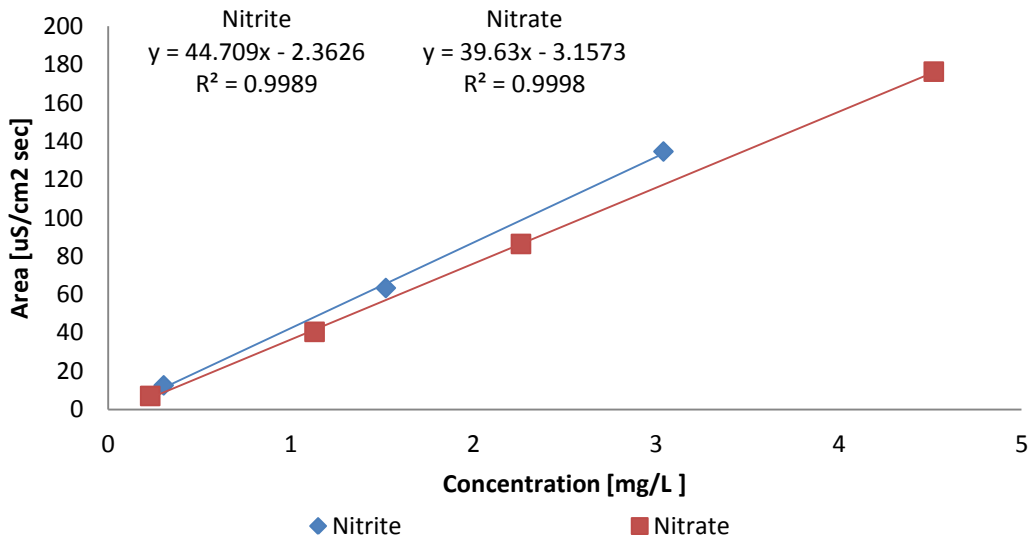
Appendix D: Standard Curves

$$y = 0.9494x + 0.2955$$
$$R^2 = 0.9985$$

Representative standard curve used for TOC and DOC. Obtained December 12 2013.

$$y = 0.1861x + 0.1208$$
$$R^2 = 0.9998$$

Representative standard curve used for ammonium determination. Obtained December 13 2013.

Nitrite
$$y = 44.709x - 2.3626$$
$$R^2 = 0.9989$$

Nitrate
$$y = 39.63x - 3.1573$$
$$R^2 = 0.9998$$

Representative standard curve used for nitrite/nitrate determination. Obtained December 10 2013.