



Doctoral Thesis

Adsorption capacity and biological activity of biological activated carbon filters in drinking water treatment

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**ADSORPTION CAPACITY AND BIOLOGICAL ACTIVITY OF
BIOLOGICAL ACTIVATED CARBON FILTERS IN
DRINKING WATER TREATMENT**

A dissertation submitted to
Swiss Federal Institute of Technology Zurich

for the degree of
Doctor of Sciences

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Abstract

Granular activated carbon (GAC) filters have been used for decades to remove various kinds of organic micropollutants (MP), disinfectant by-products and taste and odor (T&O) compounds from water by adsorption. In recent years chemical oxidation by ozonation was implemented in many treatment plants before GAC filtration. During ozonation a substantial fraction of the natural organic matter (NOM) present in surface waters is oxidized to smaller and biodegradable compounds thus giving rise to elevated assimilable organic carbon (AOC) concentrations. This fraction is readily metabolized by the biomass present in the GAC filter. To date, the removal processes occurring in GAC filters are not completely understood and therefore most GAC filters have been designed empirically. Improved drinking water quality requirements (regulations of European Union and U.S. Environmental Protection Agency) and the availability of innovative treatment technologies make it necessary to rethink the role of activated carbon applications in water works. This necessitates gaining a more detailed understanding of simultaneously occurring processes in GAC filters, in particular with regard to adsorption and microbiological processes.

The goal of this thesis is to determine the significance of GAC filtration for drinking water treatment within future process schemes. The research described in this thesis focused on:

- (1) Quantification of biomass in GAC filters,
- (2) Determination of biofilm development and growth rates,
- (3) Adsorption of individual NOM fractions,
- (4) Adsorption of methyl *tertiary*-butyl ether (MTBE), as an example of a hazardous MP in the absence and presence of adsorbed NOM and
- (5) Removal of 2-isopropyl-3-methoxypyrazine (IPMP), as a problematic T&O compound.

The first section of the thesis deals with the development and the implementation of innovative new analytical methods. A new method for the quantification of active biomass in GAC filters, based on ATP analysis in combination with flow cytometry was developed. Compared to existing methods, this method provides the advantage of direct and rapid biomass quantification leading to reproducible results. In addition, AOC was measured by enumerating the growth of a natural microbial consortium with fluorescence staining combined with flow cytometry. Compared to the conventional use of pure cultures combined with plating, the new AOC assay has the advantage of providing data rapidly. Another

sophisticated analytical method was used for the analysis of NOM with the help of size exclusion chromatography (SEC), which allows quantification of individual NOM fractions. Both methods have been newly established at Eawag. GAC surface area and pore size characterizations were performed based on the standard method of N₂ adsorption.

Attached biomass was quantified over time and space in three different GAC filters operated under similar conditions and with similar influent water quality. Starting with fresh GAC, biomass growth was observed as a function of time and filter depth. Over a time period of 90 days, biomass increased steadily, but at different rates in all investigated filter layers and leveled off at a constant value after ~ 90 days. The steady-state biomass concentration developed after this stage was comparable in the top layer of all three GAC filters. Biomass stratification was followed in a pilot-scale GAC filter over the entire investigation period of 198 days. Biomass concentration was highest at a depth of 45 cm from the GAC filter top and decreased with increasing filter bed depth. The biomass growth rates changed with time and space in the GAC filter during the entire growth period. The highest growth rates were determined in the upper 45 cm of the GAC filter. Variations could be ascribed to changes in AOC influx and NOM concentrations in the GAC filters.

NOM adsorption was determined over time and space in a pilot-scale GAC filter. Concentration of humics, building blocks, and LMW organics increased in the effluent until reaching a pseudo-steady-state after 168 days (12.21 min EBCT). Biopolymers were practically not removed and appeared from the beginning in the effluent. The characterization of different NOM fractions showed that the adsorbability of NOM increased with decreasing size: biopolymers < humics < building blocks < LMW organics. The adsorption capacity of GAC for NOM was influenced mainly by the pore volume in the pore size fraction between 1-50 nm and less by the total surface area and was already exhausted after 6 months (15.8 min EBCT). Therefore GACs with a high pore volume in the pore size fraction between 1-50 nm should be applied for the removal of mainly NOM.

When NOM adsorbs on the GAC surface, the GAC becomes preloaded and pore entrances get blocked. The consequence is a decrease in adsorption capacity for MPs, this process is very dynamic and takes place in a very short time (< 30 days). MTBE was chosen as a representative micropollutant typically found in most surface waters in small concentrations. During adsorption GAC experiments, changes in MTBE adsorption capacity were more pronounced than changes in total surface area and micropore volume. The preloading effect of NOM was more important than direct site competition with MTBE. The pore volume in the pore size fraction of 5.2-5.7 Å correlated most strongly with the MTBE

adsorption capacity. Thus, adsorbents with a narrow pore size distribution and a high pore volume in the 5.2-5.7 Å range seem most suited for the removal of MTBE. However, MTBE is a highly hydrophilic molecule and adsorbs only poorly on GAC. For an efficient MTBE removal, alternative processes, such as advanced oxidation, should be considered.

Removal of a frequently occurring T&O compound, 2-isopropyl-3-methoxypyrazine (IPMP), was investigated with GAC. Experiments were conducted with fresh GAC, used GAC and biologically active GAC in NOM containing and NOM free water, respectively. In bottle-kinetic experiments with fresh GAC, the IPMP concentration decreased to 20%, independently of the water source. On the contrary, isotherm experiments showed a decrease in adsorption capacity in the presence of NOM. Biological degradation of IPMP could not be detected. GAC pilot scale filtration showed a 100% removal within the upper 50 cm of a GAC filter (with fresh GAC), which is in agreement with the results of a lab-scale GAC filter. However, bottle-kinetic experiments results did not reflect these findings. Summarizing the different results of this study, it must be concluded that no reliable data could be gained which would allow describing the exact mechanisms and the extent of IPMP removal. System losses might provide a partial explanation for the inconsistent results.

The present investigations have shown that the explicit consideration of all aspects influencing GAC filters operated for adsorption and biological removal of organic matter is not a trivial task. It becomes obvious that not all desired tasks can be met in a single GAC step. Therefore the combination of GAC and eventually of PAC with other treatment steps has to be considered. Future research should consider the position of GAC within whole treatment trains including pre-treatment such as flocculation and ozonation as well as post-treatment such as disinfection and membrane filtration. It would also be of great help to establish computer tools based on the new experimental findings to mathematically describe the system such that simultaneously occurring physico-chemical and biological processes are taken into account. This would allow for the design and the optimization of GAC filters and of reduced amounts of selective experiments and analyses.

Zusammenfassung

Granulierte Aktivkohle (GAK) wird seit Jahrzehnten in der Trinkwasseraufbereitung eingesetzt, um verschiedene organische Spurenstoffe, Desinfektionsnebenprodukte und Geruchs- und Geschmacksstoffe durch Adsorption zu entfernen. In den letzten Jahren wurde in vielen Trinkwasserwerken die Ozonung als Vorstufe zur GAK Filtration eingeführt. Ein beträchtlicher Teil des im Zulauf, d.h. in Oberflächengewässern enthaltenen, natürlichen organischen Materials (NOM) wird während der Ozonung zu kleineren und biologisch abbaubaren Verbindungen oxidiert. Dies führt zu einer signifikanten Zunahme an assimilierbarem organischen Kohlenstoff (AOC), der durch die im GAK Filter etablierte Biomasse leicht abgebaut wird. Da die Entfernungsprozesse in GAK Filtern bisher nicht vollständig verstanden sind, werden GAK Filter in der Regel empirisch dimensioniert. Erhöhte Anforderungen an die Trinkwasserqualität (Regelungen der European Union und U.S. Environmental Protection Agency) sowie die Verfügbarkeit innovativer Behandlungstechnologien bedingen ein Überdenken der Rolle von GAK in der Trinkwasseraufbereitung. Dies macht ein detailliertes Verständnis der im GAK Filter zeitgleich stattfindenden Prozesse, insbesondere der Adsorptions- und mikrobiologischen Prozesse, erforderlich.

Das Ziel dieser Arbeit ist die Bedeutung von GAK Filtern zur Trinkwasseraufbereitung innerhalb zukünftiger Prozesskonzepte zu untersuchen. Der Schwerpunkt liegt hierbei auf:

- (1) Quantifizierung der Biomasse in GAK Filtern
- (2) Analyse der Entwicklung von Biofilmen und Bestimmung von Wachstumsraten in Biofilmen
- (3) Adsorption individueller NOM-Fractionen
- (4) Adsorption von Methyl-*tertiär*-butylether (MTBE) als Beispiel eines bedenklichen Spurenstoffs in Anwesenheit und Abwesenheit von adsorbiertem NOM und
- (5) Entfernung von 2-isopropyl-3-methoxypyrazine (IPMP) als Beispiel eines problematischen Geruchs- und Geschmacksstoffs.

Der erste Teil dieser Arbeit beschäftigt sich mit der Entwicklung und Anwendung neuer und innovativer analytischer Methoden. Für die Quantifizierung von Biomasse in GAK Filtern wurde eine neue Methode entwickelt, welche auf der Kombination von Adenosintriphosphat-Analyse (ATP) und Durchflusszytometrie beruht. Der Vorteil dieser Methode besteht in der

schnellen und direkten Quantifizierung, welche zudem reproduzierbare Ergebnisse liefert. Zur Quantifizierung von AOC wurde das Wachstum eines natürlichen mikrobiologischen Konsortiums anhand von Fluoreszenzfärbung und Durchflusszytometrie bestimmt. Im Vergleich zur konventionellen Methode, die auf dem Ausplattieren von Reinkulturen basiert, bietet die neue Methode den großen Vorteil der schnellen Datengenerierung. Eine weitere hochentwickelte analytische Methode, Size Exclusion Chromatography (SEC), wurde zur Analyse von NOM eingesetzt. Hierbei wird NOM nach Molekülgrößen fraktioniert, so dass einzelne NOM Fraktionen quantifiziert werden können. Diese drei Methoden wurden neu an der Eawag etabliert. Die Oberflächen- und Porengrößenverteilungen wurden mithilfe der Standardmethode der N₂ Adsorption durchgeführt.

Die Biofilm-Biomasse wurde in drei AK Filtern, welche unter ähnlichen Bedingungen und mit ähnlichen Wasserzusammensetzungen betrieben wurden, als Funktion von Zeit und Filtertiefe quantifiziert. Ausgehend von Filtern mit frischer GAK wurde das Biomassenwachstum als Funktion von Zeit und Filtertiefe untersucht. Innerhalb von 90 Tagen nahm die Biomasse in allen untersuchten Filterschichten mit unterschiedlichen Wachstumsraten zu und erreichte dann eine Gleichgewichtskonzentration. Die Biomassenkonzentration im Gleichgewichtszustand war in der jeweils oberen Schicht der drei GAK Filter vergleichbar. Die Stratifizierung der Biomasse wurde in einem GAK-Pilotfilter über den gesamten Untersuchungszeitraum von 198 Tagen verfolgt. Die Biomassenkonzentration war 45 cm unterhalb der GAK Filteroberfläche am höchsten und nahm mit zunehmender GAK Filterbetttiefe ab. Die Wachstumsraten der Biomasse variierten ebenfalls über die Versuchszeit und mit der Filterbetttiefe und waren in den oberen 45 cm des GAK Filters am höchsten. Schwankungen der Wachstumsraten konnten Änderungen der AOC Zulaufkonzentration und der NOM Konzentrationen im GAK Filter zugeschrieben werden.

Die NOM Adsorption wurde ebenfalls als Funktion von Versuchszeit und Filterbetttiefe in einem GAK-Pilotfilter untersucht. Die Konzentrationen von Huminsäuren, Building Blocks und niedermolekularen Säuren im Ablauf des GAK Filters nahmen stetig zu bis nach 168 Tagen (12.21 min EBCT) ein Gleichgewichtszustand erreicht wurde. Biopolymere wurden praktisch nicht entfernt und waren von Anfang an im Ablauf vorhanden. Die Charakterisierung der verschiedenen NOM-Fraktionen zeigte, dass die Adsorbierbarkeit mit abnehmender Molekülgröße zunimmt: Biopolymere < Huminsäuren < Building Blocks < niedermolekulare Säuren. Dabei wurde die Adsorptionskapazität der GAK für NOM hauptsächlich durch das Porenvolumen in der Porengröße 1-50 nm und weniger durch die Gesamtoberfläche bestimmt und war bereits nach 6 Monaten (15.8 min EBCT) erschöpft.

Wenn die Entfernung von NOM das Hauptziel ist, sollte eine AK mit hohem Porenvolumen in der Porengröße von 1-50 nm verwendet werden.

Durch die Adsorption von NOM an der GAK Oberfläche wird die GAK vorbeladen und Poreneingänge werden blockiert. Als Konsequenz kommt es zu einer Abnahme der Adsorptionskapazität für Spurenstoffe. Dieser Prozess ist sehr dynamisch und findet innerhalb kürzester Zeit statt (< 30 Tage). MTBE, welches in geringen Konzentrationen in nahezu allen Oberflächengewässern vorkommt, wurde als repräsentativer Spurenstoff ausgewählt. In GAK Adsorptionsexperimenten waren Änderungen der MTBE Adsorptionskapazität ausgeprägter als physikalische Änderungen der Gesamtoberfläche und des Mikroporenvolumens. Der Effekt der Vorbeladung mit NOM an der GAK hatte einen größeren Einfluss auf die Abnahme der MTBE Adsorptionskapazität als die konkurrierende Adsorption von NOM. Stärker als andere Faktoren, korrelierte das Porenvolumen in der Fraktion von 5.2-5.7 Å mit der MTBE Adsorptionskapazität. Dementsprechend scheinen Adsorber mit enger Porengrößenverteilung und hohem Porenvolumen im 5.2-5.7 Å Bereich für die effiziente Entfernung von MTBE am besten geeignet zu sein. Da MTBE sehr hydrophil ist, adsorbiert es allerdings nur schwach an GAK. Um eine effiziente Entfernung von MTBE zu erzielen sollten, daher alternative Prozesse, wie die Advanced Oxidation, berücksichtigt werden.

Die Entfernung eines häufig auftretenden Geruchs- und Geschmacksstoffs, 2-isopropyl-3-methoxy-pyrazine (IPMP), wurde mit GAK untersucht. Experimente mit frischer, gebrauchter und biologisch aktiver GAK wurden in Gegenwart und Abwesenheit von NOM durchgeführt. In Batchexperimenten mit neuer GAK nahm die IPMP Konzentration unabhängig von der Wassermatrix auf 20% ab. Im Gegensatz dazu zeigten Adsorptionsisothermen eine Abnahme der Adsorptionskapazität in Gegenwart von NOM. Ein biologischer Abbau von IPMP konnte nicht bestätigt werden. Experimente mit einem mit frischer GAK beladenen Pilotfilter zeigten eine 100%-ige IPMP-Entfernung innerhalb der oberen 50 cm des Filters. Dies ist in Übereinstimmung mit den Resultaten der GAK Batchfilterexperimente, jedoch nicht mit den Ergebnissen der Batchexperimente. Zusammenfassend war es anhand der Ergebnisse dieser Untersuchung nicht möglich, zuverlässige Daten zur Beschreibung der genauen Mechanismen und des Ausmasses der IPMP Entfernung zu generieren. Die Inkonsistenz der Ergebnisse könnte möglicherweise zum Teil durch Systemverluste erklärt werden.

Diese Arbeit zeigt, dass eine detaillierte Berücksichtigung aller Einflussfaktoren auf GAK Filter, welche für Adsorption und biologische Entfernung von organischen Substanzen

eingesetzt werden, eine anspruchsvolle Aufgabe ist. Es wurde deutlich, dass nicht alle angestrebten Ziele mit einem einzigen GAK Schritt erreicht werden können. Eine Kombination von GAK bzw. eventuell Pulveraktivkohle mit weiteren Aufbereitungsschritten sollte daher in Erwägung gezogen werden. Weitere Untersuchungen sollten auf die Positionierung des GAK Filters innerhalb einer Aufbereitungskette, einschließlich einer Vorbehandlung, wie Flockung und Ozonung, aber auch einer Nachbehandlung, wie Desinfektion und Membranfiltration, ausgerichtet sein. Es wäre ebenfalls hilfreich, basierend auf den neuen experimentalen Ergebnissen, Computermodelle zu entwickeln, welche das System unter Berücksichtigung zeitgleich ablaufender physikochemischer und biologischer Prozesse mathematisch beschreiben. Diese könnten bei dem Design und der Optimierung von GAK Filtern unterstützend eingesetzt werden. Des Weiteren könnten Experimente und Analysen durch den Einsatz von Modellen besser geplant und damit gezielt reduziert werden.

Contents

| | |
|--|-----|
| Acknowledgements | I |
| Abstract | III |
| Zusammenfassung | VII |
| Introduction | 1 |
| | |
| Chapter 1 Rapid and direct estimation of active biomass on granular activated carbon through adenosine tri-phosphate (ATP)..... | 17 |
| Chapter 2 Biomass development and stratification in a drinking water granular activated carbon (GAC) filter..... | 41 |
| Chapter 3 Characterization of natural organic matter adsorption on granular activated carbon adsorbers..... | 63 |
| Chapter 4 MTBE adsorption capacity and corresponding physical characteristics of granular activated carbon..... | 79 |
| Chapter 4A Changes in physical characteristics and MTBE adsorption capacity of granular activated carbon during operation of a pilot-scale adsorber..... | 81 |
| Chapter 4B Effects of natural organic matter preloading on physical characteristics and remaining MTBE adsorption capacity of granular activated carbon..... | 101 |
| Chapter 5 Removal of 2-isopropyl-3-methoxypyrazine (IPMP) with granular activated carbon: from lab scale to pilot scale..... | 109 |
| Conclusions | 125 |
| Curriculum Vitae | 137 |

Introduction

In Switzerland, granular activated carbon (GAC) filters are used in most modern water works treating surface waters. GAC is usually applied for a variety of reasons such as removing taste and odour (T&O) compounds and improving the biological stability of drinking water.

In recent years, GAC filters are mostly combined with a preceding ozonation step where substantial fractions of natural organic substances are oxidized to biodegradable compounds that are subsequently biologically degraded in GAC filters (Lee et al., 1981; Servais et al., 1991; Velten et al., 2007; Hammes et al., 2008). The latter step, also called biofiltration, is a biofilm process that stabilizes drinking water biologically, i.e. it prevents potential bacterial re-growth during distribution. In addition, biofiltration avoids the manifold quality problems associated with biological instability: high chlorine demand, formation of disinfection by-products, accelerated corrosion, T&O compounds, high turbidity, and increased numbers of coliforms (Rittmann and Stilwell, 2002).

Concurrently, GAC filters are used in adsorption mode for the removal of micropollutants (MP) such as pharmaceuticals, halogenated hydrocarbons and T&O compounds (Knappe et al., 1999; Knappe et al., 2003; Rossner and Knappe, 2007). Apart from the chemical substance characteristics, the effectiveness of adsorption processes strongly depends on the physical characteristics of the GAC (Lee et al., 1981; Summers and Roberts, 1988; Karanfil and Kilduff, 1999). Natural organic matter (NOM) also adsorbs on GAC, thereby decreasing the MP adsorption capacity of GAC, thus, leading to considerable economic losses. Due to the fact that water treatment plants generally operate GAC adsorbers continuously, the presence of background NOM decreases GAC adsorption capacity even when the target MP is absent in the source water (Summers et al., 1989; Munz et al., 1990).

The main aim of this thesis was to determine the significance of GAC filtration within future process schemes for drinking water treatment that include membrane and ozonation treatment steps. The focus was upon biological activity and adsorption capacity for NOM and MPs, with the objective to provide further insight into crucial adsorption processes allowing for further improvement of process reliability and efficiency of GAC filters.

The main contribution of this thesis is a better insight and understanding of the development and stratification of biofilms in GAC filters over time and space by using a newly developed method for the quantification of bacterial biomass based on ATP (adenosine-tri-phosphate) measurements. Further, the role of GAC filters as adsorbers for the removal of NOM and for methyl *tertiary*-butyl ether (MTBE) and 2-isopropyl-3-methoxypyridine (IPMP),

as a relevant MP in natural waters, is investigated and evaluated in view of a consistent and cost efficient operation of activated carbon filters in potable water treatment.

Problem identification

GAC filters have been used for decades to remove organic compounds from water by adsorption. Due to its large surface area and its chemical surface characteristics, GAC is an ideal solid material to remove dissolved organic compounds in water. Removal of DOC is important because some organic substances may act as precursors in the formation of disinfection by-products that may be carcinogenic or alter the organoleptic perception such as taste and odor, and biodegradable compounds can lead to bacterial re-growth in the distribution system (Servais et al., 1991).

Numerous studies have been performed on the adsorption capacity of GAC for a large range of organic compounds. Filtration by GAC has proven very effective for the removal of certain compounds present at high concentrations. At low concentrations and in the presence of a variety of compounds, the adsorption process shows to be less effective. When GAC filters are applied as biofilters, the removal continues to remove organics far beyond the point at which the adsorption capacity would normally be exhausted (Jekel, 1982). It has been suggested that this removal is the result of the activity of microbial communities that colonize the external surface and macropores of the GAC granules (Servais et al., 1991; Urfer et al., 1997; Fonseca et al., 2001).

When the ultimate purpose of GAC filters is adsorption of NOM and/or MPs, the carbon is replaced or reactivated frequently in order to maintain sufficient adsorption capacity (Munz et al., 1990). Alternatively, some drinking water works use the GAC over an extended time period (up to 20 years). In this case, the focus shifts from adsorption towards biological degradation for the removal of organic carbon (Lee et al., 1981; Servais et al., 1991; Velten et al., 2007; Hammes et al., 2008). Most biofilters are designed empirically. However, a detailed understanding of the simultaneous biological and physico-chemical adsorption processes in GAC filters is necessary. Also models need to be developed that can help to set up criteria for design and optimization of GAC filters to ensure an efficient and safe drinking water production.

In Switzerland, an appreciable number of treatment plants need to be renovated or reconstructed within the next 20-30 years. Also, improved drinking water quality requirements (regulations of EU and USEPA), the availability of new and innovative

treatment technologies and the need for more efficient treatment scenarios are the most important factors arising at the moment, giving rise to rethink present water treatment schemes. The significance of GAC filters within this framework needs to be identified.

The present studies were conducted as part of the Project Wave21', an interdisciplinary project which was set up at Eawag in collaboration with the Zürich waterworks (WVZ) and the industrial partner WABAG, Winterthur. Within Eawag, several groups including environmental microbiologists, chemists and engineers interacted within Wave21. The project focused on the supply of drinking water from surface waters in Switzerland and investigated the treatment technologies ozonation, activated carbon filtration and ultrafiltration. In particular, the relationship between raw water parameters and treatment processes was studied to gain a better understanding of the performance of processes and the resulting drinking water quality. In addition to already established methods, methods newly developed at Eawag, such as size exclusion chromatography for NOM, new T&O analytical methods, analysis of assimilable organic carbon and biomass determination on GAC were applied.

Research questions addressed

Methods and criteria for the determination of the biological activity of GAC filters

The presence of microbial biofilms in GAC filters has been evident for decades. Bacteria colonize the external surface of GAC granules and reach at stable treatment conditions a steady state, assuming that the amount of biomass is in a state of dynamic equilibrium between growth and decay. These bacteria contribute to the functionality of the treatment system through the removal of biologically available organic carbon. Removal of the biodegradable organic carbon is an essential step in the drinking water treatment chain. Such a removal of growth-supporting nutrients contributes to the biological stability of the water and may avoid the use of disinfectants (van der Kooij, 2000; Hammes et al., 2007).

Various methods have been developed to assess the activity of biomass present in a GAC filter (Dewaters and Digiano, 1990; Stewart et al., 1990; Servais et al., 1991; Servais et al., 1994; Wang et al., 1995; Fonseca et al., 2001; Urfer and Huck, 2001; Magic-Knezev and van der Kooij, 2004; Seredynska-Sobecka et al., 2006). The main problems that most of these methods face are the heterogeneity of colonised GAC and the correct quantification of

natural bacterial communities (Magic-Knezev and van der Kooij, 2004). In order to deal with these problems, several methods use additional steps to remove the biomass from the GAC surface before analysis. However, the additional analytical treatment steps require additional equipment. They also make the determination complex time consuming and can lead to errors. Therefore a direct and straight-forward method for the estimation of active biomass on GAC granules is essential. The following questions were addressed in this context:

1. How can the active biomass on GAC be quantified with an accurate and reproducible method? Which analytical methods are appropriate for this purpose?

(Chapter 1)

2. How does biomass development during start-up of a GAC filter proceed and what are the biomass concentrations reached at steady state?

(Chapter 1, 2)

Quantification of biomass over time and space for the characterization of biological filters

Since a considerable part of the DOC removal can be attributed to biological processes, it is important to be able to quantify the microbial component responsible for these processes. In dynamic phases, any growth in the filter amounts to an increase in biomass, in both biofilm and suspended cells. In dynamic and steady states, the biomass that is washed out requires additional treatment.

Whichever post-treatment is applied, a clear understanding and quantification of the biomass in and released from the filter are necessary. In addition, the determination of kinetic parameters such as growth rates and DOC and assimilable organic carbon (AOC) removal rates are important. Quantitative knowledge of the system would allow optimization in design, operation and monitoring of the system, as well as contribute to the development of models describing these systems (Rittmann and Stilwell, 2002). The following questions were addressed:

3. How does biomass develop over filter depth? Can a vertical stratification effect of fixed biomass be identified?

(Chapter 2)

4. How do NOM and AOC influx concentrations and subsequent adsorption in the depth of the GAC filter influence biomass growth during GAC start-up and steady state in different layers?

(Chapter 2)

Characterization of NOM adsorption on GAC

NOM interferes in most processes utilized for drinking water treatment. During ozonation, for example, NOM can act as precursor for halogenated disinfection by-products (DBPs) and AOC (von Gunten, 2003). During GAC filtration NOM adsorbs and rapidly decreases the adsorption capacity of GAC. The extent of NOM adsorption and the consequences on MP removal effectiveness are difficult to predict because aquatic NOM varies in character both spatially across different water sources and temporally within a water source (Owen et al., 1993; Matsui et al., 2002). To date, little is known about the adsorption behavior of individual NOM fractions during the start-up phase of a GAC filter when adsorptive removal dominates. For the improvement of GAC filter treatment efficiency it is essential to understand the adsorption and breakthrough behavior of DOC and individual NOM fractions. Therefore, it is necessary to consider effects of preceding and subsequent processes in the treatment chain. Therefore the following question was asked:

5. What is the adsorption behavior of individual NOM fractions and what is the adsorption capacity of GAC for individual NOM fractions?

(Chapter 3)

Changes in physical GAC characteristics and concurrent loss in MP adsorption capacity over time

GAC filters are also applied to remove certain organic MPs from drinking water sources. At the same time NOM is usually present in the water source in much higher concentrations and adsorbs on GAC. As GAC filters are operated on a continuous basis, NOM decreases the GAC adsorption capacity also when MPs are absent. GAC filters are often used for many years because of their biological activity and are therefore heavily loaded with adsorbed NOM. Thus, adsorption capacity for MPs is reduced substantially by the preloading effect of NOM. (Munz et al., 1990; Knappe et al., 1998; Newcombe et al., 2002; Quinlivan et al., 2005). The effect of GAC service time on concurrent losses of MP adsorption capacity and on the changes in physical GAC characteristics need to be understood. Furthermore, a correlation

between physical GAC characteristics and the remaining MP adsorption capacity would be useful to determine GAC replacement needs. The following questions were addressed:

6. What are the effects of GAC service time on GAC characteristics and MP adsorption capacity?

(Chapter 4)

7. How does pore size distribution correlate with MP molecule size during adsorption? How important is the pore volume in the relevant pore size for the removal of a specific MP?

(Chapter 4)

Removal of T&O compounds with GAC

The presence of T&O compounds in drinking water is a frequent problem for drinking water works. Although T&O compounds do not pose any toxicological threat to humans, it affects the public's perception concerning the safety of drinking water already in ng/L concentrations. The combination of ozone together with hydroxyl radicals has shown to be a promising treatment (Peter and von Gunten, 2007). Depending on the molecular structure of T&O compounds, the residuals leaving the ozonation step may still be significant. These residuals, however, can be removed by GAC filtration below threshold concentrations. Among several T&O compounds, occurring seasonally in lake water, 2-isopropyl-3-methoxypyrazine (IPMP) is a relevant compound.

To date, only a few studies have been carried out on the removal of IPMP with GAC. Firstly, it is important to gain an understanding of the processes responsible for the removal, whether they are biological or adsorptive. Further information on removal kinetics and adsorption capacities for fresh and aged GACs is required. The following questions were addressed:

8. What is the responsible process for the removal of IPMP? What is the adsorption capacity of GAC for IPMP?

(Chapter 5)

9. What is the effect of GAC service time on the removal kinetics and the removal efficiency of IPMP?

(Chapter 5)

Outline of the thesis results

This thesis is structured as a paper dissertation. The different chapters have been either published, submitted for publication or are in preparation for publication. For this reason, not all the content follows a linear presentation and some information overlaps. The thesis was built up following the structure of the chapters described below.

Chapter 1 “**Rapid and direct estimation of active biomass on granular activated carbon through adenosine tri-phosphate (ATP)**” presents the development of an accurate and sensitive method to assess the amount of active biomass in GAC filters. In this method, we combined newly established analysis of flow-cytometric absolute cell counting and ATP analysis to derive case-specific ATP/cell conversion values as an innovative approach. As a result, measured ATP results could be converted to active cell numbers in all cases tested. Additionally, an uncertainty assessment has shown the percentage contribution of different parameters to the total uncertainty of the ATP method. A standard uncertainty of 15% shows that the ATP method is sensitive and applicable to cases where large variations can be expected, such as the start-up phase of a GAC reactor. The ATP method was applied to investigate biofilm formation during the start-up phase of a pilot-scale GAC filter and to assess the amount of active biomass in a full-scale GAC filter. Similar influent characteristics resulted in comparable biomass concentrations of 609 ng ATP/g GAC and 1820 ng ATP/g GAC, respectively.

Chapter 2 “**Biomass development and stratification in a drinking water granular activated carbon (GAC) filter**” focuses on the complete biomass quantification of a pilot plant GAC filter treating ozonated lake water as part of a drinking water treatment chain. Cultivation-independent tools were applied to assess biofilm formation on GAC and the release of suspended cells as a function of filter depth and time. Stratification of sessile and suspended biomass concentration during both the start-up phase and the steady state phase was observed in different layers. At steady state, the average biofilm concentrations over the GAC filter depth ranged from 800 to 1830 ng ATP/g GAC. These results are similar to values reported previously. Furthermore, different growth rates for biomass fixed on GAC could be calculated for both space and time variations. Also, the development of biomass on GAC and as suspended cells could be described by changes in availability of AOC and DOC, respectively.

Chapter 3 “**Characterization of natural organic matter adsorption on granular activated carbon adsorbers**” analyses the breakthrough behaviour of DOC and individual NOM fractions such as biopolymers, humic substances, building blocks and low molecular weight organics in pilot-scale GAC adsorbers and compares the adsorbability of individual NOM fractions on two GACs with different physical characteristics. Concentrations of humic substances, building blocks and low molecular weight organics increased gradually in the effluent of the GAC filter until reaching a steady state. Biopolymers were poorly removed, which may be due to their large size preventing access to the internal pore structure of GAC as well as their hydrophilicity. NOM adsorption uptake was higher for the GAC with a higher accessible surface area. Partition coefficient values (K_p) suggest that the adsorbability of NOM fractions increased with decreasing size; i.e. biopolymers < humics < building blocks < LMW organics.

Chapter 4 “**MTBE adsorption capacity and corresponding physical characteristics of granular activated carbon**” Referring to this research topic, two papers have been produced with a somewhat different content. The publication mentioned under chapter 4A represents a description of the research carried out with MTBE adsorption in lab and pilot scale during my stay at North Carolina State University. A shorter version is accepted as a conference paper. The second paper under chapter 4B includes also results on MTBE adsorption in full scale GAC investigations at the Zurich water works.

Chapter 4A “**Changes in physical characteristics and MTBE adsorption capacity of granular activated carbon during operation of a pilot-scale adsorber**” shows the impact of GAC service time on changes in physical GAC characteristics and the loss of MTBE adsorption capacity. NOM preloading strongly affected the remaining adsorption capacity of the GAC treating low DOC water. The remaining adsorption capacity of the preloaded GAC in ultra pure water and NOM containing water was similar at a given service time, suggesting that direct site competition between MTBE and NOM did not occur. GAC characteristics, such as the total surface area and micropore volume, did not correlate well with the loss in MTBE adsorption capacity. However, the pore volume in the 5.2-5.7 Å pore range correlated well with the remaining MTBE adsorption capacity, suggesting that the pore volume fraction, with a pore size similar to the dimension of MTBE, is mainly responsible for MTBE adsorption. A comparison of two tested GACs with different primary micropore volume showed that the higher the primary micropore volume, the higher the adsorption capacity for MTBE.

Chapter 4B “**Effects of natural organic matter preloading on physical characteristics and remaining MTBE adsorption capacity of granular activated carbon**” compares the MTBE adsorption capacities of preloaded GAC samples obtained from full-scale GAC adsorbers with those of corresponding fresh GAC samples and quantifies changes in the physical GAC characteristics that occur during full-scale GAC operation. MTBE adsorption capacities of used GACs were lower than those of the corresponding fresh GACs. Also, with increasing time of operation, the remaining MTBE adsorption capacity of the used GACs decreased. After 12 months of operation, the remaining adsorption capacity decreased to 11% of the initial. On the other hand, after 4 and 9 months of operation, BET surface area and micropore volume decreased only slightly (< 20%). Comparing fresh and used GACs, changes in MTBE adsorption capacities were more pronounced than changes in physical characteristics.

Chapter 5 “**Removal of 2-isopropyl-3-methoxypyrazine (IPMP) with granular activated carbon: from lab scale to pilot scale**” shows the results of different experimental conditions for the removal of IPMP including variation of the NOM matrix in the water and the GAC characteristics. Experiments with fresh, used and biological active GAC were conducted in nano-pure water and DOC containing water, respectively. Bottle kinetic experiment with fresh and 20-years-old GAC showed, independent of the water source, an IPMP removal of 80% and 60%, respectively. Isotherm experiments in contrast revealed a decrease in adsorption capacity in the presence of NOM. In fixed-bed kinetic experiments with fresh GAC, 100% of the initial IPMP concentration was removed. Biological degradation of IPMP could not be proven in bottle-kinetic experiments. This study has shown that experiments with T&O compounds are challenging and that the results are not consistent. Thus, we have observed that filter experiments have a higher removal capacity for IPMP than bottle experiments; however, we can not give an explanation for this finding. It became obvious that considerably more research would have to be carried out in order to come up with reliable data on the IPMP removal performance of GAC filters.

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Rapid and direct estimation of active biomass on granular activated carbon through adenosine tri-phosphate (ATP)

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Abstract

Granular activated carbon (GAC) filtration is used during drinking water treatment for the removal of micropollutants such as taste and odour compounds, halogenated hydrocarbons, pesticides and pharmaceuticals. In addition, the active microbial biomass established on GAC is responsible for the removal of biodegradable dissolved organic carbon compounds present in water or formed during oxidation (e.g., ozonation and chlorination) processes. In order to conduct correct kinetic evaluations of DOC removal during drinking water treatment, and to assess the state and performance of full-scale GAC filter installations, an accurate and sensitive method for active biomass determination on GAC is required. We have developed a straight-forward method based on direct measurement of the total adenosine triphosphate (ATP) content of a GAC sample and other support media. In this method, we have combined flow-cytometric absolute cell counting and ATP analysis to derive case-specific ATP/cell conversion values. In this study, we present the detailed standardisation of the ATP method. An uncertainty assessment has shown that heterogeneous colonisation of the GAC particles makes the largest contribution to the combined standard uncertainty of the method. The method was applied for the investigation of biofilm formation during the start-up period of a GAC pilot-scale plant treating Lake Zurich water. A rapid increase in the biomass of up to 1.1×10^{10} cells/g GAC dry weight (DW) within the first 33 days was observed, followed by a slight decrease to an average steady-state concentration of 7.9×10^9 cells/g GAC DW. It was shown that the method can be used to determine the biomass attached to the GAC for both stable and developing biofilms.

Keywords

ATP, Biomass, Granular activated carbon (GAC), Drinking water

Introduction

Granular activated carbon (GAC) filters have been used for decades to remove organic compounds by adsorption. In addition to the adsorption of organic matter, GAC is also an excellent support material for the development of biofilms. GAC filters continue to yield effective organic matter removal far beyond the point where adsorption capacity is normally exhausted (Jekel, 1982). This removal is a result of the activity of autochthonous microbial communities that colonise the external surface and the macropores of GAC particles (Urfer et al., 1997; Fonseca et al., 2001). In drinking water treatment, GAC filters are often placed

directly after oxidation reactors. During ozonation, for example, natural organic matter (NOM) is oxidised to low molecular weight oxygen-containing organic carbon molecules (von Gunten, 2003). This increases the biodegradable fraction of dissolved organic carbon (DOC), which is usually expressed as the concentration of assimilable organic carbon (AOC) (van der Kooij et al., 1989; Volk and Lechevallier, 2002; Hammes et al., 2006), biodegradable dissolved organic carbon (BDOC) (Escobar and Randall, 2001) or “fast/slow” BDOC (Yavich et al., 2004), depending on the analysis method used. Removal of this biodegradable fraction is an essential step in the drinking water treatment chain (van der Kooij et al., 1989).

In order to conduct correct kinetic evaluations of DOC removal during drinking water treatment, and to assess the state and performance of full-scale GAC filter installations, an accurate and sensitive method for active biomass determination on GAC is required. Various methods have been developed to assess the activity or biomass present in a GAC filter. These include epifluorescence microscopic total cell counts (Dewaters and Digiano, 1990; Servais et al., 1994), heterotrophic plate counts (HPCs) (Stewart et al., 1990), reduction of 2-(p-iodo-phenyl)-3-(p-nitrophenyl)-s-phenyltetrazolium chloride (INT) (Fonseca et al., 2001), phospholipid analysis (Wang et al., 1995; Seredynska-Sobecka et al., 2006), uptake of labelled substances (Servais et al., 1991), biomass respiration potential (BRP) (Urfer and Huck, 2001) and adenosine tri-phosphate (ATP) analyses (Magic-Knezev and van der Kooij, 2004).

The main problems that most of these methods face are the natural heterogeneity of colonised GAC and the correct quantification of natural bacterial communities. In order to deal with these problems, several methods use additional steps, such as sonication, to remove the biomass from the GAC surface before analysis (Magic-Knezev and van der Kooij, 2004). However, additional treatment steps require additional equipment, make the determination complex and time consuming, and can lead to errors. While cultivation-independent methods (e.g., ATP, phospholipids and INT) are favoured above HPCs, conversion value problems (e.g., INT/cell or ATP/cell) for natural microbial communities have still not been successfully answered.

ATP is used as primary energy currency by all organisms, from the simplest bacteria to humans. Therefore, ATP is a parameter suited for the quantification of the active biomass in GAC filters. The main advantages of this parameter are that it requires rather simple analytical equipment, allows analysis within a short time period and has sensitive detection limits. Moreover there is a significant amount of knowledge about the ecological and

physiological significance of ATP (Harrison and Maitra, 1969; Chapman et al., 1971; Magic-Knezev and van der Kooij, 2004).

This study aims to develop and describe a direct and straight-forward method for the estimation of active biomass on GAC particles. The method combines the direct ATP determination on GAC particles with the determination of the case-specific ATP/cell value. The method was developed considering the characteristics of GAC, particularly taking into account physical particle heterogeneity and patchy biofilm coverage. We demonstrate the application potential of this method by following the development of a biofilm in a pilot-scale GAC filter during the start-up period.

Nomenclature

| | | | |
|--------|--|-----|--|
| ATP | adenosine tri-phosphate | INT | 2-(p-iodo-phenyl)-3-(p-nitrophenyl)-s-phenyltetrazolium chloride |
| AOC | assimilable organic carbon | | |
| (B)DOC | (biodegradable) dissolved organic carbon | NOM | natural organic matter |
| BRP | biomass respiration potential | RLU | relative light unit |
| DW | dry weight | SD | standard deviation |
| EBCT | empty bed contact time | TDC | total direct count |
| GAC | granular activated carbon | WW | wet weight |
| HPC | heterotrophic plate count | | |

Materials and methods

Sample collection and pre-treatment

GAC samples were collected from a full-scale GAC filter at the Zurich water works (Lengg, Zurich, CH). The GAC type was ROW 0.8 SUPRA (Norit, Kempen, D) and has been in use in the filter for 20 years. This GAC filter is positioned directly after intermediate ozonation (Müller et al., 2003) and operated with an average empty bed contact time (EBCT) of 12.5 min and an average filtration rate of 6.5 m/h. Samples were collected from the filter bed surface (upper 10 cm) and stored before use in 1 L screw-capped glass flasks in the filtrate at 4°C in darkness. For pre-treatment, 5 g wet weight (WW) of GAC was rinsed three times gently in 100 mL phosphate buffer (3 mg/L KH_2PO_4 and 7 mg/L K_2HPO_4 , pH 7, (Sigma-Aldrich, Buchs, CH)).

Calculation of the external surface area of GAC

Digital images of the GAC sample at 6x magnification with an optical microscope (Wild, Heerbrugg, CH) were captured with a C-5050 camera (Olympus, Schwerzenbach, CH). The images were analysed using Olympus DP-soft software (Olympus), during which the length and width of 168 GAC particles were assessed. The external surface area of each particle was calculated based on a cylindrical shape, which is typical for ROW 0.8 SUPRA particles.

Calculation of GAC particle number per dry weight

Eppendorf tubes (2 mL; Greiner Bio-One, Frickenhausen, D), each containing about 200 mg GAC WW, were dried at 70 °C for 24 h. GAC DW was calculated from the measured weight by subtracting the weight of the same Eppendorf tube determined before use. In order to determine the number of GAC particles per gram of DW, the dried particles were spread evenly on a Petri dish, placed in a plate count reader (Acolyte Symbiosis, Hingham, MA, USA) and counted using Acolyte Super Count software (Acolyte Symbiosis).

Scanning electron microscope (SEM) characterisation

A 200 mg rinsed sample of GAC WW (described above) was prepared for observation in a Philips XL30 SEM (Philips, Eindhoven, NL) by critical point drying. The sample was first immersed stepwise in 20%, 40%, 60%, 80% and 100% of ethanol. Each step had a minimum duration of 20 min, except the last step, during which the GAC was left in the pure ethanol over night. The sample was thereafter placed in the critical point dryer where the chamber was slowly flushed 12 times over a period of about 2 h with CO₂ until the specimens were above the critical point.

Epifluorescence microscopic assessment of biofilm density

A 200 mg GAC WW sample was rinsed and re-suspended in 1 mL of phosphate buffer (described above). The sample was then stained with SYBR[®]gold (Molecular Probes, Basel, CH) (1.5 mL/mL of stock solution) and incubated for at least 15 min in the dark. The GAC was analysed with an inverted epifluorescence microscope (IX51, Olympus) with illumination from a 100 W mercury short-arc lamp and detection with a standard FITC filter. Digital images were taken as described above. For quantitative purposes, 15 images of separated

GAC particles were captured at 400x magnification, and the surface area and number of positively stained cells were determined with Olympus DP-soft software.

ATP method development

ATP measurement directly on GAC

The direct measurement of ATP contained on cells adhering to GAC was performed as follows (Fig. 1): 200 mg GAC WW was weighed into an Eppendorf tube to which 100 μ L of phosphate buffer (as above) was added. The tube was then placed in a water bath at 30 °C. Simultaneously, 300 μ L of BacTiter-Glo™ reagent (Promega Corporation, Madison, WI, USA) was transferred to a second Eppendorf tube and was also incubated at 30 °C for 3 min. After 3 min incubation the BacTiter-Glo™ reagent was added to the GAC sample. After being mixed gently for 5 s, the mixture was then placed for a further 1.5 min into the water bath. The Eppendorf tube was mixed gently every 30 s to enable optimal contact between the GAC and the BacTiter-Glo™ reagent. Subsequently, the tube was removed from the water bath and 200 μ L of the supernatant was transferred into an unused Eppendorf tube. Exactly 30 s later, the relative light units (RLU) were measured in a luminometer (Glomax, Turner Biosystems, Sunnyvale, CA, USA). The result was then converted to an ATP concentration using a calibration curve constructed with a pure ATP standard (Promega Corporation, Madison, WI, USA). Various individual aspects of this method will be discussed below.

Determining the best time point for ATP measurement

Sufficient reaction time is required to release ATP from all microbial cells. This required time was determined for direct ATP method set-up with GAC, in four separate series consisting of seven samples each. The ratio between the sample (200 mg GAC WW), the phosphate buffer (100 μ L) and the BacTiter-Glo™ reagent (300 μ L) was kept the same as for the experiments (described above). Each of the seven tubes of a series was placed in the water bath for 1, 2, 3, 4, 5, 6 or 7 min, respectively. A 200 μ L aliquot of the supernatant was taken out of the Eppendorf tube and transferred into a new Eppendorf tube and measured as described above.

ATP calibration curve with GAC

A calibration curve specific to the method described above was performed by inactivating the microbial cells on the GAC by incubating 5 g GAC WW, suspended in 5 mL of phosphate buffer (see above) in a falcon tube, for 21 h in a water bath at 60 °C.

Afterwards the GAC was washed gently five times with 15 mL of phosphate buffer. The determination of the calibration curve followed the same set-up as the basic ATP method described above. However, instead of 100 μL of phosphate buffer, 100 μL of an ATP standard solution in a concentration range from 0.05 to 1 mM was added to separate samples. The data were plotted and the calibration curve was determined with Microsoft Excel. A new calibration curve was established for every new buffer solution. The detection limit was 0.01 nm ATP.

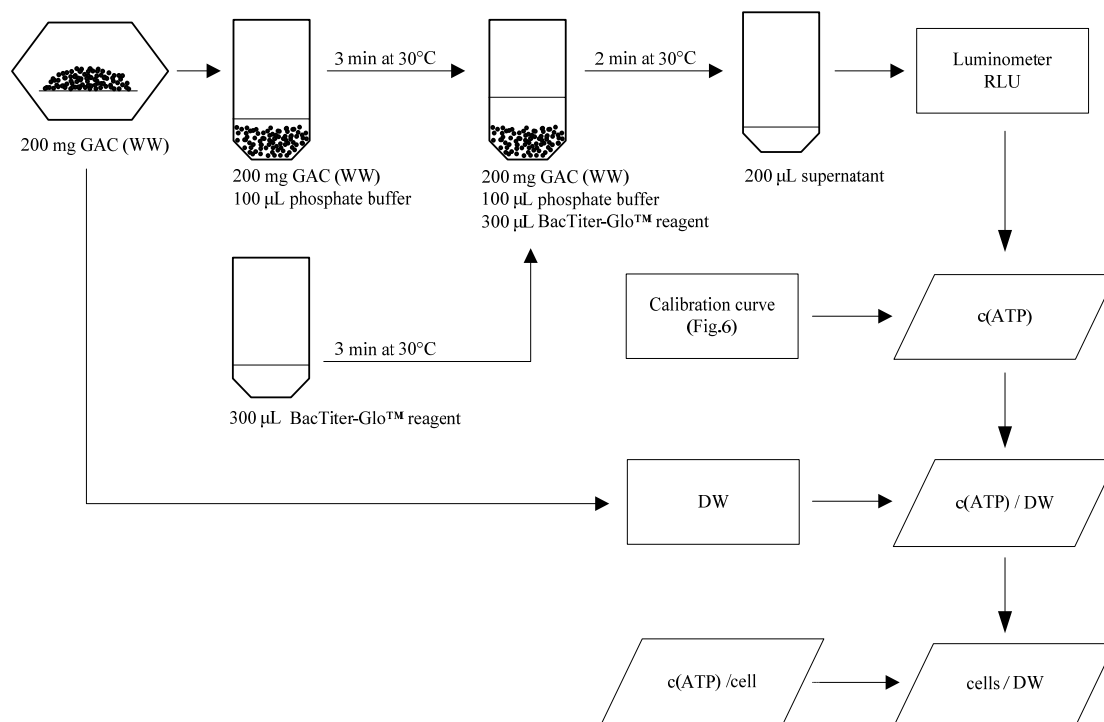


Fig. 1 Schematic layout of the direct ATP method, in which rectangular text boxes illustrate processes and rhombuses denote data. For the method set-up, 200 mg GAC WW, 100 μL of phosphate buffer and 300 μL of BacTiter-GloTM reagent were mixed and incubated for 2 min. Thereafter, the ATP content of 200 μL supernatant was determined. By combining the parameters concentration of ATP per unit of DW ($c(\text{ATP})/\text{DW}$) or per cell ($c(\text{ATP})/\text{cell}$), respectively, the cells/DW value was calculated.

Determining a case-specific ATP concentration

To obtain the case-specific ATP/cell concentration, a fraction of the bacteria from the rinsed GAC sample (see above) was removed from the GAC surface by gentle manual shaking for 1 min. The ATP concentration of these suspended bacteria was determined with the luminometer (using the method as described by the manufacturer). The number of cells in the sample was measured after SYBR[®]green-staining with flow cytometry (Cyflow Space, Partec, Münster, Germany) as described by Hammes and Egli (2005). By assuming that detached and GAC-associated cells exhibit similar properties, the case-specific ATP/cell concentration was determined. This was performed for different GAC samples and different

times to obtain a representative average value, both for samples collected from the full-scale GAC filter as well as the pilot GAC filter.

Repeatability

For determining the statistical repeatability of the method, three series with 10 samples each were carried out at separate times on separate batches of GAC, exactly as described above.

Uncertainty assessment

An uncertainty assessment of the ATP method was performed by applying the Eurachem/citac guide (Ellison et al., 2000), which provides standard operation procedures for the evaluation and expression of uncertainty in quantitative chemical analysis, based on the approach taken in the ISO “Guide to the Expression of Uncertainty in Measurement” (ISO, 1993). This assessment was carried out to determine the standard uncertainty of the method and to identify the highest error-contributing parameters. For the uncertainty quantification we developed a mathematical model of 22 parameters (e.g., error of the pipette, error of the balance and preparation of the sample). The parameters are assumed to be independent. The contributions were expressed as standard deviations (SDs) and combined according to the linear error propagation to give a combined standard uncertainty. The SD values were derived from expert knowledge, previous results and some specific experiments (where necessary).

Application of the ATP method

A GAC filter in pilot scale was set up at Zurich Water Works (WVZ, Lengg, Zurich, CH) and the formation of the biofilm on the GAC particles was monitored during the start-up period (112 days). The filter was fed with water from an intermediate ozonation reactor and was run in down-flow mode (13.5 m³/day, 1.65 min EBCT, 0.96 mg/L DOC) (Müller et al., 2003). The composition of the ozonated Lake Zurich water was: pH = 8.1 (±0.3); DOC = 0.96 (±0.03) mg/L; alkalinity = 2.74 (±0.01) mmol/L; hardness = 1.37 (±0.06) mmol/L. The fraction of 0.125 to 0.71 mm of the activated carbon F 400 (Chemviron, Brussels, Belgium) was used in this experiment. The effective GAC layer had a height of 22 cm and a diameter of 30 cm. To provide a homogeneously developed biofilm in the filter bed, the filter was backwashed once a day for 10 min with reservoir water (27 L/min). Samples were taken from the GAC filter bed surface (upper 10 cm) and stored before use in a 50 mL Schott flask in the filtrate at 4 °C in darkness. The samples were investigated on the day of sampling. GAC samples were

treated as described above and analysed for ATP. Liquid samples were taken at influent and effluent sampling points and kept in 10 mL DOC-free flasks. Glass vials for DOC analysis were cleaned and muffled at 450 °C for 4 h to remove all remaining traces of organic compounds. The DOC concentrations were measured using liquid chromatography organic carbon detection (LC-OCD) (Huber and Frimmel, 1992). The detection limit was 10 µg C/L.

Results and discussion

Heterogeneous nature of used GAC

The 20-year-old Norit ROW 0.8 SUPRA GAC which was used in this study had extremely high heterogeneity in size distribution, surface roughness and biofilm coverage (Figs. 2–5). Fig. 2A and B show the degree to which the GAC particles disintegrated over time, rendering smaller particles with a larger surface area per weight. The process of regular backwashing of the GAC filter contributes to a break-up of the particles and consequently increases the particle size distribution in the system (Sontheimer et al., 1988). The calculated average external surface area for the GAC investigated was 24×10^6 ($\pm 12 \times 10^6$) $\mu\text{m}^2/\text{mg}$ GAC DW, based on a typical cylindrical shape that was still maintained after long operation (Fig. 2C). Even though the contribution of macropores, which were evident on the carbon surface (Fig. 2D), was not accounted for in the direct microscopic surface area measurement, the obtained value still exceeds reported values ($7.92 - 9.95 \times 10^6$ $\mu\text{m}^2/\text{mg}$ GAC DW) for this type of GAC before use (Sontheimer et al., 1988).

The statistical distribution of the measured external surface area per GAC particle is shown in Fig. 3. The distribution ranges from 1×10^6 $\mu\text{m}^2/\text{particle}$ up to 12×10^6 $\mu\text{m}^2/\text{particle}$, with a mean of 3.2×10^6 ($\pm 1.5 \times 10^6$) $\mu\text{m}^2/\text{particle}$. This heterogeneous distribution is also evident from the number of particles per milligram DW. A mean number of 7.52 (± 1.5) particles/mg GAC DW was recorded ($n = 2713$ particles), which is significantly higher than the expected value (1.18 ± 0.2) for unused carbon of the same type. Fig. 4 shows the ATP content of 50 single GAC pieces, revealing even more heterogeneity in the concentration of ATP/ μm^2 than in the actual size distribution. The direct ATP assay described below utilises 200 mg GAC WW per analysis, which corresponds on average to 71.4 (± 3.8) mg GAC DW, 526 (± 110) particles and an external surface area 1.8×10^9 ($\pm 8.5 \times 10^8$) μm^2 (Table 1). This represents a significant number of particles to compensate for the natural heterogeneity of GAC.

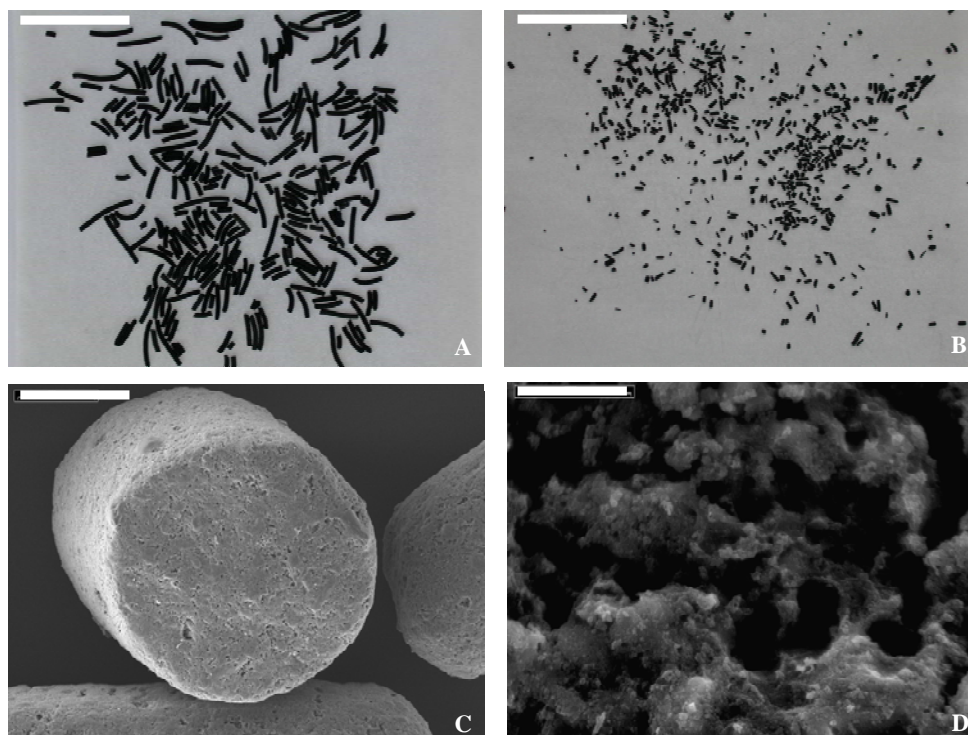


Fig. 2 The heterogeneous nature of used GAC. (A) Light optical microscope picture of unused Norit ROW 0.8 SUPRA; (B) characteristic sample of the same GAC type after 20 years use in a full-scale filter; (C) SEM image of the used GAC showing that the cylindrical shape remained; and (D) SEM close-up clearly showing an uneven surface with macropores. Scale bars represent 2 cm (A, B), 280 μm (C) and 10.4 μm (D).

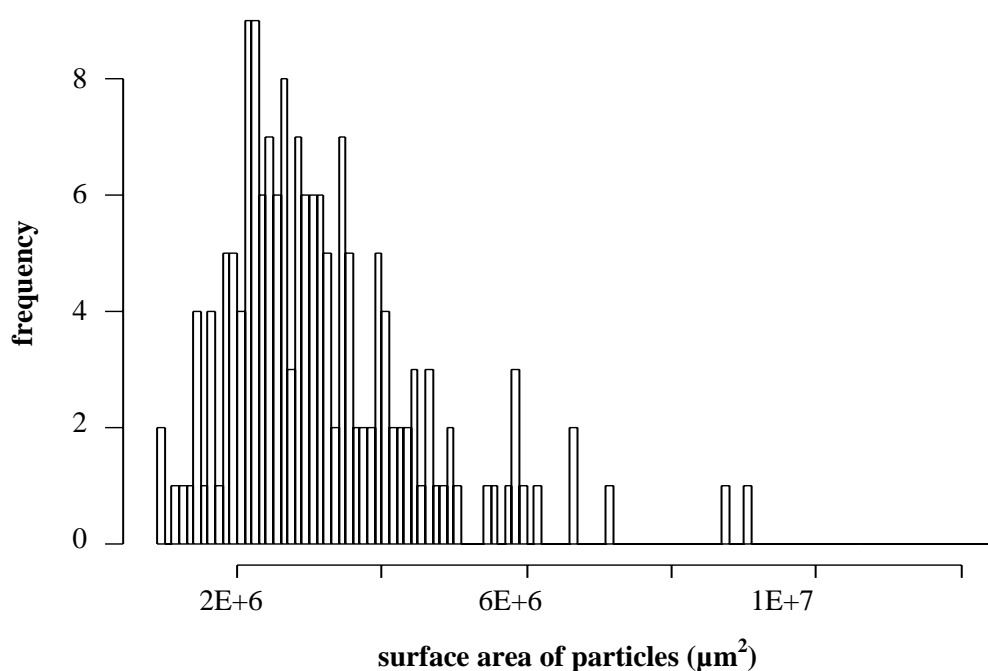


Fig. 3 Heterogeneity of the surface area per GAC particle. A log normal surface area distribution of 338 GAC particles. The mean particle surface area was $3.2 \times 10^6 (\pm 1.5 \times 10^6) \mu\text{m}^2$.

Estimation of biofilm density with direct epifluorescent microscopy

A high degree of surface roughness (Fig. 2D) and uneven distribution of the biofilm on separate and individual GAC particles (Figs. 5A–C) rendered direct microscopy impractical for quantitative purposes. At low magnification (40 x) after SYBR[®]gold staining (Fig. 5A) the heterogeneous distribution of microbial cells can clearly be seen, which further confirm the variations in ATP/ μm^2 reported in Fig. 4 for individual GAC particles. This can be attributed to differences in nutrient exposure and mineral supply in the full-scale GAC filter, and also to shear effects during back-washing (Ahmad et al., 1998). The heterogeneous distribution of microbial cells may also be attributable in part to small localized differences relating to the ease of initial bacterial attachment and subsequent biofilm development. Magnifications of 400 x were used to attempt quantification as this gave the best resolution without extreme interference of surface roughness (Fig. 5B). A total of $1.27 \times 10^5 \mu\text{m}^2$ GAC surface area was investigated and 2230 cells were detected (within 15 digital images similar to Fig. 5B). The total coverage of this GAC sample with bacteria was therefore calculated to be $0.02 (\pm 0.011)$ cells/ μm^2 . Based on the average size (calculated above), the DW, and number of particles per DW, this amounts to $4.9 \times 10^8 (\pm 2.7 \times 10^8)$ cells/g GAC DW. However, numbers should be taken with caution due to bacteria proliferating in macropores, as seen in Fig. 5C, and also owing to the low number of bacteria per surface area that can be assessed microscopically. Furthermore, microscopy allows just a relatively small surface area ($1.27 \pm 10^5 \mu\text{m}^2$ in this example) to be investigated. This is considerably less than the total surface area of 200 mg GAC WW ($1.8 \times 10^9 \mu\text{m}^2$), which is used in the direct ATP method described herein.

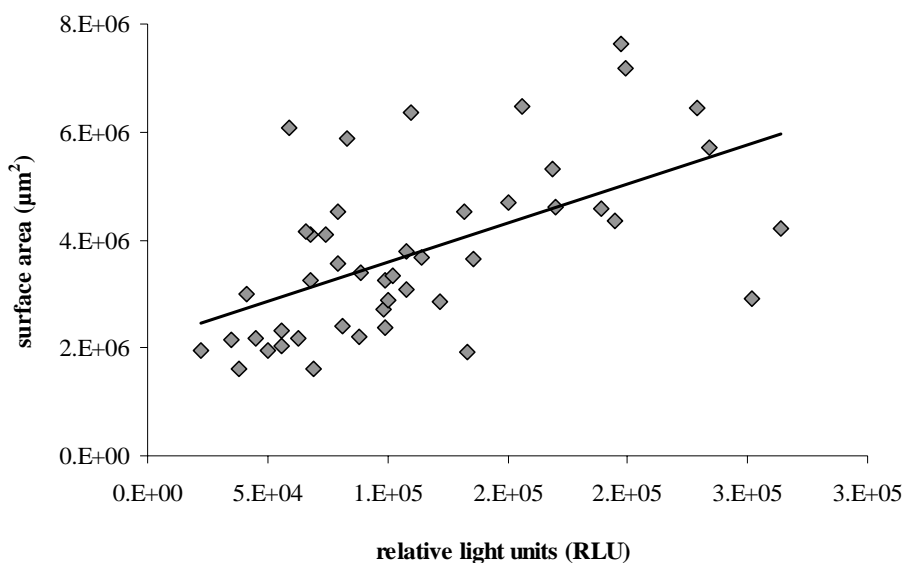


Fig. 4. Heterogeneity of the relative light unit values per surface area. ATP relative to surface area was measured for 50 individual pieces of GAC ($R^2 = 0.32$). A high heterogeneity results from patchy colonization of individual GAC particles.

Tab. 1. Experimental characteristics of the 20-year-old GAC that was used to assess repeatability of the direct ATP method. Repeatability was tested in 3 separate series, each using 10 samples. Here the results of one of three series are shown.

| | WW | DW | WW/DW | ATP | ATP/DW |
|------------------|-------------|-------------|--------------|-------------|---------------|
| | (mg) | (mg) | | (ng) | (ng/g) |
| 1 | 202.4 | 70.5 | 2.87 | 39.8 | 565 |
| 2 | 190.4 | 67.5 | 2.82 | 48.0 | 711.4 |
| 3 | 222.4 | 77.3 | 2.88 | 41.7 | 539.9 |
| 4 | 203.6 | 70.8 | 2.88 | 44.7 | 631.6 |
| 5 | 201.9 | 72.5 | 2.79 | 46.2 | 638.1 |
| 6 | 213.1 | 75.8 | 2.81 | 42.6 | 562.6 |
| 7 | 204.6 | 70.2 | 2.91 | 45.8 | 652.3 |
| 8 | 207.6 | 75.3 | 2.76 | 55.9 | 742.3 |
| 9 | 195.7 | 68.6 | 2.85 | 44.9 | 654.8 |
| 10 | 191.5 | 66.6 | 2.92 | 41.0 | 625.6 |
| Mean | 203.3 | 71.4 | 2.85 | 45.1 | 643.5 |
| Stdev | 9.7 | 3.8 | 0.05 | 4.6 | 64.4 |
| Stdev (%) | 4.8 | 5.3 | 1.9 | 10.2 | 10.2 |

Direct ATP measurement on GAC

Ratio between phosphate buffer, BacTiter-Glo™ reagent and the GAC sample

The suppliers of BacTiter-Glo™ reagent recommend using the product in a ratio of 1:1 with the targeted bacterial sample. However, this is recommended specifically for bacterial suspensions. While other studies have aimed at removing the biomass from GAC before commencing with ATP measurement (Magic-Knezev and van der Kooij, 2004), we have strived for a direct method of detection (Fig. 1). It was therefore necessary to determine the optimum ratio between reagent and sample, which had to take into account the efficacy of the measurement, practical sampling issues and the costs involved. 200 mg WW was chosen as a sufficient amount of GAC to compensate for the natural heterogeneity of the GAC (Figs. 3 and 4). The highest extraction efficiencies were gained when 300 µL of BacTiter-Glo™ reagent was added to 100 µL of sterile phosphate buffer and 200 mg GAC WW sample (data not shown).

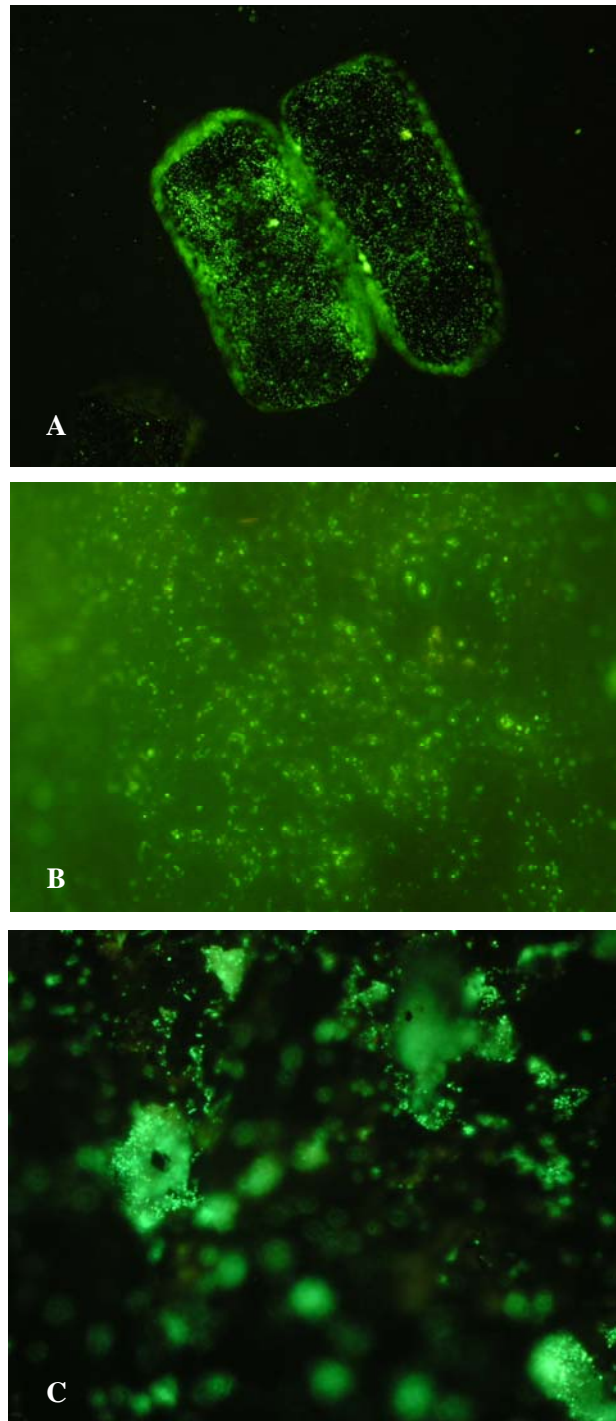


Fig. 5. Patchy biofilm distribution on 20-year-old GAC exposed after SYBR®gold staining. (A) Low magnification (40 x) showing uneven distribution on separate and individual GAC pieces; (B) 400 x magnification that was used for direct enumeration; (C) differential colonisation in macro-pores giving rise to erroneous quantification with microscopy (600 x magnification).

Best time point for ATP measurement

Upon exposure of the GAC sample to the ATP reagent, the measured ATP concentration increased initially; the maximum ATP extraction was reached at 2 min and the ATP concentration remained steady thereafter (Fig. 6). This result is different to the behaviour of bacterial suspensions with the ATP reagent (Fig. 6). The measured ATP concentration in a bacterial suspension decreases quickly after exposure to the reagent; whereas ATP in the presence of GAC is relatively stable (Magic-Knezew and van der Kooij, 2004). In repeated experiments, a maximum concentration was always obtained at 2 min and therefore this was chosen as the optimum time for ATP extraction and, subsequently, for the measurement (not all data shown).

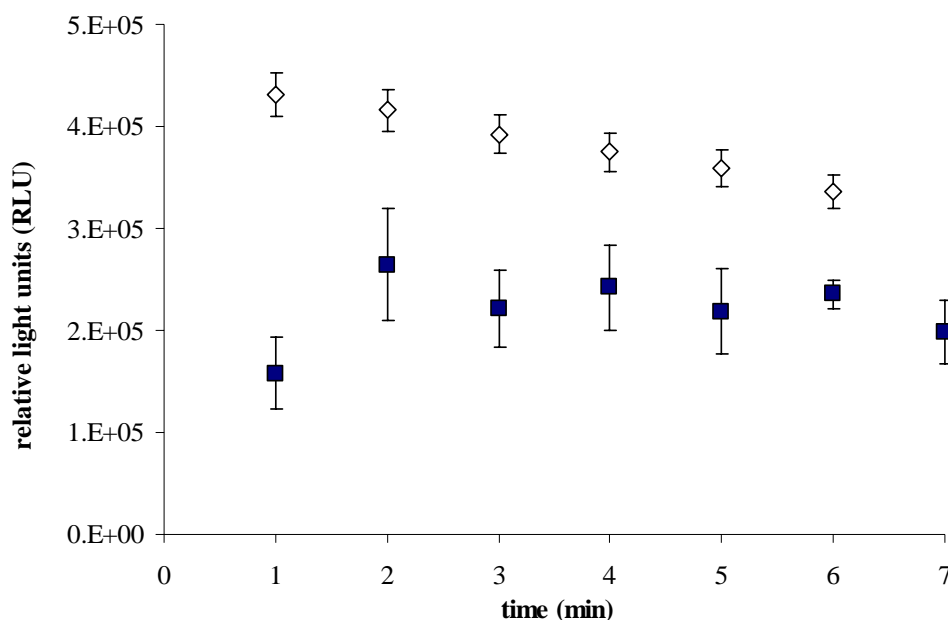


Fig. 6. Variation of RLU values over time for a planktonic cell suspension (\diamond) of natural aquatic bacteria (GAC reactor effluent) and for GAC particles (\blacksquare) after exposure to ATP reagent. For cell suspensions, the highest values are obtained when the RLU is measured as early as possible. In contrast, the best time point of measurement for the RLU concentration in a GAC system is at 2 min.

ATP calibration curve with GAC

A calibration curve representative of the GAC sample and the method was produced using inactivated GAC and an ATP standard (Fig. 7). The bacteria on the GAC were inactivated with heat (60 °C, 21 h), and as a result, the RLU value decreased to 1% of the original RLU value. By using inactivated GAC instead of fresh unused GAC, the surface characteristics of the GAC remained the same. In order to obtain accurate results, we recommend the

preparation of a new calibration curve for each new batch of BacTiter-Glo™ reagent and sample.

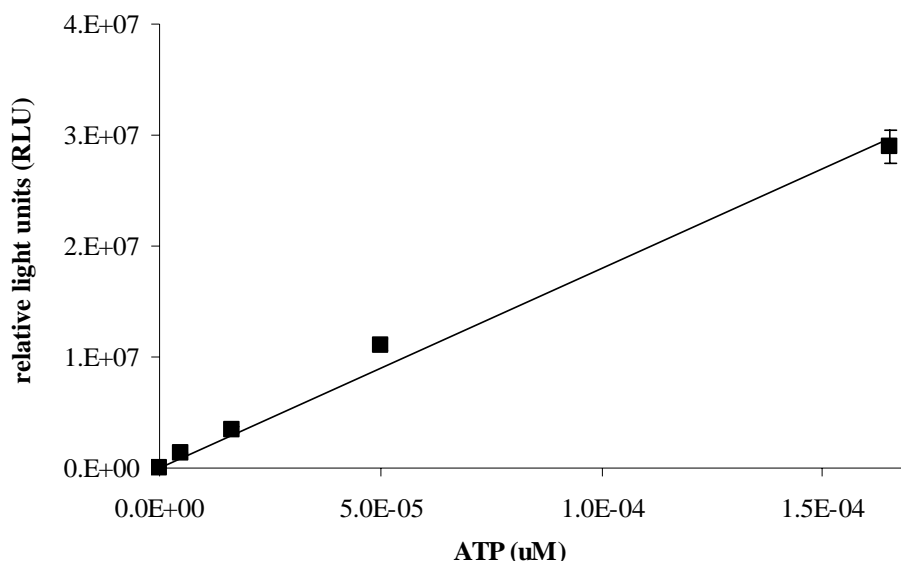


Fig. 7. The ATP calibration curve ($R^2 = 0.99$) was produced by using GAC on which the biology was inactivated by applying a high temperature treatment, and spiking the sample with known amounts of ATP.

Case-specific ATP concentration

In order to determine the case-specific ATP content per cell, we combined flow cytometry and ATP analysis. We obtained a median value of 6.7×10^{-17} ($\pm 4.3 \times 10^{-17}$) gATP/cell for the full-scale plant and 2.3×10^{-16} ($\pm 1.2 \times 10^{-16}$) gATP/cell for the pilot-scale plant. This is in the same order of magnitude as reported previously, e.g., 2.1×10^{-17} gATP/cell, attached to GAC (Magic-Knezev and van der Kooij, 2004), $0.2 - 4 \times 10^{-16}$ gATP/cell for ground water bacteria (Jensen, 1989) and $0.2 - 7 \times 10^{-16}$ gATP/cell for bacteria on membranes (Vrouwenvelder et al., 1998). Large variations in the ATP content per cell have often been reported, and can be explained by the dependence on growth phase, cell size and specific microbial species.

Repeatability of the method

The ATP method described herein was developed on a GAC sample that has been in use for 20 years. The attached biomass concentration can consequently be assumed to be in a steady-state. Three separate series of GAC samples returned SDs varying from 7.1%, 10.2% to 17.3% ($n = 10$; data of series 2 are shown in Table 1). Evidently, the error in the determination of the ATP concentration per tube primarily contributes to the overall error, which again highlights the influence of the heterogeneous biofilm distribution (Fig. 4) on the

overall result. To gain a statistically reliable result, we recommend investigating samples in triplicate and to use the mean for further calculations.

Uncertainty analysis of the ATP method

The standard uncertainty calculated for the direct ATP method (cells/GAC) was 15%. Three parameters contributed significantly more to this value than others. Of the total uncertainty (15%), 35% is attributed to the heterogeneity of the GAC sample, 30% to the overall repeatability of ATP/g GAC measurement and 12% to the repeatability of ATP/cell determination. The other 19 parameters together contributed 23% to the total uncertainty of the method. For these parameters, the individual uncertainty is relatively small (<3%); therefore their contribution to the total uncertainty remains small. A standard uncertainty <15% implies that the method is sensitive enough for characterisation of activated carbon samples and other similar systems. However, particular care must be taken when analysing dynamic systems for which only small variations are expected.

Characterisation of GAC pilot-plant start-up period

The direct ATP method, described above, was tested in practise for the characterisation of the start-up period of a new GAC pilot-scale reactor. Only about 50 days were required for the establishment of a stable biofilm on fresh GAC particles in a drinking water pilot-plant. The development phase of the biofilm was characterised by a continuous decrease in DOC adsorption on the GAC (due to gradual saturation), and a concomitant increase in ATP on the GAC particles (Fig. 8). The maximum ATP concentration (2480 ng ATP/g GAC) was measured after 33 days, decreasing thereafter to a stable average of 1820 ng ATP/g GAC after 75 days of operation. This start-up period was at the lower end of previously reported data, i.e., 6 weeks (Seredynska-Sobecka et al., 2006) and 3–6 months (Servais et al., 1994). Operational and calculated parameters for the pilot-plant are given in Table 2. The rapid increase of biomass concentration in the start-up phase can be ascribed to the high amount of DOC that was initially adsorbed on the GAC surface (Fig. 8). The adsorbed DOC fraction was then probably assimilated by attached microorganisms in addition to the continuously fed DOC load in the influent water, which resulted in a rapid biomass increase until a maximum was reached. Hence, it was demonstrated that the direct ATP method sufficed to characterise the dynamic changes occurring during the start-up phase of a new GAC reactor.

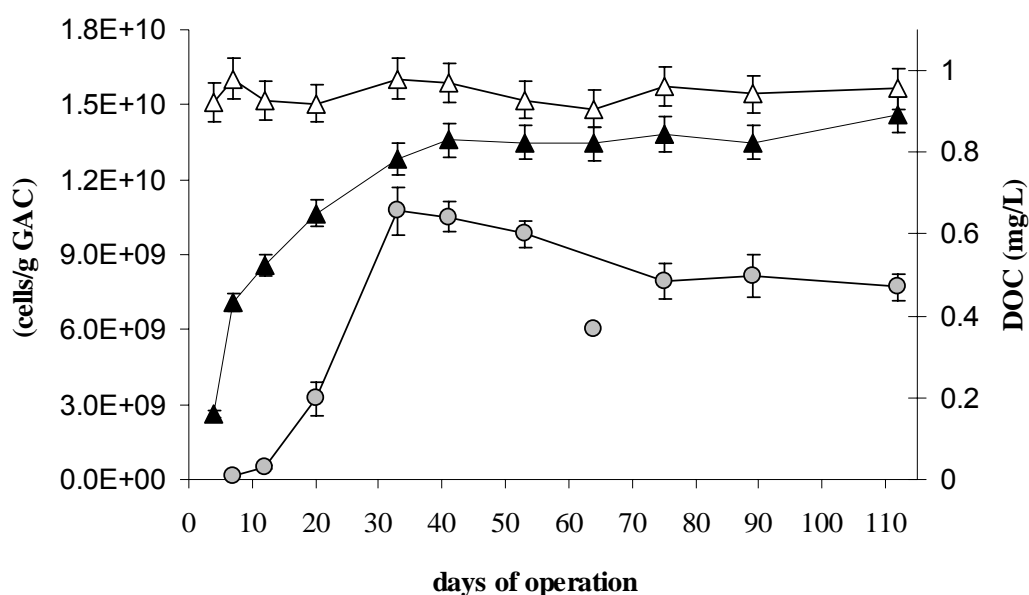


Fig. 8. Biofilm formation in a GAC filter pilot-scale reactor over time. Shown are number of cells (\circ), the DOC of the influent (Δ) and the DOC of the effluent (\blacktriangle). The reactor was fed with ozonated lake water (Lake Zurich). The error bars on the #cells/DW values indicate standard deviations of triplicate measurements. The error on the DOC values is 10% ($0.1 < x < 1$ g C/L) and 20% ($x < 0.1$ g C/L) respectively.

Tab. 2. Operational and experimental parameters of the full-scale and pilot-scale GAC filters analysed in this study. Both filters were installed after the intermediate ozonation reactor at the Lengg drinking water treatment plant (Zürich, CH).

| | | Full-scale plant | Pilot-plant |
|------------------------|-------------------|---|---|
| carbon type | | Norit ROW 0.8 SUPRA | Chemviron F400 |
| reactor volume | (m ³) | 57 | 0.015 |
| filtration rate | (m/h) | 6.5 | 8 |
| backwash rate | (m/h) | 27.4 | 22.9 |
| contact time | (min) | 12.5 | 1.65 |
| DOC (influent) | (mg/L) | 0.96 (\pm 0.03) | 0.96 (\pm 0.03) |
| ATP/cell | (g/cell) | 6.7×10^{-17} (\pm 4.3×10^{-17}) | 2.3×10^{-16} (\pm 7.8×10^{-18}) |
| ATP/GAC | (ng/g DW) | 609 (\pm 61) | 1820 (\pm 147) |
| cells/GAC | (cells/g DW) | 9.1×10^9 (\pm 1.3×10^9) | 7.9×10^9 (\pm 1.2×10^9) |

Comparison with alternative GAC biomass quantification methods

The various methods described in the literature which are presently used to determine biomass attached to GAC often result in differences in the specific biomass values reported, and several conversion factors are usually required to obtain comparable results. In this study, we have characterised GAC from two drinking water treatment reactors, i.e., a full-scale, stable-operating reactor and a pilot-plant reactor during the start-up period. Both these reactors were exposed to the same influent (0.96 mg/L DOC) at a similar flow rate. During the period of study, the full scale reactor GAC measured on average 609 ng ATP/g GAC and the pilot-plant GAC measured a steady value of 1820 ng ATP/g GAC after an initial start-up phase. This unit (ng ATP/g GAC) was selected because it can easily be obtained with limited equipment and is universally applicable.

We have used either measured or published conversion factors in order to compare our data with previously reported findings. Magic-Knezev and van der Kooij (2004), using a slightly different ATP-based method, reported 25–5000 ng ATP/cm³ from various full-scale installations in the Netherlands, while van Leeuwen et al. (1985) also found 60–100 ng ATP/cm³ for GAC reactors. Conversion of GAC mass to volume for our data resulted in 380 ng ATP/cm³ for the full-scale reactor and 1139 ng ATP/cm³ for the pilot-plant reactor. Magic-Knezev and van der Kooij (2004) also measured the cell concentration on the GAC separately from the ATP using fluorescence microscopy, and reported values of 0.1–4 x 10¹⁰ cells/cm³. Using the community specific ATP/cell values that we derived in combination with flow cytometry, our transformed results yield 5.73 x 10⁹ cells/cm³ for the full-scale reactor and 4.95 x 10⁹ cells/cm³ for the pilot-plant reactor (calculated with a GAC density of 626 kg/m³). Fonseca et al. (2001) and Sereczynska-Sobecka et al. (2006) employed phospholipids analysis for GAC biomass quantification. These authors reported values of 50–100 nmol PO₄/g and 70–120 nmol PO₄/g for colonised sand and GAC. Using the conversion value of 1 nmol PO₄ equals 10⁸ cells, proposed by Sereczynska-Sobecka et al. (2006), the above data lead to mass-specific cell numbers between 0.5 and 1.2 x 10¹⁰ cells/g of GAC, which falls well within the range our findings (7.9–9.1 x 10⁹ cells/g of GAC). Finally, Servais et al. (1991) employed radio-labelled tracers for biomass quantification on GAC from full-scale reactors and came up with a figure of 2.5–10.9 mg C/cm³. If one utilises the conversion value of C = 250 x ATP (Karl, 1980), this is equal to < 9.1 x 10⁸ cells/g of GAC, which is considerably less than the values reported above. This confirms that extreme care should be taken with the use of general conversion values. Also, it should be noted that the biofilm concentration is dependant on the biodegradable fraction in the influent; variations in the cell number can be justified by various environmental conditions (Fonseca et al., 2001).

Conclusion

- Evidently, the direct ATP method described herein provides realistic and reproducible results which are comparable to data from other alternative methods. The method is particularly favoured for its simplicity and speed of analysis (about 45 min per sample).
- A standard uncertainty of 15% was obtained for the entire method, which shows that the method is sensitive and applicable to cases where large variations can be expected, such as the start-up phase of a GAC reactor.
- The results furthermore suggest that this method would be applicable for the characterisation of other similar systems such as rapid sand filters, slow sand filters, soil samples and (with minor adaptation) biofilms on membranes.
- In a next step, we will apply the direct ATP method in subsequent studies to DOC and AOC removal kinetics during granular media filtration and GAC applications.

Acknowledgements

We acknowledge financial assistance from the EAWAG Wave21 project, the Zurich Water Works (WVZ) and the EV project TECHNEAU (018320), and thank Iris Hülshoff, Hans-Peter Kaiser, Sébastien Meylan, Jörg Rieckermann and Brian Sinnet for technical and scientific assistance.

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2

Biomass development and stratification in a drinking water granular activated carbon (GAC) filter

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manuscript in preparation

Abstract

We followed biofilm formation and development in a drinking water granular activated carbon (GAC) filter treating ozonated surface water, during the first six months of operation. Water samples were taken from six different levels of the reactor and analyzed for dissolved and assimilable organic carbon (DOC and AOC) and flow cytometric total cell counts (TCC), as well for all conventional parameters. GAC particles were sampled from four different levels and attached biomass was measured with adenosine tri-phosphate (ATP) analysis. The attached biomass accumulated rapidly on the GAC particles throughout all levels in the filter during the first 90 days of operation and reached a steady state afterwards. Clear stratification with regards to biomass densities and growth rates was observed during start-up and in steady state. At steady state, the highest biomass concentration (1.83×10^{-6} g ATP/g GAC) was established in the second layer (45 cm from top) and this decreased considerably with the filter depth (0.8×10^{-6} g ATP/g GAC at 115 cm from top). During steady state operation, 22% of the total DOC was removed from the water and the total biomass production was about 1.8×10^{12} cells/m²h, which represents a yield of 1.26×10^6 cells/ μ g. A carbon balance of the GAC filter showed that the bacteria assimilated only 3% of the removed carbon as biomass. The concentration of AOC in the reactor influent was not reflecting the total concentration of biodegradable DOC that was removed during GAC filtration. In addition, it was shown that phytoplankton concentrations in the influent had a significant influent on biomass production in the GAC filter. Understanding the basic microbiological performance parameters will allow improved monitoring, modeling and operation of biological filters used during drinking water treatment.

Keywords

Granular activated carbon (GAC), biomass, drinking water, filtration, stratification

Introduction

Granular activated carbon (GAC) filters are commonly used during drinking water treatment for the removal of dissolved organic carbon (DOC), including micropollutants such as pharmaceuticals, halogenated hydrocarbons and taste and odor compounds, or for the removal of biodegradable organic carbon fractions (Servais et al., 1994; Urfer et al., 1997; Fonseca et al., 2001; Velten et al., 2007). When the ultimate purpose of a GAC filter is

adsorption, the GAC is replaced or reactivated frequently in order to maintain sufficient adsorption capacity (Munz et al., 1990). Alternatively, some drinking water works use the GAC over an extended time period (up to 20 years), where the ultimate focus shifts from adsorption towards biological degradation for the removal of organic carbon (Lee et al., 1981; Servais et al., 1991; Moll et al., 1999; Velten et al., 2007; Hammes et al., 2008). When the focus is on biodegradation, the carbon is also referred to in literature as biological activated carbon (BAC), and filters that are operated in this manner are also known as 'biofilters'.

The presence of microbial biofilms in GAC filters has been evident for decades (Weber et al., 1978; Camper et al., 1985). Bacteria colonize the surfaces of the GAC particles and exist not merely opportunistic, but contribute also to the functionality of the treatment system through the removal of biologically available organic carbon (Servais et al., 1991; Lehtola et al., 2002). When the intended function is biodegradable organic carbon removal, GAC filters are typically placed in a treatment train after an ozonation step. During ozonation natural organic matter (NOM) is oxidized to low molecular weight oxygen-containing organic carbon molecules (von Gunten, 2003). This increases the biodegradable fraction of DOC (Volk and Lechevallier, 2002; Hammes et al., 2006). Removal of this biodegradable fraction contributes to the biological stability of the water and is therefore an essential step in the drinking water treatment chain (van der Kooij et al., 1989). Since a major part of DOC removal during GAC filtration can be attributed to biological processes, it is important to be able to quantify the microbial component responsible for this process. Heterotrophic microbial growth basically encompasses substrate (organic carbon) removal and concurrent biomass production, both of which are measurable variables. These two variables are linked by more complex physiological, stoichiometric and kinetic parameters. Quantitative knowledge of these microbiological processes would allow optimization in design, operation and monitoring of the system, as well as aid the development of models describing these systems (Rittmann and Stilwell, 2002). Previous studies have usually focused on stratification at a single specific point in time (Servais et al., 1994; Carlson and Amy, 1998; Urfer and Huck, 2001) or on just one sampling point during filter operation (Wang et al., 1995; Magic-Knezev and van der Kooij, 2004; van der Aa et al., 2006; Velten et al., 2007). As a result, little is still known about biomass stratification over time in GAC filters, especially during the start-up period when the particles are colonized. In addition, little is also known about DOC removal efficiency, biomass growth rates and yields, and bacterial release/detachment into the effluent of the filters.

In this study we present a complete quantification of a pilot plant GAC filter treating ozonated lake water as part of a drinking water treatment chain. We have used cultivation-

independent flow cytometry and ATP analysis to assess (1) biofilm development on the GAC particles and (2) the release of suspended cells, as a function of filter depth and time. These data were in turn compared to (3) influent water composition and (4) DOC and assimilable organic carbon (AOC) removal capacity of the filter, in order to derive some of the kinetic parameters that drive the main biological functions in these filters.

Material and Methods

Pilot plant lay-out and operation

The experiments were conducted at a pilot plant that was set up at the Zurich Waterworks (WVZ Lengg, CH). The pilot plant consisted of pre-filtration (20 mm), ozonation, GAC filtration and ultrafiltration and has been described previously (Hammes et al., 2008). The GAC filter was operated in down-flow mode with ozonated surface water (Table 1). The design of the GAC filter allowed sampling of both water and GAC particles over the filter bed, as well as influent and effluent water samples (Figure 1). GAC was sampled at four sampling points that were distributed over the filter with interspaces of 35 cm. Figure 1 shows that sample points are named from the top of the GAC filter downwards; thus the GAC 1 sample was taken 10 cm below the top of the filter. Similarly, water sample 1 (WS 1) was taken at the same height. The data reported herein cover the first 6 months of operation. For the explicit purpose of studying stratification, no backwashing was applied to the filter during this initial period.

Tab. 1. GAC filter and water quality parameters

| | | |
|-------------------------------|----------------------|--------------------|
| carbon type | (-) | Chemviron SGL 8x18 |
| packed bed density | (kg/m ³) | 460 |
| reactor volume | (m ³) | 1.47 |
| GAC depth | (m) | 1.55 |
| column diameter | (m) | 1.1 |
| filtration velocity | (m/h) | 5.9 |
| empty bed contact time | (min) | 15.76 |
| influent DOC | (mg/L) | 1.1 (± 0.04) |
| influent pH | (-) | 7.79 (± 0.14) |
| temperature | (°C) | 7.05 (± 0.7) |

Sampling

For GAC sampling, a metal tube (inner and outer diameter 0.9 and 1.1 cm, respectively) was inserted 0.8 m into the GAC filter from the side through purpose-build sampling ports and about 20 g GAC particles were collected from each sampling point. Water samples (250 mL) were taken from taps located at the side of the GAC filter, as well as above and below the filter. These samples were collected in sterile, carbon-free glassware prepared as described previously (Hammes and Egli, 2005). During the start up phase (first 70 days), samples were taken twice a week and afterwards sampling was reduced to once every two weeks. GAC samples were analyzed for biomass concentrations (see below for details), while the water samples were divided and analyzed for microbial abundance with flow cytometry and NOM analysis (see below for details). All samples were transported to the laboratory in cold storage, and analyzed within 3 hours of sampling.

Quantification of biomass on GAC particles

GAC samples were treated as described in Velten et al. (2007). In short, the GAC particles were rinsed thrice in phosphate buffer. Thereafter, 200 mg (wet weight) was transferred to an Eppendorf tube together with 100 μ L sterile phosphate buffer and 300 μ L BacTiterGlo™ (Promega Corporation, Madison, WI, USA), and the resulting luminescence was measured as relative light units (RLU). Results were converted to ATP concentrations using a calibration curve and, where applicable, converted to a corresponding number of cells by using a case-specific cellular ATP concentration (see below). The GAC samples were analyzed in triplicate.

Determining a case-specific cellular ATP concentration

To obtain the case-specific ATP/cell value, a fraction of the bacteria from the rinsed GAC sample (see above) was removed from the GAC surface by gentle manual shaking for 1 minute. The ATP concentration of these suspended bacteria was determined as described previously (Velten et al., 2007; Hammes et al., 2008). The number of cells in the sample was measured after SYBR® Green I staining with flow cytometry (Cyflow Space, Partec, Münster, D) as described previously (Hammes et al., 2008). From the combination of the data, a case-specific ATP/cell value was derived.

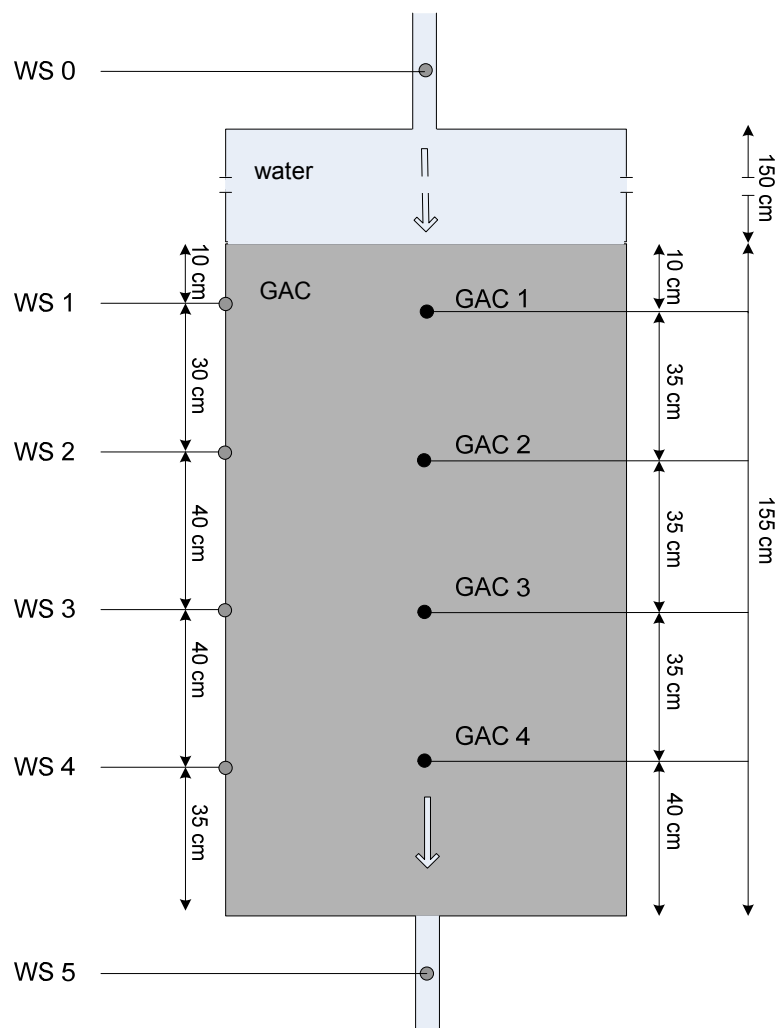


Fig. 1. Schematic presentation of the pilot scale granular activated carbon (GAC) filter that was studied. The influent was ozonated surface water (Lake Zurich). Water samples (WS 0 – 5) and GAC samples (GAC 1 – 4) were sampled from different depths over the filter.

Calculation of growth rate in filter

The biofilm specific growth rate (μ) was calculated from the ATP measurements as follows (Equation 1):

$$\mu = (\ln(n_t) - \ln(n_0)) / \Delta t \quad (\text{Equation 1})$$

where n_t , and n_0 are the biofilm cell concentrations (cells/g GAC) measured at subsequent time points and Δt is the expired time interval between these points. The yield was calculated as follows (Equation 2):

yield = biomass production / DOC removal

(Equation 2)

Total suspended cell concentration measurements with flow cytometry

Total cell concentration (TCC) in the water samples was measured with SYBR[®] Green I staining and flow cytometry as described previously in detail (Hammes et al., 2008). In short, for working solutions, SYBR[®] Green I (SG) (Invitrogen AG, Basel, CH) was diluted 100x in anhydrous dimethylsulfoxide (DMSO) and stored at -20 °C until use. From every water sample, a 1 mL sub-sample was stained with 10 µL/mL SG and incubated in the dark for 10 minutes. Prior to flow cytometric analysis, the water samples were diluted with 0.22 µm filtered commercially available bottled water (Evian, F) to 10% v/v of the initial concentration. FCM was performed using a Partec CyFlow Space instrument (Partec GmbH, Münster, D), equipped with a blue 200 mW solid state laser emitting light at a fixed wavelength of 488 nm. Green fluorescence was collected at 520 ± 10 nm, red fluorescence above 630 nm, and high angle sideward scatter (SSC) at 488 nm. The trigger was set on the green fluorescence channel and data were acquired on two-parameter dot-plots while no compensation was used for any of the measurements. The CyFlow Space is equipped with volumetric counting hardware and has an experimentally determined quantification limit of 1000 cells/mL (Hammes et al., 2008). Every one out of ten water samples was measured in triplicate with both stains, to control the standard instrumental error, which never exceeded 5%.

DOC measurement

DOC was detected by an infrared (IR) detector after complete oxidation of DOC to CO₂ in a Graentzel Thin-Film Reactor (DOC-Labor Dr. Huber, D). The detection limit was 10 µg/L (Huber and Frimmel, 1996).

Assimilable organic carbon (AOC) measurement

Sterile organic carbon-free borosilicate glass vials (20 mL) that were used for the AOC assay, were prepared as described previously (Hammes and Egli, 2005). AOC was measured with a method comprising the use of a site-specific natural microbial community, fluorescent staining and flow cytometry for growth quantification (Hammes and Egli, 2005; Hammes et al., 2006). In short, a natural microbial community is inoculated into a cell-free water sample (0.22 µm filtered) and incubated at 30 °C until stationary phase is reached. The

cell concentration at stationary phase is converted to a concentration of AOC with a conversion factor of 1 μg AOC giving 1×10^7 cells (Vital et. al, 2007). All samples were measured in triplicate.

Analysis of phytoplankton

Phytoplankton in the lake water was measured as described in Müller et al. (2003). For the analysis, the samples were immediately fixed with Lugol's solution. Phytoplankton genera species were differentiated and counted by means of an inverted microscope (Zeiss AXIOVERT 10, D). The biomass was calculated by multiplying the counts of the different phytoplankton's species by their respective biovolume and following by their specific weight.

Results and discussion

Spatial and temporal development of biofilm biomass in the GAC filter

Attached biomass accumulated rapidly on the GAC particles throughout all levels in the filter during the first three months of operation (t_1 : -11 to 91 days) (Figure 2). The biomass accumulation ceased after about 90 operational days (= 8300 empty bed volumes (EBV)) in all layers, indicating the establishment of a steady state (t_2 : 91 to 198 days). The steady state was defined by the period when the total biomass growth rate decreased to nearly zero and remained constant with only minor fluctuations. Both during the initial development period and in the steady state, stratification with regards to biomass concentrations and growth rates was clearly observed in the filter (Figure 2).

The GAC was first analyzed 11 days prior to the actual initialization of the GAC filter. These first 11 days were used for testing the hydraulics of the filter using treated water without disinfectant residuals, which exposed the raw GAC to initial colonization. Once the ozonation reactor was activated ($t = 0$ days), the concentration of suspended cells in the influent became insignificant due to complete destruction of the bacterial cells by ozone (Hammes et al., 2008). All subsequent biomass increase is therefore regarded as growth and not as attachment. In the first period (t_1), initial biofilm development (expressed as the growth rate) proceeded at the highest rates in the upper layer of the filter (GAC 1 = 0.0041 h^{-1}) and about 50% slower in the bottom layer (GAC 4 = 0.0019 h^{-1}). Such stratified behavior is ascribed directly to a decreasing availability of organic nutrients downward through the filter.

The adsorption capacity of fresh GAC is high and therefore very little DOC reaches the bottom of the filter in the initial stage of operation (Figure 3)

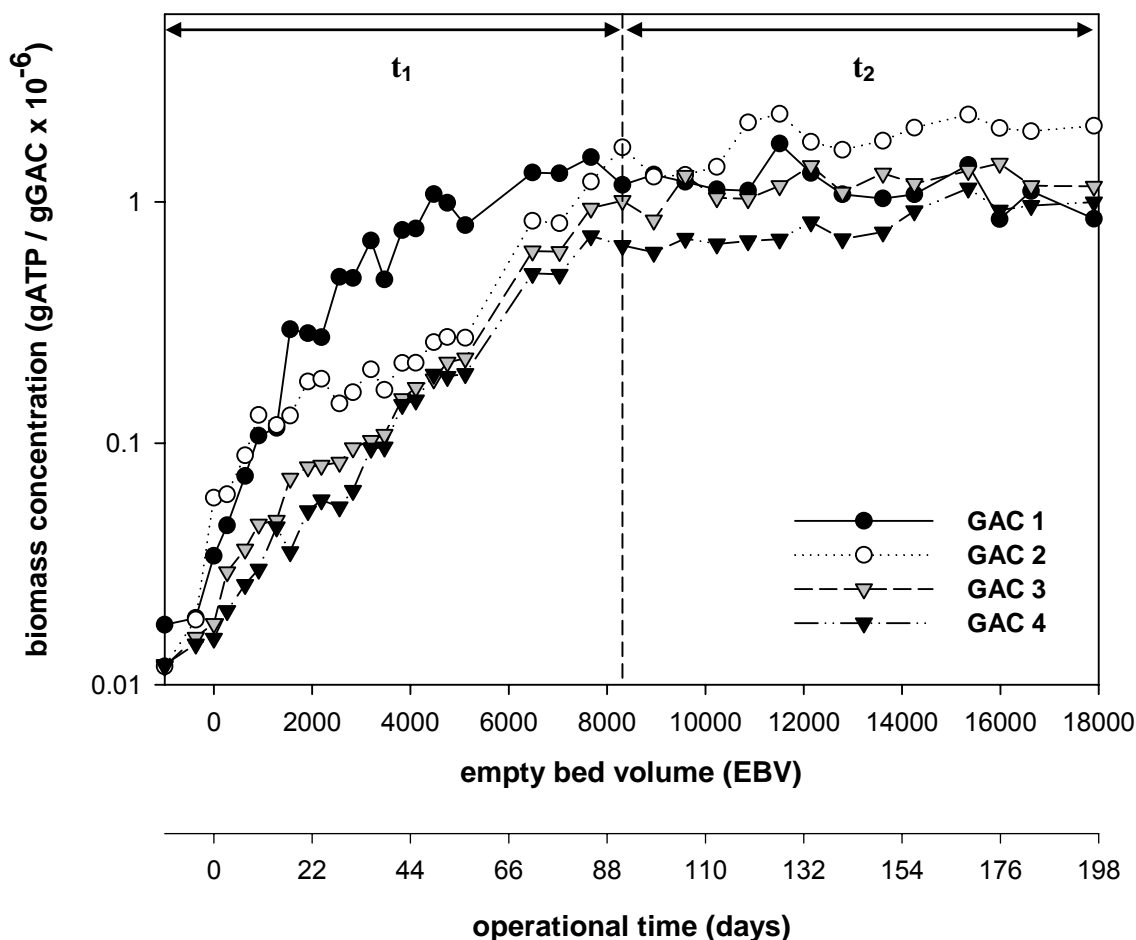


Fig. 2. Development of biomass (g ATP/g GAC) at different depths in the GAC filter over time. From the top of the filter, GAC 1 = 10 cm; GAC 2 = 45 cm; GAC 3 = 80 cm; GAC 4 = 115 cm. All data points are average values of triplicate measurements, with an average standard deviation always below 15%.

Figure 3 shows an example of the DOC profile through the filter on day 14 (1300 EBV) and day 196 (17906 EBV), respectively. Evidently, less than 20% of the initial DOC concentration reaches the bottom levels of the GAC filter in the first period (t_1), which is predominantly ascribed to adsorption. In addition, size fractionation of the DOC has suggested a greater adsorbability of smaller NOM constituents, and therefore a lower concentration of easily available carbon reaches the bottom layers compared to the top. In fact, about 50% of low molecular weight organic carbon compounds were retained in the top two layers of the filter in the initial stages of development (data not shown). This adsorption process is likely to result in a double advantage for biofilm development in the upper layers of the filter: while bacteria in the bottom layers are deprived of easily available DOC, adsorption

in the upper layers would also create a nutrient-rich micro-environment on the surface of the GAC granules that is favorable to biological growth (Li and Digiano, 1983; Urfer et al., 1997; Herzberg et al., 2003).

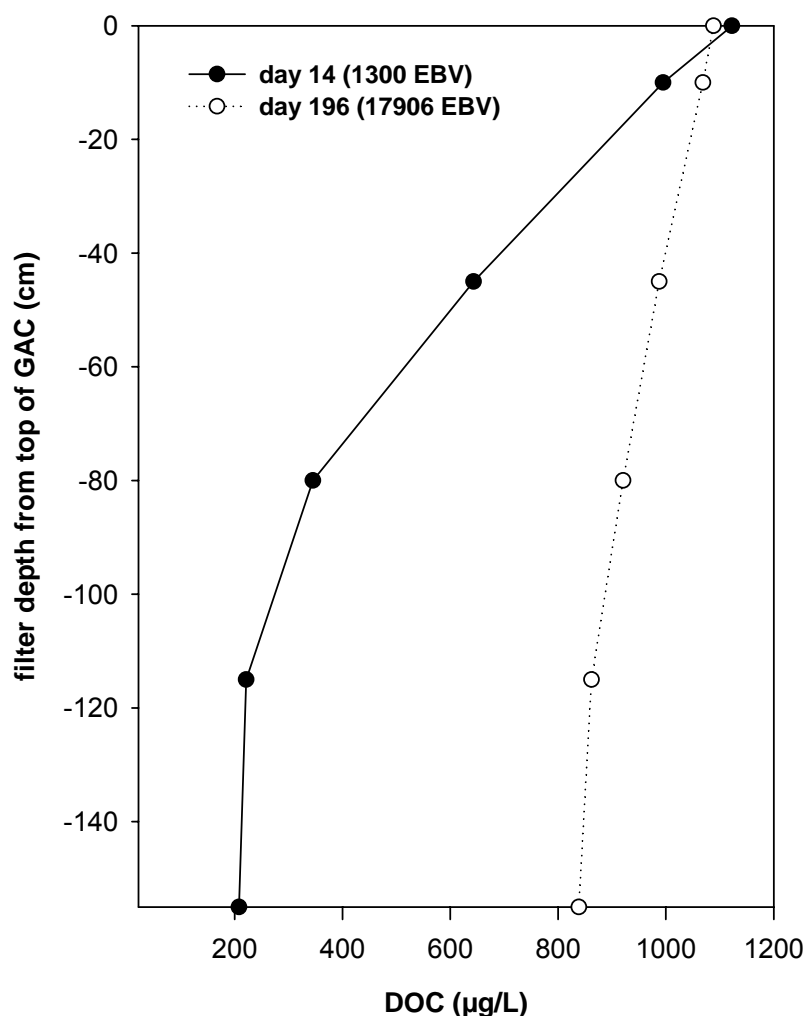


Fig. 3. Typical DOC filter profiles for two sampling days. At day 14 (1300 EBV) a high adsorption capacity for DOC still existed, whereas at day 196 (17906 EBV) the adsorption capacity decreased and resulted in an increased DOC effluent concentration. The standard error is 10%.

In the 1st period, the growth rates in the middle layers (GAC 2 and GAC 3) fluctuated but increased markedly at about day 60 (Figure 2). The cause of this increase was directly related to a significant influx of algal organic matter that typically occurs during this time of the year. Phytoplankton in the raw water, predominantly cyanobacteria from the species *Planktothrix rubescens*, increased from an average biomass concentration of 300 µg/L up to 1530 µg/L between day 50 - 70 and remained relatively high until day 198 (see also Figure 6B below). The algal cells are severely damaged by ozonation, and release/form AOC that stimulates growth in the GAC filter (Müller et al., 2003; Hammes et al., 2007). In addition, since no backwashing was applied to the filter, the dead algal cells accumulated visibly on

top of the filter bed (data not shown), where ongoing chemical degradation (residual ozone is on average 0.22 mg/L) and enzymatic degradation contribute to increased AOC concentrations in the water. This represents a significant addition of bio-available organic carbon, which could most likely not be used entirely in the top of the filter, and thus supported increased growth in the lower layers. Figure 4 shows average AOC profiles in the filter for the periods before and after the increased algal influx. Before the influx, an expected pattern was observed, where AOC produced during ozonation (average = 80 µg/L) was removed during the GAC filtration. During the period of increased algal influx, the AOC concentration after ozonation is higher (average = 110 µg/L) while a further increased concentration of AOC at level WS 1/GAC 1 (average = 145 µg/L) is evident. As a result of these additional nutrients, the biomass concentration in the middle layers (GAC 2 and GAC 3) developed extensively in this period. As shown below, the increased phytoplankton concentration directly affected the number of planktonic cells in the effluent of the filter.

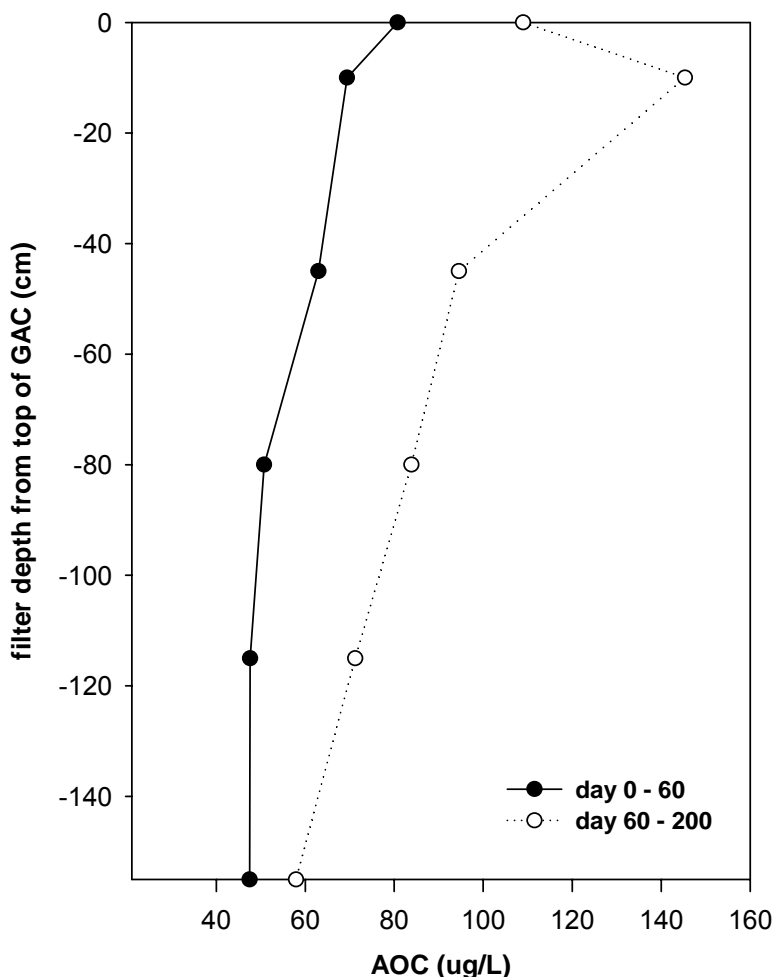


Fig. 4. AOC filter profiles for two periods, the first average data from 0-60 days and the second average data from 60-200 days showing the impact of the high algae influx. Data points are mean values of 12 data points (statistical difference).

Throughout the initial biofilm development periods, the growth rates obtained were about 10 times lower than those reported by Servais et al. (2002), which were growth rates of 0.038 - 0.16 h⁻¹ for similar empty bed contact times (EBCT) at temperatures of 9 - 22 °C. This can be ascribed to the temperature factor, which was up to 15 °C higher than in the present study (7.05 (± 0.7) °C) and to considerably higher influent DOC concentrations (1.7 - 2.95 mg/L), which would all be supportive of higher growth rates (Servais et al., 2002). In addition, Servais et al. (2002) utilized a different approach for the determination, which might have contributed to differences with the present study.

In the 2nd period (t₂), a steady state in terms of biomass concentrations was observed in all levels, and evidently, differences of up to 2.3 times in biomass concentrations occur in the separate levels. The average concentration (n = 14) for each level during the steady state period was

GAC 1 (10 cm) = 1.17 (±0.2) x 10⁻⁶ g ATP/g GAC;

GAC 2 (45 cm) = 1.83 (±0.4) x 10⁻⁶ g ATP/g GAC;

GAC 3 (80 cm) = 1.18 (±0.2) x 10⁻⁶ g ATP/g GAC;

GAC 4 (115 cm) = 0.8 (±0.2) x 10⁻⁶ g ATP/g GAC.

These values are in the same range (0.3 - 1.8 x 10⁻⁶ g ATP/g GAC) of previous reported data for GAC filters (Velten et al., 2007; van der Aa et al. 2006). The variations in biomass concentrations reported in different studies can be the result of different methodologies for biomass determination, different types of GAC and different water qualities used for operation.

The highest biomass concentration was established in level GAC 2 (45 cm from the top; Figure 1). Urfer and Huck (2001) also determined a higher biomass concentration at a second sampling point (9 cm) compared to a first one (4 cm). These authors explained the lower concentration at the first sampling point as a result of the presence of residual ozone in the influent of the filter. The same explanation would suffice in the present study: residual ozone on top of the GAC filter was 0.22 mg/L. In addition, Urfer and Huck (2001) demonstrated that even when a GAC filter was backwashed twice a week, the higher biomass concentration was constantly established in the second sampling point. This illustrates that stratification effects occur also in backwashed GAC filters between backwashing events. In both the present study and that reported by Urfer and Huck (2001), the biomass concentration decreased likewise with the GAC filter depth from the second sampling point on. Such vertical stratification was also shown by Wang et al. (1995). Interestingly, Servais et al. (1994) showed a stratification effect over the filter bed only during operational periods of 20°C, and not for the low temperatures (e.g. 9°C), as in this study.

Knowledge about this stratification effect is important because it impacts on sampling strategies that are used when GAC filters are assessed. Filters that are sampled from only one location (usually at the top) might not provide a complete picture of the actual biomass distribution throughout the filter, and result in erroneous total biomass calculations.

Estimation of total biofilm biomass

At steady state, the entire filter contained in total an amount of about 2.7×10^{15} cells, which was estimated from the concentration of ATP measured at the different levels and specific ATP-per-cell values measured for this particular system. Figure 5 gives an example of the concentration of ATP across the depth of the GAC filter at one specific point in time (EBV = 14251; time = 156 days; from Figure 2). For the calculation of the total biomass, the filter was partitioned into four segments, with the intersection half of the distance between adjacent sampling points. For each segment, the mass (dry weight) of GAC was calculated from the known volume and density of the GAC (Table 1). Each sampling point was assumed to give the average ATP concentration of the segment that it represented. Using the operational parameters (Table 1), the total ATP content for the entire GAC filter for every time point was calculated. For example, the average concentration at steady state ($n = 14$) results in the following calculation for layer GAC 1 and the filter in total:

$$\begin{aligned} \text{Total ATP (GAC 1)} &= \text{ATP concentration (GAC 1)} \times \text{mass of GAC (segment GAC 1)} \\ &= 1.17 \times 10^{-6} \text{ g ATP/g GAC} \times 120\,000 \text{ g GAC} \\ &= 0.14 \text{ g ATP} \end{aligned}$$

$$\begin{aligned} \text{Total filter ATP} &= \text{GAC 1} + \text{GAC 2} + \text{GAC 3} + \text{GAC 4} \\ &= 0.14 \text{ g} + 0.28 \text{ g} + 0.18 \text{ g} + 0.2 \text{ g} \\ &= 0.8 \text{ g ATP} \end{aligned}$$

During the course of the experimental period, we have also measured the specific cellular ATP concentration (ATP/cell) for bacteria removed from the GAC. This was on average $3 \pm 1.5 \times 10^{-16}$ g ATP/cell ($n=105$), which is similar to values reported previously (MAGIC-Knezev and van der Kooij, 2004; van der Aa et al., 2006; Velten et al., 2007; Hammes et al., 2008). Using this value, combined with the total ATP content, we have calculated the total cell content in the filter at every sampling time point (Figure 6A). For example, the average cell content in the filter during steady state was 2.67×10^{15} cells, derived from the total ATP concentration (0.8 g ATP, above). Considering an average cell biovolume of $0.065 \mu\text{m}^3/\text{cell}$

(Wang et al. 2009) this amount of biomass represents an overall biovolume of approximately $1.75 \times 10^{-4} \text{ m}^3$ in the GAC filter. According to studies on the head-loss development in deep bed filters by Boller and Kavanaugh (1995), this amount of biomass can lead to only minor head-losses in the order of a few millimeter water column. Therefore, if a GAC filter is operated in such a manner that no additional particles would enter the filter (e.g. GAC after ultrafiltration and ozonation) backwashing of the GAC filter would hardly be necessary.

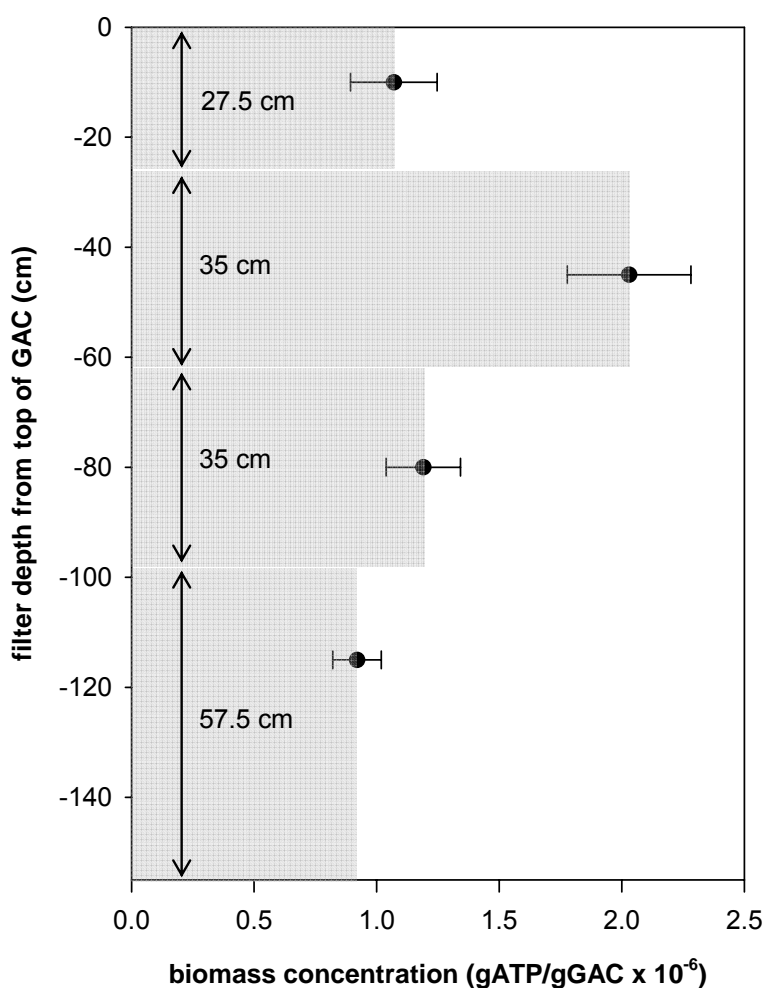


Fig. 5. Example of the concentration of biomass (g ATP/g GAC) at different depths in the GAC filter (Figure 1) at one specific time point (EBV = 14251; Time = 156 days). Blocks indicate the model that was used to convert biomass concentration to total filter biomass. Error bars represent standard deviation on triplicate measurements.

DOC removal and biomass production in steady state

Figure 6A shows how the DOC concentration in the GAC effluent continuously increased from the start-up, while at the same time, attached biomass increased on the GAC particles. The increasing DOC concentrations in the effluent is the direct result of the decreasing adsorption capacity of the carbon becoming exhausted (Figure 3). The biomass steady state is established at about the same time (90 days) as when the adsorption capacity of the GAC nears exhaustion. During this period, the primary function of the GAC filter – removal of DOC – is taken over by biological processes. It is difficult to estimate exactly how much of the DOC removal can be ascribed to adsorption still, how much is direct biological removal, and how much is a combination of the two processes (i.e., adsorption followed by biological degradation). For the purpose of this paper we considered the adsorption after 90 days to be negligible. A combination of bacterial respiration and biomass assimilation should predominantly account for the DOC removal. Biomass production can be measured as the concentration of suspended cells detached in the effluent of the reactor (Figure 6B), as well as the increase of attached biomass on the GAC particles (Figure 6A). The average DOC removal in the steady state was $240 (\pm 24) \mu\text{g/L}$ ($n = 14$), which equals 22% of the influent DOC concentration and which implies a removal of $1.41 \text{ g/m}^2\text{h}$ (flow rate of $5.6 \text{ m}^3/\text{h}$). The studies from Volk and LeChevallier (2000) and Servais et al. (1991) suggest that in surface waters on average 5 – 49% of the total DOC can be present as BDOC. The average concentration of suspended cells was $2.53 \times 10^5 \text{ cells/mL}$ ($\text{sd} = 5.6 \times 10^4 \text{ cells/mL}$, $n=14$), which equates to an average cell production of $1.49 \times 10^{12} \text{ cells/m}^2\text{h}$. The attached biomass displayed only a slight increase at a rate of about $0.0001/\text{h}$ (Figure 6A), which equates to an average cell production of $2.74 \times 10^{11} \text{ cells/m}^2\text{h}$ ($2.67 \times 10^{11} \text{ cells/h}$). This implies that about 84% of biomass formed during steady state is present in the effluent as suspended cells. The total biomass production of $1.78 \times 10^{12} \text{ cells/m}^2\text{h}$, combined with the total DOC removal ($1.41 \text{ g/m}^2\text{h}$) translates to a yield of $1.26 \times 10^6 \text{ cells}/\mu\text{g}$. This value is about 10-times lower than yield values for suspended cells of natural microbial communities in drinking water growing under optimal conditions (van der Kooij, 2002; Vital et al., 2007). However, it should be considered that these cells grew in biofilms where severe nutrient limitation prevailed. Coupled with the low temperatures and a high dilution rate (Table 1) a lower yield can be expected (Vital et al., 2008). This is also similar to data found in our group for full-scale sand filters and GAC filters (unpublished data). By using an average cellular carbon content of $2 \times 10^{-14} \text{ g}$ per cell (Servais et al., 1991; Batté et al., 2003), it was calculated that $0.035 \text{ g/m}^2\text{h}$ was assimilated as biomass. This fraction is only 3% of the total DOC amount removed in the filter ($1.41 \text{ g/m}^2\text{h}$), which is slightly lower than the findings of 8% from Servais et al. (1991). AOC was used as an indicator of the biodegradable organic carbon fraction in the water.

However, the AOC analysis typically detected only 35% of the DOC that was removed during steady state, confirming the considerable differences between AOC and BDOC observed in previous studies (Volk and LeChevallier 2000; Escobar and Randall 2001). Moreover, the data in Figure 4 clearly demonstrates how the AOC fluctuated during the period of high algal concentrations in the water, suggesting that AOC turnover in the filter can potentially lead to localized differences in AOC concentrations. From these observations the conclusion can be drawn that AOC analysis is not the optimal method to study biodegradability in GAC reactors.

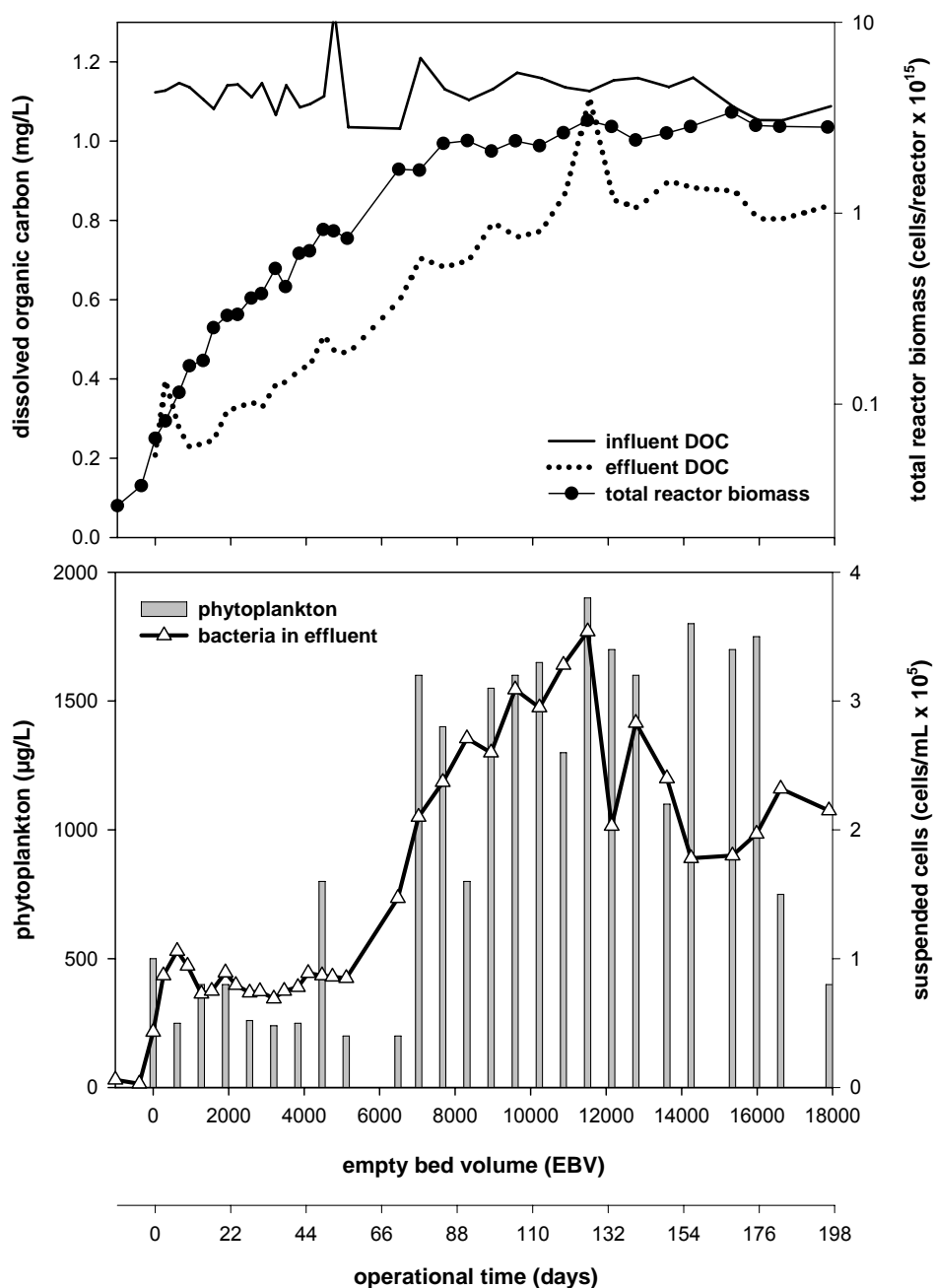


Fig. 6. Presentation of the evolution of influent DOC, effluent DOC, total filter biomass, phytoplankton in the influent and bacteria in the effluent of the filter as a function of the empty bed volume (EBV) and operational time.

It is furthermore interesting to note that the concentrations of suspended cells in the effluent follow the same pattern as phytoplankton in the influent to the pilot plant. Figure 6B shows the development of suspended cells over time in the effluent and the corresponding influx of algae's to the GAC filter. This behavior could also be followed for the biomass on the GAC in the two middle layers (GAC 2 and GAC 3), as described above. Thus biomass concentrations for both, suspended and biofilm biomass, are apparently strongly correlated to the substrate influx in the GAC filter: the higher the available carbon/nutrient concentration the higher the biomass amount in the GAC filter and in the effluent ($R^2 = 0.71$).

Monitoring and optimization of GAC filter performance

An important practical point is how biofiltration processes can/should be monitored, and if and how filter performance can be improved. The GAC-ATP method provided meaningful scientific information, but regular sampling from different levels of a full-scale filter is usually not practical. Straightforward DOC analysis and FCM total cell counts provided useful data, which described both the general filter performance as well as specific changes/events in the water quality (e.g. TCC increase during algal intake). These methods are fast and easy to use, and therefore have considerable practical value. It is also imperative to know the total concentration of biodegradable organic carbon in the water, in order to evaluate whether the filter performs optimally. In the present study, AOC analysis clearly did not suffice for this purpose. Consequently, consideration should be given to BDOC analysis as an alternative tool for this purpose (Escobar and Randall 2001, Prevost et al. 2005).

One approach towards improving the filter performance would be to increase the total microbial growth rate (thus DOC degradation rate), for example by increasing the operational temperature. However, in a full-scale treatment plant, considerable changes in bulk water temperature is not feasible at all, while increased temperatures may provide better opportunities for pathogenic bacteria to proliferate (Vital et al. 2008). A second approach would be to increase the EBCT in the filter by either using a slower filtration rate or a larger filter bed (Prevost et al. 2005). The extension over a threshold limit may not significantly increase BOM removal, and straightforward modeling of our data suggested that the filter investigated in this study already had an optimal filter bed depth. A larger filter bed would also increase the investment costs and also existing EBCT's cannot be augmented easily. Using a decreased filtration rate to achieve a larger EBCT might suffice, but a slower filtration rate would have a negative impact on the general operation (less water production). However, it is interesting to note that some full-scale systems are operated with a slow sand filtration

as the final treatment step, which provides significantly longer EBCT's than what can be obtained with conventional GAC filtration.

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3

Characterization of natural organic matter adsorption in granular activated carbon adsorbers

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Abstract

The removal of natural organic matter (NOM) from ozonated lake water was followed during the operation of two pilot-scale granular activated carbon (GAC) adsorbers containing coal-based GACs with different physical properties. To study the adsorption behavior of individual NOM fractions as a function of time and adsorber depth, NOM was fractionated by size exclusion chromatography (SEC) and NOM fractions were quantified by both ultraviolet and organic carbon detectors. High molecular weight biopolymers were not retained in the two adsorbers. In contrast, humic substances, building blocks and LMW organics were initially well removed, and their effluent concentrations increased gradually in the outlet of the adsorbers until a pseudo-steady state concentration was reached. Poor removal of biopolymers was likely a result of their comparatively large size that prevented access to the internal pore structure of the GACs. In both GAC adsorbers, adsorbability of the remaining NOM fractions, compared on the basis of partition coefficients, increased with decreasing molecular size, suggesting that increasingly larger portions of the internal GAC surface area could be accessed as the size of NOM decreased. Overall DOC uptake at the onset of pseudo-steady state differed among the two tested GACs (18.9 g-C/kg GAC versus 28.6 g-C/kg GAC), and the percent difference in DOC uptake closely matched the percent difference in the volume of pores with widths in the 1-50 nm range that was measured for the two fresh GACs. These results illustrate the importance of the pore size distribution (PSD) on the adsorber effluent water quality.

Keywords

Adsorption, granular activated carbon, natural organic matter (NOM), NOM characterization

Introduction

Granular activated carbon (GAC) filters are widely used to remove micropollutants and natural organic matter (NOM) from drinking water. One beneficial result of NOM removal is that precursors for halogenated disinfection by-products (DBPs) are eliminated (1). NOM removal can result in a reduction of membrane fouling and thus increases membrane filtration efficiency (2).

Because aquatic NOM varies in character both spatially across different water sources and temporally within a water source (3), the rate and extent of NOM adsorption and the consequences on MP removal effectiveness are difficult to predict (4). Aspects of NOM character such as molecular weight distribution (MWD), degree of hydrophobicity, charge distribution, and ability to hydrogen bonds affect the NOM adsorption capacity of activated carbon (AC). In addition, physical (surface area; size, shape and volume of pores) and chemical (charge, type, and number of surface groups; ash content) AC characteristics influence NOM adsorption (5). Furthermore, solution pH, ionic strength, and hardness influence the adsorption of NOM (6).

Physical effects are largely governed by the MWD of NOM relative to the pore size distribution (PSD) of AC (7, 8). NOM adsorption primarily takes place in mesopores (2-50 nm width) and large micropores (1-2 nm width) (5, 8-12) and is negligible on AC that primarily contains small micropores (<1 nm in width) (11, 12). The high molecular weight (HMW) fraction of NOM does not readily adsorb because of size exclusion effects; however, this NOM fraction is generally well removed by coagulation and is frequently present only at low concentrations in GAC adsorber influents (13, 14). In contrast, intermediate molecular weight fractions (~500-4000 Da) are well removed by GAC. Although low molecular weight (LMW) NOM constituents have access to a large percentage of the GAC pore volume and thus could be well removed based on size considerations alone, low MW compounds may also be relatively hydrophilic and, hence, less adsorbable, and/or they may represent metabolic products of microorganisms living in the GAC filter (13).

Chemical interactions are influenced by characteristics of the adsorbate, the adsorbent surface, and the water matrix. Because of the presence of carboxylic acid and phenolic groups in the NOM structure, NOM carries a negative charge at pHs typically encountered in drinking water treatment (15). Depending on the solution pH, the AC base material and the activation process, the net surface charge of AC can be positive, negative, or neutral (7). Consequently, electrostatic interactions can affect NOM adsorption. Overall, however, the adsorbent pore size distribution appears to be the principal factor controlling NOM uptake by GAC while electrostatic effects play a secondary role (16, 17).

To date, little is known about the adsorption behavior of individual NOM fractions during the operation of fixed bed GAC adsorber when adsorptive NOM removal dominates. The objectives of this study were (1) to determine the breakthrough behavior of dissolved organic carbon (DOC) and individual NOM components such as biopolymers, humic substances,

building blocks and LMW organics in pilot-scale GAC adsorbers and (2) to compare the adsorbability of individual NOM fractions on two GACs with different physical characteristics.

Tab. 1. Operational and influent water quality parameters for GAC 1 and GAC 2 adsorbers.

| parameters | | GAC 1 | GAC 2 |
|----------------------------|----------------------|----------------|--------------------|
| carbon type | | Chemviron F400 | Chemviron SGL 8x18 |
| reactor volume | (m ³) | 0.015 | 1.47 |
| filtration velocity | (m/h) | 8 | 5.9 |
| backwash rate | (m/h) | 22.9 | n/a |
| backwash time | (min/d) | 10 | n/a |
| empty bed contact time | (min) | 1.65 | 15.76 |
| GAC depth | (m) | 0.22 | 1.55 |
| column diameter | (m) | 0.3 | 1.1 |
| GAC particle diameter | (mm) | 0.125 - 0.71 | 1 - 2.5 |
| bed porosity | (-) | 0.47 | 0.39 |
| packed bed density | (kg/m ³) | 425 | 460 |
| influent DOC | (mg/L) | 0.96 (± 0.03) | 1.1 (± 0.04) |
| influent UV ₂₅₄ | (1/m) | 1.07 (± 0.14) | 1.84 (± 0.18) |
| influent SUVA | L/(mg·m) | 1.12 (± 0.12) | 1.58 (± 0.18) |
| influent pH | (-) | 8.1 (± 0.3) | 7.79 (± 0.14) |

Materials and methods

Experimental setup and water characteristics

Two GAC adsorbers, GAC 1 and GAC 2, were set up at the Zurich Water Works (WVZ-Lengg, Zurich, Switzerland). GAC 1 was operated with ozonated water from the intermediate ozonation step of the full-scale water treatment plant while GAC 2 was part of a pilot plant that included ozonation, GAC filtration and ultrafiltration. Both reactors were operated in down flow mode. Operational and influent water quality parameters for the two GAC adsorbers are given in Table 1. The design of the GAC 2 filter allowed sampling over the entire filter bed. Samples were taken at four sampling points that were distributed over the

whole filter with an interspace of 30-40 cm. To not disturb the mass transfer zone in GAC 2, the adsorber was not backwashed during the course of this study.

Activated carbons and activated carbon characterization

Two bituminous-coal based GACs (Chemviron SGL 8x18 and Chemviron F400, Chemviron, Feluy, Belgium) were used. GAC characteristics are summarized in Table 2.

Tab. 2. Physical characteristics of two GACs that were used in the GAC filters to assess the NOM adsorption. BET surface area and pore volume distributions were obtained from N₂ adsorption isotherm data.

| parameters | | GAC 1 | GAC 2 |
|---|----------------------|----------------|--------------------|
| Carbon Type | | Chemviron F400 | Chemviron SGL 8x18 |
| BET Surface Area | (m ² /g) | 1060 | 790 |
| Primary Micropore Volume ^a | | | |
| 0 - 10 Å | (cm ³ /g) | 0.175 | 0.165 |
| Secondary Micropore Volume ^a | | | |
| 10 - 20 Å | (cm ³ /g) | 0.207 | 0.127 |
| DFT Mesopore Volume ^b | (cm ³ /g) | 0.203 | 0.124 |
| BJH Mesopore Volume ^c | (cm ³ /g) | 0.232 | 0.146 |

^a Micropore volume calculated by density functional theory (DFT) for pores with widths less than 20 Å

^b Mesopore volume calculated by density functional theory (DFT) for pores with widths ranging from 20 to 360 Å (upper limit for DFT model)

^c Mesopore volume calculated by Barrett, Joyner, and Halenda (BJH) method for pores with widths ranging from 20 to 500 Å

NOM characterization

Glass vials for DOC sampling were acid washed and baked at 450°C for 4 hours. NOM was fractionated by size exclusion chromatography (SEC) and quantified by both ultraviolet (UV) and organic carbon (OC) detectors. The SEC column (Toyopearl TSK HW-50S, 250 x 20 mm) has a fractionation range of 100-20,000 Da and fractionates NOM in a water sample such that HMW compounds elute first and LMW compounds elute last. The UV detector (Knauer K-200) provides an online UV signal and OC is detected by an infrared (IR) detector after

oxidation of NOM to CO₂ in a Graentzel Thin-Film Reactor (DOC-Labor Dr. Huber, Germany). Chromatograms were interpreted based on a previously developed procedure (18). Hydrophobic organic carbon (HOC) that did not elute from the SEC column was quantified by determining the difference between DOC and the sum of the detected chromatographic OC. A phosphate buffer was used as the eluent (24 mM, pH 6.6) and the flow rate was set at 1 mL /min. The detection limit was 10 µg C/L.

Results and discussion

GAC 1

NOM adsorption in GAC 1 was studied for 112 days or 98,000 empty bed volumes (EBV). Panels A and B of Fig. 1 show DOC and UV absorbance data collected at the inlet and outlet of GAC 1. Following rapid initial breakthrough, effluent DOC and UV absorbance values reached a pseudo-steady state after about 40 days of operation or 36,000 EBV. At that time, the UV absorbance values measured in the adsorber inlet and outlet were almost identical whereas of the DOC data differed by about 0.1 mg-C/L (Fig. 1). This difference may be explained by biodegradation of a DOC fraction with low UV absorbance.

For GAC 1, 50% DOC breakthrough was reached after ~2,400 EBV. When GAC is used to remove NOM with the goal to minimize disinfection by-product formation during chlorination, full-scale experience suggests that 50% total organic carbon (TOC) breakthrough is reached after ~6,400 and ~7,900 EBV for empty bed contact times (EBCT) of 10 and 20 minutes, respectively (19). The earlier occurrence of 50% DOC breakthrough obtained here resulted from the short EBCT of GAC 1 (1.65 min) relative to those used in practice. Regarding the onset of the pseudo-steady state region, results obtained with GAC 1 were similar to those of a prior study (20), during which a pseudo-steady state TOC concentration was reached after 35,000-40,000 empty bed volumes when evaluating TOC removal from ozonated water in a GAC adsorber with an EBCT of 1.2 min.

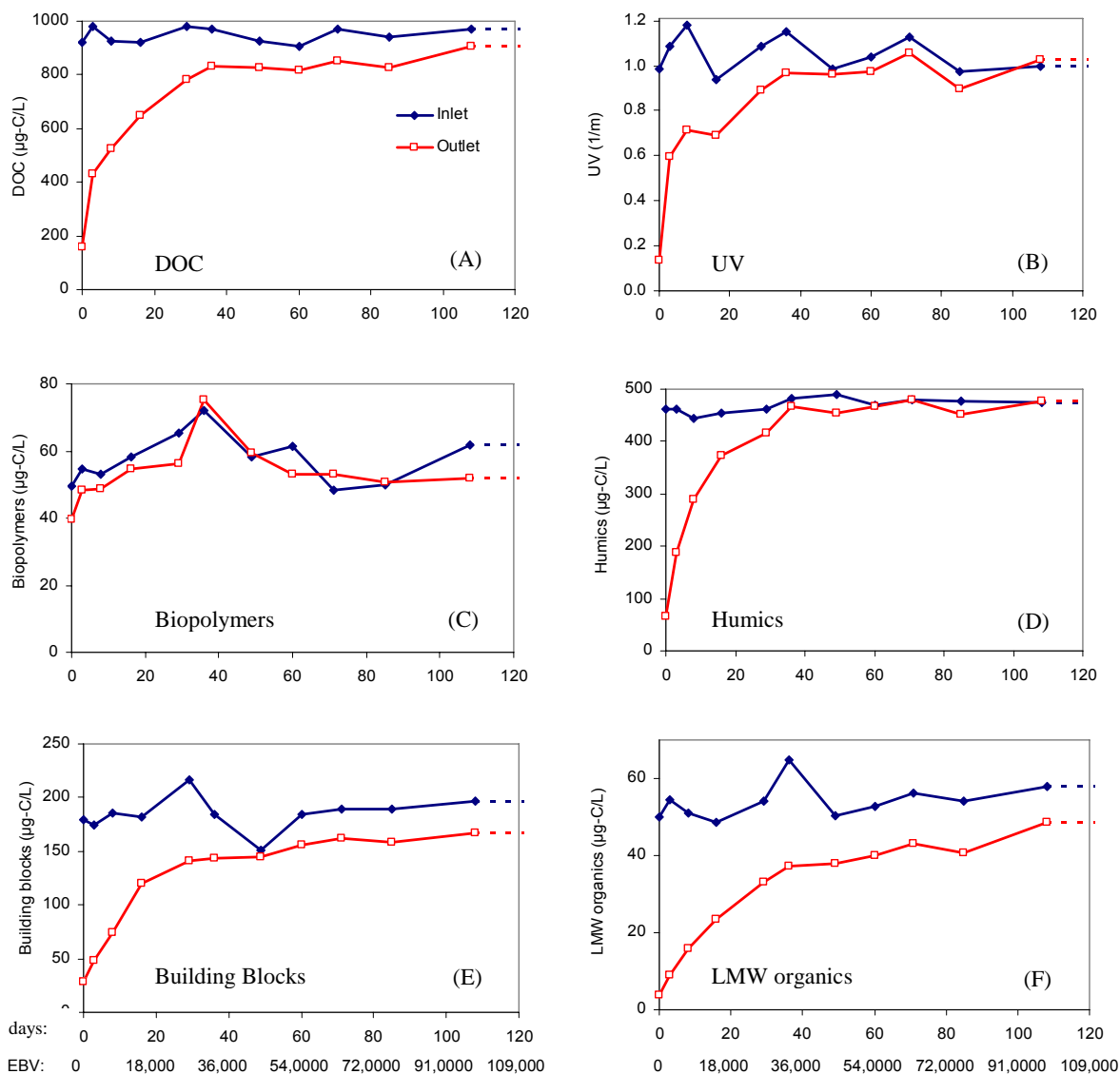


Fig. 1. Influent and effluent concentrations of DOC, UV absorbance, biopolymers, humics, building blocks and LMW organics measured for GAC 1.

NOM characterization

Fig. 2 compares size exclusion chromatograms obtained with OC (panel A) and UV detection (panel B) of influent and effluent samples obtained from GAC 1 during the first 50 days of operation. The size exclusion chromatogram of the influent that was obtained with OC detection exhibits a peak for biopolymers (28 min retention time) followed by a large humic substances peak (42 min retention time) that constituted ~50% of the total DOC. Building blocks (45 min retention time) are degradation products of humic substances. LMW organics (51 min retention time) are composed of LMW acids and LMW humics that elute simultaneously. LMW neutrals (>55 min retention time) are neutral or amphiphilic molecules

that interact with the column and consequently have a longer retention time than the elution time of water (55 min). Compared to the size exclusion chromatogram obtained with OC detection, that obtained with UV detection differs in three aspects: (1) the biopolymer peak is absent, (2) the relative signal strength for building blocks is lower, and (3) the relative signal strength for LMW organics is higher. Fig. 2 qualitatively shows the removal of individual NOM fractions during the start-up phase of the GAC adsorber. Biopolymers were not retained by the GAC filter as influent and effluent concentrations were practically identical after one day of operation. Concentrations of humics, building blocks and LMW organics increased gradually in the effluent during the first 50 days of operation. The three dominant NOM fractions (humics, building blocks, and LMW organics) were initially all well removed in the GAC adsorber, and this observation was consistent between chromatograms obtained with OC and UV detection. After 50 days of operation, the removal of humics became negligible while a small percentage of the two smaller NOM fractions (building blocks and LMW organics) continued to be removed across the GAC adsorber (Fig. 2).

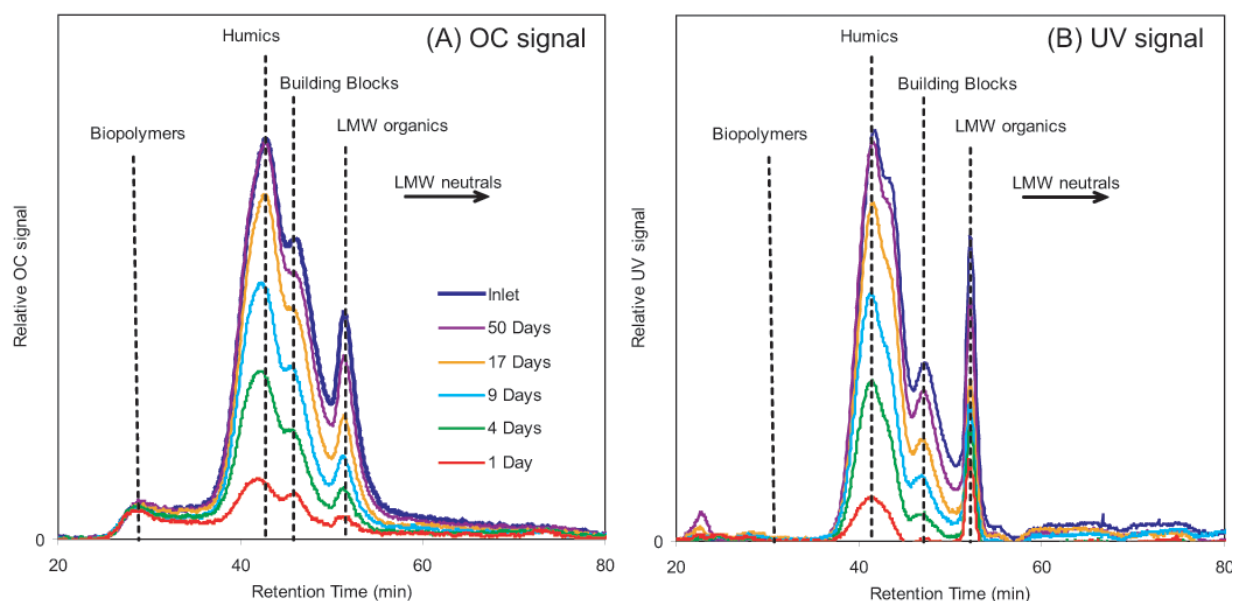


Fig. 2. SEC chromatograms obtained with OC detection (A) and UV detection (B) for influent and effluent samples of GAC 1.

Breakthrough curves for biopolymers, humics, building blocks and LMW organics are depicted in Fig. 1. Panel C confirms that biopolymers removal was negligible in GAC 1 (Fig. 1). Biopolymers such as protein- and polysaccharide-like substances are large molecules with MW > 20,000 Da. The number of adsorption sites for such large molecules on AC is limited because of size exclusion effects. Humics were initially well retained by GAC 1 but the AC rapidly lost its adsorption effectiveness (Fig. 1D). Fifty percent humics removal

was reached after ~4,500 EBV and the inlet concentration was reached after ~30,000 EBV. Compared to biopolymers, humics are much smaller molecules with an average molecular weight of ~1,000 Da and a diameter of < 2 nm; they can therefore enter the mesopores and larger micropores of activated carbon (18, 21). Similarly the building blocks are well retained during the start-up phase and 50% building blocks removal was reached after ~9,000 EBV. Complete breakthrough of building blocks was not reached during the operation time of GAC 1 (Fig. 1E), and about 20% of the influent building blocks were removed in the GAC filter at pseudo-steady state. LMW organics followed a similar pattern as building blocks with 50% LMW organics removal after ~17,000 EBV (Fig. 1F) and approximately 25% removal at pseudo-steady state. The decrease of building blocks and LMW organics is most probably due to biodegradation in the biofilm that developed in GAC 1. A concurrent study focusing on the development of the microbiology on GAC 1 showed that the number of microorganisms reached a maximum after 33 days of operation (30,000 EBV) (22).

Tab. 3. Solid-phase concentrations and partition coefficients (K_p) of DOC and individual NOM fractions on GAC 1 and GAC 2 at pseudo-steady state. Pseudo-steady state was reached in GAC 1 after 36,000 EBV or 40 days and in GAC 2 at 120 cm after 20,000 EBV or 168 days.

| fractions | GAC 1 | | GAC 2 | |
|-----------------|--|-----------------|--|-----------------|
| | solid-phase concentration (g-C/kg GAC) | K_p (L/g GAC) | solid-phase concentration (g-C/kg GAC) | K_p (L/g GAC) |
| DOC | 28.6 | 34.4 | 18.9 | 22.8 |
| Biopolymers | 1.1 | 14.7 | 0 | 0.0 |
| Humics | 11.3 | 24.2 | 7.8 | 16.7 |
| Building Blocks | 7.1 | 49.7 | 3.8 | 26.8 |
| LMW organics | 6.8 | 53.5 | 1.6 | 41.0 |

Table 3 summarizes adsorption capacities and partition coefficients of DOC and individual NOM fractions after pseudo-steady state was attained in GAC 1. Overall DOC uptake in GAC 1 was 28.6 g-C/kg GAC. Humics exhibited the highest solid-phase concentration on the GAC (11.3 g-C/kg GAC) followed by building blocks (7.1 g-C/kg GAC) and LMW organics (6.8 g-C/kg GAC) and finally biopolymers (1.1 g-C/kg GAC). The high solid-phase concentration of humics can in part be explained by its dominance in the influent NOM composition (50%). To compare the adsorbability of DOC and individual NOM fractions,

partition coefficients (K_p) were calculated from the pseudo-steady state solid phase concentration and the corresponding aqueous-phase concentration in the GAC 1 effluent ($K_p = q/C$). K_p values suggest that the adsorbability of NOM constituents increased with decreasing size; i.e. biopolymers < humics < building blocks < LMW organics. The greater adsorbability of smaller NOM constituents is likely the result of their ability to access a larger percentage of the total AC pore volume.

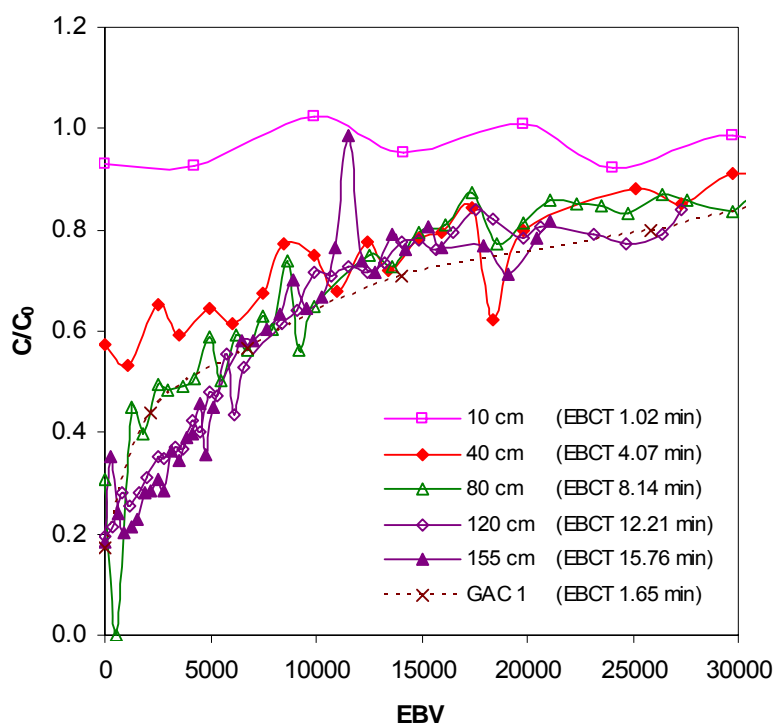


Fig. 3. DOC breakthrough curves obtained with GAC 2 at different empty bed contact times and with GAC 1: effluent DOC concentration normalized with respect to influent DOC concentration versus empty bed volumes treated.

GAC 2

Upon start-up of GAC 2, NOM removal was studied at different depths over a 4-month period. Fig. 3 depicts the evolution of DOC concentrations as a function of operation time and depth. Fifty percent DOC breakthrough in GAC 2 was reached immediately after start up of the reactor in the top 2 layers (10 and 40 cm) and was reached after 4,300 EBV at 80 cm (EBCT = 8.1 min); 5,300 EBV at 120 cm (EBCT = 12.2 min); and 6,500 EBV at 155 cm (EBCT = 15.8 min). EBV values to 50% DOC breakthrough that were obtained with GAC 2 are typical when compared to U.S. data that was gathered as part of the information collection rule (6449 ± 3935 EBV at an EBCT of 10 minutes, 20). Plotting normalized effluent

DOC concentrations as a function of treated EBV, a comparison of the breakthrough curves at different filter depths (Fig. 3B) shows improved DOC removal with increasing EBCT up to an EBCT of 12.2 min; an increase in EBCT from 12.2 to 15.8 min did not offer an advantage in terms of decreasing carbon usage rate, however.

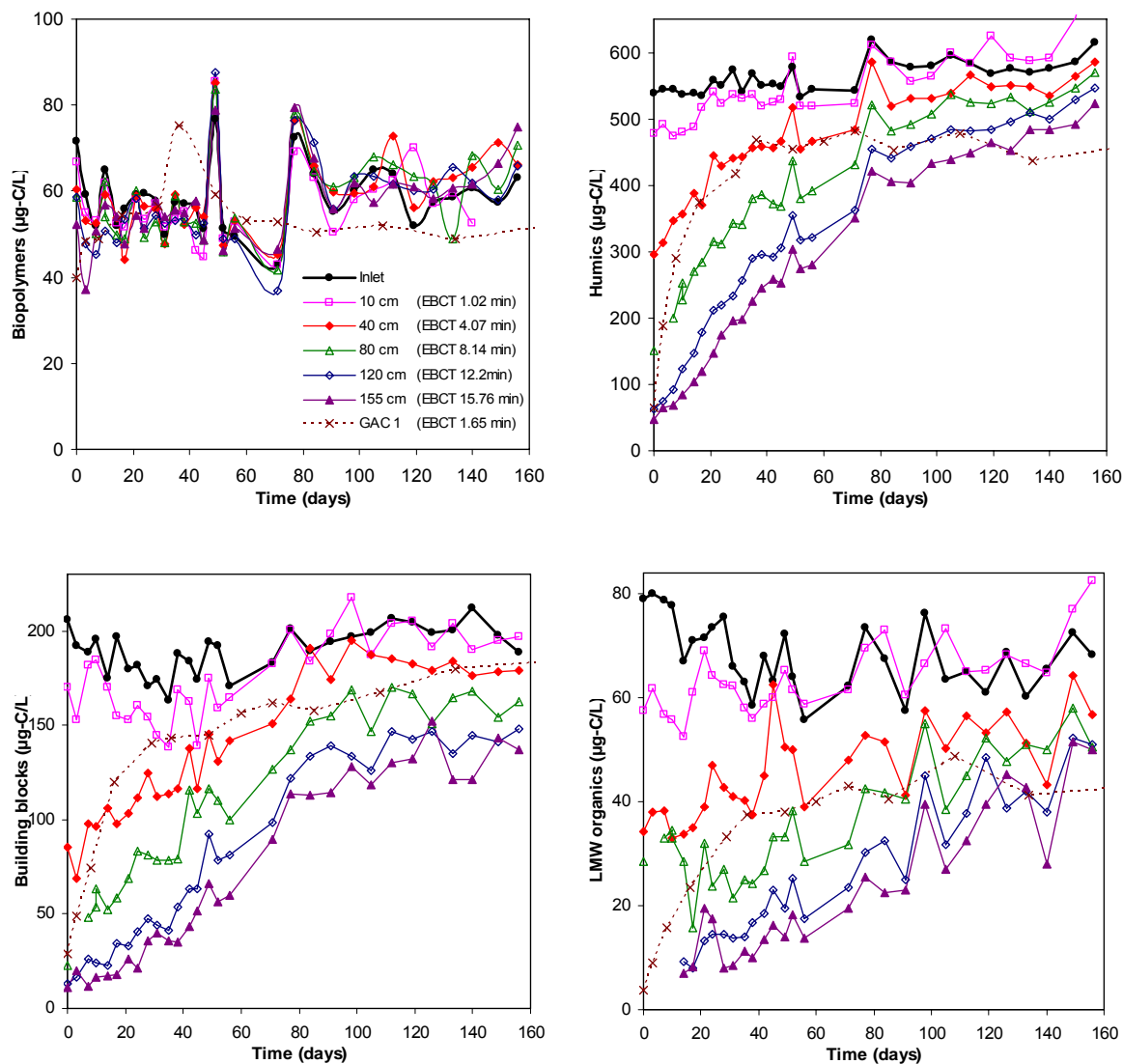


Fig. 4. Evolution of biopolymers, humics, building blocks and LMW organics during the load of GAC 2 at different levels of the reactor as a function of the operation time and depth compared to GAC.

Fig. 4 depicts breakthrough curves for biopolymers, humics, building blocks and LMW organics obtained with GAC 2 at different depths. In addition, results obtained with GAC 1 are included for comparison. As was the case with GAC 1, biopolymers were only slightly retained in GAC 2. Humics and building blocks were well retained during the start-up phase, and concentrations decreased with increasing filter depth. At an EBCT of 15.8 min, 50%

breakthrough of humics, building blocks, and LMW organics was reached after 5,100 EBV (56 days), 6,500 EBV (71 days), and 10,300 EBV (112 days), respectively.

Adsorption capacities and partition coefficients of DOC and individual NOM fractions for GAC 2 are summarized in Table 3. The overall uptake of DOC in GAC 2 was 18.9 g-C/kg GAC. As was the case with GAC 1, humics showed the highest solid-phase concentration on GAC (7.8 g-C/kg GAC), followed by building blocks (3.8 g-C/kg GAC), LMW organics (1.6 g-C/kg GAC), and biopolymers (negligible adsorption). Partition coefficients for individual NOM fractions were calculated once the effluent DOC concentration reached a pseudo-steady state (~168 days at an EBCT of 12.21 min). The order of NOM fraction adsorbability matched that obtained with GAC 1 (i.e., biopolymers < humics < building blocks < LMW organics).

Comparison of GACs

In this study two adsorbers containing GACs with different physicochemical properties were tested. The BET surface area of the AC used in GAC 2 exhibited a BET surface area that was 75% of that used in GAC 1; furthermore, the AC used in GAC 2 had secondary micropore (1-2 nm pore width range) and mesopore (2-50 nm pore width range) volumes that were approximately 60% of those measured for the AC used in GAC 1 (Table 2). In contrast, primary micropore volumes (< 1 nm width) were similar for the two ACs. Also, a smaller grain size was used in GAC 1 (US mesh 25x120) compared to GAC 2 (US mesh 8x18). Results of prior studies suggest that NOM adsorbs primarily in secondary micropores and mesopores. Therefore, DOC uptake was expected to be greater on the AC used in GAC 1. The solid-phase concentrations and partition coefficients shown in Table 3 indeed confirm that the AC used in GAC 1 was more effective for NOM removal than that used in GAC 2. At pseudo-steady state, DOC uptake in GAC 2 was approximately 66% of that obtained in GAC 1, a result that is in reasonable agreement with the difference in mesopore and secondary micropore volumes between the two tested ACs. This result illustrates that extent of NOM uptake in GAC adsorbers is largely controlled by pores with widths in the 1-50 nm range. This finding further confirms a result that has been obtained in previous batch tests.

To assess whether GACs with different physical properties fractionate NOM differently, size exclusion chromatograms for the influent and effluent of GAC 1 and GAC 2 were compared at points of operation, at which similar overall DOC removal was measured [for GAC 1 after 8 days or 7230 EBV and for GAC 2 after 42 days or 7434 EBV of operation

(EBCT 8.14 min), see Fig. 3]. As illustrated in Figure 5, all NOM fractions adsorbed similarly in the two GAC adsorbers even though the physical characteristics of the two GACs differed. Consequently, the effluent NOM composition at a given DOC removal percentage did not appear to be affected by differences in GAC pore structure. Finally, it should be noted that the smaller grain size of the AC used in GAC 1 aided the rate of NOM removal (Fig. 4). As illustrated in Fig. 4, the initial performance of GAC 1 (EBCT = 1.65 min) was similar to that of the GAC 2 layer with an EBCT of 8.14 min.

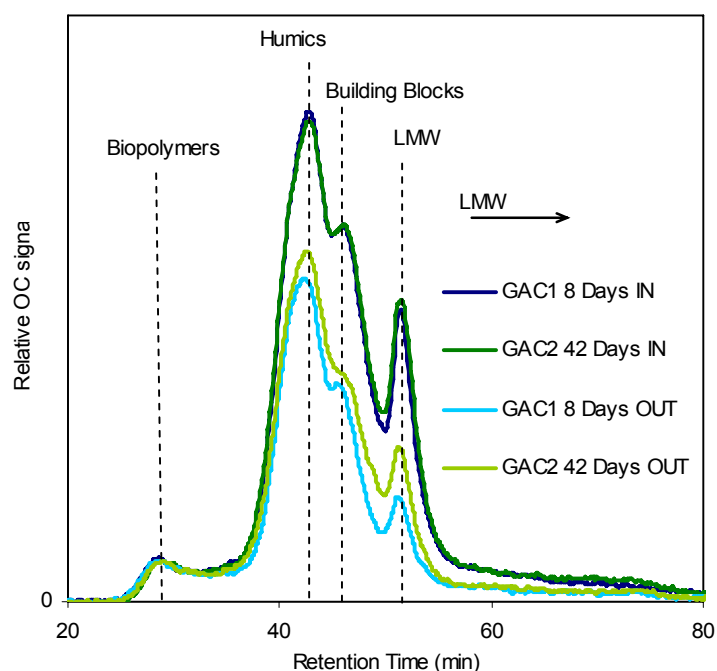


Fig. 5. SEC-OCD chromatograms for influent and effluent concentrations of GAC 1 and GAC 2 after treating 7230 and 7434 EBV, respectively.

In order to achieve a high removal efficiency of NOM from the water source, GAC adsorbers with a high surface area, combined with a high pore volume in the widths of 1-50 nm should be used in surface water treatment. In a treatment chain with GAC filtration followed by ultrafiltration, a reduction of the biopolymer and humic fractions which are mainly responsible for membrane fouling occurs only during the first three months of the start-up phase. Thus, GAC filtration does not lead to substantial fouling reduction of ultrafiltration membranes on a long term basis. Other means of fouling reduction such as the use of powdered activated carbon (PAC) or pre-coagulation have to be considered.

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4

**MTBE adsorption capacity and corresponding
physical characteristics of granular activated
carbon influenced by NOM**

4A

Effects of natural organic matter preloading on physical characteristics and remaining MTBE adsorption capacity of granular activated carbon

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Abstract

The objectives of this research were to quantify (1) changes in physical granular activated carbon (GAC) characteristics and (2) the loss of methyl *tertiary*-butyl ether (MTBE) adsorption capacity that takes place during GAC adsorber operation. An additional objective was to identify physical GAC characteristics that correlate directly with the remaining MTBE adsorption capacity of GAC in operating adsorbers. GAC samples were collected from a pilot-scale GAC filter that was operated for 298 days as well as from three full-scale GAC adsorbers. The remaining MTBE adsorption capacity at a concentration of 10 µg/L (q_{10}) decreased to 30 and 6% of that measured for fresh GAC after operating times of 3 and 298 days, respectively. Among the physical GAC characteristics that were determined (BET surface area, micropore volume, and pore volume in different size ranges), the pore volume in the 5.2-5.7 Å pore width range correlated most strongly with the remaining MTBE adsorption capacity. Other GAC characteristics did not change as dramatically as the MTBE adsorption capacity or the pore volume in the 5.2-5.7 Å range. For example, after 298 days, BET surface area, micropore volume, and pore volume <10 Å were 75, 74, and 71% of the values measured for fresh GAC. The relationship between remaining MTBE adsorption capacity and pore volume in the 5.2-5.7 Å range that was developed from the pilot-scale GAC adsorber effectively described the remaining MTBE adsorption capacity of GAC samples that had been collected from full-scale GAC adsorbers after service times of 112 and 365 days. An additional GAC sample that had been collected from a GAC adsorber after a service time of 20 years exhibited a negligible MTBE adsorption capacity and pore volume in the 5.2-5.7 Å range.

Keywords

Adsorption, granular activated carbon (GAC), methyl *tertiary*-butyl ether (MTBE), pore volume, surface area

Introduction

Granular activated carbon (GAC) adsorbers are frequently used to remove organic micropollutants from drinking water sources. In addition, natural organic matter (NOM) adsorbs on GAC and adversely affects the micropollutant adsorption capacity and kinetics, leading to considerable economic losses (Knappe et al. 1998, Munz et al. 1990, Newcombe et al. 2002, Quinlivan et al. 2005). Because water treatment plants typically operate GAC

adsorbers on a continuous basis, the presence of background NOM decreases the micropollutant adsorption capacity and kinetics even when the targeted micropollutant is absent in the source water (Kilduff et al. 1998, Munz et al. 1990, Summers et al. 1989). NOM is a heterogeneous mixture that, based on size, can be fractionated into biopolymers, humics, building blocks, low molecular weight (LMW) organics (Huber and Frimmel 1996). Biopolymers do not adsorb due to size exclusion effects, whereas humics, building blocks and LMW organics are well removed by GAC (Velten et al. submitted). NOM of similar size to micropollutants can directly compete with micropollutants for adsorption sites while larger NOM components are thought to cause pore blockage by adsorbing in mesopores and secondary micropores (Li et al. 2003a, Li et al. 2003b, Newcombe et al. 2002). While the directly competing NOM components primarily decrease the remaining micropollutant adsorption capacity, the pore blocking NOM primarily reduces micropollutant adsorption rates (Li et al. 2003a, Li et al. 2003b, Newcombe et al. 2002)

The effectiveness of adsorption processes strongly depends on the physical GAC characteristics (Karanfil and Kilduff 1999, Lee et al. 1981, Summers and Roberts 1988). In practice, many utilities rely on iodine number determinations to monitor the degree of GAC exhaustion. However, the iodine number is not a good predictor of remaining GAC life for a given micropollutant (Knappe et al. 2003). Since many micropollutants are small ($\sim 5 - 10 \text{ \AA}$ diameter), the presence of micropores of similar size primarily determines the effectiveness of activated carbon adsorption processes (Li et al. 2002). For micropollutants, whose adsorption region overlaps with that of NOM, GACs with a broad pore size distribution (PSD) (ranging from primary micropores to a large volume of secondary micropores and some mesopores) exhibited a smaller reduction in micropollutant adsorption capacity than GACs that essentially contained primary micropores only. For small micropollutants that adsorb in pores with widths $< 10 \text{ \AA}$, on the other hand, micropollutant uptake was least affected by NOM for GACs with a high volume of pores smaller than 10 \AA and a minimal volume of pores larger than 10 \AA (Guo et al. 2007). The latter scenario would apply to methyl *tertiary*-butyl ether (MTBE), which adsorbs in pores with widths of about $5.1\text{-}5.6 \text{ \AA}$ (Rossner and Knappe 2008).

In this study, MTBE was investigated because of its adverse impacts on drinking water odor and its potential carcinogenicity. MTBE is credited with reducing the emission of air pollutants from gasoline-powered vehicles, but it has also contaminated many water supplies. Because of its high solubility, low octanol/water partition coefficient, and low Henry's constant, MTBE is difficult to remove from water. The U.S. Environmental Protection Agency (EPA) concluded that concentrations in the range of 20 to 40 $\mu\text{g/L}$ are likely to lead to

unpleasant taste and odor effects (Melin 2000). In Europe, regulations for MTBE in drinking water exist only in Denmark, where a limit value of 30 µg/L applies (Kolb and Puttmann 2006).

The objectives of this work were to quantify the effect of GAC service time on (1) physical GAC characteristics and (2) remaining MTBE adsorption capacity. An additional objective was to identify physical GAC characteristics that correlate directly with the remaining MTBE adsorption capacity of preloaded GAC.

Materials and methods

Sample collection

GAC samples were collected from a pilot-scale GAC adsorber that was operated at the Zürich Water Works (WW Lengg, Switzerland). The GAC adsorber contained the 0.125 - 0.71 mm grain size fraction of Filtrasorb[®] 400 (Chemviron, Be) and was fed with ozonated Lake Zürich water ($Q = 13.5 \text{ m}^3/\text{day}$, EBCT = 1.65 min, $v_f = 8 \text{ m/h}$, DOC = 0.96 mg/L) (see Velten et al. 2007 for additional operational details). GAC samples were collected from the filter bed surface (upper 5 cm) over the first 298 days of operation. In addition, three full-scale GAC adsorbers treating ozonated Lake Zürich water were sampled. GACs in the full-scale adsorbers were SGL 8x18 and SGL 8x16 (both Chemviron, Be) and ROW 0.8 SUPRA (Norit, Kempen, D). Samples were collected after 112 and 365 days and after over 20 years of operation, respectively. All GAC samples were drained and stored in 200-mL screw-capped glass flasks in the dark at 4°C.

Adsorbent characterization

Brunauer, Emmett and Teller (BET) surface areas, micropore and mesopore volumes, and pore size distributions (PSDs) were determined from N₂ adsorption isotherm data collected at 77 K (Autosorb-1-MP, Quantachrome, Boynton Beach, FL, USA). Prior to analysis, adsorbent samples were outgassed for 24 hours at 423 K. BET surface areas were determined from 18-point adsorption isotherms that were completed with a 0.1-g sample in the 0.01 to 0.3 relative pressure range. PSDs were determined by conducting N₂ adsorption experiments in two separate phases: high and low pressure phase. Adsorption isotherms from both pressure phases were combined to produce one isotherm. Micropore volume and

PSD were computed from N₂ adsorption isotherm data using the Density Functional Theory (DFT) with the N2_carb1.gai kernel (PC software version 1.51, Quantachrome, Boynton Beach, FL, USA). In addition, the mesopore volume was computed using the Barrett, Joyner, and Halenda (BJH) method which captures the entire mesopore range (20 to 500 Å). Additional details of the experimental procedure are described in Knappe et al. (2007).

Isotherm experiments

Single-solute adsorption MTBE adsorption isotherm experiments were conducted in ultrapure laboratory water (UPW), which was produced by treating Raleigh, NC, tap water. UPW was amended with a 1 mM phosphate buffer (0.5 mM Na₂HPO₄•2H₂O and 0.5 mM NaH₂PO₄•7H₂O) to maintain a pH of 7. The effect of NOM on GAC adsorption capacity was evaluated with raw Tar River water (TRW). TRW was collected by the Greenville Utilities Commission (Greenville, NC, USA). Prior to its use in experiments, TRW was vacuum-filtered through a 0.45-µm membrane filter (Millipore, Durapore®) that was placed in a 47-mm glass microanalysis filter holder (Fisher Scientific, Pittsburgh, PA). Filtered TRW was diluted with UPW to a dissolved organic carbon (DOC) concentration of 1.1 mg/L (pH 7.8). To both UPW and TRW, 400 mg/L sodium azide (NaN₃) was added to avoid interferences associated with biological activity.

MTBE served as model organic contaminant in this study (HPLC grade, Fisher Scientific). MTBE stock solutions were prepared in UPW at a concentration of ~ 4,900 µg/L. Adsorption isotherm experiments (T = 25°C) were performed in UPW and TRW using a bottle-point technique (Knappe et al. 2003). GAC was not pulverized to avoid altering the adsorption capacity of preloaded GAC (Knappe et al. 1999). Adsorbent doses between 5 and 6,400 mg/L were applied. Upon weighing, dry adsorbents were transferred into 4-oz., 8-oz., 16-oz or 32-oz. amber glass bottles (smaller bottles received larger adsorbent doses). After filling the isotherm bottles with amended UPW or TRW, a pre-determined volume of target contaminant stock solution (MTBE) was added with a constant rate syringe (CR-700-200, Hamilton Co., Reno, NV) to yield an initial concentration of ~ 130 µg/L (single-solute isotherms) or ~ 20 µg/L (isotherms in the presence of co-adsorbing NOM). Once MTBE was added to a bottle, it was topped off immediately with amended UPW or TRW to create headspace-free conditions and capped using PTFE-faced silicon septa and open-top closures. A mixing time of 3 weeks in a rotary tumbler was sufficient to reach adsorption equilibrium, as established in screening tests.

MTBE analysis

Aqueous MTBE concentrations were determined by gas chromatography (GC). The GC system consisted of a purge and trap concentrator (Tekmar 3100, Cincinnati, OH) that was connected to a gas chromatograph (Shimadzu 14a, Columbia, MD) equipped with a 30-m column (J&W Scientific DB-VRX, I.D. 0.45 mm, film thickness 2.55 μm , Folsom, CA) and a flame ionization detector (FID). Samples (5 mL) were purged with nitrogen gas at 36°C for 12 min. The analytes were trapped on a Vocab 3000 trap (Supelco, Bellefonte, PA) and desorbed for 2 min at 255°C. The GC oven temperature was maintained at 40°C for 3 min, was increased at 20°C/min and held at 90°C for 2.5 minutes, increased at 20°C/min and held at 140°C for 1 minute, and finally increased at 40°C/min and held at 240°C for 1 min. The detection limit was 1 $\mu\text{g/L}$.

Tab. 1. Remaining MTBE adsorption capacity measured at an aqueous-phase MTBE concentration of 10 $\mu\text{g/L}$ (q_{10}) and physical adsorbent characteristics of fresh and used GAC.

| Samples | Time in Use (days) | BET surface area (m^2/g) | Micropore Volume ^a 5.2-5.7 Å (cm^3/g) | Micropore Volume ^a 4-20 Å (cm^3/g) | BJH | MTBE q_{10} in D.I. water (mg/g) | MTBE q_{10} in TAR water (mg/g) |
|------------|-----------------------|--|---|--|---|--|---|
| | | | | | Mesopore Volume ^b 20-500 Å (cm^3/g) | | |
| F400-fresh | 0 | 1061 | 0.029 | 0.382 | 0.232 | 0.280 | 0.182 |
| F400-3 | 3 | 1088 | 0.022 | 0.370 | 0.290 | 0.085 | 0.083 |
| F400-6 | 6 | 1048 | 0.022 | 0.357 | 0.267 | 0.070 | 0.054 |
| F400-11 | 11 | 1053 | 0.021 | 0.357 | 0.292 | 0.037 | 0.037 |
| F400-19 | 19 | 970 | 0.021 | 0.334 | 0.271 | 0.036 | n.a. |
| F400-32 | 32 | 986 | 0.020 | 0.337 | 0.275 | 0.026 | n.a. |
| F400-39 | 39 | 923 | 0.022 | 0.323 | 0.237 | n.a. | n.a. |
| F400-52 | 52 | 959 | 0.021 | 0.332 | 0.260 | n.a. | n.a. |
| F400-63 | 63 | 922 | 0.019 | 0.319 | 0.260 | n.a. | n.a. |
| F400-298 | 298 | 791 | 0.020 | 0.282 | 0.215 | 0.017 | 0.017 |

n.a. - data not available

^a Micropore volume calculated by DFT for pores with widths less than 20 Å

^b Mesopore volume calculated by BJH method for pores with widths ranging from 20 to 500 Å

Results and discussion

Physical Characteristics of GAC

BET surface areas as well as micropore and mesopore volumes of the fresh and used GAC samples are summarized in Table 1. With increasing service time or degree of NOM preloading, the BET surface area, micropore volume, and mesopore volume of the GAC decreased (Table 1). As shown in Figure 1, BET surface areas decreased more rapidly during the first 70 days of adsorber operation and more gradually thereafter. Relative to the BET surface area of the fresh GAC (1061 m²/g), BET surface area values decreased to 87% and 75% after 70 and 298 days of operation, respectively (Figure 1). The loss in micropore volume followed a trend similar to that observed for the BET surface area. The micropore volume decreased from 0.382 cm³/g for the fresh GAC to 0.282 cm³/g for the GAC sampled after 298 days of operation, which represents a loss of 26%. In contrast, the loss of pore volume in the mesopore range was less pronounced; BJH mesopore volumes of 0.232 cm³/g GAC and 0.215 cm³/g GAC were obtained for the fresh GAC and the GAC after 298 days of use, respectively, a decrease of 7% (Table 1).

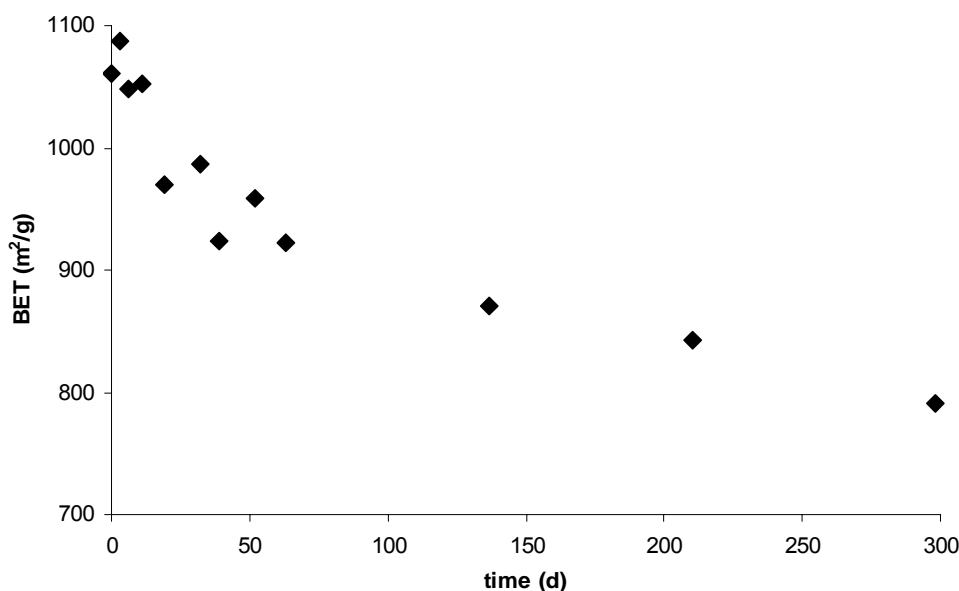


Fig. 1. Changes in BET surface area as a function of GAC service time.

Figure 2 shows the relationship between the DOC loading on the GAC (obtained influent and effluent DOC concentrations measurements, Velten et al., submitted) and both BET surface area and micropore volume. After 40 days of operation, effluent DOC concentrations

reached a pseudo-steady state, and the solid-phase DOC concentration reached a value of 28.6 g-C/kg GAC (Velten et al., submitted). Both BET surface area and micropore volume decreased linearly with increasing DOC loading (Fig. 2), and the loss in micropore volume was proportional to the loss in BET surface area (remaining BET surface area was 87% of the starting value after 40 days of operation while the remaining micropore volume was 85%).

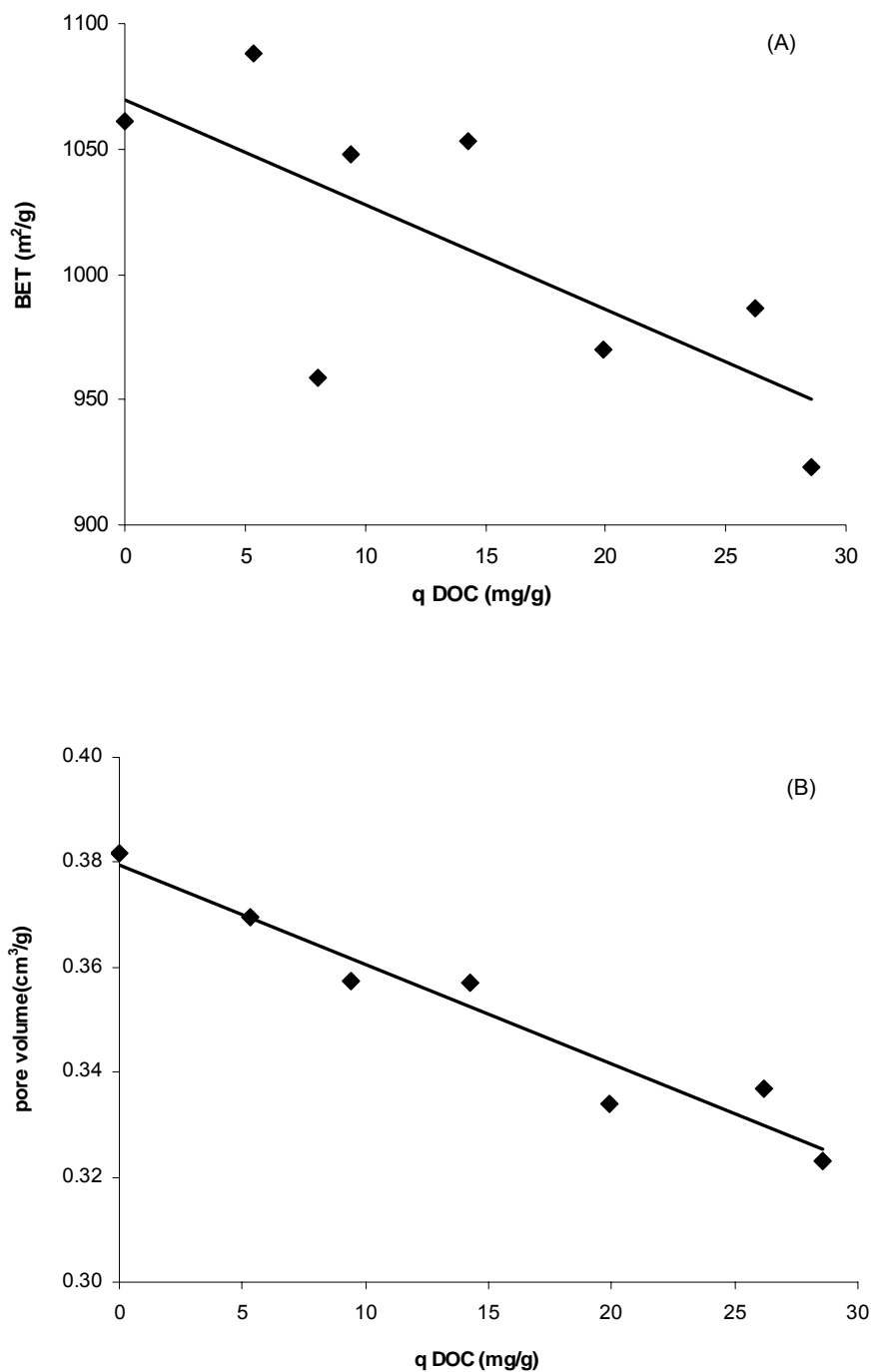


Fig. 2. Linear decrease of (A) BET surface area ($R^2 = 0.8$) and (B) micropore volume (4-20 Å) ($R^2 = 0.91$) with increasing DOC load on GAC.

The effect of GAC service time (or degree of NOM preloading) on the differential pore volume distribution in the micropore size range is shown in Figure 3. Figure 3 illustrates that the pore volume in the 5-7 Å range decreased quickly during the first three days of operation and more gradually thereafter. Also, the pore volume in the 11-12 Å range was strongly affected by NOM preloading and decreased steadily over the 298-day GAC service time. The micropore size distributions exhibit a minimum at about 9-10 Å for all adsorbents. Similar minima on pore size distribution curves calculated by means of DFT models have previously been presented (Jagiello and Thommes 2004, Olivier 1998). The proposed explanation is that of a model-induced artefact arising from the packing effect of filling 9 - 10 Å micropores at a relative pressure near 1×10^{-4} , which coincides with that for abrupt monolayer formation (Jagiello and Thommes 2004).

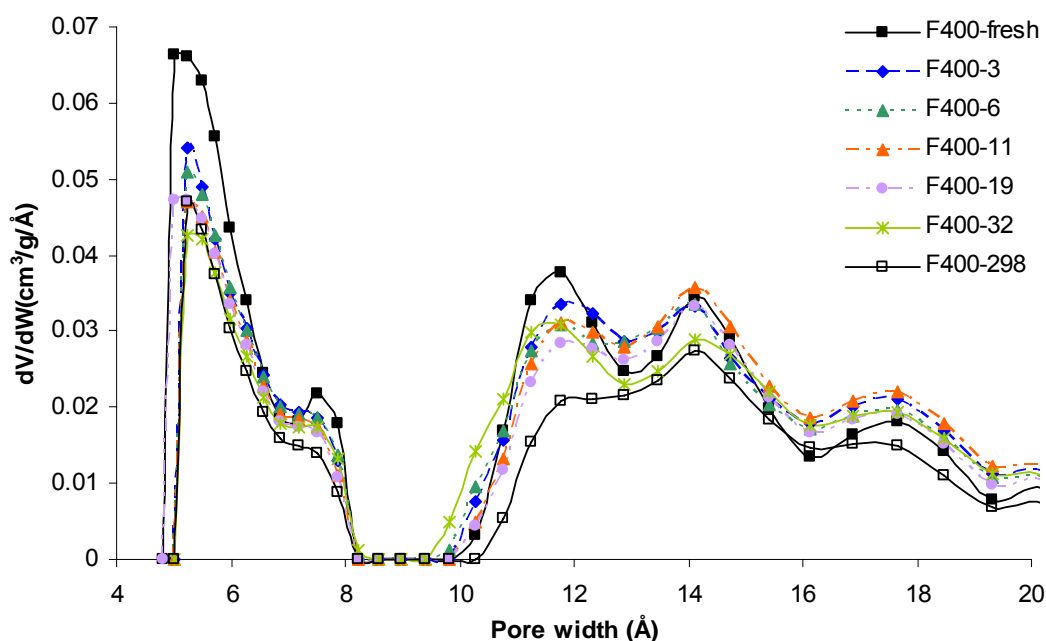


Fig. 3. Micropore volume distribution in the pore width range of 4-20 Å.

Figure 4 summarizes changes in GAC pore volume in different size ranges. At a given service time, the pore volume in a given size range was normalized with the pore volume in the same size range that was measured for the fresh GAC. During the first month of operation, the loss in pore volume that resulted from NOM uptake was most dramatic for the smallest pores (5.2-5.7 Å, <6 Å) and less severe when the upper bound of the considered pore size range was increased. Given that NOM does not adsorb in pores with widths <10 Å (e.g. Guo et al. 2007, Pelekani and Snoeyink 1999), this result suggests that NOM preloading blocked the entrances to small micropores in a manner that even prevented N_2

access when GAC samples were characterized via N_2 adsorption. During the second month of operation, the volume of the smallest pores ($<10 \text{ \AA}$ and subsets thereof) actually increased while that of the larger pores decreased. This result suggests that NOM adsorption caused a decrease in pore width that was manifested by a loss of larger pores and the concurrent appearance of smaller pores. Between day 63 and day 298, pore volume losses occurred primarily in larger pores, suggesting that NOM continued to fill large micropores ($10 - 20 \text{ \AA}$) and mesopores with widths $<100 \text{ \AA}$. The pore volume in the pore width range of $5.2 - 5.7 \text{ \AA}$ decreased to 76% ($0.022 \text{ cm}^3/\text{g GAC}$) of that measured for fresh GAC within the first 6 days and to 69% ($0.020 \text{ cm}^3/\text{g GAC}$) after 298 days of operation. The results obtained here show some similarities with those of Moore et al. (2001) who also found that changes in pore volume during NOM loading occur primarily in small micropores. For example, Moore et al. (2001) measured a pore volume loss of 30 - 35% in the size range $<10 \text{ \AA}$ after 30 days treating river water with a TOC of about 1.5 mg/L . However, for the system studied by Moore et al. (2001), the pore volume in the $<10 \text{ \AA}$ size range began to rise rapidly between days 70 and 150. In this study, a similar, but smaller rise in pore volume was observed between days 30 and 40, suggesting that the adsorption of NOM from Lake Zurich water did not lead to the narrowing of pores in a manner observed by Moore et al. (2001) with Ohio River water.

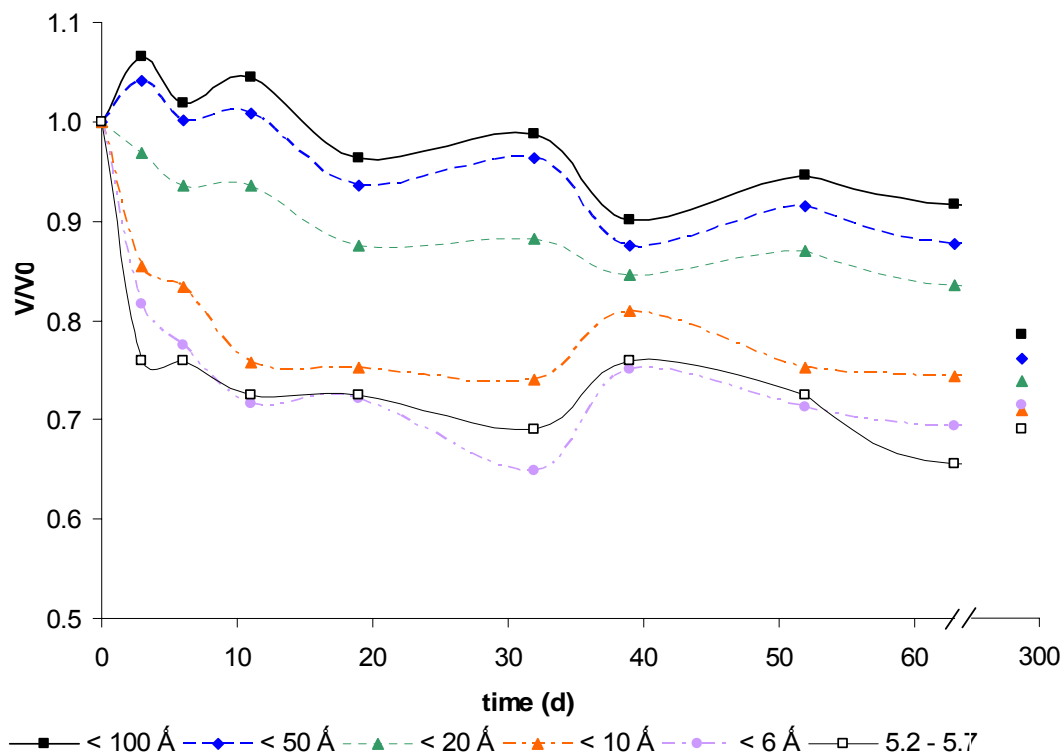


Fig. 4. Micropore and mesopore volume in different pore widths as a function of time. The impact of NOM preloading is the strongest pronounced in the pore width of $5.2-5.7 \text{ \AA}$

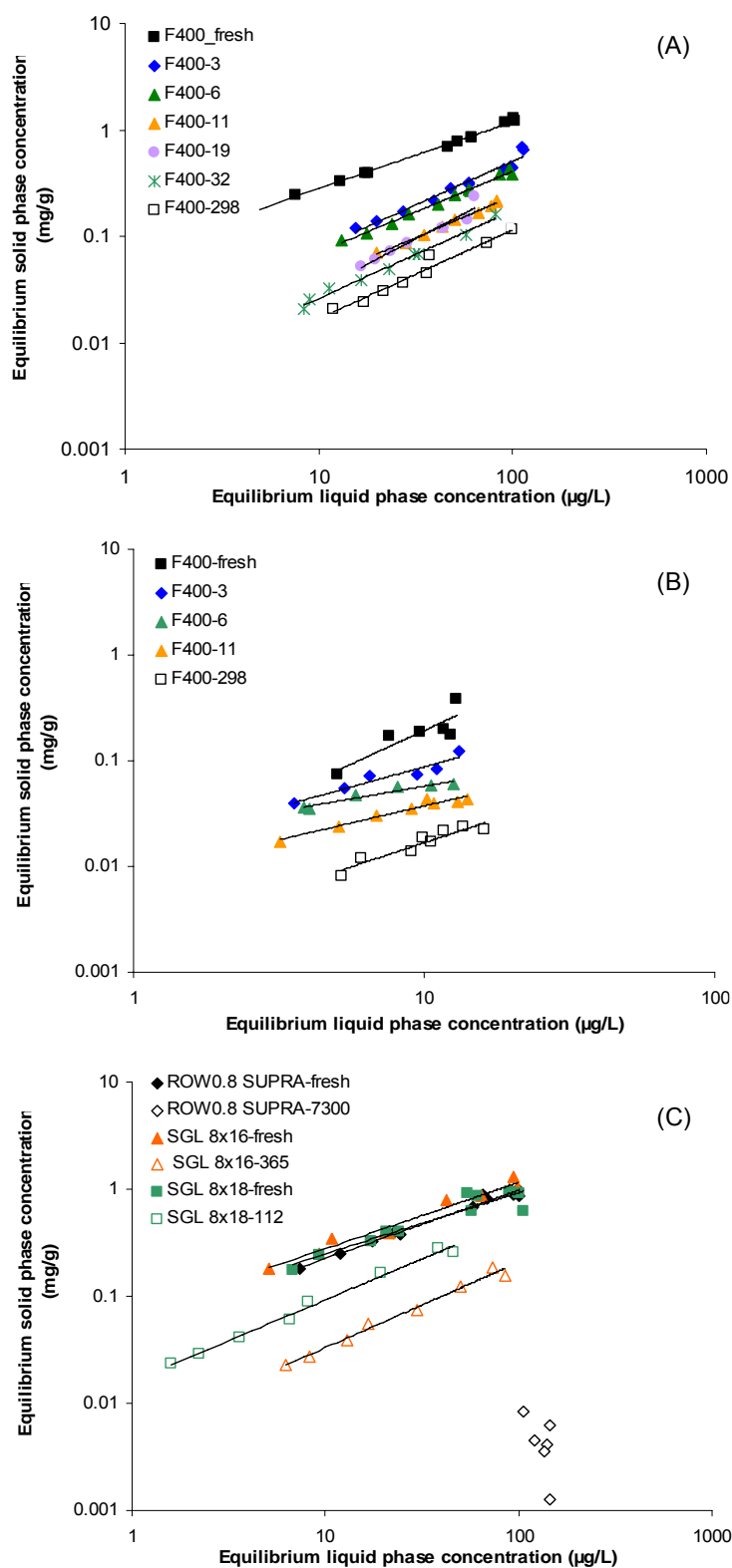


Fig. 5. MTBE isotherms for fresh and used GAC samples. Panel (A) depicts single-solute isotherms while panel (B) depicts isotherm data collected in TRW. Panel (C) shows MTBE isotherms for GACs from water works treating Lake Zürich water.

MTBE adsorption on GAC

MTBE adsorption isotherms for fresh and used GAC samples are summarized in Figure 5. Isotherms were described by the Freundlich model [$q_e = K (C_e)^{1/n}$], where q_e and C_e are the equilibrium solid-phase and liquid-phase concentrations, respectively, and K and $1/n$ are fitting parameters. Results of MTBE adsorption isotherm experiments conducted in UPW are given in Figure 5A for fresh GAC as well as used GAC samples that were taken after 3, 6, 11, 19, 32, and 298 days of operation of the GAC pilot filter. As expected, MTBE adsorption capacities of used GAC decreased with increasing time of operation and were lower than that of the fresh GAC. To assure a valid comparison among all isotherms, q_{10} (the solid phase MTBE concentration at $C_e = 10 \mu\text{g/L}$) values were calculated and compared. After GAC operating times of 3 and 298 days, q_{10} values decreased to 0.085 mg/g GAC (30%) and 0.017 mg/g GAC (6%), respectively, compared to that measured for fresh GAC (0.28 mg/g GAC).

Results of MTBE adsorption isotherm experiments conducted in TRW are summarized in Figure 5B for fresh GAC and used GAC samples that were taken after 3, 6, 11 and 298 days of pilot plant operation. Apart from the results for fresh GAC, q_{10} values obtained for MTBE in UPW and TRW were similar, suggesting that direct adsorption competition between MTBE and NOM constituents in TRW for remaining adsorption sites did not take place. In other words, MTBE had unimpeded access to the remaining adsorption sites on preloaded GAC. The decrease in MTBE adsorption capacity (q_{10}) that was observed with increasing GAC service time was therefore a result of NOM preloading only. For the fresh GAC, q_{10} in TRW (0.182 mg/g GAC) was 65% of that measured in UPW (0.28 mg/g GAC). This is an expected result for fresh activated carbon, where direct adsorption competition between NOM constituents and the micropollutant is important (e.g., Rossner and Knappe 2008).

Correlation of physical GAC characteristics and remaining MTBE adsorption capacity

Among the physical GAC characteristics that were determined (BET surface area, pore volume in different size ranges), the pore volume in the 5.2 - 5.7 Å pore width range correlated most strongly with the MTBE adsorption capacity (Figure 6). This result agrees well with the observation that MTBE adsorbs particularly well on silicalite zeolites that exhibit uniform pores with dimensions in the 5.1 - 5.6 Å range (Knappe et al. 2007, Rossner and Knappe 2008). The fresh GAC exhibits a pore volume of 0.029 cm³/g in the 5.2 - 5.7 Å range.

The trendline shown in Figure 6 suggest that $q_{10} = 0$ at a pore volume of $0.019 \text{ cm}^3/\text{g}$. It therefore appears that N_2 , the adsorbate used to determine physical GAC characteristics, was able to access pores that could not be accessed by MTBE and that $\sim 65\%$ of the total volume in the $5.2\text{-}5.7 \text{ \AA}$ range was “lost” for the adsorption of MTBE. The inability of MTBE to access pores that can be accessed by N_2 may be explained by (1) ink-bottle-shaped pores and/or (2) by pore entrances that were partially blocked by NOM and produced an ink-bottle shaped pore. Other GAC characteristics did not change as dramatically as the pore volume in the $5.2 - 5.7 \text{ \AA}$ range and could not explain the measured loss in MTBE adsorption capacity.

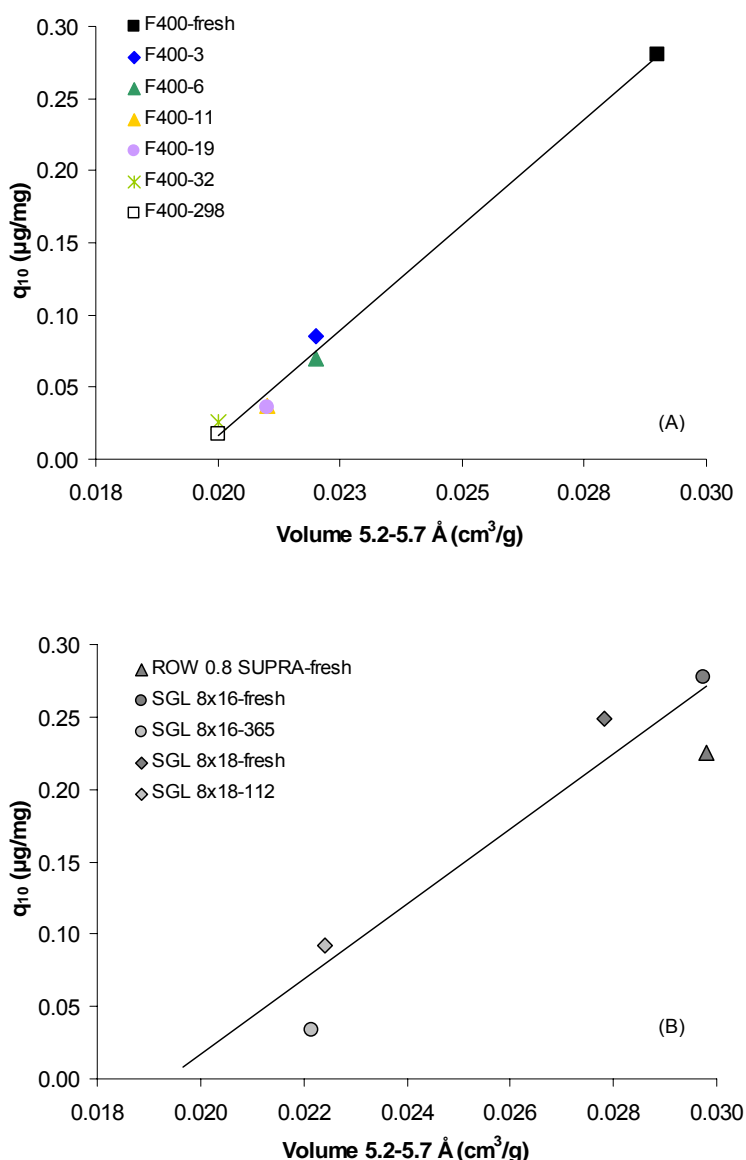


Fig. 6. Correlation between pore volume in the $5.2\text{-}5.7 \text{ \AA}$ range and MTBE adsorption capacity measured at an aqueous-phase MTBE concentration of 10 µg/L (q_{10}) (A) for GAC F 400 ($R^2 = 0.99$) and (B) water works GACs ($R^2 = 0.95$).

Three additional GACs from water works treating Lake Zurich water were evaluated in conjunction with their corresponding fresh GACs. Table 2 summarizes physical adsorbent characteristics as well as MTBE adsorption capacities at an equilibrium liquid-phase MTBE concentration of 10 µg/L (q_{10}), and Figure 5C depicts the corresponding MTBE adsorption isotherm. The results in Table 2 illustrate that the GAC sample that had been in service for 20 years exhibited a micropore volume that was 25% of that measured for the corresponding fresh GAC. Micropore volumes of the GACs that were sampled after 112 and 365 days of full-scale operation were ~87 and 92%, respectively, of those measured for the corresponding fresh GAC. After service times of 112 and 365 days, MTBE adsorption capacities (q_{10}) were ~37 and 12%, respectively, of those measured for the corresponding fresh GACs while the 20-year-old sample exhibited negligible MTBE uptake (Table 2, Figure 5C).

Tab. 2: MTBE adsorption capacity measured at an aqueous-phase MTBE concentration of 10 µg/L (q_{10}) and physical adsorbent characteristics of 3 fresh and used water works GACs.

| Carbon typ | Time in Use | BET surface area | BJH Mesopore Volume | Micropore Volume 5.2-5.7 Å | Micropore Volume 0 - 20 Å | MTBE q_{10} in D.I. water |
|---------------------------|-------------|---------------------|----------------------|----------------------------|---------------------------|-----------------------------|
| | (days) | (m ² /g) | (cm ³ /g) | (cm ³ /g) | (cm ³ /g) | (mg/g) |
| ROW 0.8 SUPRA-fresh | 0 | 946 | 0.258 | 0.03 | 0.331 | 0.225 |
| ROW 0.8 SUPRA-7300 | >7300 | 317 | 0.242 | 0.005 | 0.084 | n.a. |
| SGL 8x16-fresh | 0 | 944 | 0.179 | 0.03 | 0.343 | 0.277 |
| SGL 8x16-365 | 365 | 905 | 0.216 | 0.022 | 0.317 | 0.033 |
| SGL 8x18-fresh | 0 | 973 | 0.191 | 0.028 | 0.358 | 0.249 |
| SGL 8x18-112 | 112 | 856 | 0.174 | 0.022 | 0.312 | 0.092 |
| n.a. - data not available | | | | | | |

The correlation between remaining MTBE adsorption capacity and the pore volume in the 5.2 - 5.7 Å pore width range (Figure 6A) also applied to the full-scale GAC adsorber samples (Figure 6B). Overall, the results of this research show that the MTBE adsorption capacity of fresh and used GACs is strongly dependent on the pore volume in the 5.2 - 5.7 Å width range. As a result, indices such as the BET surface area, micropore volume, or iodine number cannot be used as an indicator for predicting the remaining MTBE adsorption capacity of GAC in full-scale adsorbers after different service times.

Conclusion

- NOM preloading strongly decreased the MTBE adsorption capacity of GAC treating low-DOC lake water. Relative to the single-solute MTBE adsorption capacity of fresh GAC, MTBE adsorption capacities after 3 and 298 days of service time were 30 and 6%, respectively.
- Direct adsorption competition between NOM and MTBE adsorption was not important on preloaded GAC samples.
- The pore size range of 5.2-5.7 Å appeared to be the most important for MTBE adsorption. Consequently, effective adsorbents for MTBE should contain a large pore volume within this pore size range.
- Comparing fresh and used GACs, changes in MTBE adsorption capacities were more pronounced than changes in physical characteristics derived from N₂ adsorption isotherms. Some of the pore volume in the 5.2-5.7 Å size range appeared to be accessible to N₂ but not to MTBE. Both ink-bottle shaped pores and pore entrances partially blocked by NOM may explain the discrepancy in pore accessibility. As a result, it is difficult to directly relate physical GAC characteristics derived from N₂ adsorption isotherm data to the adsorption of organic micropollutants from drinking water sources.

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4B

Effects of natural organic matter preloading on physical characteristics and remaining MTBE adsorption capacity of granular activated carbon

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Introduction

Because water treatment plants typically operate granular activated carbon (GAC) adsorbers continuously, background natural organic matter (NOM) adsorbs on GAC even when targeted micropollutants (MPs) are absent in the source water. As a result, GAC becomes loaded with or fouled by NOM such that the MP adsorption capacity decreases with increasing time of operation (e.g. Summers et al. 1989, Kilduff et al. 1998). In practice, many utilities rely on iodine number determinations to monitor the degree of GAC exhaustion. However, the iodine number is not a good predictor of remaining GAC life for a given MP (Knappe et al. 2003). The objectives of this work were to (1) compare the MTBE adsorption capacities of preloaded GAC samples obtained from full-scale GAC adsorbers with those of corresponding fresh GAC samples and (2) quantify changes in the physical GAC characteristics that occur during full-scale GAC operation. An ongoing research objective is to identify physical GAC characteristics that correlate directly with the remaining MP adsorption capacity of preloaded GAC.

Keywords

Adsorption, granular activated carbon (GAC), methyl *tertiary*-butyl ether (MTBE), natural organic matter (NOM)

Materials and methods

GAC samples were obtained from full-scale GAC adsorbers at four Swiss water treatment plants (WTPs) that use Lake Zurich as a raw water source. At the time of sampling, GAC samples had been in operation for 4, 9, and 12 months as well for 20 years. In addition, matching fresh GAC samples (Chemviron F400, Chemviron 8x16, Chemviron SGL 8x18, Norit ROW Supra 0.8) were characterized. Treatment trains prior to GAC adsorbers differed at the four WTPs, but a typical GAC influent (ozonated Lake Zurich water) exhibits a DOC of 1.1 mg/L and a pH of 7.8.

BET surface areas as well as micropore and mesopore volumes were determined from N₂ adsorption isotherm data collected at 77 K (Autosorb-1-MP, Quantachrome, Boyton Beach, FL); see Knappe et al. (2007) for a detailed description of the experimental procedure.

Adsorption isotherm experiments ($T = 25^{\circ}\text{C}$) were performed in ultrapure water (UPW) using a bottle-point technique (Knappe et al. 2003). Use of UPW did not change the MTBE adsorption capacity of preloaded GAC compared to that obtained with Lake Zurich water. GAC was not pulverized to avoid altering the adsorption capacity of preloaded GAC (Knappe et al. 1999); a mixing time of 3 weeks in a rotary tumbler was sufficient to reach MTBE adsorption equilibrium, as established in screening tests.

Results and discussion

Figure 1 summarizes MTBE adsorption isotherms for fresh and used GACs. MTBE adsorption capacities of the four fresh GACs were very similar. As expected, MTBE adsorption capacities of used GACs were lower than those of the corresponding fresh GACs (Fig. 1). Also, with increasing time of operation, the remaining MTBE adsorption capacity of the used GACs decreased; after 4, 9, and 12 months of operation, the remaining MTBE adsorption capacities at a concentration of $10\ \mu\text{g/L}$ were, respectively, 36%, 19%, and 11% of those measured for the corresponding fresh GACs. For the GAC that had been in operation for 20 years, no measurable MTBE adsorption capacity remained (Fig. 1).

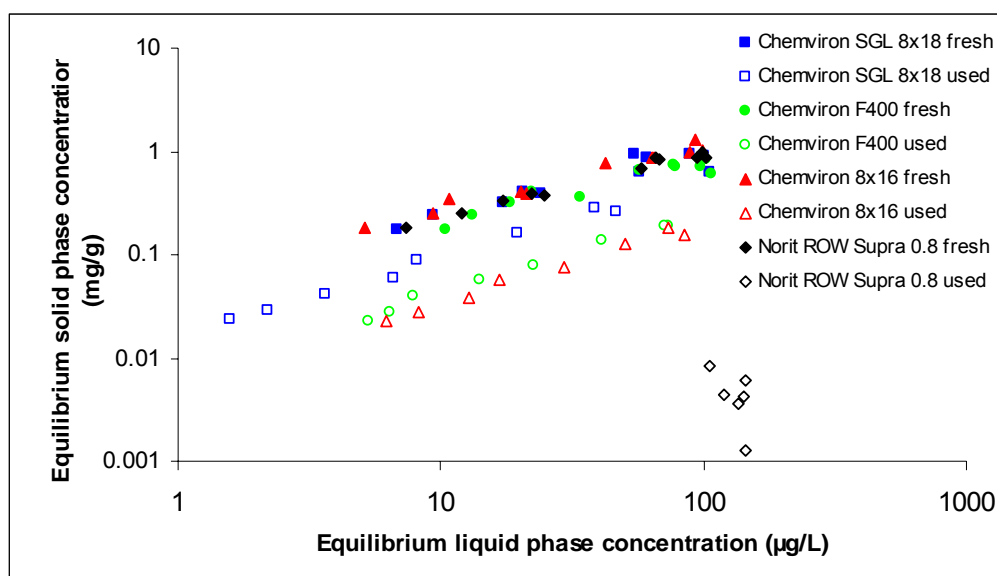


Fig. 1. MTBE adsorption isotherms for fresh and used GACs

To date, physical characterizations have been completed for three of the four GAC sample pairs (Table 1). After 4 and 9 months of operation (SGL and F400 samples, respectively), BET surface area and micropore volume decreased only slightly (<20%) relative to the values measured for the corresponding fresh GACs. For the GAC that had

been in operation for 20 years (Norit), losses in BET surface area and micropore volume were more dramatic. For none of the tested GACs could changes in the physical characteristics shown in Table 1 explain changes in MTBE adsorption capacity between the fresh and used samples. It appears that N₂, the adsorbate used to determine physical GAC characteristics, was able to access pores that appeared to be in the 5-6 Å width range, where MTBE is expected to adsorb (Knappe et al. 2007), but that could not be accessed by MTBE. Both ink-bottle-shaped pores and pore entrances partially blocked by NOM may explain these results.

Tab.1. Physical adsorbent characteristics

| Carbon Type | Time in Use (months) | BET surface area (m ² /g) | Micropore Volume ^a 0 - 10 Å (cm ³ /g) | Micropore Volume ^a 10 - 20 Å (cm ³ /g) | DFT Mesopore Volume ^b (cm ³ /g) | BJH Mesopore Volume ^c (cm ³ /g) |
|---------------------------|-------------------------|---|--|---|---|--|
| Chemviron SGL 8x18 fresh | 0 | 973 | 0,18 | 0,18 | 0,16 | 0,19 |
| Chemviron SGL 8x18 used | 4 | 856 | 0,15 | 0,16 | 0,14 | 0,17 |
| Chemviron F400 fresh | 0 | 879 | 0,19 | 0,14 | 0,17 | 0,20 |
| Chemviron F400 used | 9 | 834 | 0,17 | 0,14 | 0,11 | 0,13 |
| Norit ROW Supra 0.8 fresh | 0 | 946 | 0,19 | 0,14 | 0,25 | 0,26 |
| Norit ROW Supra 0.8 used | 240 | 317 | 0,03 | 0,05 | 0,23 | 0,24 |

^a Micropore volume calculated by density functional theory (DFT) for pores with widths less than 20 Å

^b Mesopore volume calculated by density functional theory (DFT) for pores with widths ranging from 20 to 360 Å (upper limit for DFT model)

^c Mesopore volume calculated by Barrett, Joyner, and Halenda (BJH) method for pores with widths ranging from 20 to 500 Å

Conclusion

NOM preloading strongly affected the remaining MTBE adsorption capacity of GACs treating low-DOC lake water. Comparing fresh and used GACs, changes in MTBE adsorption capacities were more pronounced than changes in physical characteristics derived from N₂ adsorption isotherms.

Acknowledgements

The authors kindly acknowledge financial assistance through the EAWAG Wave21 project and the Zurich Water Works (WVZ) as well as David Black at NCSU for his assistance with MTBE measurements.

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5

Removal of 2-isopropyl-3-methoxypyrazine (IPMP) with granular activated carbon: from lab scale to pilot scale

Silvana Velten, Dietmar Strübing, Andreas Peter, Markus Boller

Introduction

2-isopropyl-3-methoxypyrazine (IPMP) is an actinomycetal metabolite that occurs at nanograms per liter levels in drinking water supplies using lake water and is responsible for many taste and odor (T&O) complaints about the aesthetics of drinking water. Although IPMP does not pose a toxicological threat to humans, it affects the public's perception concerning the safety of drinking water. This negative perception has a great influence on the image of the drinking water suppliers.

IPMP occurs, as many other T&O compounds, seasonally due to its natural origin and, thus, it is difficult to control T&O compounds from a source point of view. An often applied technology is the combination of chemical oxidation and (biological) granular activated carbon (GAC) filtration. Previous studies on ozonation have shown that ozone in combination with hydroxyl radicals can be an effective tool for the removal of T&O compounds (Peter and von Gunten, 2007). However, it was also shown that the oxidation efficiency is depending on the structure of the T&O compound. IPMP was shown to be a slow reacting compound with ozone ($k = 50 \text{ M}^{-1}\text{s}^{-1}$). Ozonation experiments, conducted in a batch system with a dissolved organic carbon (DOC) containing water, showed a IPMP removal efficiency of 76% (contact time 10 min) (Peter and von Gunten, 2007). GAC filtration following ozonation is intended to remove the residual concentrations. Previous studies on the removal of T&O compounds showed that ozonation followed by biofiltration is an effective treatment method (Kim et al., 1997). A few studies have focused on the removal of IPMP with the help of powdered activated carbon (PAC) (Liang et al., 2005).

However, the case specific results can often not be transferred to other water treatment plants. We therefore conducted experiments in the laboratory with nano pure water (NPW) and DOC containing water in order to investigate the influence of natural organic matter (NOM) preloading and simultaneous adsorption of NOM on the GAC removal efficiency of IPMP.

The objectives of this study were to quantify the effect of GAC service time (1) on the adsorption capacity for IPMP, (2) to determine the influence of NOM on the adsorption capacity and (3) to evaluate the potential of biological degradation. Adsorption isotherms and bottle kinetic experiments as well as column tests were conducted in laboratory scale. Continuous spiking experiments showed the removal of IPMP in a pilot-scale GAC filter.

Materials and methods

Standards and Reagents

2-isopropyl-3-methoxypyrazine (IPMP) and 2-isobutyl-3-methoxypyrazine (IBMP) were purchased from Sigma-Aldrich (Buchs, Switzerland) in the highest purity available. Stock solutions (1 mM and 50 μ M, respectively, depending on the water solubility) were prepared in NPW. All chemicals used were reagent grade and used without further purification. NPW was produced using a NANOpure[®] DIamond[™] system (Barnstead International, Dubuque, IA, USA). DOC containing lake water was taken after the intermediate ozonation step (prior to GAC filtration) of the full-scale water treatment plant from Zurich water works (WVZ Lengg, Zurich, Switzerland).

Activated carbon

Laboratory-scale experiments were conducted with GAC ROW 0.8 SUPRA (Norit, Kempton, D). Used GAC was sampled from the full scale GAC filter (empty bed contact time (EBCT) = 12.5 min, v_f = 6.5 m/h). This GAC was in use for 20 years and therefore assumed to be totally saturated. The GAC pilot reactor contained the bituminous-coal based GAC SGL 8x18 (Chemviron, Feluy, Belgium). More information on the two GACs is given in Table 1.

Analytical methods

Samples were analyzed using solid-phase micro extraction (SPME) combined with gas chromatography – mass spectrometry (GC–MS). For that purpose, 6 mL of the samples were transferred into 10 mL head space vials. Sodium chloride (1.2 g) was added to each sample, in order to enhance the transfer of the compounds from the liquid into the gas phase. IBMP was used as an internal standard and added at a concentration of 100 ng/L. SPME was carried out using 1 cm DVB-Carboxen-PDMS fibers (Supelco, Bellefonte (PA)) mounted on a Combi PAL auto sampler (CTC, Switzerland). The sample was first heated to 65°C and shaken for 5 minutes, followed by 30 minutes head-space sampling at 65°C and desorption in a SPME liner sealed with a MERLIN micro seal at 250°C (2 minutes splitless). GC-separation was done with a GC 8000 (Fisons) using a SLB-5MS column (30x0.25x0.25; Supelco) and Helium was used as a carrier gas in a constant pressure mode (50 kPa). The following temperature program was applied: 2 minutes at 50°C, then heated at 10°C/min to 150°C and 5°C/min to 200°C. Detection and quantification was performed on an MS detector

(MD800, Fisons), which was operated in the SIM mode. The following masses were used for detection: 124 and 137 for IPMP; 124 and 151 for IBMP. The method showed good linearity in the range of 2 - 200 ng/L. The detection limit was 1 ng/L.

Experimental set up

Previous to the experiments, the saturated GAC was treated with sodium acid (NaN_3 ; Merck, D) at a concentration of 400 mg/L in NPW. The purpose of this treatment was to inhibit the bacterial activity in order to ensure adsorption as the main removal process. Used GAC was filled in a Scott flask and turned in an overhead mixer at 3-4 rpm for 7 days. Afterwards the GAC was rinsed 3 times in NPW and used directly after in the experiment. The GAC dry weight was determined subsequent to the experiments. Therefore the GAC was extracted from the bottles and dried at 70°C for 2 days before weighing. Lake water (LW) was sampled after ozonation in the full-scale plant. 1L Schott flasks were used to perform isotherm and bottle-kinetic experiments. All experiments were performed in darkness at 18°C ($\pm 0.5^\circ\text{C}$).

Bottle-kinetic experiments

1L Scott flasks were filled with either NPW or LW and IPMP was spiked in different concentrations (75-150 ng/L) to the water. Samples for determining the initial IPMP concentrations were taken immediately after. Following, 70 mg fresh GAC or 155 mg used GAC were added. Liquid samples were taken over a period of 216 hours. To be able to differentiate between biological degradation and adsorption, biological active GAC from the full-scale treatment plant (20 years in use) was sampled and used in kinetic experiments.

Isotherm experiments

Single-solute adsorption isotherm experiments of IPMP were conducted in NPW. The effect of NOM on GAC adsorption capacity was evaluated with LW. Adsorption isotherm experiments were performed using a bottle-point technique (Knappe et al., 2003). GAC was not pulverized to avoid altering the adsorption capacity of preloaded GAC (Knappe et al., 1999). After filling the isotherm bottles with amended NPW or LW, a pre-determined volume of target IPMP stock solution was pipetted to yield initial concentrations ranging from 100 to 1200 ng/L. Once IPMP was added, the start concentration was measured and the adsorbents were transferred into the bottles. Adsorbent doses of 20 mg fresh GAC and 160

mg used GAC were applied. All bottles were placed in an overhead mixer for 216 h. This time was estimated to be sufficient for bottle kinetic experiments.

Fixed-bed-kinetic reactor

Figure 1 illustrates the set up for the fixed bed kinetic experiment. The column was set up as a tubular glass reactor with an inner diameter of 2.5 cm and a length of 40 cm. The column was tightly packed with GAC at a filter bed depth of 3 cm. A water column of about 6 cm was kept to avoid disturbances of the filter bed. The column was operated in down flow mode. Feed water was pumped with a gear pump (MVZ, ISMATEC SA, Glattbrugg, CH) from the feed tank into the column at a constant rate of 3 L/h corresponding to a filter velocity of 6 m/h. The effluent stream was recycled back to the feed tank. The feed tank had a volume of 250 L and was made of PE. The water was continuously stirred to simulate a completely stirred batch reactor (CSBR). Tubes of the type Tygon MHSL 2001 were obtained from ISMATEC SA (Glattbrugg, CH). These tubes were chosen due to the limited interaction with the water content.

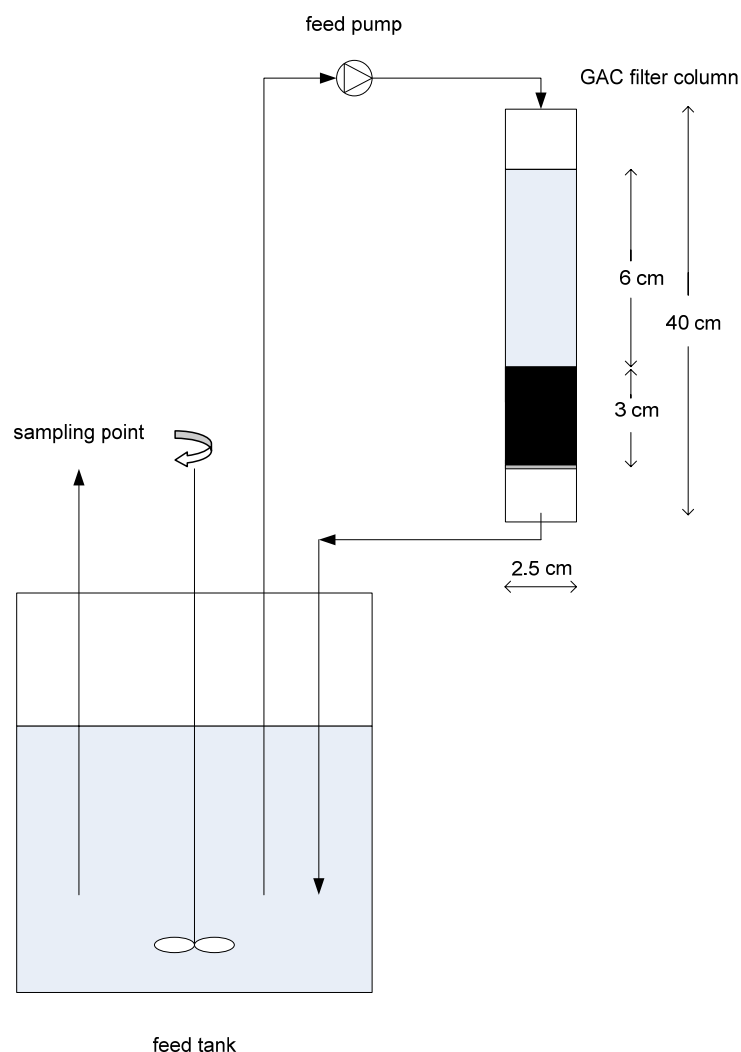


Fig. 1. Flow scheme of the shallow fixed-bed recycle GAC filter for testing adsorption kinetics.

First, 5.1 g fresh GAC was filled in the GAC column. After, the feed tank was filled with 80 L NPW and spiked to an initial IPMP concentration of 150 ng/L. After initial mixing, the starting concentration was determined and the experiment was started. The samples were taken in the feed tank over a period of 10 days with a decreasing frequency from once per hour in the beginning to once per day when the steady state was reached.

Previous studies showed a high system loss for T&O compounds in laboratory scale experiments. Therefore, the specific loss of the applied system was determined before the experiment. The IPMP system loss experiment was performed in 100% recycle mode (closed loop system) at an initial concentration of 150 ng/L (in NPW and without GAC) and a filtration rate of 6 m/h.

Pilot GAC reactor

The GAC filter was part of a pilot plant that included ozonation, GAC filtration and membrane filtration. The GAC reactor was operated in down-flow mode. Operational and influent water quality parameters for the GAC adsorber are given in Table 1.

Tab. 1. Operational and influent water quality parameters for full scale and pilot scale plant adsorbers.

| parameter | | full scale plant | pilot scale plant |
|------------------------|----------------------|---------------------|--------------------|
| carbon type | | Norit ROW 0.8 SUPRA | Chemviron SGL 8x18 |
| reactor volume | (m ³) | 57 | 1.47 |
| filtration velocity | (m/h) | 6.5 | 5.9 |
| empty bed contact time | (min) | 12.5 | 15.76 |
| GAC depth | (m) | 1.3 | 1.55 |
| column diameter | (m) | n/a | 1.1 |
| influent DOC | (mg/L) | 0.96 (± 0.03) | 1.1 (± 0.04) |
| influent pH | (-) | 8.1 (± 0.3) | 7.79 (± 0.14) |
| GAC particle diameter | (mm) | > 0.6 | 1 - 2.5 |
| bed porosity | (-) | 0.52 | 0.39 |
| packed bed density | (kg/m ³) | 390 | 460 |

Two spiking experiments with IPMP were performed with the pilot GAC reactor. The first experiment was carried out shortly after the installation of the pilot plant with fresh GAC in the filter while the second experiment occurred six months later when the GAC was saturated with NOM (influent concentration 1.1 mg-C/L). In the two experiments, IPMP was

dosed to the reactor in a pre-concentrated solution to reach an inflow concentration of 1.5 µg/L. IPMP dosing was maintained during two hours accompanied by regular sampling of the filter at the inflow and outflow as well as depths of 10 cm, 20 cm, 30 cm, 40 cm, 50 cm and 90 cm. The sampling was continued for four hours after the IPMP dosing had been stopped to follow the decrease in IPMP concentration in the filter.

Results and discussion

Bottle-kinetic experiments

Bottle-kinetic experiments were performed for fresh and used GAC in NPW and LW, respectively (Figure 2). The equilibrium was reached after about 170 hours for all experiments. As expected, the fresh GAC exhibits a higher adsorption capacity than the GAC that has been used for 20 years. The initial IPMP concentration was reduced to about 20% in NPW and LW with fresh GAC at adsorption equilibrium. The used GAC was still able to reduce the initial IPMP concentration to 40% in NPW and LW. The percentage removal for fresh and used GAC was independent of the water matrix, which let us conclude that the IPMP adsorption was not influenced by the presence of NOM.

The IPMP removal efficiency of the 20 year old GAC, which is assumed to be saturated, was unexpectedly high. One possible explanation for the removal could be the loss of IPMP by adsorption on the systems surface. If this is the case, system losses would account for the removal in all experiments. System losses in bench-scale will be discussed in the section 3.3 of this paper. In drinking water treatment plants the contact time in GAC filters is up to 30 minutes. The removal of IPMP in the kinetic experiments at this time was insignificant. Concluding from these preliminary results, it would mean that the removal of IPMP by adsorption in a full-scale plant is hardly feasible.

Kinetic experiments with biologically active carbon (BAC) showed an IPMP removal to 40% in NPW and LW. The removal was similar compared to the results of the same GAC, on which the biomass was inhibited (Figure 3). The water matrix did not influence the removal efficiency for IPMP. If the biofilm on the GAC was able to metabolize IPMP, the removal would be higher. Yet the effect of biological degradation was not evident.

Since the BAC was sampled from the full-scale plant, treating Lake Zurich with seasonal IPMP loads, the biomass should be adapted to metabolize IPMP. Nevertheless, the results show that no further increase in IPMP concentrations with BAC was achieved.

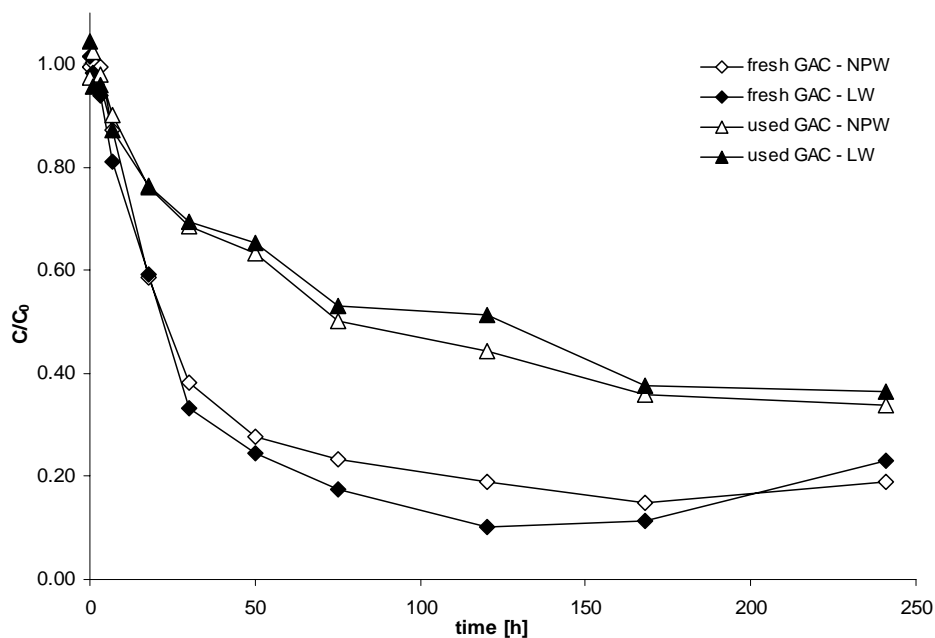


Fig. 2. Presentation of the bottle kinetic experiments conducted in NPW and LW with fresh and used GAC, respectively. The percentage removal was independent from the water source, but depending on the age of the GAC (fresh/used).

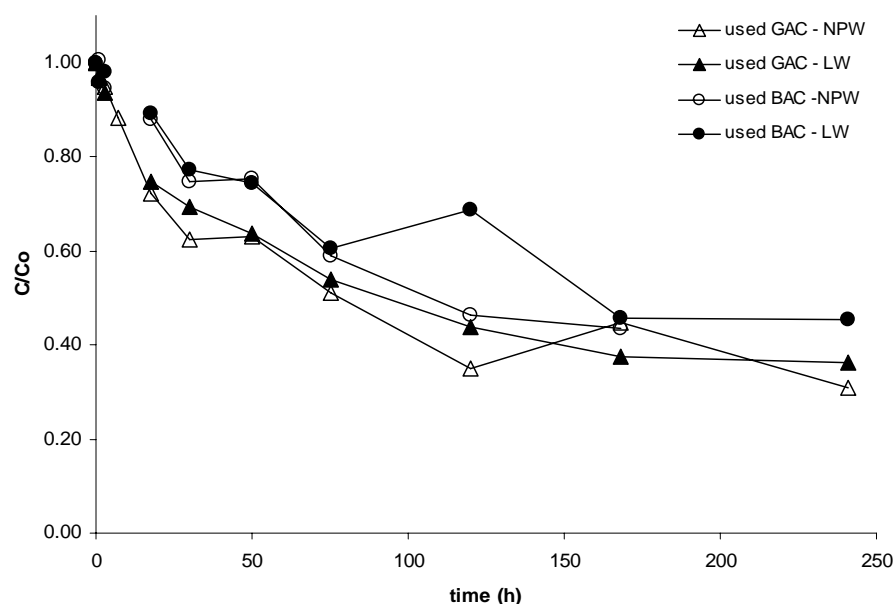


Fig. 3. Presentation of the bottle kinetic experiments conducted with used GAC in NPW and LW. For the first set of experiments, biological active carbon (BAC) was used; for the second set, inactivated GAC was used. The percentage removal was independent of the existence of biomass

Isotherm experiments

The IPMP adsorption isotherms for the fresh and the used GAC samples are shown in Figure 4. The isotherms are described by the Freundlich equation [$q_e = K (C_e)^{1/n}$], where q_e and C_e are the equilibrium solid-phase and liquid phase concentrations, respectively. K and $1/n$ are Freundlich fitting parameters. As expected, the IPMP adsorption capacity of used GAC was lower than that of the fresh GAC. In order to assure a valid comparison among the isotherms, q_{50} (50 ng/L) values were calculated and compared (Quinlivan et al., 2005). The q_{50} value presents the solid phase concentrations at a liquid phase concentration of 50 ng/L. The adsorption capacity for fresh GAC in NPW reached a q_{50} value of 44.63 ng/mg GAC, compared to only 8.56 ng/mg GAC (19%) in LW. The adsorption capacity of the used GAC in NPW was very low (0.45 ng/mg) and similar to the one obtained in LW (0.4 ng/mg GAC). The remaining IPMP adsorption capacity of the used GAC compared to the fresh GAC in LW was only 5%.

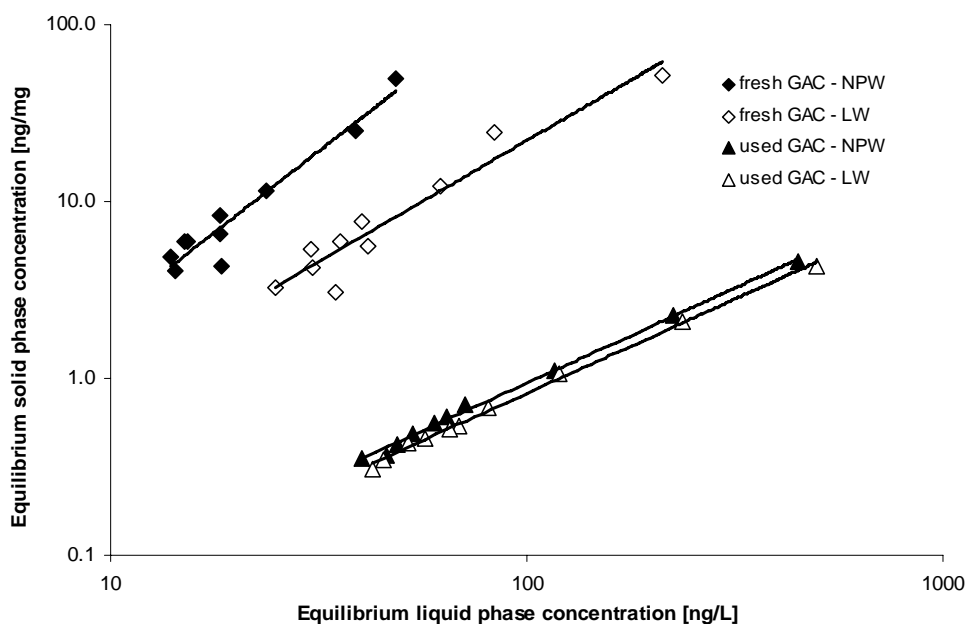


Fig. 4. IPMP Freundlich isotherms for fresh and used GACs. Compared to fresh GAC, the IPMP adsorption capacity in natural water was substantially lower. No influence of concurrent DOC adsorption was observed on the used GAC.

In the presence of NOM, the adsorption capacity of the fresh GAC in LW was lower than the adsorption capacity in NPW. NOM competes with IPMP for the adsorption sites and, in addition, blocks the entrances to the pores for IPMP adsorption. Thus the adsorption capacity in the presence of NOM is decreased strongly. For saturated GAC the effect of preloading with DOC is such dominant, that the impact of simultaneous NOM adsorption

becomes negligible. Bottle kinetic experiments with fresh GAC did not show the influence of NOM competition, which is contrary to the results above. But NOM competition was insignificant in the kinetic experiments with used GAC. Comparing the endpoints of the kinetic experiments with the results of the isotherm experiments, the observed equilibrium values in the bottle kinetic experiments matched the isotherm results with the used GAC well. In the case of the fresh GAC, the equilibrium concentrations of the bottle kinetic experiments showed lower concentrations than expected from the isotherm results. One possible explanation could be volatilization of IPMP and losses during sampling.

Fixed bed kinetic experiments

Prior to the fixed bed kinetic experiment, we tested the system loss for IPMP. The experiment showed a 38% decrease of IPMP in absence of GAC. Previously reported data (Elhadi et al., 2004) show similar system losses of 42% and 30% for other T&O compounds such as Geosmin and MIB, respectively. These authors describe the loss to physical adsorption occurring on glass materials and pump tubing. Volatilization may have played a role in experiments involving glass columns.

Following to the system loss experiment we performed a desorption experiment. Thereby we wanted to determine the amount of IPMP which was adsorbed on the system surface and could be desorbed again (results not shown). The system was run with NPW and the IPMP concentration was measured. No IPMP was detected in the sample. Possible explanations are: (1) IPMP adsorbed permanently and could not be desorbed from the systems surface and (2) the loss of IPMP is mainly due to volatilization. Thus the quantitative influence of system-surface-adsorption of IPMP on adsorption rates of IPMP onto GAC could not be determined.

Figure 5 shows the result of the fixed-bed kinetic experiment which was carried out at an initial IPMP concentration of 150 ng/L in NPW with 5.1 g fresh GAC (ratio of 2.34 ng IPMP/mg GAC). The 50% removal was reached within the first 24 hours. A total IPMP removal in the fixed-bed-kinetic experiments was achieved after 120 h. Compared to the bottle-kinetic experiments, the steady state in the fixed-bed kinetic experiment was reached faster with a higher removal, even though the ratio between IPMP and GAC was higher. It seems that with fixed-bed experiments higher IPMP removal rates can be achieved. Again, the higher removal could be also due to the loss of IPMP by volatilization. Although the system was sealed best possible, losses by volatilization can not be excluded.

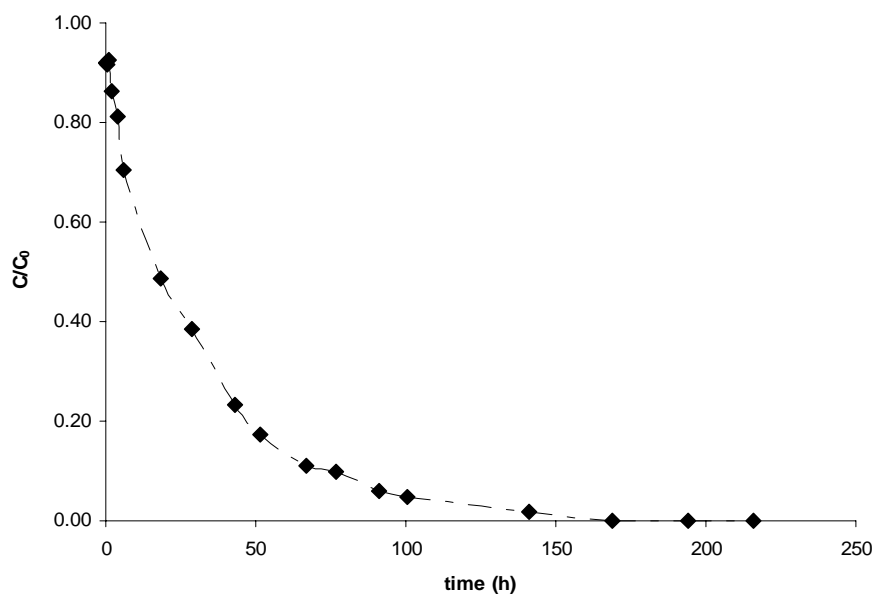


Fig. 5. Fixed bed kinetic experiment for the removal of IPMP at a concentration of 150 ng/L.

Pilot-scale GAC filter

The removal efficiency for IPMP was investigated in the pilot-scale GAC filter over 180 minutes during the first day of operation with fresh GAC. IPMP was continuously spiked over a period of 120 minutes. The results show a nearly 100% retention in the upper 50 cm of the filter (EBCT 5 min) (Fig. 6A). Already the upper 10 cm of the filter showed a high retention capacity. At this sampling point, the IPMP concentration reached a maximum of 50% relative to the inflow concentration after two hours of spiking. Below 50 cm, the IPMP concentrations remained below detection limit during the whole experiment. After 120 minutes, when spiking of IPMP was stopped, the concentrations in the upper part of the filter dropped immediately and the previously adsorbed IPMP did not desorb. The observed 100% reduction of IPMP by GAC filtration in this experiment is in contrast to the findings of Kim et al. (1997). These authors determined a 35% removal efficiency at an EBCT of 5 minutes. The higher efficiency in our experiments can be explained by the high adsorption capacity of the fresh GAC. In contrast, bottle kinetic experiments with fresh GAC did not show any removal after 5 minutes.

Figure 6B shows the results of the spiking experiment 6 months after start of the pilot-plant. At this time the concentrations in all layers increased faster and remained at a higher percentage. In the upper 10 cm, the IPMP concentration was removed by a maximum of 40%. Comparing the fresh and the used GAC, the IPMP concentration decreased from 90% to 75%. When spiking was stopped, the concentrations decreased more slowly, compared to the previous experiment. After 6 months of carbon use, it was still possible to remove IPMP

by 80% within the first 30 cm of the GAC filter bed, although other micropollutants such as methyl *tertiary*-butyl ether (MTBE) showed no removal anymore.

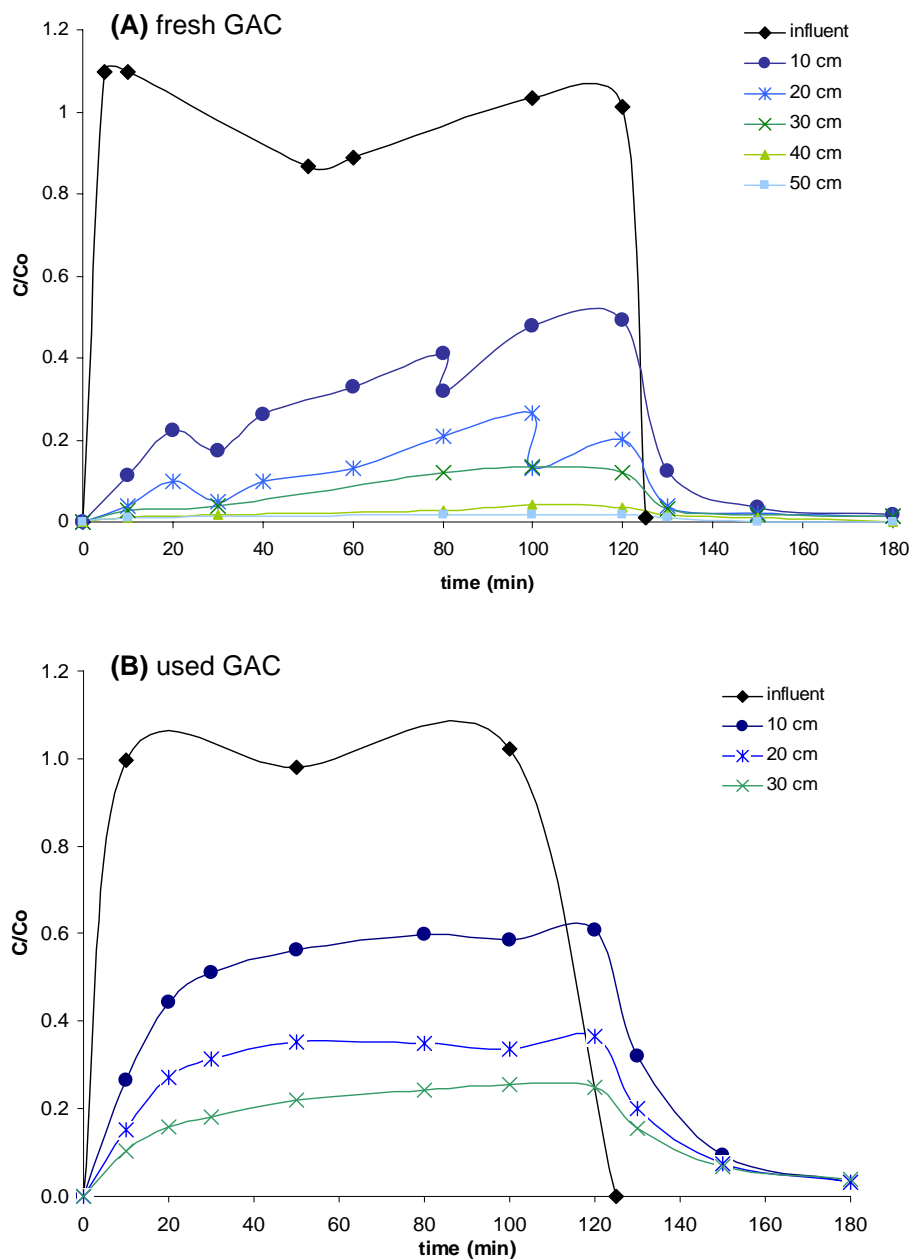


Fig. 6. Continuous IPMP spiking experiments on the pilot-scale GAC filter. (A) In the upper 50 cm of a GAC filter bed (fresh GAC) a 100% IPMP removal was reached over a spiking period of 120 minutes. (B) After 6 months of operation the adsorption capacity for IPMP decreased to 80% in the upper 30 cm.

The results of this study contain many uncertainties and thus conclusions are partially speculative. We could not present a clear scientific proof, but from the available results we can conclude that GAC filtration is an efficient treatment technology for the removal of IPMP. We have observed that filter experiments have a higher removal capacity for IPMP than bottle experiments; however, we can not give an explanation for this finding.

Conclusion

- Bottle-kinetic experiments have shown that it is possible to remove IPMP to a certain percentage with fresh (80%) and used GAC (60%), respectively. Thus, the presence of NOM did not show an influence on the IPMP removal efficiency of the fresh GAC, which could not be explained so far.
- Biological degradation of IPMP could not be proved in bottle kinetic experiments.
- Isotherm experiments showed the highest removal with fresh GAC, compared to the used GAC. The presence of NOM decreased the adsorption capacity of IPMP on the fresh GAC, which is reasonable but contradictory to the results from the kinetic experiments.
- The results of the fixed-bed kinetic experiments showed a 100% removal of IPMP with fresh GAC. These results are not in good agreement with the lower removal in the bottle kinetic experiments.
- System losses of 38% were determined for bottle-kinetic experiments, thus it was not possible to differentiate between fractions of physical adsorption and of volatilization.
- Under the given circumstances, using IPMP as target compound, bottle-kinetic experiments seem not to be an adequate set-up to replace fixed-bed-kinetic experiments operated in batch mode.
- Pilot-scale experiments showed a 100% IPMP reduction within the upper 50 cm of the fresh GAC filter. Still, after 6 month of continuous operation with NOM containing lake water, the removal was 80% within the upper 30 cm. GAC filtration showed to be a promising technology for the removal of IPMP from drinking water. Still, we can not explain the differences to other settings in this study.
- This study has shown that experiments with T&O compounds are challenging and not easy to interpret. The results of this study are not consistent or even partly contradictory. It was not possible to gain stable and reasonable results reaching from lab-scale experiments up to pilot-scale experiments. Nevertheless, T&O compounds are of substantial interest for many water works which asks for the need of further research.

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Conclusions

Conclusions

The present work focuses on the characterization of biologically active GAC filters. Specific focus was placed on the quantification of active biomass over time and space in different GAC filters for which a new method, based on ATP and flow cytometry, was developed. Additionally, the understanding of the role of such GAC filters as an adsorber for the removal of NOM, MTBE and IPMP at different settings was investigated.

The questions stated at the beginning of this project will be answered shortly:

Method development for the quantification of active biomass on GAC

The direct ATP method developed during this thesis provides realistic and reproducible results for the quantification of active biomass on GAC. Its standard deviation of 15% shows that the method is sensitive and also applicable to situations where slight variations over a large period can be expected, such as in start-up phases of GAC filters. Advantages as simplicity, speed and cultivation independency favor this method. Moreover, the set up of this method may easily be adapted for the quantification of fixed biomass in similar systems such as rapid sand filters and slow sand. The ATP method has been already adapted and applied successfully for biomass quantifications on ultrafiltration membranes.

Biomass quantification of dynamic systems and pseudo-steady state conditions

For a GAC pilot-scale filter, which was investigated over time and space during the start-up phase, it was shown that biomass accumulated rapidly on the GAC particles throughout all layers. The biomass accumulation ceased after about 90 operational days in all layers, indicating the establishment of a steady state. Both during the initial development and in the steady state, stratification with regard to biomass concentration was clearly observed in the different layers.

The highest biomass concentration was established in the 2nd layer (GAC 2; 45 cm). Below this layer the concentration decreased likewise with the GAC filter depth from GAC 2 to GAC 4 (115 cm). This stratification effect is important because it impacts on the sampling strategies and more over on the design of GAC filters.

In a second pilot-scale filter, biomass development over time was characterized. Therefore, samples were taken once every fifth to tenth day. The maximum ATP

concentration was measured after 33 days with a following decrease thereafter to a pseudo-steady state after 75 days of operation.

For the full-scale GAC plant in Lengg, Zürich, which has been operating for over 20 years without replacing the GAC, we determined the steady state concentration. The treatment conditions and water compositions of all three GAC filters were similar and comparable results of $4.15 - 9.1 \times 10^9$ cells/g GAC were obtained. This biomass concentration results in a biomass volume of $1.75 \times 10^{-4} \text{ m}^3$ for the entire GAC filter. Compared to the GAC interstitial volume, this biomass volume is insignificant and leads therefore only to minor head-losses in GAC filters.

Vertical stratification in biomass concentration can be explained by NOM and AOC influx concentration and subsequent adsorption in the GAC filter

Stratification during the start-up and the steady state phase can be ascribed directly to differences in the availability of nutrients on the different layers. Biomass accumulation was followed for four individual GAC layers (GAC 1-4). Two distinct periods of biofilm development were observed in the individual layers: t_1 (-11-91 days) and t_2 (91-198 days). In the first period (t_1), initial biofilm development proceeded at the highest rates in the upper layer of the filter and about 50% slower in the bottom layer. Such stratified behavior is ascribed directly to a decreasing availability of organic nutrients downwards through the filter. The adsorption capacity of fresh GAC is high and therefore very little DOC reaches the bottom of the filter in the initial stage of operation.

In the 2nd period (t_2), a steady state in biomass concentration in all levels was reached, still with a slight biomass increase (growth rate = 0.0001 h^{-1}). The highest biomass concentration was established in the second layer and decreased following over the filter bed depth. The lower biomass concentration at the upper layer can be explained by the residual ozone concentration in the influent of the GAC filter.

The increase at about day 60 in the layers GAC 2 and GAC 3 was directly related to a significant influx of algal organic matter. The algal cells were severely damaged by ozonation, and release/form AOC that stimulated growth in the GAC filter. Before the algae influx, the AOC influent concentration was on average $80 \text{ } \mu\text{g/L}$. During the period of increased algal influx, the AOC concentration in the influent was higher (average = $110 \text{ } \mu\text{g/L}$) while a further increased concentration of AOC at level GAC 1 (10 cm) was evident (average = $145 \text{ } \mu\text{g/L}$).

This represented a significant addition of bio-available organic carbon, which was most likely not used entirely in the top of the filter, and thus supported further growth in the lower layers.

Adsorption behavior of different NOM fractions

Biopolymers were poorly removed in GAC filters. Concentrations of humics, building blocks and LMW organics increased gradually in the outlet of the filters until reaching a steady state after 168 days (EBCT of 12.21 min). In order to compare the adsorbability of DOC and individual NOM fractions, partition coefficients (K_p) were calculated from the steady state solid phase concentrations and the corresponding aqueous phase concentrations in the two GAC effluents ($K_p=q/C$). K_p values suggest that the adsorbability of NOM constituents increased with decreasing size: biopolymers < humics < building blocks < LMW organics. The greater adsorbability of smaller NOM constituents is likely the result of their ability to access a larger percentage of the total GAC pore volume. Biopolymers are fibrils with a height of a few nm and a length of several 100 nm. Poor removal of biopolymers was likely a result of their comparatively large size that prevented access to the internal pore structure of the GAC and their hydrophilicity.

The NOM adsorption uptake was higher for the GAC with the higher accessible surface area, which is in a reasonable agreement with the difference in mesopore and secondary micropore volumes between the two tested GACs. An increase in EBCT from 12.2 min to 15.8 min (entire GAC filter) did not offer any advantage in terms of decreased carbon usage rate.

Effect of GAC service time on the changes in GAC characteristics and the concurrent loss of MTBE adsorption capacity

The increase in DOC load on GAC over time resulted in a linear decrease of the BET surface area and the micropore volume. After 298 days of continuous operation, the BET surface area and micropore volume decreased by 25% of the original values. In contrast, preloading strongly affected the remaining MTBE adsorption capacity. Already after 3 days of operation, the remaining MTBE adsorption capacity decreased to 30% of that measured for fresh GAC (at a concentration of 10 $\mu\text{g/L}$ in ultra pure water). After 298 days of operation the MTBE adsorption capacity decreased further to low 6%.

For the fresh GAC, the adsorption capacity in NOM containing water was 35% lower compared to that measured in UPW. After 3 days of service time the remaining MTBE adsorption capacity in UPW and in the presence of NOM was already similar. This suggests

that direct site competition between MTBE and NOM did not occur on preloaded GAC. This preloading effect was most probably mostly affected by the blockage process of micro and mesopores. Hence the influence of NOM preloading is higher than direct site competition.

Correlation of GAC pore size distribution with MTBE molecule size

The pore volume of 5.2 - 5.7 Å size range correlated most strongly with the MTBE adsorption capacity along with other physical GAC characteristics. The kinetic diameter of MTBE (6.2 Å) is comparable to the pore width of 5.2 - 5.7 Å of the targeted adsorbate.

Removal of IPMP with GAC

The removal of IPMP was investigated with different experimental set ups, ranging from bottle kinetic experiments to pilot-scale studies with GAC filters. Bottle kinetic experiments showed a reduction of IPMP to about 20% by applying fresh GAC. The IPMP concentration was reduced to 40% of the initial by the 20 year old GAC. The decrease in adsorption capacity of fresh GAC at the presence of NOM, determined in isotherm experiments, was not confirmed in batch kinetic experiments. Biological active carbon showed no increased removal rate, compared to the biologically inhibited carbon (both to 40%). Fixed-bed filter experiments in lab-scale and pilot-scale showed a quantitative IPMP removal, compared to a 60-80% removal in corresponding bottle-experiments. This removal was reached after 150 h in fixed-bed kinetic experiments and after 5 min EBCT in the pilot-scale GAC filter. Nevertheless we have to conclude that the results of this study are not consistent and not absolutely reasonable. Considerable system losses might partially explain inconsistent results.

The main scientific contributions of the work can be summarized as follows:

- Development of a new straight-forward method to quantify active biomass on GAC.
- Application of the newly developed ATP-method for the determination of active biomass in different GAC filters in time and space.
- Characterization of adsorbability of different NOM fractions from lake water on GAC.
- Investigation of changes in GAC characteristics by NOM preloading and impact on GAC adsorption capacity for MTBE.
- Characterization of IPMP removal with GAC

Concluding remarks

The investigations have shown that the explicit considerations of all aspects within GAC filters operated for adsorption and biological removal is not a trivial task. Extensive expert knowledge is required in order to describe the system in a mathematically correct way. Experts should also consider influences of pretreatment such as ozonation as well as the influence of the GAC effluent on post treatment such as membrane filtration.

Outlook

The GAC treatment fulfils in the present process chain with O₃, GAC and UF three different tasks: particle separation, adsorption and fixed bed biofiltration. The main fraction of the suspended particles in the lake water has to be eliminated in the GAC filter, which acts hereby as a rapid filter. On the other hand, the requirements for particle removal are not very strict since further particle separation takes place during the following ultrafiltration.

The main task of GAC is to remove undesired dissolved compounds by adsorption on the GAC surface area. Thereby different categories of substances are addressed which have different demands for the GAC application: removal of T&O compounds, synthetic organic micropollutants in a concentration of ng/L and NOM in mg/L concentrations. In cases of accidental spills the GAC filter shall also act as a protection barrier for a short period.

It is well established that ozonation increases the fraction of NOM that is biodegradable. This AOC fraction is degraded by the biomass established on the GAC and results in biological stable water of which the re-growth potential is very low.

These three tasks have different requirements on GAC operation, which can not be fulfilled concurrently in an optimal way. Experiments on the GAC pilot filter and results from lab scale experiments served to gain further insight of the performance of such GAC filters.

If the main task of a GAC filter is biological removal, the impact of NOM preloading is not crucial. Yet, in the case of concurrent adsorption of MP, possible treatment steps before GAC filtration should be evaluated to decrease NOM preloading.

NOM removal before GAC filtration

One possible option for the NOM removal before GAC filtration would be the implementation of a pre-coagulation step. This practice has been already established as an essential pre-treatment step in many water treatment plants. Suspended solids agglomerate together with NOM into larger flocks so that physical filtration processes can more easily remove them. As a result less NOM adsorbs on GAC and thus prolong the application time of GAC. The process requires chemical knowledge of source water characteristics to ensure that an effective coagulant mix is employed. The ultimate effectiveness of coagulation is also determined by the efficiency of the filtering process with which it is combined.

Early elimination of natural organic matter (NOM) can also be achieved by ion exchange (IEX) in water treatment which improves subsequent water treatment processes and the final drinking water quality. Depending on the IEX characteristics, the removal of NOM fractions, specifically humic substances and biopolymers, is thereby achieved (Boyer and Singer, 2008). Also, the fractions responsible for membrane fouling are decreased. Still, the application of IEX is expensive.

Optimization of GAC operation

The phenomenon of GAC preloading was described already by several authors and is characteristic especially for deep GAC filters treating water with high NOM concentrations. Different treatment possibilities for the reduction of NOM preloading have been investigated in the past. In the case of little and known micropollutants in the influent water the layered upflow carbon adsorber (LUCA) offers good options (Munz et al., 1990). The principle of its application is the addition of always fresh GAC in shallow layers on top of the filter as soon as the breakthrough of a substance is monitored. Another promising technique is the application of activated carbon fibers (ACF) (Hopman et al., 1995). The pore entrances of the ACF are very narrow and thus access for higher molecular weight substances as humics and biopolymers is prevented. Thus the entire internal ACF surface area is available for the adsorption of low molecular weight substances. However, the removal of NOM does not take place in this process and can influence subsequent treatment steps.

Influence of GAC filtration on membrane systems

The influence of GAC filtration on the following membrane filtration shows advantages. Humics, the highest concentrated fraction in the water source, responsible for most of the membrane fouling, are removed. However, the adsorption capacity for humics is depleted

already after six months. Further, biopolymers, which are also responsible for membrane fouling, are only poorly removed in GAC filters. Thus GAC filtration does not lead to substantial fouling reduction of ultrafiltration membranes on a long term basis. Though the composition and amount of humics in surface water can vary highly across different water sources and seasonally within a water source, the rate and extent of humic adsorption and the consequences on the removal efficiency are difficult to predict.

An alternative to polyethersulphone membranes (PES) are ceramic membranes, with the advantage of lower fouling rates. It was determined that ceramic membranes can be operated longer than PES membranes before backwashing/cleaning with a high permeability. Thus this technology is still more expensive compared to PES membranes.

Application of PAC as an alternative to GAC filtration

In order to eliminate the effect of preloading on GAC and thus increase the cost efficiency, the application of powdered activated carbon (PAC) should be considered. Spent PAC is replaced continuously, which guarantees constant removal efficiency for micropollutens and NOM. In combination with membrane filtration, PAC shows advantages over GAC with regard to (1) constant NOM removal and thus lasting reduction of membrane fouling and (2) steady adsorption capacity for micropollutants. The combined application of PAC and membranes already exists and is applied in the so called *Crystal Process* (Pianta et al., 1998) for the treatment of e.g. karstic spring water.

However, the use of PAC is in contradiction with the application of ozone. The desired biological reduction of AOC does not occur when PAC is used. Because the residence time of PAC in the system is short, it does not serve as carrier material for the growth of substantial amounts of bacteria and thus AOC is not degraded biologically. Additionally, in a case of unknown accidental spills no protection barrier would exist in this set-up. However, in known accident spills, PAC could be dosed specifically on a case to case base.

Important future research tasks

A long term goal is to understand the dependence of biofilm dynamics in GAC filters. The outcome of this thesis showed already the influence of AOC and NOM influent composition on biofilm dynamics, growth rates and DOC removal capacity in a GAC filter and the corresponding effluent concentrations in one setting. Thus, changes in given water quality parameters such as fluctuations in AOC loads have to be investigated in more detail to

understand apparent changes in suspended and attached biomass concentrations. Also, the influence of reactor design and operation (e.g. reactor volumes, flow rate, empty bed contact time and backwashing regime) on the biological and chemical GAC effluent composition needs further investigation. In our opinion, it is important to be able to differentiate between biological degradation and adsorption of NOM in GAC filters, which would be the outcome of further experiments.

Last but not least, the question is whether it is possible to describe biological and adsorption processes together in one mathematical model and how transferable the results are to other settings. A mathematical description is important, because it is the basis for application in the design and optimization of GAC filters in order to ensure an efficient and safe drinking water production. Several models either describe adsorption processes in detail (Kilduff et al., 1998; Knappe et al., 1998; Graham et al., 2000) or characterize biological processes in the GAC filter (DiGiano et al., 2001; van der Aa, 2006), but a successful combination has not been presented yet. It is also not certain whether it is possible to apply a combined model, often developed under specific conditions for GAC filters in pilot-scale, for a full-scale GAC filter under different settings (differences in water and biomass compositions, GAC product).

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