

EFFECT OF LIME SOLIDS AND NATURAL ORGANIC
MATTER ON GEOSMIN REMOVAL VIA POWDERED
ACTIVATED CARBON

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Abstract

Minneapolis Water Works, a 60 million gallon per day water treatment facility, experiences seasonal taste and odor episodes that result in customer complaints. Geosmin, which imparts an earthy or musty odor, is one taste and odor causing compound that has been detected at levels exceeding its odor threshold concentration. Powdered activated carbon (PAC) is added in the lime softening plant to remove geosmin via sorption. It is important to understand how lime solids, contact time, and natural organic matter (NOM) affect PAC performance so that the correct PAC dose and application point are used in order to maximize geosmin removal and minimize PAC cost. Results from jar test experiments suggest that lime and alum do not inhibit the sorption of geosmin when added simultaneously with PAC but that contact time is the most important parameter. Therefore, PAC should generally be added to the water at the point which maximizes contact time. Conversely, PAC contained in settled lime solids exhibited a reduced sorption capacity compared to fresh PAC, indicating that PAC contained in recycled lime solids has minimal impact on geosmin removal at the full-scale treatment plant. Additionally, the impact of NOM on PAC performance was investigated. Using Suwanee River (SR) NOM, an increase in 1 mg/L dissolved organic carbon resulted in a decrease in geosmin removal efficiency of 2.7% (at a PAC dose of 7.5 mg/L). Suwanee River humic acid, SR fulvic acid, and Pony Lake fulvic acid also inhibited geosmin sorption, but the effect was significantly lower. For the three SR NOM types, the inhibitive effective increased as average molecular weight of the NOM decreased. Data from the full-scale plant were in reasonable agreement with laboratory jar test data for PAC added immediately before or after lime. For PAC added at the recarbonation tanks, geosmin removal efficiencies were much higher at the full-scale plant than in the jar test experiments. This could be due to the small sample size (n=4) of the full-scale data set or differences in DOC levels between jar tests and the full-scale plant.

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1. Introduction

Taste and odor episodes are problematic for drinking water utilities as most consumers evaluate water quality based solely on aesthetic indicators. In North America, approximately 43% of water utilities receive complaints about taste and odor in their drinking water (Suffet et al. 1996). Water utilities in Europe and Asia also receive a high number of complaints due to taste and odor issues (Lalezary et. al 1986). Taste and odor (T&O) causing compounds generally do not pose a threat to human health, and are therefore not regulated in the United States. Nevertheless, it is vital that water utilities have the capacity to remove these compounds when they occur in order to maintain high consumer confidence.

1.1. Minneapolis Water Works

Minneapolis Water Works (MWW) in Minneapolis, MN treats and distributes an average of 60 million gallons per day (MGD). Water is withdrawn from the Mississippi River and treated by lime softening, disinfection, and filtration. The treatment scheme is shown in Figure 1 (Minneapolis Water Works, 2010).

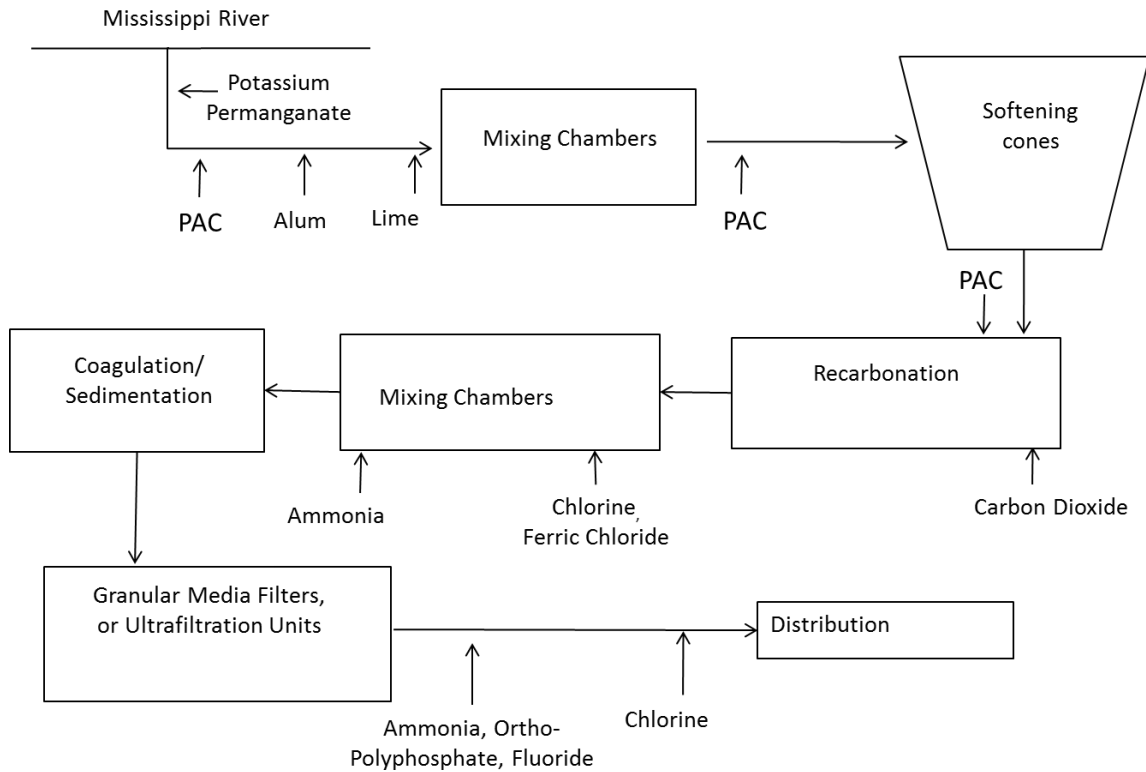


Figure 1: Treatment scheme at Minneapolis Water Works (MWW 2010)

Between October 2007 and February 2012, raw water and finished water were tested for ten known taste and odor-causing compounds (

Table 1). Raw water was tested on 107 dates and finished water was tested on 82 dates. Most compounds never exceeded the odor threshold concentration (OTC) in the raw or finished water. The OTC's for 2,3,6-trichloroanisole (2,3,6-TCA), 2,4,6-trichloroanisole (2,4,6-TCA), 2-isopropyl-3-methoxyprazine (IPMP), and 2-isobutyl-3-methoxyprazine (IBMP) were below the reporting limit, so it is possible that these compounds could have exceeded their OTC without being detected. Geosmin, a known earthy/musty odor-causing compound, was detected in nearly every sample and geosmin concentrations were frequently above the OTC (4 ng/L; Young et al. 1996).

Table 1: Detection data for ten T&O compounds for 2007-2010

Compound	Descriptor	Percentage of samples above OTC, raw water ¹	Percentage of samples above OTC, finished water ¹
Cis-3-Hexene-1-ol	Grassy ²	0%	0%
Heptanal	Fatty Oily ^{3,4}	0%	0%
Cis-3-Hexenyl acetate	Grassy ²	0%	3%
Trans,trans-2,4-Heptadienal	Fishy ²	0%	0%
2-Isopropyl-3-methoxyprazine	Earthy, Potato bin ⁵	2%	0%
2-Methylisoborneol	Musty, earthy, brazil nuts, peaty ⁵	1%	1%
2-Isobutyl-3-methoxypyrazine	Woody, Stale, musty, coal dust, ash ⁵	0%	0%
2,4,6-Trichloranisole	Dusty, musty, earthy, rotten vegetable ⁵	13%	5%
2,3,6-Trichloranisole	Dusty, musty, earthy, rotten vegetable ⁶	2%	3%
Geosmin	Musty, Earthy, stagnant, grassy, beetroot mold ⁵	61%	13%

¹CH2M HILL Applied Sciences Laboratory, Analytical Reports, 2007-2010

²Suffet et al. (1999)

³Burlingame et al. (2004)

⁴Buttery et al. (1988)

⁵Young et al. (1996)

⁶Montiel et al. (1999)

Between January 2008 and December 2010, MWW received approximately 330 complaint calls regarding taste and odor issues. The majority of the complaints (60%) were classified as fishy, musty, or swampy. The remaining complaints were due to unspecified taste and odors, with isolated complaints of chlorine, plastic, metallic, and chemical tastes or odors. One customer even reported that their water tasted like a gin and tonic. In addition, observations by MWW personnel indicate that the finished water has a

noticeable earthy or musty odor over 80% of the year. Complaint calls, particularly those due to fishy, musty, or swampy odors, are most frequent between March and September.

Total complaint calls, earthy/musty complaint calls, and geosmin concentrations in the finished water from 2008-2010 are shown in Figure 2. The horizontal shaded region on the graph represents the range of reported OTC values for geosmin. Geosmin concentrations within or above this region are detectable by humans. Because it is difficult to describe faint odors emanating from drinking water without proper training, consumer descriptions of the odor may not be accurate. The volume of consumer complaints, however, is a good indicator of whether or not there is an aesthetic problem with the water.

There were only two serious taste and odor episodes between 2008 and 2010. In July of 2008, a high number of complaint calls, many of them due to earthy/musty odors, corresponded to geosmin concentrations well over the OTC. In 2009, MWW received very few complaint calls, though the geosmin concentration on April 1 and 3 slightly exceeded the OTC range. Most of the complaints in March 2010 were due to a fishy odor, and the corresponding geosmin concentrations were not significantly higher than in other months that year. 2011 is not shown in Figure 2 because MWW received less than 10 complaint calls due to taste and odor. In 2011, the geosmin concentration in the finished water only exceeded 4 ng/L twice and never exceeded 10 ng/L.

It has thus been concluded that geosmin, though detectable year-round, is only a potential problem in the spring and summer months when concentrations above the OTC occur. Fortunately, serious geosmin episodes are infrequent, only occurring once every few years. The earthy-musty/geosmin problem, however, is not the only concern. Some early spring odor episodes appear to be due to a fishy/swampy odor and the causative compound or compounds have not been identified. Trans, trans-2, 4-decadienal is one known fishy odor, but MWW has routinely tested for this compound and never detected it above the OTC in either the raw or finished water. Trimethylamine is also a known fishy odor (Suffet et al. 1999) and could be responsible for the fishy taste and odor.

Unfortunately, trimethylamine is difficult to detect analytically at low, odor-producing levels.

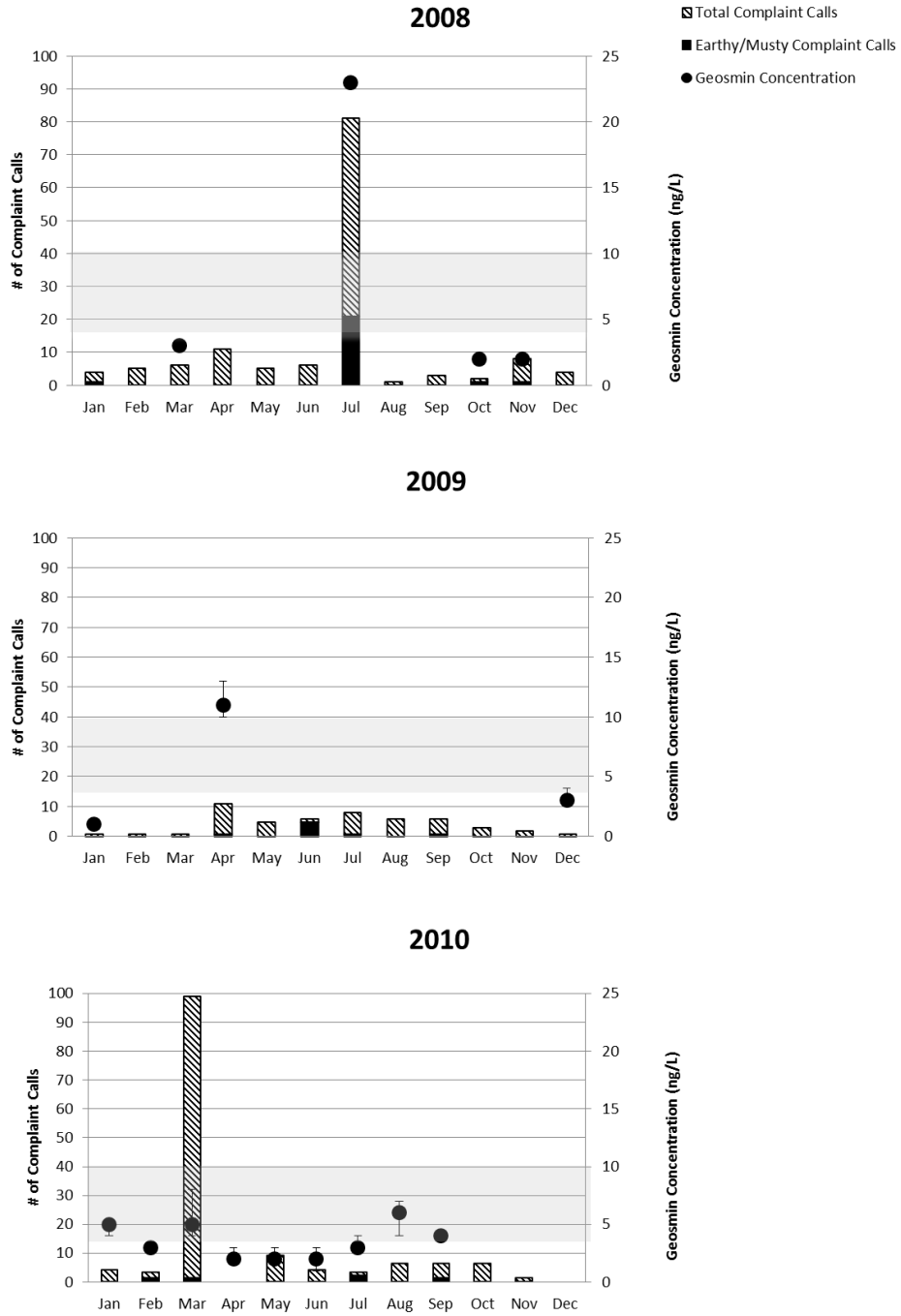


Figure 2: Total complaint calls, earthy/musty complaint calls, and finished water geosmin concentrations for 2008 - 2010

Geosmin concentrations are averages- error bars represent the high and low for a given month.

Minneapolis Water Works has applied powdered activated carbon (PAC) and potassium permanganate in an attempt to mitigate the taste and odor problems, yet geosmin concentrations in the finished water occasionally exceed the upper bound of the OTC resulting in earthy/musty complaints. PAC performance is shown in Figure 3, which shows geosmin removal efficiency as a function of PAC dose. The slope is statistically significant ($p < 10^{-4}$) and suggests that removal efficiency increases at a rate of 3.1% for every 1 mg/L increase in PAC dose. Ideally, MWW would adjust PAC dose in proportion to raw water taste & odor levels. It is clear from Figure 4 that PAC dosing does not correlate with raw water geosmin concentration. It is difficult to apply PAC based on geosmin concentrations, however, as concentration data are not available in real time. In addition, as indicated above, geosmin is not the only taste & odor compound of concern. Nevertheless, the primary goal of this research was to optimize PAC application for geosmin removal.

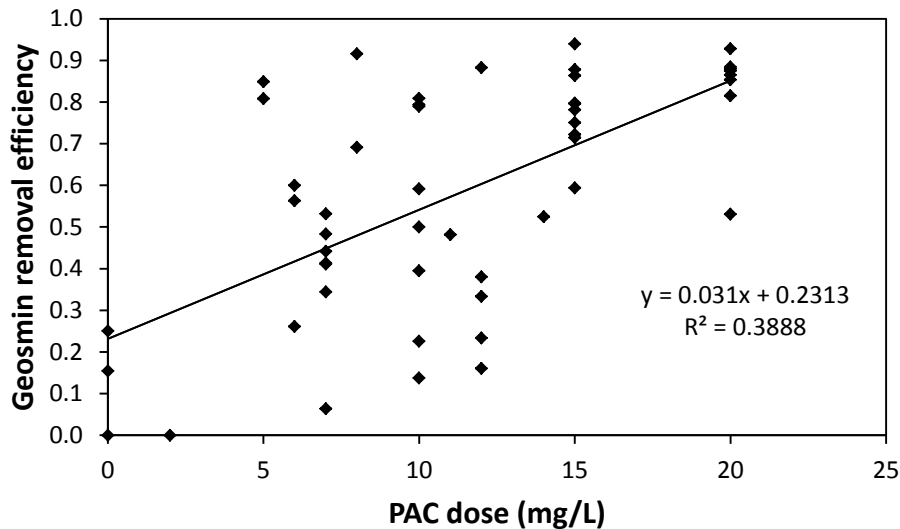


Figure 3: Geosmin removal efficiency increases with PAC dose (MWW, data from 2007-2011)

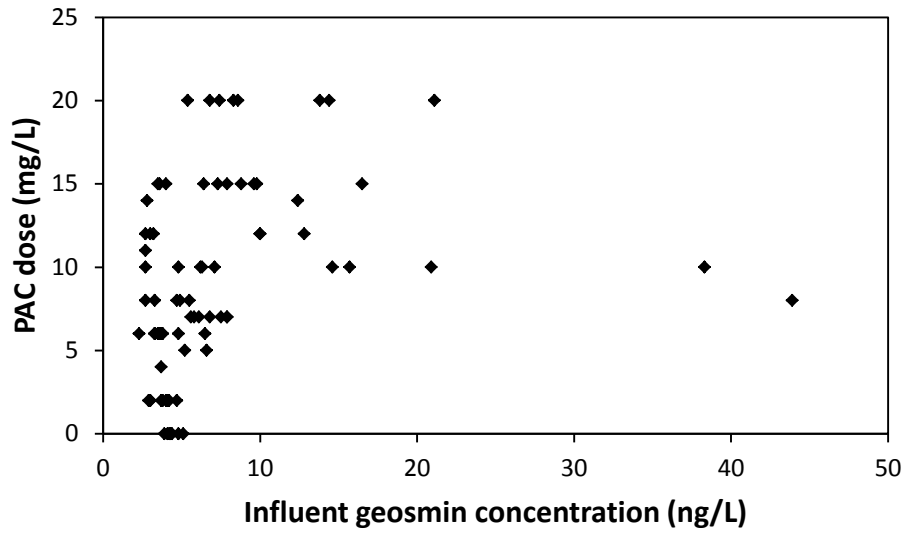


Figure 4: PAC dose increases with raw water geosmin concentration (MWW, data from 2007-2011)

2. Literature Review

There are many different classes of taste and odor compounds, summarized by Suffet et al. (1999) in the “Taste and Odor Wheel” (Figure 5). Of these classes, earthy/musty odors are often the most problematic because compounds in this class have low OTCs and are not effectively removed by conventional treatment processes. The most commonly detected earthy/musty compounds are trans-1, 10-dimethyl-trans-9-decalol (geosmin) and 2-methylisoborneol (MIB). Others include 2,4,6-TCA, IPMP, and IBMP (Suffet et al. 1999). Problems due to other classes of compounds are less common, as the compounds occur infrequently, have relatively high OTCs, or are removed by conventional treatment processes.

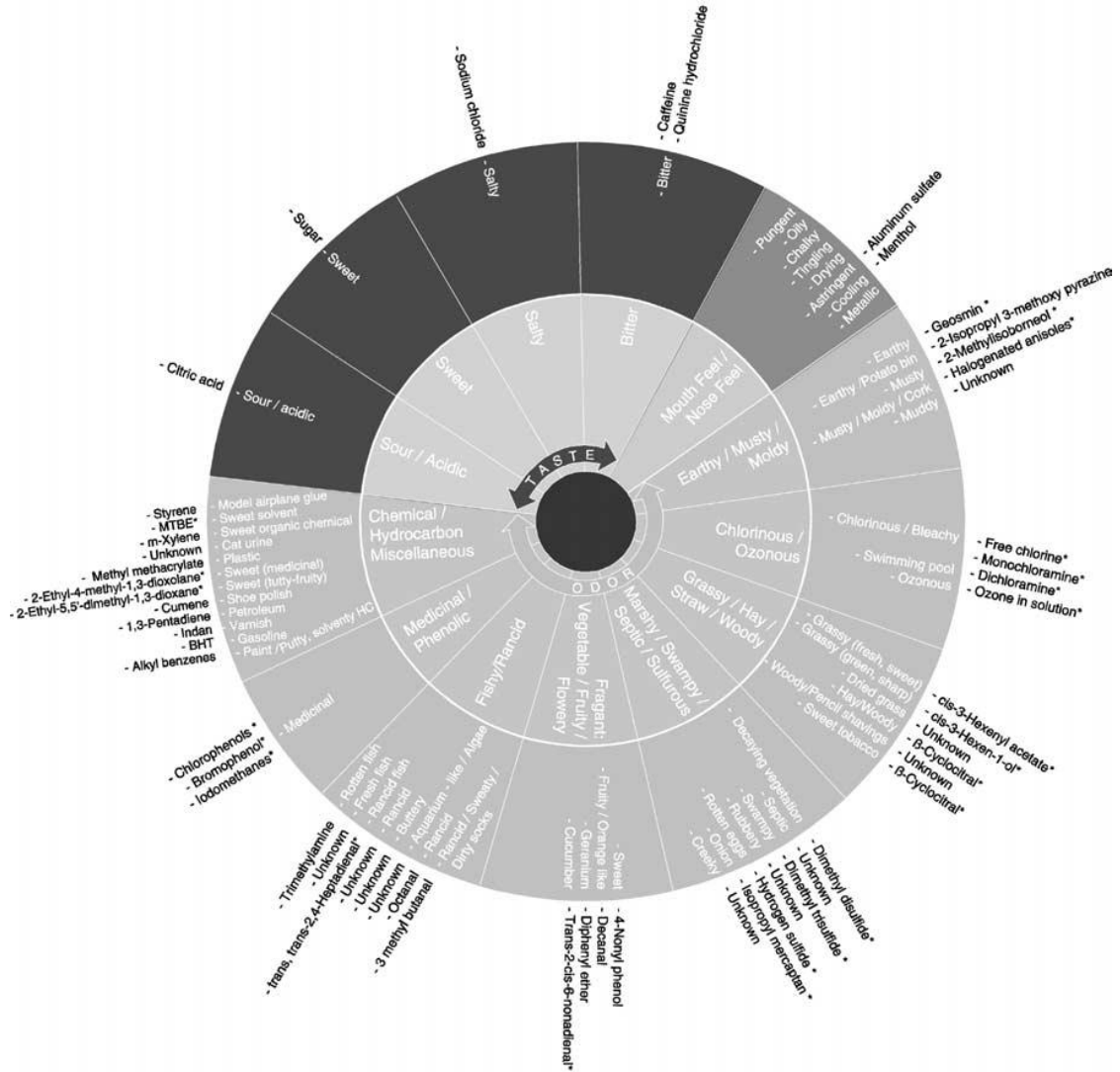


Figure 5: Drinking water Taste and Odor Wheel (Suffet et al. 1999)

2.1. Earthy/Musty compounds Geosmin and MIB

Geosmin and MIB, first identified in the 1960's (Gerber and Lechevalier 1965, Medsker et al. 1969), are byproducts of actinomycetes and cyanobacteria (formerly known as blue-green algae) in surface water supplies (Zaitlin and Watson 2006). In addition, both compounds can be released upon cell lysis (Juttner and Watson 2007). Forty one species of cyanobacteria have been linked to geosmin and MIB production

(Izaguirre et al. 2004), and at least 11 species of actinomycetes are known to produce geosmin and MIB (Izaguirre et al. 1982). Both compounds are tertiary alcohols, and their structures are shown in Figure 6.

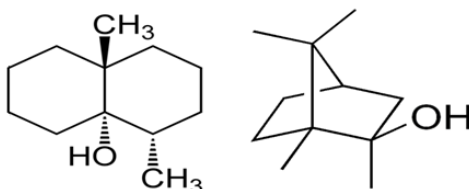


Figure 6: Structures of geosmin (left) and MIB (right)

One factor contributing to the problematic nature of geosmin and MIB is their relatively low OTCs. Reported OTCs range from 4-20 ng/L (Persson 1980, Young et al. 1996, Rashash et al. 1997). Young et al. (1996) reported an OTC for geosmin of 4 ng/L at 40° C and 16 ng/L at 25° C. Rashash et al. (1997) conducted tests at 45° C, and reported that the OTC of both compounds ranged from 6-10 ng/L. For MIB, Young et al. (1996) reported that the OTC ranges between 15-18 ng/L. For the purpose of this review, 10 ng/L will be considered the OTC for both compounds unless stated otherwise (note that in Table 1, 4 ng/L was used for the OTC of geosmin).

2.2. Fishy Compounds

Fishy and rancid odors are responsible for customer complaints across the United States. Known fishy compounds include: trans,trans-2,4-heptadienal, trimethylamine, octanol, and 3-methyl butanal (Suffet et al. 1999). Fishy odors are often associated with phytoplankton blooms, which also frequently coincide with earthy/musty episodes (Dixon et al. 1993, Hargesheimer et al. 1996).

2.3. Water Treatment Processes

The effectiveness of conventional and advanced treatment processes for removal of taste and odor-causing compounds has been the subject of numerous research reports.

While most conventional treatment methods are not effective at removing these compounds, advanced oxidation processes and sorption are often effective at reducing the concentrations of taste and odor compounds to below their OTCs. (Lalezary et al. 1986, Glaze et al. 1990, Bruce et al. 2002, Jung et al. 2004, Scharf et al. 2010).

2.3.1. Conventional Treatment Processes

2.3.1.1. CGS and DAF

Conventional gravity sedimentation (CGS) and dissolved air flotation (DAF) are two traditional treatment methods that can reduce odor intensity. DAF is significantly more effective at reducing odor intensity than CGS because the addition of air results in stripping of the volatile/semi-volatile taste and odor-causing compounds. Neither method, however, is sufficiently effective at removing odors from drinking water (Hargesheimer et al. 1996).

2.3.1.2. Coagulation

Many researchers have proven that coagulation is not an effective process to remove taste and odor-causing compounds, especially earthy/musty odors. Bruce et al. (2002) reported that neither alum (20 mg/L) nor ferric chloride (2 mg/L) had any effect on geosmin or MIB concentrations.

2.3.1.3. Traditional Oxidation Processes

Chemical oxidants commonly used in water treatment plants, including chlorine, chlorine dioxide, and potassium permanganate, are not effective at removing geosmin or MIB. Lalezary et al. (1986) and Glaze et al. (1990) were the first researchers to report on the effectiveness of chemical oxidation at removing geosmin and MIB, with reported removal efficiencies below 50% for all oxidants except ozone. Others (Jung et al. 2004, Liang et al. 2006) have since reported similar results. For example, Jung et al. (2004) observed that doses of 1.5 mg/L of Cl_2 and ClO_2 removed little or no geosmin and MIB.

Additionally, the application of chlorine (or other oxidants) can cause lysis of actinomycetes or cyanobacteria. When the cells are lysed, geosmin and MIB can be released. Therefore, if an oxidant is added before the actinomycete or cyanobacteria cells are removed, there is a risk of increasing the geosmin concentration (Juttner and Watson 2007).

Furthermore, researchers have also demonstrated that chlorine and chloramine residuals do not reliably mask the smell of the earthy/musty compounds. While some studies report that the presence of residual chlorine confuses panelists, the earthy/musty smell is not eliminated (Oestman et al. 2004).

2.3.2. Advanced Treatment Processes

2.3.2.1. Oxidation with Ozone

It is well established that ozonation can effectively remove geosmin and MIB (Bruce et al. 2002). Ozone can react with compounds in two ways: directly as molecular ozone or indirectly as radical species formed when molecular ozone decomposes (including hydroxyl and peroxy radicals) (Hoigne & Badner 1975). Research suggests that the oxidation of geosmin is mediated primarily by hydroxyl radicals, and not molecular ozone (Bruce et al. 2002, Westerhoff et al. 2006, Scharf 2007). For example, Westerhoff et al. (2006) reported that the geosmin removal for a 2 mg/L ozone dose was 24% in the presence of a hydroxyl radical quencher but 98% in the absence of the quencher.

There are a number of ways to encourage hydroxyl radical formation: addition of hydrogen peroxide, increasing pH (pH>8), or a reduction in alkalinity (Bruce et al. 2002). The simultaneous addition of hydrogen peroxide and ozone is considered an advanced oxidation process (AOP).

The use of ultraviolet (UV) light irradiation with ozonation is also an AOP, and it has been successful in removing geosmin and MIB. Glaze et al. (1990) observed 87-99% removal of geosmin and 71-83% removal of MIB. More recently, Collivignarelli and

Sorlini (2004) observed complete removal of geosmin and MIB when UV irradiation and ozone were used together.

Ozone doses in the range of 1-2 mg/L often are not effective at removing taste and odor compounds from raw waters (<90% MIB removal), while doses in the range of 3-7 mg/L are usually highly effective (75-99% MIB removal) (Lundgren et al. 1988, Glaze et al. 1990, Jung et al. 2004). In addition, all researchers that have studied both geosmin and MIB removal indicate that the latter is more difficult to remove, meaning that if MIB was removed at 75-99%, similar or higher removal efficiencies could be expected for geosmin.

Ozone doses along with corresponding removal efficiencies are shown in Table 2. As it is not uncommon for raw waters to have a concentration of 100 ng/L MIB, 90% would be the minimum removal efficiency necessary to reduce the concentration to below the OTC of 10 ng/L. It is apparent from the varying results that oxidation of MIB and geosmin is strongly affected by raw water characteristics.

Table 2: MIB removal by ozone

Ozone Dose (mg/L)	Contact time (min)	Initial concentration (ng/L)	MIB removal (%)	Source
1.5	10	50	75	Lundgren et al. (1988)
7	10	50	>95	
2	20	NA	40	Glaze et al. (1990)
4	20	NA	73-83	
1	12	100	60-65	Ferguson et al. (1990)
2	12	100	78-90	
4	12	100	80-90	
1.3-1.6	NA	37-43	54-65	Nerenberg et al. (2000)
1.5	6	66-108	<20	Jung et al. (2004)
3.8	6	66-108	88	

Ozone is an attractive option for water treatment because it is a strong oxidant and there is no risk of halogenated disinfectant byproduct formation. Disadvantages to ozone

include high cost, lack of residual, possible bromate formation, and production of labile carbon. Much of the research suggests that ozone should be used in series with a biologically-active filter to remove the labile carbon that is produced (Rice et al. 1981).

2.3.2.2. Ultraviolet Irradiation and Hydrogen Peroxide

While UV irradiation alone is not effective at removing geosmin or MIB (Rosenfeldt et al. 2005, Kutschera et al. 2009), the AOP of coupling UV irradiation with hydrogen peroxide is capable of removing geosmin and MIB. Glaze et al. (1990) first observed 40% removal of geosmin and 29% removal of MIB using the UV/H₂O₂ process (with a 0.56 W lamp and an H₂O₂ dose of 5 mg/L). Rosenfeldt et al. (2005) reported greater than 70% removal of both geosmin and MIB at a UV fluence of 10000 J/m² and a H₂O₂ dose of 7.2 mg/L. While UV/ H₂O₂ has proven capable of removing geosmin and MIB at high UV doses in the laboratory, removal efficiencies are likely to be insufficient at typical UV doses needed for disinfection. The Environmental Protection Agency (1999) reports that a UV dose of 20-60 J/m² is necessary for 1-log inactivation of most bacteria and viruses while in two pilot plants, a UV dose of 1000 J/m² provided more than 4-log inactivation of bacteriophage MS-2.

2.3.2.3. Other Advanced Treatment Methods

Ultrasonic irradiation and nanofiltration are two treatment methods that have shown promise for removal of geosmin and MIB. Song et al. (2007) reported that ultrasonic irradiation at 640 kHz provided 90% removal of both geosmin and MIB within 30 minutes. Several researchers have demonstrated that nanofiltration membranes are effective at removing earthy/musty odors. Choi et. al. (2010) observed 98% rejection of geosmin and MIB, and Dixon et al. (2010) reported >90% rejection of both compounds. While both of these methods have shown potential for T&O removal, at this point they are expensive and in the case of nanofiltration, produce a concentrate stream that must be disposed of.

2.4. Sorption

Geosmin and MIB can also be removed by sorption to activated carbon. For sorption to occur, the sorbate must diffuse from the bulk solution through the liquid film layer to the carbon surface. The sorbate can then be transferred to the internal pores of the activated carbon by surface diffusion (along the pore surfaces) or pore diffusion (through the liquid in the pores) (Sontheimer et al. 1988).

Batch equilibrium experiments are typically conducted to determine the capacity of an activated carbon to sorb a sorbate in a particular raw water. The results are frequently modeled using the two-parameter Freundlich or Langmuir isotherm equations. The sorption results are commonly expressed as solid phase concentration (mass sorbate/mass sorbent) versus liquid phase concentration (mass sorbate/volume of liquid) at equilibrium. The Langmuir model is shown in equation 1:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

where: q_e is the solid phase concentration at equilibrium (ng geosmin/mg activated carbon), q_m is the sorption capacity or maximum solid phase concentration (ng geosmin/mg activated carbon), C_e is the liquid phase concentration at equilibrium (ng/L), and K_L is the Langmuir equilibrium constant (L/ng) (Sontheimer et al. 1988).

The Freundlich model is as follows:

$$q_e = K_f C_e^n \quad (2)$$

where: q_e and C_e are the same as for the Langmuir isotherm, while n (unitless) and K_f ((ng/mg)·(ng/L)⁻ⁿ) are constants for a sorbate and sorbent at a particular temperature.

Activated carbon is used in drinking water treatment plants either in granular (GAC) or powdered (PAC) form. GAC is used as filter media in filter/sorbers while PAC is added directly into the water and is later removed by filtration or sedimentation. Activated carbon is most commonly made from coal, wood, coconut shell, or peat. A brief list of activated carbons used for taste and odor removal is shown in Table 3.

Table 3: Information on activated carbons used for drinking water taste and odor control

Manufacturer	Carbon name	PAC/GAC	Material	Size	
				GAC ¹	PAC ²
Calgon	Filtrisorb 200	GAC	coal	.55-.75 mm	
Calgon	Filtrisorb 820	GAC	coal	1-1.2 mm	
Norit	Norit GAC 400	GAC	coal	0.7 mm	
Calgon	WPH	PAC	coal		95%
Carbon Resources	CR325AA-10	PAC	coal		95%
Norit	Hydrodarco W	PAC	coal		95%
Norit	Norit PAC 20 B	PAC	coal		88%
Meadwestvaco	Aqua Nuchar	PAC	wood		95%
General Carbon Corp	Watercarb	PAC	coal		95%

¹ Effective size

² % by weight smaller than 0.75 μm in diameter

Factors that affect activated carbon performance include properties of the sorbate and sorbent and raw water characteristics, most notably the concentration and character of natural organic matter (NOM). NOM is present in most raw waters at low mg/L levels, which is four to five orders of magnitude higher than the concentration of geosmin or MIB. MIB is more difficult to remove by activated carbon compared to geosmin, which is partially due to the fact that NOM competes directly for sorption sites with MIB but not geosmin (Newcombe et al. 2002). Another contributing factor is that geosmin has a higher log K_{ow} (3.7) compared to MIB (3.1) and is thus more hydrophobic (Pirbazari et al. 1992).

2.4.1. Granular Activated Carbon

GAC beds are very effective at removing many T&O compounds, including geosmin and MIB. Batch sorption tests can be conducted to find equilibrium isotherms for individual carbons. Pilot-scale studies or rapid small-scale column tests (RSSCTs) can then be used to determine a breakthrough curve.

Many researchers have investigated geosmin/MIB removal by GAC and have reported that more geosmin was removed than expected by adsorption alone. These results pointed to another mechanism at work in addition to adsorption. Researchers have since proven that biodegradation plays a major role in the geosmin removal that occurs in GAC filter/sorbers. Herzberg et al. (2005) reported that GAC is a good host for biofilm, and Hoefel et al. (2009) identified specific bacteria active in geosmin-degrading GAC biofilms. In addition, McDowall et al. (2009) demonstrated the potential of seeding bacteria in new filters to decrease the lag time before onset of bioactivity. Several researchers have observed high removal efficiencies in pilot-scale GAC filter/sorbers as shown in Table 4. Ozonation can be used in series with GAC filter-sorbers, and the easily biodegradable organic matter, formed during ozonation, helps support growth of a biofilm that can degrade odorous compounds.

Table 4: Geosmin and MIB Removal by GAC Filters

Geosmin removal	MIB removal	Source
75-84%	52-78%	Ridal et al. (2001)
76-100%	47-100%	Elhadi et al. (2004)
	90-100%	Ho et al. (2010)

2.5. Powdered Activated Carbon

Powdered activated carbon (PAC) is often used to remove geosmin and MIB from water, especially when the problem is episodic in nature. In 1977, Hertzling et al. studied the application of PAC for the removal of geosmin and MIB. The authors reported that PAC could be effective for geosmin and MIB removal but speculated that it would ultimately be cost-prohibitive. Since then, many researchers have studied PAC for geosmin and MIB removal, and while it can be expensive, it is often times the best option for a water utility experiencing seasonal taste and odor problems.

PAC is normally added during presedimentation or rapid mix and is removed by sedimentation or filtration (Najm et al. 1991). The contact time is generally in the range of 10-120 minutes, though this is dictated by the treatment plant design and location of PAC addition. While researchers have observed that PAC and geosmin take a minimum of 4 hours to reach equilibrium, adsorption rates decrease exponentially with time. Adsorption after the first 60 minutes is very slow and often does not substantially increase the removal efficiency (Cook et al. 2001, Bruce et al. 2002). For example, Cook et al. found that a PAC dose of 20 mg/L removed approximately 77% of the geosmin in the first 60 minutes, while an additional 60 minutes of contact time increased removal to only 85%. Also, PAC should not be added with chlorine as PAC exerts a chlorine demand and PAC sorption sites can be oxidized (Gilligly et al. 1998), decreasing geosmin removal by PAC (Lalezary et al. 1988).

The general procedure for the application of PAC is to first determine which carbon offers the highest sorption capacity for the contaminant given the particular background matrix, and to then determine what doses are necessary to reduce concentrations of geosmin or MIB to below the OTC (Cook et al. 2001). Batch equilibrium experiments either in closed containers or using a jar test apparatus are used to find the carbon with the highest sorption capacity and to determine dosing requirements. Multiple researchers have reported that for a particular raw water and carbon combination, PAC performance (geosmin/MIB removal efficiency) is independent of initial concentration (Gilligly et al. 1998, Cook et al. 2001, Graham et al. 2000). Gilligly et al. (1998) also notes that it is important to evaluate PAC on cost per mass of compound removed basis rather than by cost per mass of PAC.

A summary of experimental results from different research papers is shown in Table 5. The PAC doses given represent the required dose to remove 90% of geosmin or MIB (this would correlate to reducing 100 ng/L to the OTC of 10 ng/L). The high variation in required doses shows that carbon type, character of the raw water, and experimental conditions all have a strong influence on adsorption to PAC.

Table 5: Required PAC dose to remove 90% of geosmin and MIB

PAC dose for geosmin (mg/L)	PAC dose for MIB (mg/L)	Contact Time	Type	Source
>20	>40	50 min	Jar Test	Cook et al. (2000)
30-40	>50	30 min	Jar Test	Jung et al. (2004)
45-60		60 min	Jar Tests	Johnston (2005)
	>>20	60 min	Jar Test	Liang et al. (2005)
10	20	60 min	Jar Tests	Roh et al. (2008)
15-30+	>30	10-30 min	Pilot Scale	Kim et al. (2007)
8-16	25-35	3 days	Batch	Graham et al. (2000)
7-8	15-30	3-5 days	Batch	Cook et al. (2000)
8-20	10-50	240 min	Batch	Bruce et al. (2002)
12-25		3 days	Batch	Johnston (2005)

2.5.1. Modeling PAC Performance

Modeling of PAC performance has been accomplished using the ideal adsorbed solute theory (IAST) by Graham et al. (2000) and the homogenous surface diffusion model (HSDM) by Gillogly et al. (1996), Huang et al. (1996), and Cook et al. (2001). The equivalent background compound (EBC) has been used to model NOM (Graham et al. 2000).

2.5.1.1. Ideal Adsorbed Solute Theory (IAST)

The IAST is a model that uses the Freundlich equation for multi-component systems. Graham et. al. (2000) used the IAST to model the adsorption of geosmin and NOM. The IAST assumes that all solutes have access to the same surface area and the adsorbed phase forms an ideal solution (Graham et al. 2000). The EBC was used to model organic matter as a single compound. When considering two compounds (geosmin and NOM), the liquid phase equilibrium concentrations are given by:

$$C_{1,e} = \left(\frac{q_1}{q_1+q_2} \right) * \left[n_1 * \frac{q_1+q_2}{\frac{n_1+n_2}{K_{f_1}}} \right]^{1/n_1} \quad (3)$$

$$C_{2,e} = \left(\frac{q_2}{q_1+q_2} \right) * \left[n_2 * \frac{q_1+q_2}{\frac{n_1+n_2}{K_{f_2}}} \right]^{1/n_2} \quad (4)$$

where: K_f and n are constants from the Freundlich isotherm, C is liquid phase concentration, and q is solid phase concentration. Subscripts 1 and 2 refer to NOM and geosmin, respectively. The authors reported that the IAST was a very accurate predictor of PAC performance in three out of four raw waters (except at PAC doses less than 5 mg/L). It should be noted that several researchers (Knappe et al. 1998, Gilogly et al. 1999, Graham et al. 2000) have shown that the IAST is accurate only when the contaminant concentration is low (in relation to background organic matter concentration).

2.5.1.2. Homogenous Surface Diffusion Model (HSDM)

The HSDM is a dynamic model that can be used to predict the adsorption of geosmin and MIB to activated carbon (Huang et al. 1996). Computer programs such as AdDesignS employ the HSDM or related models such as the pore and surface diffusion model (PSDM). The HSDM assumes that surface diffusion is the rate-limiting step. The model uses equilibrium and kinetic experimental results to determine a liquid film mass transfer coefficient and the surface diffusion coefficient that best fits the data. The model then predicts geosmin or MIB liquid-phase concentration as a function of contact time for any given PAC dose by the following two equations:

$$\frac{dC}{dt} = -\frac{3C_c}{R^3} - \int_0^R qr^2 dr \quad (5)$$

$$\frac{q}{t} = D_s \left(\frac{q^2}{r^2} + \frac{2q}{r^2} \right) \quad (6)$$

with the following boundary conditions applying:

$$\frac{q}{r}(0, t) = 0 \quad (7)$$

$$\frac{q}{r}(R, t) = \frac{R^2 k_f (C - C_s)}{\rho_c} \quad (8)$$

where: C is the liquid concentration of geosmin, C_c is the concentration of activated carbon, R is the radius of the carbon particle, r is the distance from the center of the carbon particle, q is the surface concentration of geosmin, t is time, D_s is the surface diffusion coefficient, k_f is the liquid film diffusion coefficient, and ρ_c is the apparent density of the activated carbon. Freundlich isotherm constants are also necessary, as $q(R, t) = K_f C^n$. Equations 5 and 6 can be solved simultaneously to determine the liquid phase concentration. Huang et al. (1996) found the HSDM to be a good predictor of PAC performance for PAC doses between 5-30 mg/L and times ranging from 0-90 minutes. In a study by Cook et al. (2001), the theoretical results correlated well to experimental data for three out of four raw waters. The model did not fit well with data from a raw water that had high turbidity (>26 NTU).

A disadvantage to these models is that the various approaches require equilibrium isotherms and kinetic experiments for calibration and validation. In addition, researchers have demonstrated that the models are not an accurate predictor of PAC performance for all raw waters.

2.5.2. Potential Improvements for PAC Performance

Several researchers have investigated possible improvements for the application of PAC. Kim and Bae (2006) studied the effect of baffles on PAC performance in a baffled-channel PAC contactor. The authors demonstrated that baffles could slightly improve removal efficiencies. With an increased number of baffles and a decreased bend width, removal efficiencies increased by 0-15%. This difference is fairly minor, however, and would not warrant the implementation of a baffled-channel PAC contactor.

Matsui et al. (2009) studied the use of “Super-PAC” (PAC of sub-micron sizes) and reported that while Super-PAC does not increase adsorption capacity, adsorption kinetics are markedly improved. Through kinetic experiments, the authors observed that after 30 minutes, 90% removal is achieved by S-PAC, while only 30% removal was achieved by traditional PAC. One potential problem, however, is difficulty in removing the super-PAC from the water.

2.5.3. Effect of natural organic matter (NOM) on PAC Performance

The presence of NOM can inhibit the sorption of geosmin and MIB via PAC. Researchers have reported that the sorption of MIB is more sensitive to NOM character and concentration than the sorption of geosmin (Newcombe et al. 1997, Cooke et al. 2000, Sugiura et al. 1997, Newcombe et al. 2002). One potential reason is that NOM directly competes for sorption sites with MIB, but not with geosmin (Zoschke et al. 2011). Zoschke et al. (2011) speculates that this is due to the size of the molecules. MIB, which is larger than geosmin and more closely resembles NOM molecules in structure, may therefore compete directly for the same sorption sites. Newcombe et al. (1997) and Newcombe et al. (2002) observed that low molecular weight NOM compounds (<500 g/mol) were the most competitive. Hepplewhite et al. (2004) also reported that low molecular weight compounds were the most competitive, and in addition to direct competition, the authors observed pore restriction caused by larger NOM molecules. In a study by Cooke et al. (2000), sorption was tested in four different natural waters with different NOM composition. Removal efficiencies of geosmin were nearly identical in all four waters, while removal efficiencies of MIB were highly variable. Sugiura et al. (1997) also reported that the type of organic compounds present has a greater impact on adsorption capacity of MIB than geosmin.

Zoschke et al. (2011) observed sorption of geosmin and MIB to PAC in reservoir water and pre-treated water (after flocculation), and reported no significant difference between the two waters. The reservoir water had a dissolved organic carbon (DOC) concentration of 2.7 mg/L, while the DOC level in the pre-treated water was 1.8 mg/L.

This could indicate that the portion of NOM removed from the water during flocculation does not inhibit the adsorption of geosmin or MIB. It could also be that a difference of 0.9 mg/L DOC was too minor of a difference to have a noticeable effect on sorption.

2.5.4. PAC in Conjunction with Lime Softening

The use of PAC in a lime softening plant has not been thoroughly investigated. The application of lime elevates pH above 10 which could have an effect on sorption. Several researchers (including Graham et al. 2000 and Scharf et al. 2010) have investigated the effect of pH on PAC performance for geosmin removal and have reported no significant difference between a pH of 5.6 and 11.5.

Najm et al. (1991) hypothesized that if PAC is added during the lime softening process, the PAC may be coated with precipitate, thus reducing adsorption efficiency. Crozes et al. (1999) investigated PAC performance for taste and odor removal in a lime softening plant. The authors reported that while the kinetics of adsorption were independent of PAC application point, adding PAC to the softened water reduced dosage requirements from 25 mg/L to 10 mg/L. Conversely, in separate jar tests, the authors observed that the optimum alternative for reducing taste and odor intensity was dosing PAC and potassium permanganate simultaneously and allowing for 60 minutes of contact time prior to the softening process. A weakness of this study is that the authors determined taste and odor intensity by the semi-quantitative method of flavor profile analysis (FPA). The authors identified geosmin and other taste and odor-causing compounds by closed loop stripping analysis (CLSA), but conclusions regarding PAC dose point and potassium permanganate were based on FPA of the raw and finished water. Additional research, using precise methods for determining concentrations of taste and odor compounds, is needed to conclusively determine the influence of lime softening on PAC performance.

2.6. Summary and Research Needs

The presence of taste and odor compounds in drinking water is a serious problem that affects approximately 43% of water utilities. Earthy/musty taste and odors are largely responsible for customer complaints, with fishy and swampy odors also playing a role. Traditional treatment processes are largely ineffective at removing the predominant earthy/musty compounds: geosmin and MIB. One solution that has the capacity to remove geosmin and MIB is the application of activated carbon, either in granular or powdered form. PAC is an attractive option because it can be applied as needed to control seasonal taste and odor episodes. Very little work has been done to investigate the performance of PAC in a lime softening plant. Thus, the factors affecting PAC performance in a lime softening plant remain largely unknown.

The main goal of this research was to elucidate the factors affecting PAC performance in a lime softening plant including the effects of lime solids, contact time, and NOM. This information proved useful in specifying the optimum PAC application point and dosage for Minneapolis Water Works.

3. Materials and Methods

The goal of this research was to determine the effect of lime solids, contact time, NOM, and recycled solids on PAC performance. Equilibrium batch experiments and preliminary jar tests were performed to identify the highest performing PACs in Mississippi River water. Jar tests simulating the full-scale plant were conducted to investigate the effects of lime/coagulant addition and contact time on geosmin removal by PAC. Additionally, jar tests were performed to determine the effect of NOM and recycled solids on geosmin removal by PAC. A GC-MS and organic carbon analyzer were used to analyze water samples for geosmin and DOC, respectively.

3.1. Materials

All chemicals used were reagent grade unless noted otherwise. A geosmin solution in methanol (>98% purity, Wako Chemical: #072-03421) was used for making analytical standards and in equilibrium batch and jar test experiments. Neat geosmin (>95% purity, Dalton Chemical Laboratories: DC-001056) was obtained for experiments with NOM so that no DOC was added when geosmin was spiked in to the water. Naphthalene-d8 (Supelco #442716) was used as an internal standard in geosmin analysis. Equilibrium batch and jar test experiments were conducted with Mississippi River water collected at the full-scale plant. Ultrapure water (Milli-Q system, Millipore, Inc.) was used in NOM experiments. Samples of PAC were obtained from carbon distributors. The six PACs chosen were recommended by the manufacturers for removal of taste and odor compounds. PAC types and specifications are shown in Table 6.

Table 6: Characteristics of the six PAC types used in equilibrium batch experiments

Manufacturer	Carbon name	Material	Min. Iodine # (mg/g)	bulk density (g/ml)	% by weight less than:		
					150 μm	75 μm	45 μm
Norit	PAC 20BF	coal	800	0.51	96	88	50 min.
Carbon Resources	325AA-10	coal	1000	.35-.40	99	95	90
Jacobi	Aquasorb CB3	coal	NA	NA	NA	NA	NA
Calgon	WPC	coal	800	NA	99	95	90
Meadwestvaco	Aqua Nuchar	wood	900	.21-.37	99	95	90
Meadwestvaco	Nuchar DW	wood	900	.21-.37	95	85	65

3.2. Equilibrium Batch Experiments

Batch experiments were conducted to determine the equilibrium sorption capacity of six different PACs. Separate experiments were conducted with each PAC type. First, one batch of eight liters of Mississippi River water was spiked with geosmin to a concentration of approximately 100 ng/L. (Except when noted otherwise, geosmin was always spiked to a concentration of approximately 100 ng/L.) PAC was added to five 1 L amber glass bottles in varying amounts between 5-25 mg. A control bottle with no PAC was also included. After PAC was added to the bottles, the geosmin spiked water was siphoned into the bottles to a headspace free level and the bottles were sealed using polytetrafluoroethylene (PTFE) -lined screw caps. The bottles were placed horizontally on a shaker table and incubated at room temperature ($22.0 \pm 1.0^\circ\text{C}$) for 72 hours. At the end of the incubation period, water samples were withdrawn, filtered through 0.7 μm glass fiber filter (Whatman Gf/F), and analyzed for geosmin.

3.3. Jar Tests

Jar tests were performed to elucidate the factors that affect PAC performance in a lime softening plant. Preliminary jar tests were performed to identify the most effective PAC types for removing geosmin from Mississippi River water. Jar tests that simulated the full-scale lime softening plant were conducted to determine the optimum point for PAC addition. Additionally, Suwannee River and Pony Lake NOM were used to determine the effect of NOM on PAC performance. Finally, laboratory prepared recycled solids and recycled solids collected from the full-scale plant were used in jar tests to determine the impact of recycled solids on geosmin removal by PAC.

3.3.1. Preliminary Jar Tests

The four highest performing PAC types were identified from the equilibrium batch experiments and used in subsequent jar test experiments. Jar tests were conducted using a Phipps and Bird Jar Tester and 2 liter beakers (B-ker, USA Bluebook #33703). Varying amounts of PAC (5-50 mg) were added to five 1.5 mL centrifuge tubes and the PAC was pre-wetted with ultrapure water. As with the equilibrium experiments, one batch of Mississippi River water (14 L) was spiked with geosmin. Two liters of the water were added to each beaker and the beakers were placed in the jar test apparatus. The PAC was then added to each beaker with one beaker receiving no PAC (control). The procedure for mixing speeds was taken from previous experiments conducted by MWW. The three segments were as follows: (1) 80 rpm for 10 minutes, (2) 20 rpm for 50 minutes, and (3) 60 minutes of no mixing. Water samples were collected from each beaker at the end of the experiment, filtered, and then analyzed for geosmin.

3.3.2. Effect of PAC Dose Point and Contact Time

The two highest performing PAC types were identified from the preliminary jar tests and tested further in jar tests designed to mimic the full-scale treatment plant. The primary goal of these experiments was to determine the optimum location for PAC

addition in the treatment plant. There are three available PAC addition locations (Figure 7). These will be referred to as pre-softening (PAC1), mid-softening (PAC2), and post-softening (PAC3). Separate experiments were conducted with Norit PAC 20BF added at each of the three PAC addition points. An additional experiment was conducted in which the mixing speeds and PAC contact time were identical to the pre-softening location, but no lime or alum was added. Pre-softening and mid-softening experiments were also performed with Carbon Resources 325AA.

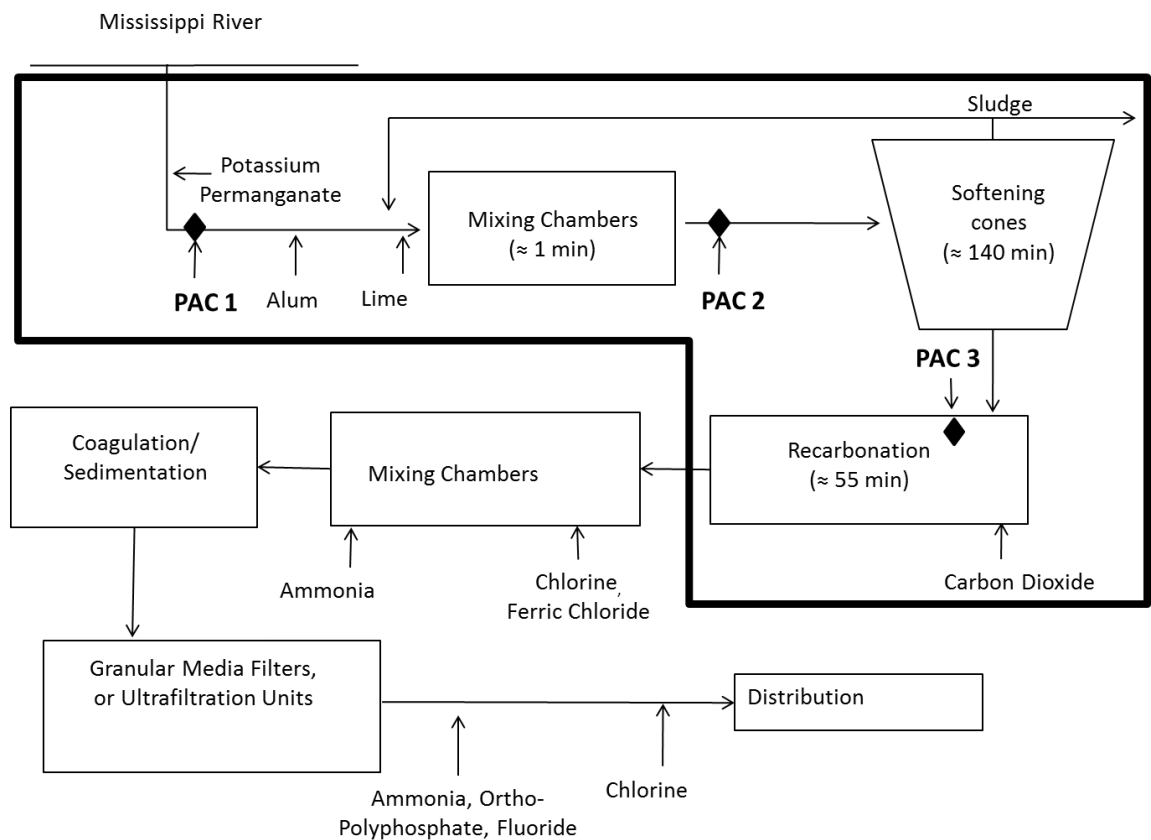


Figure 7: MWW treatment flow diagram with three PAC addition points highlighted (Box encloses the portion of the treatment scheme that is mimicked in the jar testing. The sludge recirculation was not considered in the jar tests described in this section.)

The experimental setup was identical to the jar tests described previously: Mississippi River water was spiked with geosmin and placed in 2 L beakers, and PAC was pre-wetted in centrifuge tubes. The following jar test procedure was used to simulate

the treatment plant (shown also in Table 7): (1) add 8 mg/L aluminum sulfate, or alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) followed by 10 seconds of mixing at 120 rpm, (2) add 190 mg/L calcium hydroxide, or lime ($\text{Ca}(\text{OH})_2$), followed by 1 minute at 65 rpm, (3) 140 minutes at 50 rpm and (4) 55 minutes at 10 rpm. The mixing times and speeds were chosen to mimic conditions at the full-scale plant. Additional details are provided in Appendix A. To simulate the three addition points in the jar tests, PAC was added immediately before alum addition (pre-softening), immediately after the 1 minute of mixing at 65 rpm (mid-softening), or at the very beginning of the 55 minute/10 rpm portion (post-softening).

Table 7: Comparison of jar test parameters with typical full-scale treatment plant conditions

	Jar tests			Full-scale	
	Mixing speed (rpm)	G value (s^{-1})	Time (min)	G value (s^{-1})	Time (min)
Alum injection	Add 8 mg/L $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$			Add 15 mg/L of 48.5% $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ solution	
	120	408	0.17	NA	NA
Mixing chambers	Add 190 mg/L $\text{Ca}(\text{OH})_2$			Add 140-160 mg/l CaO	
	65	163	1	156	1.1
Softening cones	50	110	140	NA	143
Recarbonation tank	10	10	55	NA	53

3.3.3. Effect of NOM

Jar tests were performed to investigate the effect of NOM concentration and type on PAC performance. 2.497 grams/L of disodium phosphate heptahydrate and 0.094 grams/L of monosodium phosphate monohydrate were added to ultrapure water to create a 10 mM phosphate buffer at pH 8. The resulting ionic strength was 2.7×10^{-2} M, which is in the range of natural freshwater systems (Brezonik & Arnold, 2011). Geosmin was spiked into the water and the water was distributed into 1 L beakers. NOM was added to the beakers at concentrations ranging from 1.8 to 16.2 mg DOC/L. A control beaker with no NOM added was also included. The same mass of Norit PAC 20BF was dosed into

each beaker (either 7.5 or 15 mg/L). The water was mixed in a jar test apparatus at 50 rpm for 120 minutes. Samples were collected at 0 and 120 minutes, filtered, and analyzed for geosmin. Four NOM types were obtained from the International Humic Substance Society (IHSS) and tested in jar tests: Suwannee River (SR) NOM, SR fulvic acid, SR humic acid, and Pony Lake fulvic acid (elemental compositions and acidic functional groups shown in Table 8).

The Suwannee River is located in southern Georgia, and NOM extracted from the Suwannee River is often used in research as a reference or standard NOM. Pony Lake is an Antarctic coastal pond that contains phytoplankton but no higher plants in the water (McKnight et al. 1994). Suwannee River NOM contains a mix of autochthonous and allochthonous dissolved organic matter (DOM) while all Pony Lake DOM is autochthonous and is thus less aromatic (McKnight et al. 2001). Fulvic acids are defined as dissolved organic matter that is soluble at all pH levels while humic acids are only soluble above pH 2 (Aiken et al. 1985). In natural water systems, fulvic acids make up a larger portion of humic substances than humic acids (McKnight and Aiken, 1998).

Table 8: Properties of four NOM types obtained from the International Humic Substances Society and used in jar tests

NOM type	Elemental compositions ¹					Acidic functional groups ²	
	C	H	O	N	S	Carboxyl	Phenolic
	%	%	%	%	%	meq/g C ³	2 × meq/g C ⁴
SR NOM	52.5	4.2	42.7	1.1	0.7	9.9	3.9
SR humic acid	52.6	4.3	42.0	1.2	0.5	9.1	3.7
SR fulvic acid	52.4	4.3	42.2	0.7	0.4	11.4	2.9
Pony Lake fulvic acid	52.5	5.4	31.4	6.5	3.0		

¹ IHSS (analysis performed by Huffman Laboratories, Wheat Ridge, CO, USA)

² IHSS (Ritchie and Perdue, 2003)

³ charge density (meq/g C) at pH 8.0

⁴ two times the change in charge density (meq/g C) between pH 8.0 and pH 10.0

3.3.4. Effect of Recycled Solids

At the treatment plant, MWW employs solids recycle to reduce the turbidity of the softened water. The solids (also called sludge) from the softening cones are collected and 50 ± 10% of the solids are re-dosed into the raw water immediately ahead of lime addition. All other solids are sent to the dewatering plant as waste. This solid mixture includes predominantly precipitated calcium carbonate (lime solids) but also PAC. This mixture will be referred to as lime/PAC solids. One goal of this research is to determine the influence of solids recycle on PAC performance. The following experiments were designed to determine the effect of recycled solids on the performance of fresh PAC and to determine the geosmin removal potential of PAC-containing recycled solids.

3.3.4.1. Effect of pre-formed PAC-free lime solids on the performance of fresh PAC

In this first experiment, recycled lime solids (without PAC) were added to geosmin spiked river water along with fresh PAC. This was done to determine the impact of the solids recycle process on the performance of fresh PAC. A jar test was conducted with 2 L of Mississippi River water and appropriate amounts of lime (190 mg/L $\text{Ca}(\text{OH})_2$) and alum (8 mg/L $\text{Al}_2(\text{SO}_4)_3$). The water was not spiked with geosmin and no PAC was added. After 140 minutes of mixing at 50 rpm (simulating the softening cones), 1.75 L of the water was collected. This contains the correct amount of solids for simulating the full-scale solids recycle process in a 2 L jar test (see Appendix B for calculations). The 1.75 L of water was then vacuum filtered through a 0.2 µm nylon filter and the solids were collected with a spatula. Next, the solids were added to a fresh 2 L batch of geosmin spiked Mississippi River water. Immediately after the solids were added, 5 mg/L Norit PAC 20BF was dosed into the water. The water was then mixed at 50 rpm for 120 minutes. Water samples were collected at 0 and 120 minutes and then filtered and analyzed for geosmin. This experiment was repeated two times. Two control experiments were conducted with the same PAC dose, contact time, and mixing speed, but no recycled solids were added.

3.3.4.2. Geosmin removal from softened water containing lime solids and PAC

A preliminary experiment to determine the sorption capacity of recycled solids was conducted by adding 1 L of geosmin spiked river water to 1 L of softened river water, which included a lime/PAC solids mixture. A jar test was first conducted by dosing 1 L of Mississippi River water with appropriate amounts of lime (190 mg $\text{Ca}(\text{OH})_2$), alum (8 mg $\text{Al}_2(\text{SO}_4)_3$), and Norit PAC 20BF (20-40 mg). This 1 L jar test was conducted in a 2 L beaker and the water was not spiked with geosmin. After 140 minutes at 50 rpm, approximately the contact time in the softening cones, the mixing speed was increased to approximately 250 rpm to re-suspend all solids. One liter of geosmin-spiked Mississippi river water (approximately 200 ng/L geosmin) was then added to the 2 L beaker. This water was mixed at 50 rpm for two hours. Geosmin concentrations were measured immediately after the second batch of water was added (time=141 min) and at the end of the experiment (time=260 min). This experiment was repeated five times. This setup does not directly simulate the treatment plant, but the sorption capacity of recycled solids is still determined by exposing the lime/PAC solids mixture to geosmin after the softening portion of the jar test. Two control experiments were also conducted in which the lime solids did not contain PAC. This was done to determine if the lime solids alone have any potential for geosmin removal.

The experiment was then repeated with one difference. In the procedure described above, the first batch of water was not spiked with geosmin. While this allows for the determination of the sorption capacity of the lime/PAC solids mixture, it does not mimic the plant (where PAC would be exposed to geosmin each time it was dosed or re-dosed into the water). For the second version of the experiment, the first batch of river water was spiked with geosmin to a concentration of approximately 100 ng/L. The geosmin concentration of the second batch of water was also 100 ng/L (instead of 200 ng/L). The water was analyzed for geosmin at the beginning of the experiment (time=0 min), immediately before (time=140 min) and after (time=141 min) the second batch of water was added, as well as at the end of the experiment (time=260 min). This experiment was

conducted five times, once each at PAC doses of 10, 15, and 20 mg/L, and twice with no PAC added.

3.3.4.3. Sorption of geosmin to laboratory-prepared lime solids containing PAC

In the next experiment, the PAC/lime solids mixture was collected from one jar test and added into a second batch of water. First, a jar test was conducted using 2 L of Mississippi River water along with 7.5 mg/L Norit PAC 20BF, 190 mg/L calcium hydroxide, and 8 mg/L aluminum sulfate. No geosmin was added. The water was mixed at 50 rpm for 140 minutes in a jar test apparatus to mimic the softening cones. After the 140 minute contact time, all solids were resuspended and two thirds of the water (1333 mL of the 2 L) was collected. Assuming the PAC was evenly distributed in the water, 1333 mL would contain 10 mg PAC (since 2 L contained 15 mg PAC). The collected water was then vacuum filtered through a 0.2 μm nylon filter. The solids were collected from the filter with a spatula and added to a 2 L batch of river water spiked with geosmin. The water and solids were mixed at 50 rpm for 120 minutes. The water was analyzed for geosmin before the solids were added and at the end of the 120 minute contact time. This experiment was repeated two times and two control experiments (with 5 mg/L fresh PAC instead of recycled PAC) were performed.

A second set of similar jar tests was also conducted in which the PAC was pre-exposed to geosmin. In the procedure described above, no geosmin was spiked into the water for the first jar test. In the second set of these jar tests, the procedure was identical except that the first jar test was spiked with 100 ng/L geosmin. This procedure was repeated two times. Again, exposing PAC to geosmin each time it is added to water better represents the treatment plant.

3.3.4.4. Sorption of geosmin to full-scale recycled lime solids containing PAC

Recycled solids were collected from the treatment plant and dosed into Mississippi River water in laboratory jar tests. It was first necessary to determine the proper amount of recycled solids to dose to two liters of river water. Using flow rate

values of 3500 gallon per minute (gpm) for the recycle and waste pumps and 50 MGD for the total water production, the ratio of recycled solids to influent water is 0.10. To mimic this in the lab, 2 L of Mississippi River water was spiked with geosmin and 0.2 L of the recycled solids slurry from the plant was added. The water and solids were then mixed at 50 rpm for 120 minutes. This experiment was repeated three times.

3.3.4.5. Simulation of the full-scale plant

In the final set of experiments, the full scale treatment scheme was mimicked as accurately as possible. A preliminary jar test was conducted to prepare recycled solids. The preliminary test was conducted with geosmin spiked river water and standard chemical doses: 190 mg/L $\text{Ca}(\text{OH})_2$, 8 mg/L $\text{Al}_2(\text{SO}_4)_3$, and 10 mg/L Norit PAC 20BF. After 140 minutes of contact time at 50 rpm, 1.75 L of the water were collected and filtered through a 0.2 μm nylon filter. The solids were collected and used for the primary jar test. For the primary jar test, chemicals were dosed in the following order: 10 mg/L Norit PAC 20BF, 8 mg/L $\text{Al}_2(\text{SO}_4)_3$, recycled solids from the preliminary jar test, and 190 mg/L $\text{Ca}(\text{OH})_2$. The mixing speeds and timing pattern were the same as discussed in section 3.3.2, except that the lime solids were added immediately before the fresh lime. Geosmin concentrations were measured at the beginning and end of both the preliminary and the primary jar test.

3.4. Full-scale testing

Full-scale tests were conducted at the treatment plant to help evaluate PAC performance. This work was conducted by MWW personnel and geosmin was analyzed by a commercial lab. PAC addition point and dose were varied and the geosmin concentrations in the raw and finished water were measured. Data was collected on 35 dates between 1/26/2011 and 9/12/2011.

3.5. Kinetics

Eight hour kinetics experiments were conducted using the jar test apparatus. Mississippi River water was spiked with geosmin and placed in 2L beakers. To determine volatilization rates, no PAC was added to the beakers. To determine sorption rates, 7.5 mg/L Norit PAC 20BF was added to the beakers. The water was mixed at 50 rpm for the entire experiment. In the beakers with no PAC, samples were taken for geosmin analysis every 60-120 minutes. In the beakers with PAC, samples were taken every 30 minutes for the first 90 minutes, and every 60-120 minutes for the remainder of the experiment.

3.6. Analytical Methods

3.6.1. Geosmin Analysis

Geosmin was extracted from the water samples by headspace solid phase microextraction (SPME) and analyzed via gas chromatography-mass spectrometry (GC-MS). The method was adapted from Watson et al. (2000). Sample water or ultrapure water (10 mL) was filtered through a 0.7 μm glass fiber filter (Whatman Gf/F) and added to a 20 mL vial along with 3 grams of sodium chloride. Twenty microliters of a naphthalene-d8 stock (250 $\mu\text{g/L}$ in methanol) was added to each sample and standard to achieve a concentration of 50 ng/L.

The headspace SPME process was automated using an HTA 280T autosampler (HTA- Scientific Instruments). The autosampler first placed the sample vial in an oven at 65°C and incubated it for 5 minutes. Then, a polydimethylsiloxane (PDMS) SPME fiber (Sigma Aldrich) was extended into the sample headspace for 60 minutes, during which time analytes volatilized and adsorbed onto the SPME fiber. The sample was agitated during both the five minute incubation period and the 60 minute extraction period. The fiber was then removed from the sample headspace and inserted into the injection port of a Hewlett Packard 5890 Series II GC, where it was held for one minute to allow the analytes to desorb from the fiber and flow into the GC column. The injection port was maintained at 250°C. The temperature program for the GC column was as follows: 40°C for 5 minutes, followed by an increase of 11°C/minute for approximately 18 minutes and

a hold at 240°C for 2 minutes. A Hewlett Packard 5972 mass spectrometer was used for detection in select ion monitoring (SIM) mode. Two ions were monitored: 112 m/z for geosmin and 136 m/z for naphthalene-d8. After each run, the SPME fiber was cleaned by placing in a separate cleaning port held at 250°C for two minutes.

The method detection limit (MDL) for geosmin was determined according to *Standard Methods* (1980). One batch of water was prepared at a geosmin concentration such that the geosmin peak was approximately three times the baseline level. Seven samples of this water were then analyzed by headspace SPME. The MDL, 1.1 ng/L, was determined by multiplying the standard deviation of the seven samples by a factor of 3.17.

Relative standard deviation (RSD) was determined by spiking one liter of DI water with geosmin to a concentration of approximately 100 ng/L and then analyzing eight samples of this water. The mean concentration was 102.9 ng/L and the standard deviation was 3.9 ng/L, giving a RSD of 3.7%.

3.6.2. DOC Analysis

DOC was analyzed by a Sievers 900 Portable TOC analyzer. Samples were first acidified with sulfuric acid to $\text{pH} \leq 3$ and purged with nitrogen gas to remove inorganic carbon prior to analysis. Vials were prepared by combusting at 550°C for four hours and septa were soaked in a 10% sodium persulfate solution at 60°C for one hour (according to Kaplan et al. 1994).

4. Results and Discussion

4.1. Equilibrium batch experiments

Of the six carbons tested, Norit PAC 20BF, Carbon Resources (CR) 325AA, Calgon WPC, and Jacobi Aquasorb CB3 all removed similar amounts of geosmin while Aqua Nuchar and Nuchar DW removed less geosmin (Figure 8 and Figure 9). Conditions for the experiments as well as Freundlich isotherm constants are shown in Table 9. The $C_{f,control}$ value reported in Table 9 is the final concentration (at time=72 hours) of the control bottle (no PAC added). Removal efficiencies and solid phase concentration values were calculated from this value (final concentration of the control bottle) and not initial concentration. Thus, removal efficiencies and isotherm data are based only on removal via PAC and not via other loss mechanisms such as volatilization. Aqua Nuchar and Nuchar DW, the only wood-based PACs tested, were eliminated from the next round of experiments because they removed less geosmin than the other four types, which are coal-based.

Table 9: Experimental conditions and Freundlich isotherm parameters for equilibrium batch experiments conducted in Mississippi River water

PAC	$C_{f,control}$	Freundlich Isotherm values			T	pH	DOC
	ng/L	k	1/n	R_2	°C		mg/L
Norit PAC 20BF	83.9	1.22	0.63	0.93	22.0	7.54	11.69
Carbon Resources 325AA	64.1	2.51	0.29	0.91	23.0	7.66	11.69
Jacobi Aquasorb CB3	102.1	1.58	0.45	0.96	21.5	7.94	11.69
Calgon WPC	96.1	1.12	0.56	0.89	21.5	7.71	11.69
Aqua Nuchar	86.6	0.60	0.64	0.84	21.8	8.05	11.69
Nuchar DW	90.0	0.23	0.85	0.75	22.0	8.10	11.69

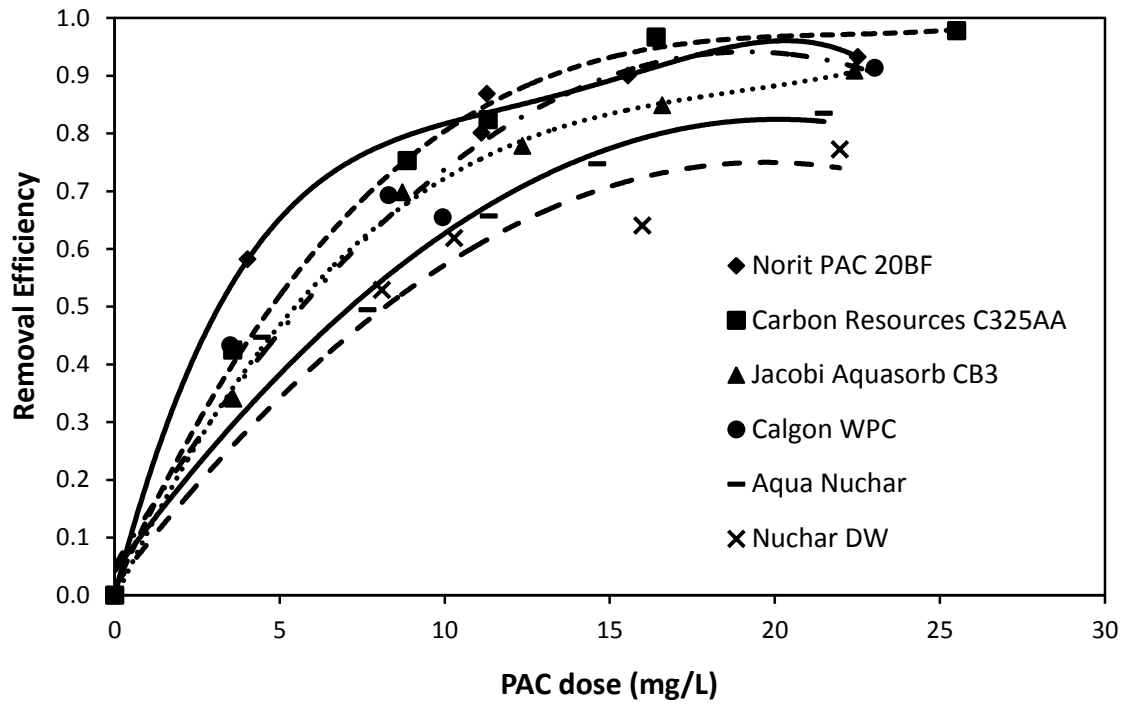


Figure 8: Effect of PAC type on equilibrium geosmin removal efficiency (trendline styles: Norit PAC 20BF: solid, Carbon Resources 325AA: dashed, Jacobi Aquasorb CB3: dotted, Calgon WPC: dashed-dotted, Aqua Nuchar: solid, Nuchar DW: dashed)

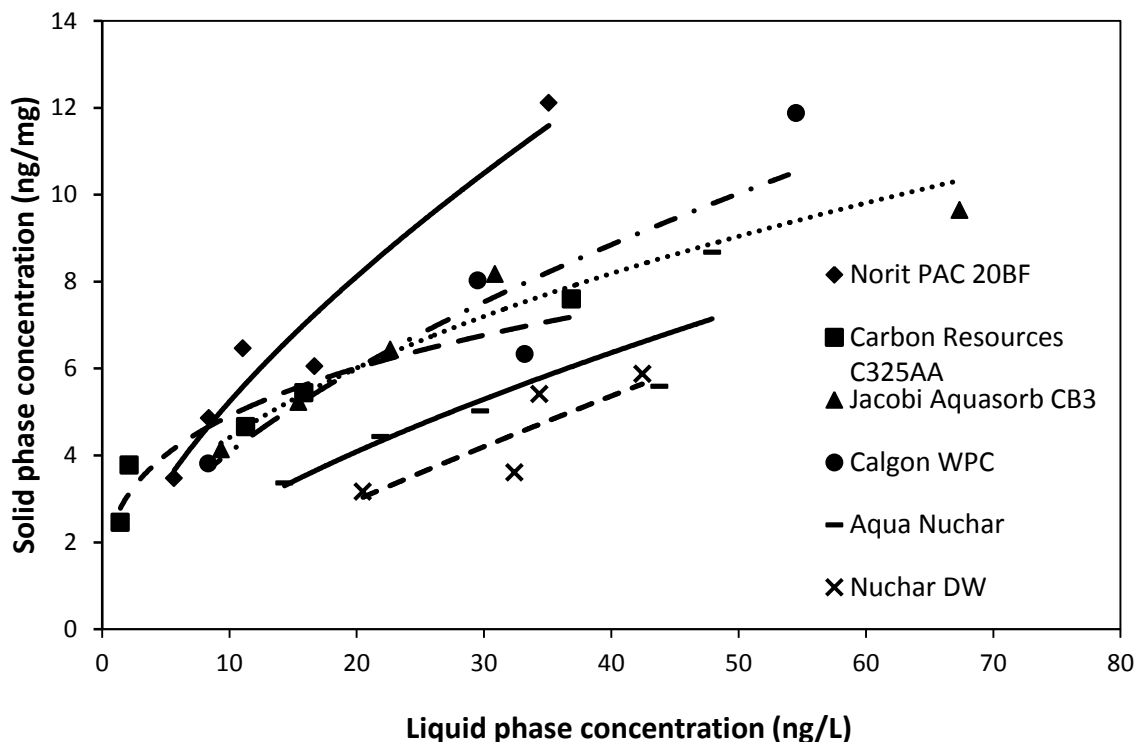


Figure 9: Freundlich isotherm plots for the geosmin sorption results shown in Figure 8 (trendline styles: Norit PAC 20BF: solid, Carbon Resources 325AA: dashed, Jacobi Aquasorb CB3: dotted, Calgon WPC: dashed-dotted, Aqua Nuchar: solid, Nuchar DW: dashed)

Discussion

The results reported in Table 9 and Figure 8 are in general agreement with other equilibrium data from the literature. At a PAC dose of 10 mg/L, geosmin removal efficiencies were between 50 and 80% for the six PAC types. Lalezary-Craig et al. (1988) reported geosmin removal efficiencies in the range of 65 to 90% at a PAC dose of 10 mg/L. In four natural waters, Graham et al. (2000) observed removal efficiencies between 60 and 85% at a PAC dose of 10 mg/L. Cook et al. (2001) observed higher geosmin removal efficiencies at the same PAC dose: between 90 and 95%. The DOC levels of all of the natural waters used in the Cook et al. and Graham et al. studies were lower than the DOC levels of the water used in the experiments shown in Figure 8. The higher geosmin

removal efficiencies observed by Cook et al. and Graham et al. can be attributed to lower DOC levels, as many authors (Hertzing et al. 1977, Graham et al. 2000) have demonstrated that the presence of NOM reduces the sorption of geosmin.

In the results shown in Table 9 and Figure 8, four coal-based PACs removed more geosmin than two wood-based PAC types. This indicates that coal-based PACs are more effective at removing geosmin from Mississippi River water than wood-based PACs. It appears that the optimum PAC type is different for different natural waters, irrespective of PAC source material. Sugiura et al. (1997) reported that a wood based PAC removed more geosmin than either a coal-based or coconut shell-based PAC. Gillogly et al. (1999) tested ten activated carbons made from five source materials (coal, wood, coconut shell, peat, and lignite) and observed that there was no relationship between PAC source material and MIB removal efficiency. Newcombe et al. (2002) reported that a wood, coal, and coconut shell-based PAC all removed similar amounts of MIB, while other wood and coconut shell based PACs were inferior for MIB removal (compared to the three top performing PACs). Furthermore, there are no specific water characteristics that indicate which PAC source material will be most effective at removing geosmin from a given water.

4.2. Jar Tests

4.2.1. Preliminary Jar Tests

In two-hour jar tests, Norit PAC 20BF and CR 325AA removed more geosmin than Calgon WPC and Jacobi Aquasorb CB3 (Figure 10-11). Furthermore, the geosmin removals by Norit PAC 20BF and Carbon Resources 325AA were similar. Again, removal efficiencies and solid phase concentrations were based on the final concentration of the control bottle ($C_{f,control}$) so that the only loss mechanism considered was sorption via PAC. The removal efficiencies (Figure 10) are not dependent on initial concentration (or, in this case, $C_{f,control}$), but because the experiment was not run to equilibrium, the isotherm plots are dependent on initial concentration (see Appendix F). Because Norit PAC 20BF and CR 325AA removed more geosmin than Jacobi Aquasorb CB3 and

Calgon WPC, only the Norit and Carbon Resources PACs were used in subsequent experiments.

Table 10: Experimental conditions for two-hour jar tests in Mississippi River water

Experiment	$C_{f,control}$	T	pH	DOC
	ng/L	°C		mg/L
Norit PAC 20BF #1	119.9	22.4	7.83	11.69
Norit PAC 20BF #2	102.1	20.5	7.66	13.65
Carbon Resources 325AA #1	100.5	20.8	7.70	13.65
Carbon Resources 325AA #2	112.1	21.5	7.63	13.65
Jacobi Aquasorb CB3	98.4	19.5	7.77	13.65
Calgon WPC	89.4	20.0	7.91	11.51

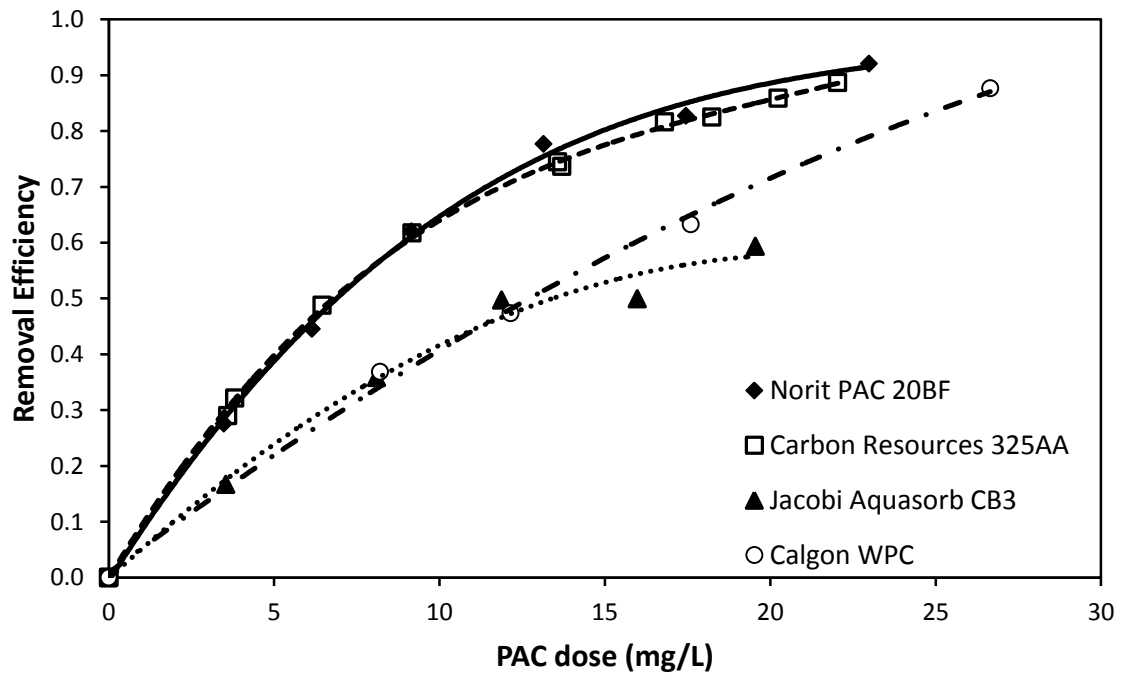


Figure 10: Effect of PAC type on geosmin removal efficiency in two-hour jar tests
 Data sets from the same carbon (e.g. Norit PAC 20BF #1 and #2 from Table 10) are combined in removal efficiency graphs
 (trendline styles: Norit PAC 20BF: solid, CR 325AA: dashed, Jacobi Aquasorb CB3: dotted, Calgon WPC: dashed-dotted)

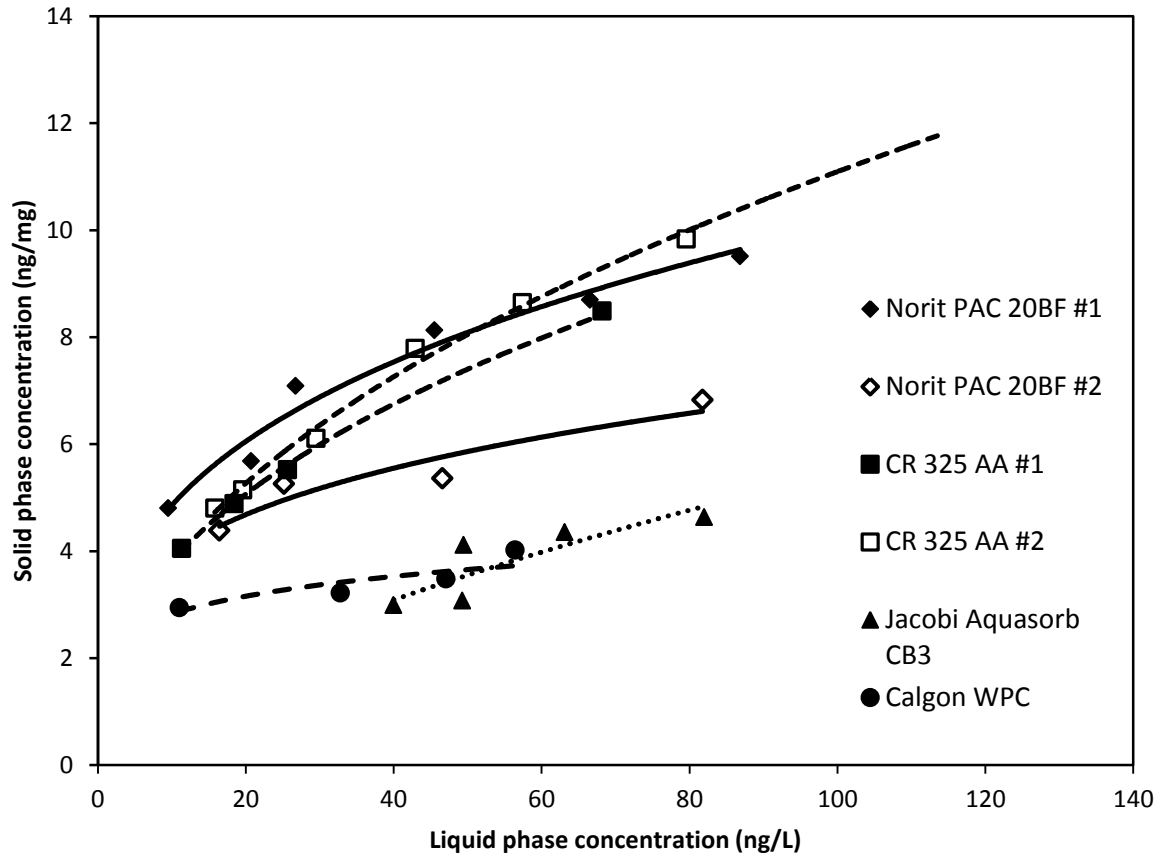


Figure 11: Isotherm plots for the geosmin sorption results shown in Figure 10 (Lines are included for visual purposes only. Line styles: Norit PAC 20BF #1 and #2: solid, CR 325AA #1 and #2: dashed, Jacobi Aquasorb CB3: dotted, Calgon WPC: dashed-dotted)

Discussion

In kinetics experiments in four natural waters, Cook et al. (2001) observed removal efficiencies of 75-85% at a PAC dose of 20 mg/L and a contact time of 120 minutes. Results shown in Figure 10 indicate that after 120 minutes, 58% and 72% of geosmin is removed by Jacobi Aquasorb and Calgon WPC, respectively, while 86 to 90% of geosmin is removed by Norit PAC 20BF and CR 325AA.

There are no known characteristics that would indicate that Norit and Carbon Resources would be more effective at removing geosmin than Jacobi or Calgon. The only

notable difference between the PACs is that Norit PAC20BF has a smaller percentage of particles pass through 44 μm and 75 μm sieves (Table 6). The larger particle size of Norit PAC 20BF with respect to the CR 325AA and Calgon WPC would suggest that the Norit PAC would be less effective at removing geosmin than the other two PAC types. Najm et al. (1991) and Matsui et al. (2004) report that the kinetics of adsorption will be faster to smaller PAC particles because in smaller particles, there is a shorter distance for the adsorbing molecule to travel from pore to sorption site. This effect, however, does not hinder the geosmin removal potential of Norit PAC 20BF in comparison to the other PAC types tested.

4.2.2. Effect of PAC dose point and contact time

In jar tests with lime and alum, three PAC addition points were simulated using two PAC types. The results for the three PAC addition points, referred to as pre-, mid-, and post-softening, as well as a control experiment are shown in Figure 12, Figure 13, and Table 11. PAC in the pre-softening and mid-softening experiments removed similar amounts of geosmin. This is expected as the only difference between the two experiments is approximately one minute in PAC contact time. More importantly, PAC in the pre- and mid-softening experiments removed similar amounts of geosmin as PAC in the control experiment. These results suggest that when lime and alum are added simultaneously with PAC, the lime and alum do not inhibit the sorption of geosmin.

Finally, PAC in the post-softening experiment removed less geosmin than PAC in the other three experiments. At a PAC dose of 20 mg/L, approximately 90% removal was observed for the control, pre-softening, and mid-softening experiments. With the post-softening experiment, the removal efficiency at a PAC dose of 20 mg/L was approximately 65%. In these experiments, contact time was the only parameter that was important in regards to geosmin sorption.

It should be noted that different water batches were used for these experiments. The DOC for the pre- and mid-softening experiments was 11.51 mg/L (water collected on

7/18/2011) while the DOC for the post-softening and control experiments was 9.05 mg/L (water collected on 9/15/2011). A difference of 2.46 mg/L DOC would result in a decrease in removal efficiency of approximately 6.6% at a PAC dose of 7.5 mg/L based on results from section 4.2.3. Applying that difference to Figure 12, the trendlines for the control, pre-, and mid-softening experiments are still similar.

Table 11: Experimental conditions for jar tests with Norit PAC 20BF simulating the three PAC addition points

Experiment	contact time	$C_{f,control}$	T	pH	DOC
	min	ng/L	°C		mg/L
Pre-softening #1	195	80.7	18.5	7.70	11.51
Pre-softening #2	195	93.7	19.5	7.90	11.51
Mid-softening	195	98.6	18.5	8.16	9.05
Post-softening	55	90.0	18.5	7.92	11.51
Control	195	97.1	19.0	8.14	9.05

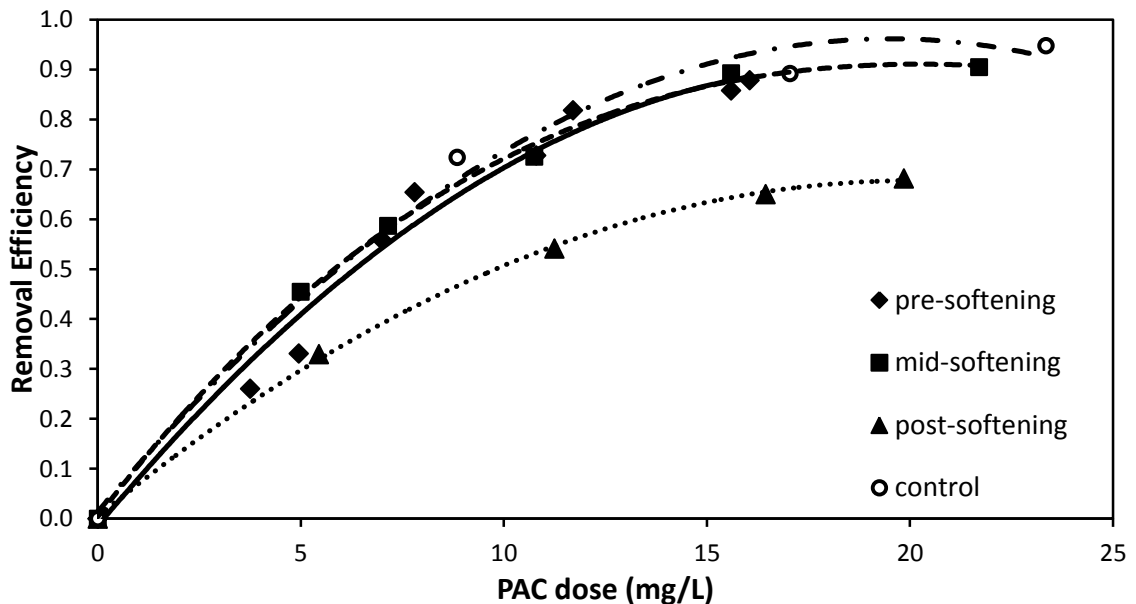


Figure 12: Effect of PAC addition point on geosmin removal efficiency in jar tests with Norit PAC 20BF

(trendline styles: pre-softening: solid, mid-softening: dashed, post-softening: dotted, control: dashed-dotted)

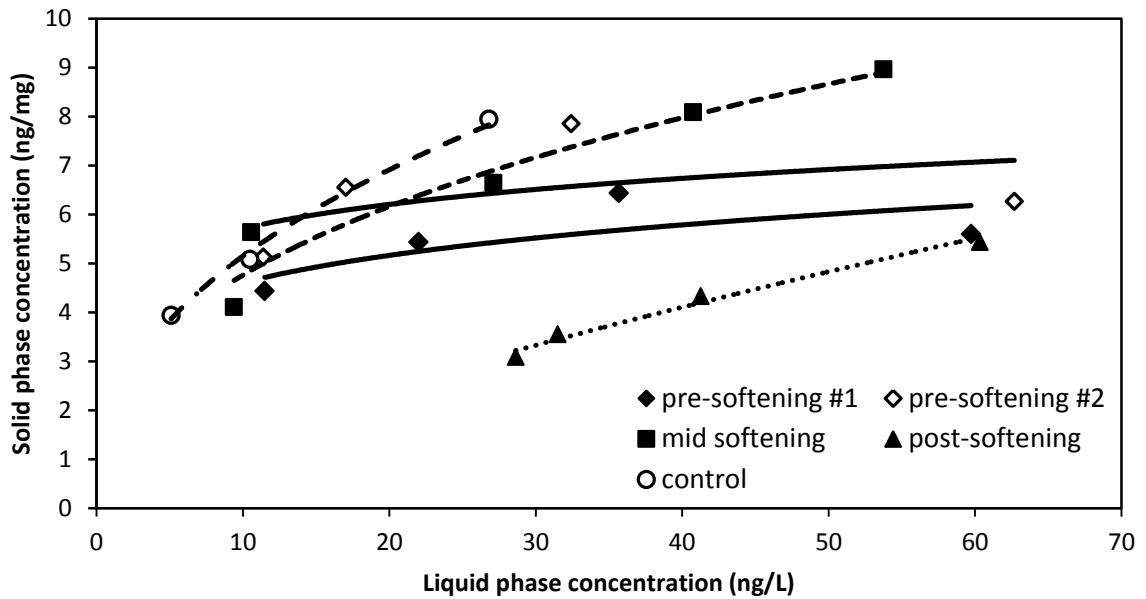


Figure 13: Isotherm plots for the geosmin sorption results shown in Figure 12 (Lines are included for visual purposes only. Line styles: pre-softening #1: solid, pre-softening #2: solid, mid-softening: dashed, post-softening: dotted, control: dashed-dotted)

Jar test experiments evaluating the different PAC addition points were also conducted with Carbon Resources 325AA. There were minor differences in performance between Norit and Carbon Resources, some of which is attributable to DOC difference. In both the pre-softening and mid-softening experiments (shown in Table 12-13 and Figure 14-Figure 17), Carbon Resources 325AA removed 5 to 20% more geosmin than Norit PAC 20BF. The water used in the Norit pre-softening experiments, however, contained 2.46 mg/L more DOC than the water used in the Carbon Resources experiments. The higher DOC concentration would result in a 6.6% decrease in geosmin removal efficiency at a PAC dose of 7.5 mg/L and a 3.0% decrease in removal efficiency at a PAC dose of 15 mg/L (section 4.2.3). It is possible that Carbon Resources removes slightly more geosmin than Norit PAC 20BF in the presence of lime and alum. It is also possible that the difference between the two carbons is due to DOC differences and experimental error.

Table 12: Experimental conditions for jar tests using the pre-softening PAC addition point with Norit PAC 20BF and CR 325AA

Experiment	$C_{f,control}$	T	pH	DOC
	ng/L	°C		mg/L
CR pre- #1	84.2	18.5	8.27	9.0
CR pre- #2	90.9	19.0	8.30	9.0
Norit pre- #1	80.7	18.5	7.70	11.5
Norit pre- #2	93.7	19.5	7.90	11.5

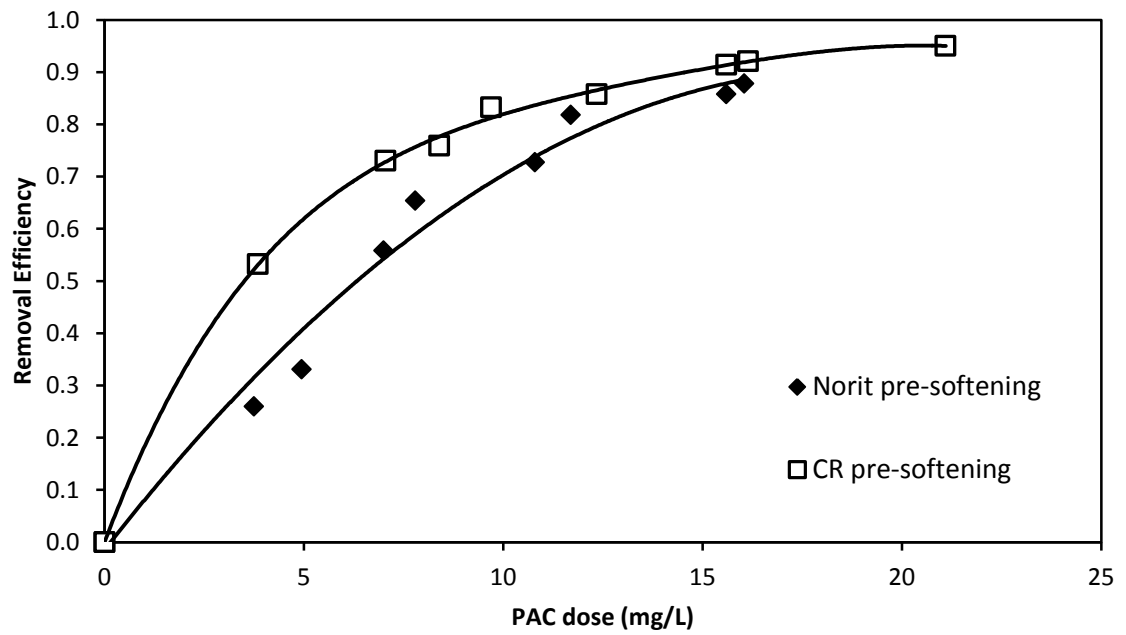


Figure 14: Comparison of the geosmin removal performance of Carbon Resources 325AA and Norit PAC 20BF for the pre-softening PAC addition point

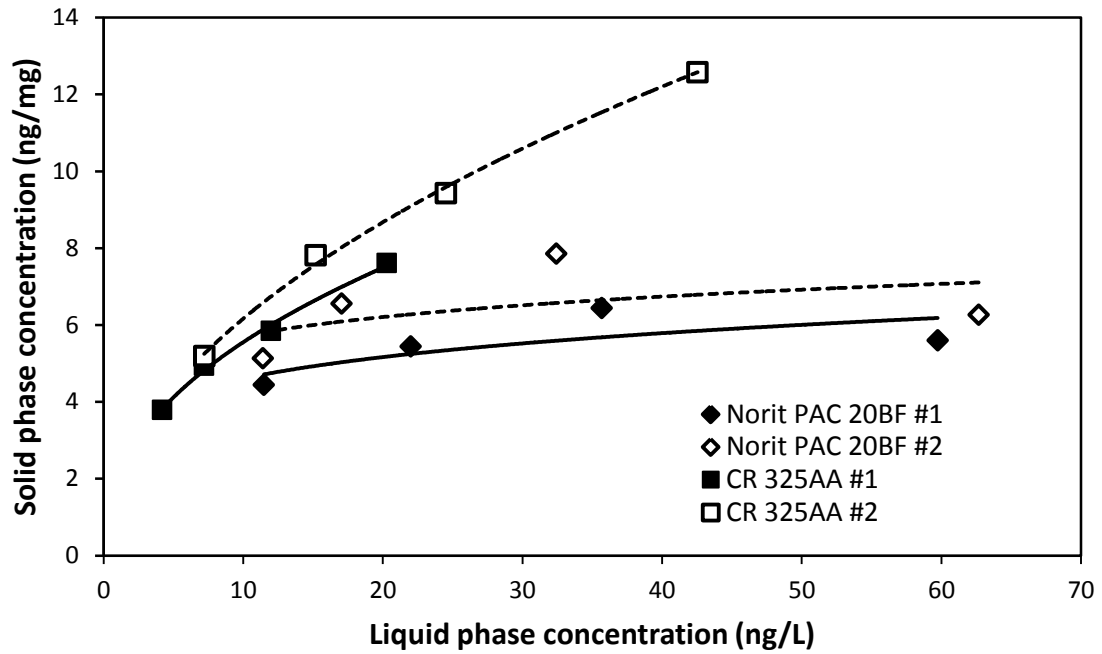


Figure 15: Isotherm plots for Carbon Resources 325AA and Norit PAC 20BF pre-softening experiments
(Lines included for visual purposes only.)

Table 13: Experimental conditions for jar tests using the mid-softening PAC addition point with Norit PAC 20BF and CR 325AA

Experiment	$C_{f,control}$	T	pH	DOC
	ng/L	°C		mg/L
CR mid-softening	81.4	19.5	8.19	9.0
Norit mid-softening	98.6	18.5	8.24	9.0

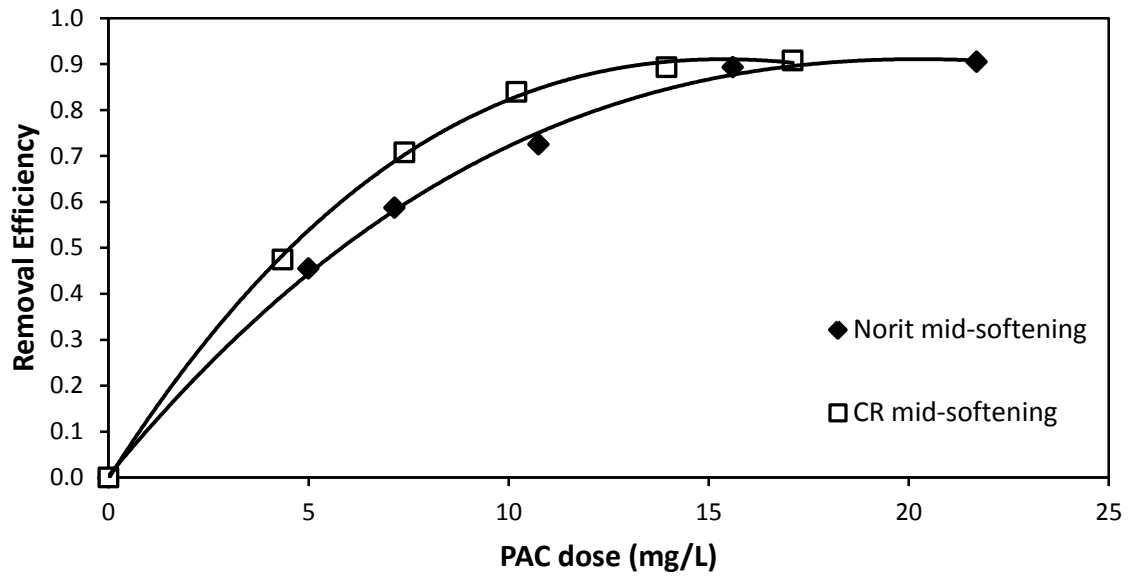


Figure 16: Comparison of the geosmin removal performance of Carbon Resources 325AA and Norit PAC 20BF for the mid-softening PAC addition point

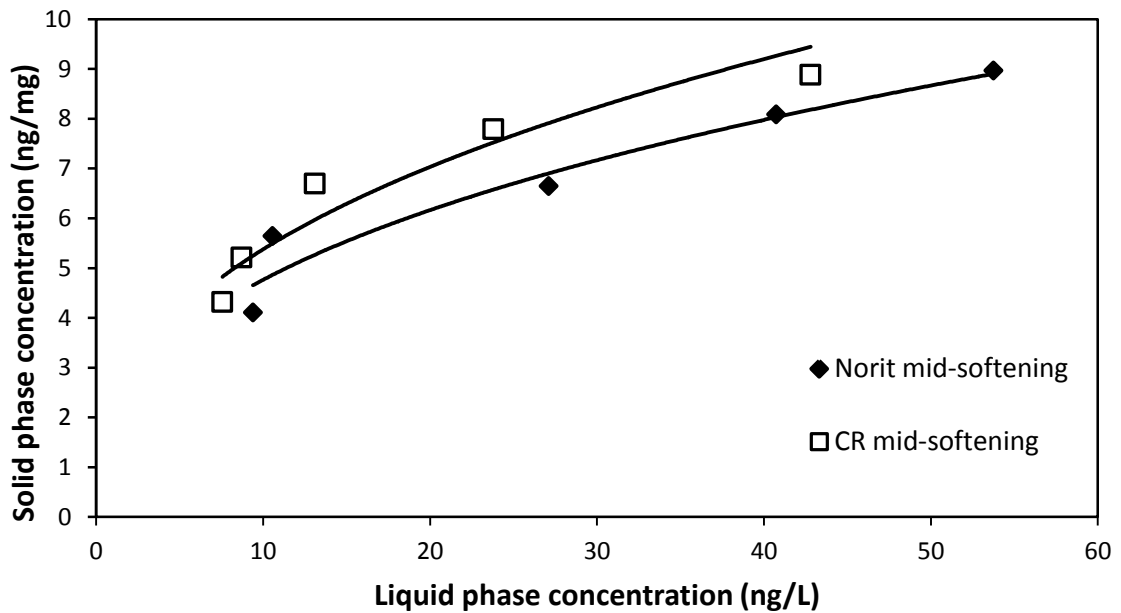


Figure 17: Isotherm plots for Carbon Resources 325AA and Norit PAC 20BF mid-softening experiments (Lines included for visual purposes only.)

Discussion

Removal efficiencies in these jar tests are in general agreement with removal efficiencies observed by Cook et al. (2001). In the article by Cook et al. (2001), 80 to 90% of geosmin was removed by 20 mg/L PAC in 195 minutes. In the pre-softening, mid-softening, and control experiments, all of which had a contact time of 195 minutes, the removal efficiencies were between 85 and 95% at a PAC dose of 20 mg/L. At the same PAC dose, but in only 55 minutes of contact time, Cook et al. (2001) observed removal efficiencies between 60 and 75%. In the post-softening experiment (contact time of 55 minutes), the removal efficiency was 68% at a PAC dose of 20 mg/L.

In the experiments simulating the full-scale plant, the presence of lime and alum did not affect the removal of geosmin by PAC (Figure 12). While Najm et al. (1999) hypothesized that adding PAC simultaneously with lime could cause the PAC particles to become coated with precipitate, there appears to be no adverse effect on geosmin removal. Additionally, the coagulant (alum) does not appear to affect geosmin removal either, although this was expected as Bruce et al. (2002) reported that 20 mg/L alum (higher than the dose used in these jar tests) had no effect on geosmin concentration.

4.2.3. Effect of natural organic matter (NOM)

The effect of Suwannee River (SR) NOM on sorption of geosmin at a PAC of 15 mg/L is shown in Figure 18. The data are plotted as the fraction of geosmin remaining after two hours as a function of DOC concentration. The slope of the regression line is 0.012, meaning that for every 1 mg/L increase in DOC, the geosmin removal efficiency will decrease by 1.2% at a PAC dose of 15 mg/L (95% confidence interval (CI) of the slope: 0.010, 0.014). The y-intercept of -0.023 (95% CI: -0.042, -0.0050) suggests that more than 100% of the geosmin would be removed when no NOM is added. The fraction remaining for a control beaker (no NOM added) was 0.018. Thus, it appears that competitive inhibition of geosmin sorption by NOM is negligible at low DOC concentrations (<3 mg/L) and relatively high PAC doses (15 mg/L).

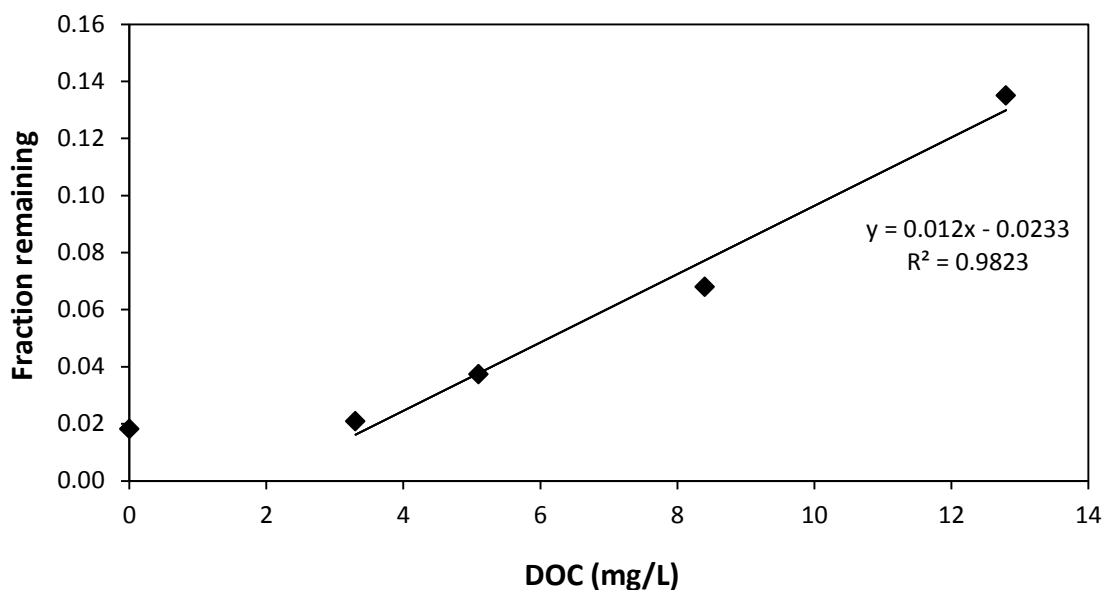


Figure 18: Effect of Suwannee River NOM concentration on removal of geosmin from ultrapure water via sorption to Norit PAC 20BF at a PAC dose of 15 mg/L
 $C_o=92.9$ ng/L, $T=21.0^\circ\text{C}$, $\text{pH}=8.0$

The results from four experiments conducted with Suwannee River NOM at a PAC dose of 7.5 mg/L are shown in Figure 19. The slope of the regression line is 0.027 with a 95% CI of 0.020, 0.034. This slope suggests that for a 1 mg/L increase in DOC, the geosmin removal efficiency will decrease by 2.7% at a PAC dose of 7.5 mg/L. The y-intercept of 0.032 (95% CI: -0.02, 0.08) indicates the fraction remaining for a beaker with no NOM added. The mean fraction remaining for nine control experiments (i.e. no NOM) was 0.069 ± 0.017 . Data points from the control beakers were not included in the regression. Two other experiments were conducted with SR NOM though the results were significantly different than the four shown below. The results for these two experiments are given in Appendix C, and the results are not included in the regression in Figure 19.

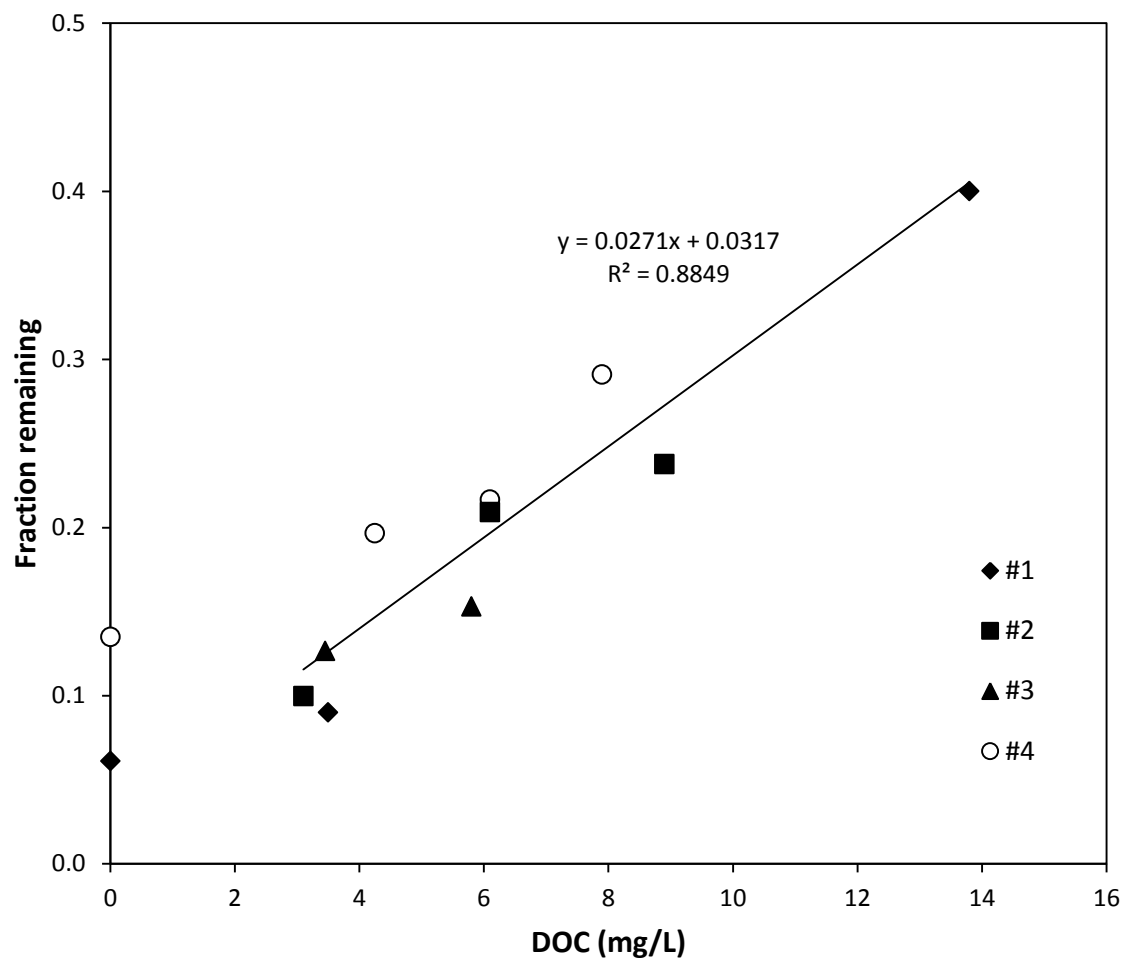


Figure 19: Effect of Suwannee River NOM concentration on removal of geosmin from ultrapure water via sorption to Norit PAC 20BF at a PAC dose of 7.5 mg/L (linear regression performed on all four data sets)

Experiment #1: $C_0=101.4$ ng/L, $T=20.0^\circ\text{C}$, $\text{pH}=8.0$

Experiment #2: $C_0=120.9$ ng/L, $T=22.5^\circ\text{C}$, $\text{pH}=8.0$

Experiment #3: $C_0=90.9$ ng/L, $T=21.5^\circ\text{C}$, $\text{pH}=8.0$

Experiment #4: $C_0=81.7$ ng/L, $T=22.0^\circ\text{C}$, $\text{pH}=8.0$

Separate experiments were conducted with Suwannee River humic acid, Suwannee River fulvic acid, and Pony Lake fulvic acid (Figure 20-Figure 22 and Table 14). In Table 14, a higher slope indicates a stronger inhibitive effect. Whole Suwannee River NOM inhibits sorption more than SR fulvic and Pony Lake fulvic acids, which in

turn inhibit sorption more than SR humic acid. A two tailed t-test was performed to determine if the slopes for SR fulvic acid and Pony Lake fulvic acid are statistically similar. The null hypothesis (H_0) was that $\text{slope}_{\text{SR fulvic acid}} = \text{slope}_{\text{Pony Lake fulvic acid}}$, and the resulting p-value was 0.21. Because the p-value was greater than the significance level of 0.05, the null hypothesis cannot be rejected, indicating that the two slopes are similar. There is, however, a significant difference between SR fulvic acid and SR humic acid (two tailed t-test, H_0 : $\text{slope}_{\text{SR fulvic}} = \text{slope}_{\text{SR humic}}$, p value=0.004). Because the slope of the line is higher for the fulvic acids, the results suggest that fulvic acids inhibit sorption of geosmin more than humic acid. There is also a significant difference between the SR fulvic/humic acids and whole SR NOM (two tailed t-test, H_0 : $\text{slope}_{\text{SR fulvic}} = \text{slope}_{\text{whole SR NOM}}$, p value=0.0008 and H_0 : $\text{slope}_{\text{SR humic}} = \text{slope}_{\text{whole SR NOM}}$, p value= 8.6×10^{-6}). Again, because the slope of the line is higher for the whole SR NOM, the results suggest that whole SR NOM reduces geosmin sorption to PAC more than either the SR fulvic or SR humic acids.

Table 14: Effect of NOM type on geosmin removal via sorption to PAC

NOM type	Slope¹	95% confidence interval
SR whole	0.027	(0.020, 0.034)
SR humic	0.008	(0.003, 0.012)
SR fulvic	0.015	(0.009, 0.021)
Pony Lake fulvic	0.013	(0.011, 0.015)

¹a slope of 0.027 indicates that upon an increase of 1 mg/L DOC, geosmin removal will decrease by 2.7%

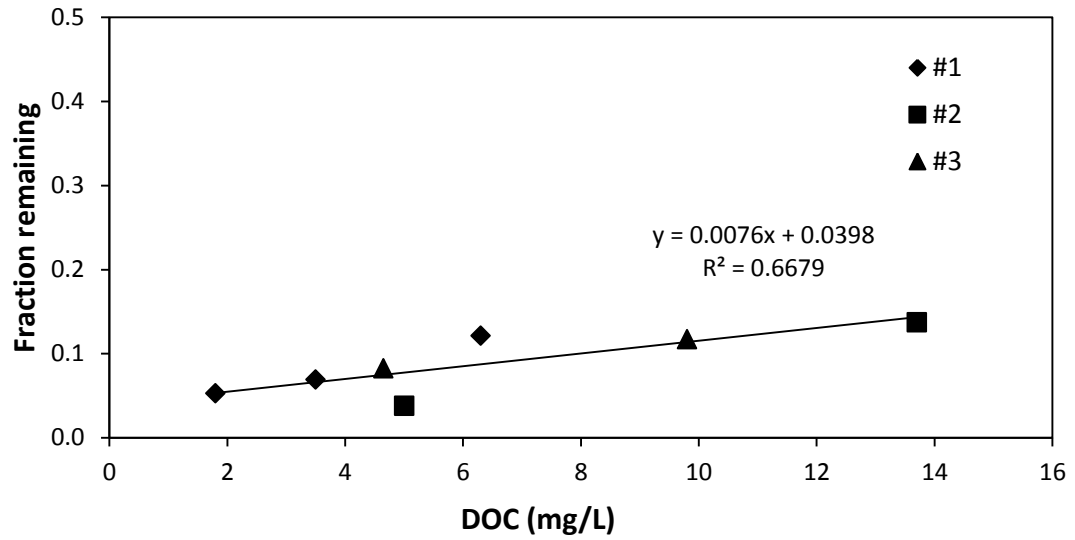


Figure 20: Effect of Suwannee River humic acid on removal of geosmin from ultrapure water via sorption to Norit PAC 20BF at a PAC dose of 7.5 mg/L

Experiment #1: $C_0=134.2$ ng/L, $T=21.0^\circ\text{C}$, $\text{pH}=8.0$

Experiment #2: $C_0=89.5$ ng/L, $T=21.0^\circ\text{C}$, $\text{pH}=8.0$

Experiment #3: $C_0=100.5$ ng/L, $T=22.0^\circ\text{C}$, $\text{pH}=8.0$

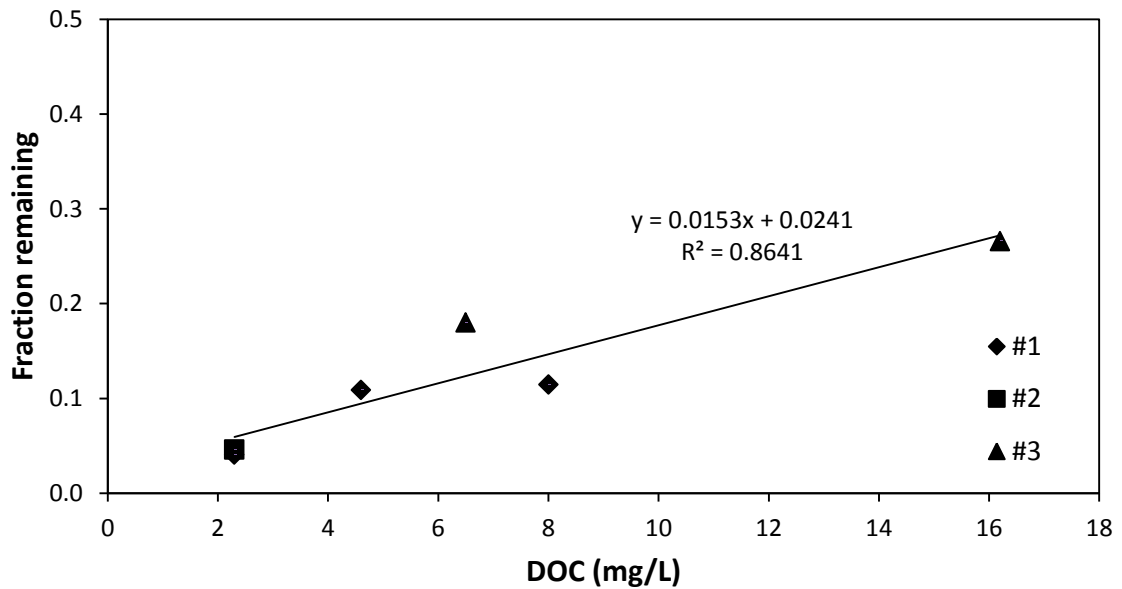


Figure 21: Effect of Suwannee River fulvic acid on removal of geosmin from ultrapure water via sorption to Norit PAC 20BF at a PAC dose of 7.5 mg/L

Experiment #1: $C_0=146.7$ ng/L, $T=21.5^\circ\text{C}$, $\text{pH}=8.0$

Experiment #2: $C_0=113.5$ ng/L, $T=21.5^\circ\text{C}$, $\text{pH}=8.0$

Experiment #3: $C_0=78.7$ ng/L, $T=21.0^\circ\text{C}$, $\text{pH}=8.0$

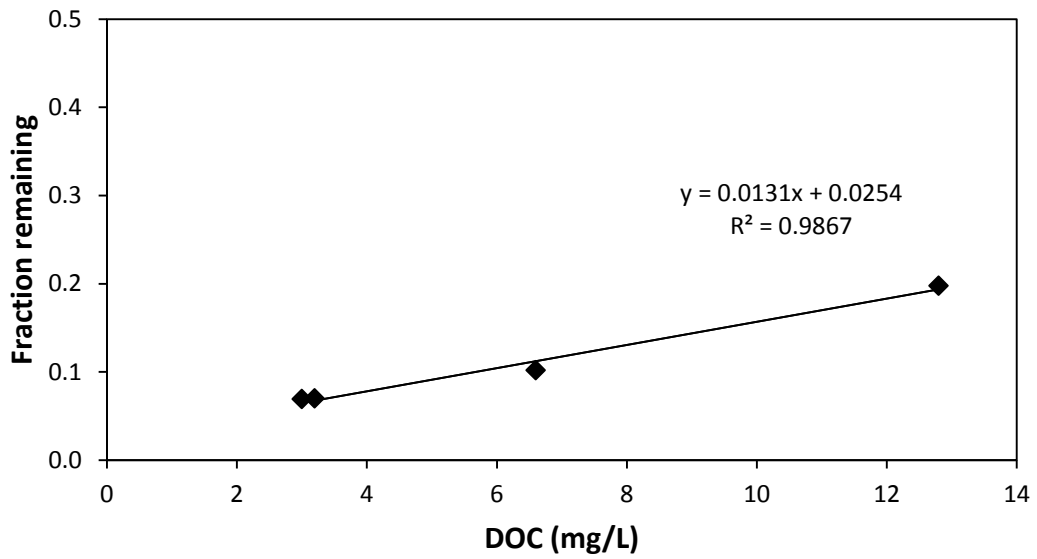


Figure 22: Effect of Pony Lake fulvic acid on removal of geosmin from ultrapure water via sorption to Norit PAC 20BF at a PAC dose of 7.5 mg/L
 $C_o=120.7$ ng/L, $T=21.5^\circ\text{C}$, $\text{pH}=8.0$

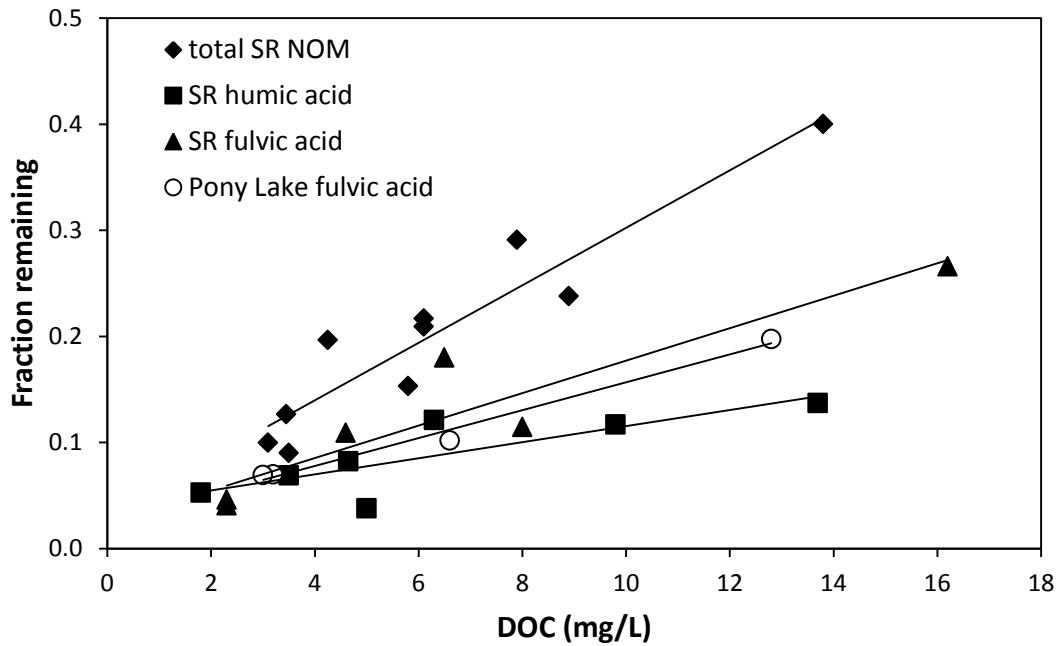


Figure 23: Effect of four NOM types on removal of geosmin from ultrapure water via sorption to Norit PAC 20BF at a PAC dose of 7.5 mg/L

Discussion

Many researchers have reported that the presence of NOM inhibits the sorption of geosmin and MIB to PAC, although most authors report that MIB sorption is more sensitive than geosmin sorption to changes in NOM concentration and characteristics. (Newcombe et al. 1997, Sugiura et al. 1997, Graham et al. 1999, Cook et al. 2000, Newcombe et al. 2002). NOM molecules adsorb to PAC and reduce accessible surface area. PAC pores become blocked and/or the NOM molecules compete directly for sorption sites with geosmin or MIB, which is referred to as a competitive effect (Newcombe et al. 1997, Newcombe et al. 2002). There are a number of factors that could impact the effect of NOM, although the most important factor appears to be the size of the NOM compounds.

Summers et al. (1988) reported that low molecular weight (MW) NOM compounds adsorb to PAC at a higher rate than higher MW compounds. Specifically, PAC had the highest adsorptive capacity for NOM compounds in the 500 to 1000 MW range. Newcombe et al. (1997) observed that low MW NOM fractions (MW<500) reduced PAC surface area and pore volume more than other NOM fractions. Adsorption kinetics may also be important. Larger NOM molecules will be slow to diffuse through PAC pores and reach sorption sites, and by the time NOM molecules reach the sorption sites, MIB or geosmin may have already adsorbed (Newcombe et al. 1997). It is therefore expected that NOM compounds with low molecular weights will inhibit geosmin and MIB sorption more than high MW NOM compounds.

Research conducted by Newcombe et al. (1997 and 2002) and Hepplewhite et al. (2004) supports the theory that low MW NOM compounds (<1000 Daltons) exert a stronger competitive effect on MIB sorption than high MW NOM compounds. Newcombe et al. (1997 and 2002) reported that the presence of NOM compounds smaller than 500 Daltons reduced MIB removal to between 55 and 60% from 98% in ultrapure water. NOM compounds between 500 and 3000 Daltons also reduced MIB sorption to PAC, but larger NOM molecules (>3000 Daltons) had little effect. Hepplewhite et al.

(2004) observed that NOM molecules between 200 and 600 Daltons provided more competition for MIB sorption sites than larger NOM molecules.

The effect that NOM character exerts on geosmin sorption, however, is different than the effect on MIB sorption. Sugiura et al. (1997) observed that different types of NOM (including humic acid) affected geosmin sorption similarly but affected MIB sorption differently. Cook et al. (2000) reported that while MIB removal was significantly different in four natural waters, similar geosmin removals were observed in each of the four waters. The only other study that investigated the inhibitory effects of isolated humic acid was conducted by Hertzog et al. (1977). The authors observed that a commercial humic acid reduced the sorption of geosmin to PAC, and speculated that a larger competitive effect would be observed with fulvic acids due to their smaller size.

In the results presented in Figure 23, geosmin sorption is very sensitive to different NOM types. Whole SR NOM, SR fulvic acid, and SR humic acid all had a significantly different effect on the sorption of geosmin to PAC. It appears that the same trend that Newcombe et al. (1997, 2002) and Hepplewhite et al. (2004) observed for MIB (that smaller NOM compounds inhibit sorption more than larger NOM compounds) also holds true for geosmin, as presented in Table 15 (with the exception of Pony Lake fulvic acid). As average molecular weight increases, the slope decreases, indicating that the inhibitive effect on geosmin sorption also decreases.

Table 15: Effect of average molecular weight on the competitive effect that a NOM type exerts on geosmin sorption

NOM type	Slope ¹	average molecular weight	
		M _n ²	M _w ³
whole SR NOM	0.027	1330 ⁴	2190 ⁴
SR fulvic acid	0.015	1360 ⁴ , 1652 ⁵	2310 ⁴ , 2290 ⁵
SR humic acid	0.008	1864 ⁵	3759 ⁵
Pony Lake fulvic acid	0.013		1200-1400 ⁶

¹from Table 14, a higher slope indicates a stronger inhibitive effect

²number averaged molecular weight

³weight averaged molecular weight

⁴Chin et al. (1994)

⁵O'Loughlin and Chin (2001)

⁶Brown et al. (2004)

One reason for the difference in average molecular weight between whole SR NOM compared to SR fulvic and SR humic acids could be the method of separation from water. The whole SR NOM was separated by reverse osmosis while the fulvic and humic acids were extracted using the XAD-8 resin adsorption method adapted from Aiken et al. (1985). Newcombe et al. (1997) speculated that some small molecular weight compounds are lost in the desalting step used to obtain NOM fractions (i.e. humic and fulvic acids), and that these small molecular weight compounds are most likely to adsorb to PAC and thus most likely to inhibit the sorption of geosmin.

While the results shown in Table 15 suggest that the same trend observed by others for MIB sorption (smaller NOM molecules exert a stronger competitive effect) is also true for geosmin sorption, the fact that some researchers reported geosmin sorption is not sensitive to different NOM types (Sugiura et al. 1997 and Cook et al. 2001) is still unexplained. There are a few possible reasons for this discrepancy. First, perhaps in the studies by Sugiura et al. (1997) and Cook et al. (2001), there were subtle differences in geosmin sorption that were not observed due to experimental error. It is possible that if experiments were conducted with SR NOMs and MIB, MIB sorption would be much more sensitive to NOM type, and in comparison, the effect of NOM type on geosmin sorption would appear small. Secondly, perhaps differences in elemental composition,

acidic groups, and aromaticity affect MIB sorption much more than geosmin sorption. All three SR NOM types (whole, fulvic, humic) tested had similar elemental compositions, carboxyl and phenolic groups, and aromaticity. It is possible that the NOMs tested in the Sugiura et al. (1997) and Cook et al. (2001) studies had significantly different elemental compositions or acidic groups. If this was true, the difference in sensitivity to NOM type between MIB sorption and geosmin sorption could be attributed to these NOM characteristics. Finally, the difference could be related to PAC type. Newcombe et al. (1997) reported that two different PAC types adsorbed different amounts of NOM. If different PACs are affected differently by NOM, perhaps the sorption of geosmin to certain PACs is less sensitive to NOM type. For example, maybe geosmin sorption to the PACs used in the Sugiura and Cook studies was less sensitive to NOM type than geosmin sorption to Norit PAC 20BF.

If the effect of NOM is dictated by the molecular weight of the NOM type, then Pony Lake should inhibit geosmin sorption more than any of the three SR NOM types. The weight-average molecular weight is 800 to 1000 Daltons lower than SR whole NOM (the next smallest NOM type that was tested). But in fact, it exerts a weaker inhibitive effect than whole NOM, and a very similar effect compared to SR fulvic.

The reason for the discrepancy could be due to the aromaticity of Pony Lake fulvic acid. The percentage of aromatic groups is much lower and the percentage of aliphatic groups is much higher compared to the Suwannee River NOM. (Table 16). The small aliphatic groups contained in Pony Lake fulvic acid may be less hydrophobic than the aromatic compounds present in SR NOM, and thus would not sorb to the NOM at the same rate as the aromatic groups, resulting in a weaker reduction of geosmin sorption. In effect, the two distinguishing properties of Pony Lake fulvic acid (smaller average molecular weight and less aromatic/more aliphatic groups) likely have opposite influences on the competitive effect. As a result, Pony Lake fulvic acid and SR fulvic acid inhibit geosmin sorption similarly.

Table 16: Percentage of aromatic and aliphatic groups present in four NOM types

NOM type	Estimates of carbon distribution	
	Aromatic	Aliphatic
	%	%
SR NOM	23	27
SR humic acid	31	29
SR fulvic acid	24	33
Pony Lake fulvic acid	12	61

All data except for SR fulvic acid are from Thorn et al. (1989). SR fulvic acid estimates were performed by Dr. Hatcher, Ohio State University.

4.2.4. Effect of Solids Recycle

4.2.4.1. Effect of pre-formed PAC-free lime solids on the performance of fresh PAC

The first set of experiments with recycled lime solids were designed to elucidate the effect that recycled solids have on the performance of fresh PAC. Recycled lime solids, containing no PAC, were added to water along with fresh PAC. The results are displayed in Table 17. When 5 mg/L Norit PAC 20BF were added along with recycled lime solids, 40% removal was observed in two separate beakers. For the control experiments, when 5 mg/L Norit PAC 20BF were added alone (no lime solids), 46% and 43% of the geosmin was removed. The difference of 4.8% between the control and the recycled solids experiment is within the error of the experiment, and the difference between the mean removal efficiencies is not significant (two tailed t-test, H_0 : Removal efficiency_{PAC} = Removal efficiency_{lime solids+PAC}, p value=0.23).

Table 17: Impact of recycled solids on the geosmin removal performance of Norit PAC 20BF at a dose of 5 mg/L

Experiment	C _o	C _{final}	Removal efficiency	T	pH	DOC
	(ng/L)	(ng/L)		(°C)		
Fresh PAC	100.8	54.1	46.3	20.4	7.49	8.8
Fresh PAC #2	125.4	71.7	42.8	20.1	7.96	8.8
Lime solids+fresh PAC	82.7	49.6	40.0	19.6	7.70	8.8
Lime solids+fresh PAC #2	95.9	58.0	39.5	21.8	7.82	8.8

Discussion

These results suggest that the addition of recycled solids has a very minor effect on the performance of freshly added PAC. It was hypothesized that if the fresh PAC attaches to the lime solids, PAC pores could become blocked leading to a reduction in geosmin sorption. This, however, does not seem to occur as the difference in mean removal efficiency between the control and recycled solids experiment is small (4.8%) and statistically insignificant.

4.2.4.2. Geosmin removal from softened water containing lime solids and PAC

In the next set of experiments, geosmin spiked water was added to softened water that included lime/PAC solids. The original batch of softened water contained no geosmin, meaning the lime/PAC solids were not pre-exposed to geosmin. Geosmin removal efficiencies for a given PAC dose were then determined. The results are shown in Table 18. When 5 mg/L PAC was pre-exposed to lime and alum for 140 minutes and then exposed to geosmin for two hours, the mean (\pm standard deviation) geosmin removal was $24.5 \pm 7.0\%$. In the control experiments, when no lime or alum was added, a dose of 5 mg/L PAC resulted in a mean removal efficiency of $44.6 \pm 2.5\%$. The difference in removal efficiencies was not statistically significant (two tailed t-test, H₀: Removal efficiency_{PAC} = Removal efficiency_{PAC/lime solids}, p value=0.11).

Table 18: Effect of PAC exposure to lime and alum on geosmin removal by 5 mg/L Norit PAC20BF

Experiment	C_o	C_{final}	Removal efficiency	T	pH	DOC
	(ng/L)	(ng/L)		(°C)		
Fresh PAC #1	100.8	54.1	46.3	20.4	7.49	8.8
Fresh PAC #2	125.4	71.7	42.8	20.1	7.96	8.8
PAC/lime solids #1	108.2	86.4	20.1	20.4	9.15	8.8
PAC/lime solids #2	108.2	86.6	20.0	20.4	9.15	8.8
PAC/lime solids #3	133.0	84.6	36.4	21.6	9.02	8.8
PAC/lime solids #4	91.2	72.4	20.6	21.9	9.34	8.8
PAC/lime solids #5	91.2	67.7	25.8	21.9	9.34	8.8

The next experiment was similar except that the PAC was pre-exposed to geosmin (prior to the addition of the second water batch). The results from these experiments (shown in Figure 24 and Table 19) indicate that recycled lime/PAC solids, when pre-exposed to geosmin, do not remove additional geosmin. In terms of geosmin concentrations, the controls (no PAC added) lost 18% and 5% over the two hour contact time, which was attributed to volatilization. With a dose of 10 mg/L PAC, a 1% decrease in geosmin concentration was observed. With 15 mg/L PAC, the geosmin level increased by 8% and with 20 mg/L PAC, the geosmin level decreased 24% over the two hours. Thus, the geosmin losses in the controls and PAC-dosed beakers were similar.

Using the isotherm equation from the equilibrium batch experiment (Table 9), it was possible to determine if additional geosmin removal would be expected after the second batch of water is added. The calculations shown in Table 19 suggest that substantial geosmin removal would be expected. There is a wide discrepancy between observed and predicted final concentrations; the predicted final concentration is always lower than the observed final concentration.

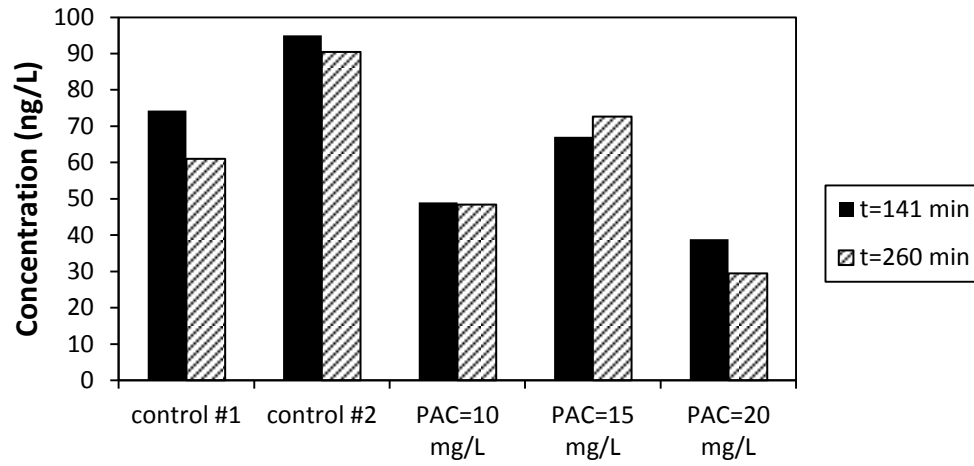


Figure 24: Effect of recycled lime/PAC solids on removal of geosmin.

Solid bars represent the geosmin concentration immediately after additional water was added (t=141 min) and striped bars represent the geosmin concentration two hours after the water was added (t=260 min)

For all experiments: DOC=6.5 mg/L, T=21.0-21.5°C

Table 19: Observed and predicted geosmin concentrations using Norit PAC 20BF (data correspond to Figure 24)

	t=0 min	t=140 min	t=141 min	t=260 min	Percent change from t=141 to t=260 min	Predicted t=260 min conc. ¹
	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(%)	(ng/L)
control #1	80.3	72.4	74.3	61.0	18	
control #2	NA	103.9	95.0	90.4	-4.8	
PAC=10 mg/L	80.3	28.0	49.0	48.4	-1.2	13.0
PAC=15 mg/L	NA	44.3	67.1	72.6	8.2	NA ²
PAC=20 mg/L	80.3	13.6	38.9	29.4	-24	5.1

¹Predicted concentration is based on the isotherm equation (1) and a mass balance equation (2). The isotherm equation is then substituted into the mass balance equation to form equation (3), and C (which is the predicted t=260 min concentration) is solved for by trial and error:

$$\begin{aligned}
 (1) \quad & q = 1.2 * C^{0.63} \\
 (2) \quad & C * V + q * m = M_{geosmin} \\
 (3) \quad & C * V + (1.2 * C^{0.63}) * m = M_{geosmin}
 \end{aligned}$$

where C is liquid phase concentration (ng geosmin/L water), V is the volume of water (L),

q is solid phase concentration (ng geosmin/mg PAC), m is the mass of PAC added (mg), and $M_{geosmin}$ is the total mass of geosmin added to the system (ng).

Example calculation (for PAC=10 mg/L):

$$C * 2L + (1.2 * C^{0.63}) * 20mg = 147 \text{ ng geosmin}$$

Solving by trial and error gives $C=13.0$ ng/L.

²Predicted t=260 min concentration is not available because of a problem with the analysis of the t=0 sample.

Discussion

While the evidence is not statistically conclusive ($p = 0.11$), the results shown in Table 18 indicate that PAC contained in lime solids removes less geosmin than PAC that has not been exposed to lime. Additionally, the discrepancy between observed and predicted final concentrations in Table 19 indicates that extended PAC exposure to lime solids reduces geosmin sorption. This effect could be due to a number of factors. One contributing factor is that the predicted concentration represents the optimal case for

geosmin removal because isotherm constants from equilibrium experiments were used, but the system does not reach equilibrium in this specific experiment (the contact time is only two hours). Another possibility is that the lime solids inhibit sorption. The results discussed in section 4.2.2 suggest that lime and alum do not inhibit sorption when added simultaneously with PAC. In this scenario, perhaps the extended contact time between the lime solids and PAC results in PAC pores becoming increasingly blocked. When geosmin spiked water is added after 140 minutes, fewer sorption sites may be available for geosmin. Additionally, pre-exposure to NOM likely plays a role in reducing PAC sorptive capacity for geosmin. As discussed in Section 4.2.3, the presence of NOM inhibits the sorption of geosmin. When Zimmer et al. (1989) exposed activated carbon to NOM for different lengths of time, adsorption capacity of chlorinated hydrocarbons decreased as activated carbon exposure to NOM increased. As PAC is exposed to NOM for longer periods of time, more NOM adsorbs to the PAC and thus reduces surface area, blocks pores, and occupies sorption sites. In the results shown in Table 19 and Table 20, the original contact time between PAC and NOM causes a reduction in the sorption of geosmin. Finally, it is also possible that in the procedure described above, the PAC quickly settles out with the lime solids, thus prohibiting a full two hours of contact time. While these procedures do not mimic the treatment plant, the results indicate that when PAC has been pre-exposed to geosmin, lime, and alum, the PAC removes less geosmin than expected when exposed to geosmin a second time.

4.2.4.3. Sorption of geosmin by laboratory-prepared lime solids containing PAC

For the next experiment, lime/PAC solids were collected from one jar test and added to a second batch of geosmin spiked river water. The results are shown in Table 20. When recycled lime solids containing 5 mg/L PAC were separated via filtration and dosed to geosmin spiked water, the removal efficiencies were 26% and 31% in two separate experiments. When 5 mg/L fresh PAC was dosed without lime solids, 44% and 48% of the geosmin was removed after the two hour contact time. With only two data points for each experiment, there is little statistical power and the removal efficiencies are

not significantly different (two tailed t-test, H_0 : Removal efficiency_{PAC} = Removal efficiency_{PAC/lime solids}, p value=0.11). Despite the lack of statistical significance, the results indicate that fresh PAC removes more geosmin than PAC contained in lime solids.

Table 20: Removal efficiencies provided by PAC/lime solids not pre-exposed to geosmin (Norit PAC 20BF dose= 5 mg/l)

Experiment	C_o	C_{final}	Removal efficiency	T	pH	DOC
	(ng/L)	(ng/L)		(°C)		(mg/L)
Fresh PAC #1	66.1	36.8	44.3	18.5	7.96	6.5
Fresh PAC #2	73.1	37.9	48.2	18.5	8.00	6.5
PAC/lime solids #1	107.7	74.6	30.7	18.7	7.88	6.5
PAC/lime solids #2	90.8	67.2	26.0	22.4	8.01	6.5

This experiment was then repeated except that the recycled PAC was pre-exposed to geosmin in the first jar test. In two separate experiments when a PAC/lime solids mixture containing 5 mg/L PAC was pre-exposed to geosmin, only 6% and 30% of the geosmin was removed when the PAC was exposed to geosmin for a second time. These results are shown in Table 21. In the first jar test, the contact time was 140 minutes and the PAC dose was 7.5 mg/L. When two-thirds of those solids (containing 10 mg PAC) were collected via filtration and dosed into a second jar test, the resulting PAC dose was 5 mg/L. Predicted concentrations were calculated based on isotherm data from section 4.1. The predicted and observed concentrations at time=140 minutes match closely for the first jar test (Jar test 1) but for the second jar test (Jar test 2), the predicted concentrations were much higher than the observed concentrations.

Table 21: Geosmin removal by PAC/lime solids pre-exposed to geosmin

	Geosmin concentration (ng/L):						removal efficiency
	Jar test 1 (PAC dose=7.5 mg/L)		predicted t=140 min	Jar test 2 (PAC dose=5 mg/L)		predicted t=120 min	
	t=0 min	t=140 min		t=0 min	t=120 min		
Experiment #1	97.6	24.0	26.5	78.7	74.0	53.8	0.06
Experiment #2	83.4	22.1	21.4	93.8	66.1	57.6	0.30

Experiment #1: Jar test 1: T=21.5°C, pH=8.0, DOC=8.8 mg/L

Jar test 2: T=20.1°C, pH=8.0, DOC=8.8 mg/L

Experiment #2: Jar test 1: T=22.0°C, pH=8.2, DOC=8.8 mg/L

Jar test 2: T=22.2°C, pH=8.2, DOC=8.8 mg/L

Discussion

These results suggest that PAC contained in recycled lime solids has reduced potential for geosmin removal compared to fresh PAC. There are three possible contributing factors to the reduction in sorption capacity of recycled PAC, all of which were discussed in section 4.2.4.2. First, pre-mixing PAC with lime for 140 minutes could result in pore blockage. The process of vacuum filtering the lime/PAC solids could exacerbate this process by compacting the lime solids into PAC pores. Second, the recycled PAC was exposed to NOM prior to geosmin exposure. As discussed in section 4.2.3 and 4.2.4.2, because the PAC was exposed to NOM twice, a reduction in geosmin removal would be expected. Lastly, if the PAC/lime solids settle out quickly, the contact time would be reduced and the recycled PAC/lime solids would not remove as much geosmin as fresh PAC.

4.2.4.4. Sorption of geosmin to full-scale recycled lime solids containing PAC

Next, recycled solids were collected from the treatment plant and dosed into Mississippi River water. When 200 mL of recycled solids were dosed into 2 L of river water, which simulates the treatment plant, an average of $25.1 \pm 6.9\%$ of geosmin was removed in three separate experiments (Table 22). The PAC dose was approximately

11.9 mg/L (see Appendix D for calculations). With that dose and an initial concentration of 100 ng/L, 85.6% removal would be expected based on the isotherm equation derived from the equilibrium experiments in section 4.1. While these experiments were only two hours long, the PAC contained in recycled solids from the plant has greatly reduced sorption capacity.

Table 22: Geosmin removal by recycled lime/PAC solids from the full-scale plant (Norit PAC 20BF dose: 11.9 mg/L)

	C_o	C_{final}	Removal efficiency	T	pH	DOC	predicted final concentration
	ng/L	ng/L		°C		mg/L	ng/L
Experiment #1	71.8	59.5	17.1	18.2	7.71	14.8	10.2
Experiment #2	86.7	61.4	29.2	22.6	7.72	14.8	13.4
Experiment #3	80.8	57.4	29.0	22.1	7.86	14.8	10.5

One potential source of error is that there could be varying amounts of solids (and thus varying amounts of PAC) in each batch of 200 mL of solids that was added to the water. To test this, 200 mL of solids was added to four beakers and dried in an oven. The average percent solids was $0.52 \pm 0.04\%$ (high of 0.57%, low of 0.46%). Thus, differing amounts of solids in each batch of 200 mL of recycled solids is likely not a major source of error.

Discussion

In previous experiments in which laboratory-prepared recycled solids were used (conducted at DOC levels of 6.5 and 8.8 mg/L), similar removal efficiencies (20.0 to 36.4%) were observed with a PAC dose of only 5 mg/L. Despite the difference in DOC concentration (the experiments in this section were conducted in water with a DOC concentration of 14.8 mg/L), the results suggest that recycled PAC from the full-scale plant has even less potential for geosmin removal than recycled PAC prepared in jar tests (since the PAC dose in these experiments was 11.9 mg/L). There could be two contributing factors: in the plant solids, some of the PAC has circulated through the

system two or more times, while PAC in the laboratory-prepared solids had been through the softening process only once. Because previous results suggest that PAC contained in lime solids has reduced sorption capacity compared to fresh PAC, the additional exposure to lime solids and NOM could further reduce sorption capacity. Finally, it is possible that the process of separating the solids and recycling them back into the water causes more pore blockage at the plant than in the laboratory. The PAC in the plant solids had not been exposed to geosmin levels above 5 ng/L, so pre-exposure to geosmin likely is not relevant

4.2.4.5. Complete full-scale plant simulation

One experiment was conducted simulating the full-scale plant (Table 23). The first jar test was simply to prepare the recycled solids. The PAC dose was 5 mg/L Norit PAC 20BF. The second jar simulates the full-scale plant in terms of chemical doses, recycled solids addition, contact times, and mixing speeds. Five mg/L of fresh Norit PAC 20BF was added in the second jar test along with recycled solids that contained 8.75 mg Norit PAC 20BF (for a resulting dose of 4.38 mg/L of recycled PAC). The resulting total PAC dose was 9.38 mg/L. In the second jar test, less geosmin was removed than would be predicted by equilibrium isotherm constants from section 4.1.

Table 23: Results from the complete full-scale plant simulation

Geosmin concentration (ng/L) at:						removal efficiency
Jar test 1		predicted t=140 min	Jar test 2		predicted t=120 min	
t=0 min	t=140 min		t=0 min	t=120 min		
93.7	39.9	36.2	61.9	38.9	26.7	37.2

Jar test 1: T=22.4 °C, pH=7.8, DOC=19.6 mg/L

Jar test 2: T=21.4 °C, pH=7.9, DOC=19.6 mg/L

Discussion

A discrepancy between observed and predicted time=120 minute geosmin concentrations is expected as the predicted concentration was calculated considering all the PAC in system (18.75 mg; recycled PAC plus fresh PAC) and all of the geosmin in the system (the initial geosmin concentration of the second jar test plus the geosmin adsorbed on the PAC contained in the recycled solids). Results from earlier sections suggest that the recycled PAC has reduced sorption capacity, so the predicted final concentration should be lower than the observed final concentration.

The removal efficiency of 37.2% is comparable to previous experiments when 5 mg/L PAC was added. At a DOC of 6.5 mg/L, the mean removal efficiency was 46.3%. At a DOC of 8.8 mg/L, the mean removal efficiency was 44.6%. Extrapolating from those removal efficiencies and DOCs, the expected removal efficiency at a DOC of 19.6 mg/L and a PAC dose of 5 mg/L would be 36.6%, almost exactly what was observed in the experiment. This indicates that the recycled PAC added did not improve geosmin removal.

4.3. Full scale results

Geosmin concentrations for the raw and finished water are shown in Figure 25. No geosmin was detected in many finished water samples. A value of 1 ng/L was assigned to these samples, which is half of the detection limit of 2 ng/L.

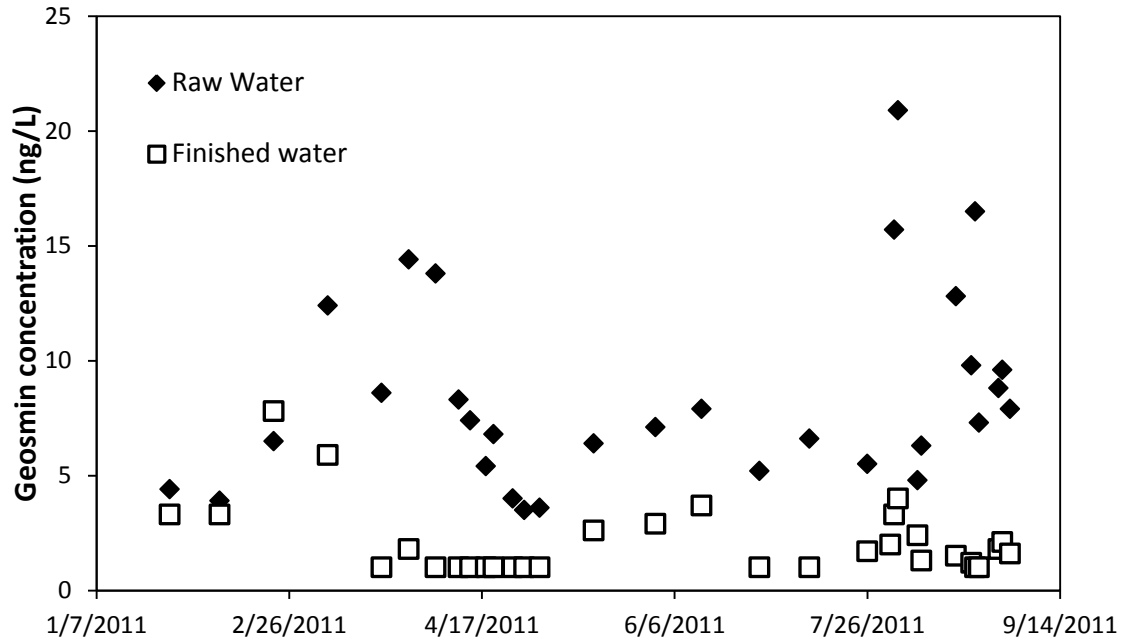


Figure 25: MWW raw water and finished water geosmin concentrations throughout 2011

It appears that there is not a major difference in removal efficiency between the three PAC addition points as all of the data points follow approximately the same pattern. Figure 26 and Table 24 show the results for the full scale test. While the removal efficiencies were higher for the post-softening addition point, the PAC dose for each post-softening data point (20 mg/L) was higher than any dose at the pre- or mid-softening locations. Also, since a value of 1 ng/L was assigned to non-detects, removal efficiency for non-detects is highly dependent on influent concentration. For example, if the influent concentration was 2 ng/L and the finished water was a non-detect, a removal efficiency of 50% was calculated. If the influent concentration was 5 ng/L and the finished water was a non-detect, the calculated removal efficiency was 80%. This is a limitation of the MDL. While the removal efficiency may in fact have been the same in both cases, substantially different removal efficiencies are calculated.

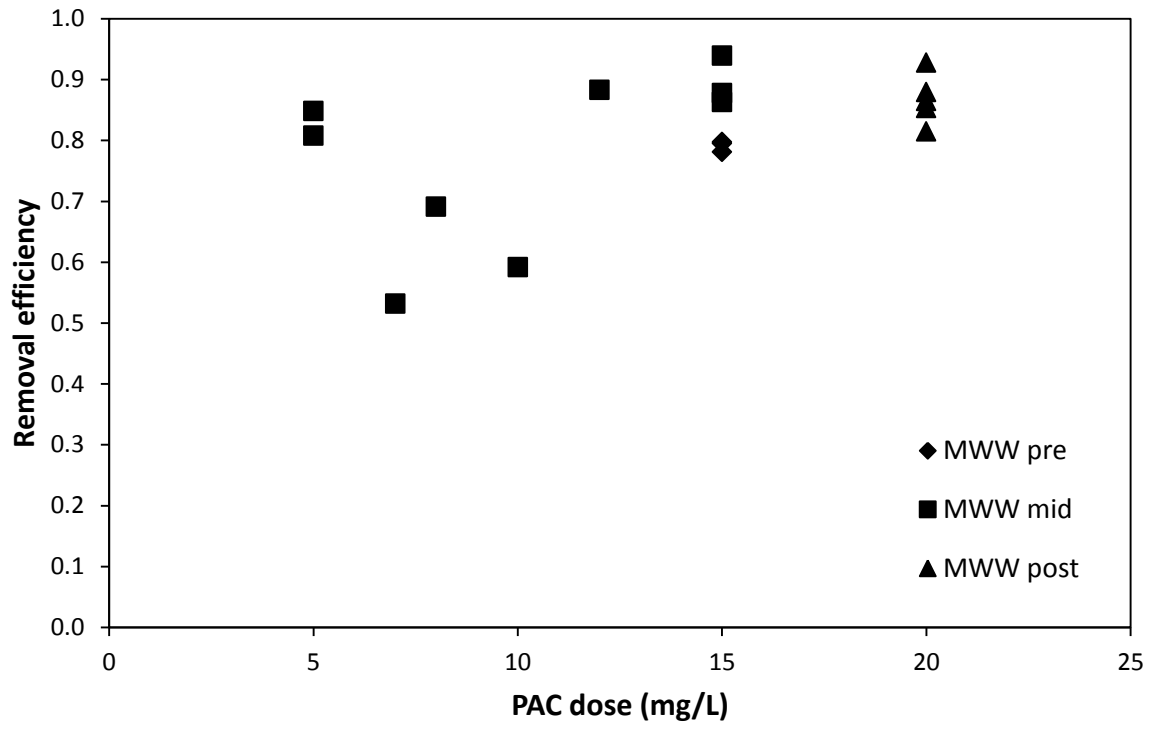


Figure 26: Full-scale testing of the three available PAC addition points using Norit PAC 20BF

Table 24: Results from full scale testing of three PAC addition points

Date	Raw water geosmin (ng/L)	Finished water geosmin (ng/L)	Pre-PAC (mg/L)	Mid-PAC (mg/L)	Post-PAC (mg/L)	% Removal
4/5/2011	13.8	1.0			20	93%
4/11/2011	8.3	1.0			20	88%
4/14/2011	7.4	1.0			20	86%
4/18/2011	5.4	1.0			20	81%
4/20/2011	6.8	1.0			20	85%
6/1/2011	7.1	2.9		10		59%
6/13/2011	7.9	3.7		7		53%
6/28/2011	5.2	1.0		5		81%
7/11/2011	6.6	1.0		5		85%
7/26/2011	5.5	1.7		8		69%
8/18/2011	12.8	1.5		12		88%
8/22/2011	9.8	1.2		15		88%
8/23/2011	16.5	1.0		15		94%
8/24/2011	7.3	1.0		15		86%
8/29/2011	8.8	1.8	15			80%
8/30/2011	9.6	2.1	15			78%
9/1/2011	7.9	1.6	15			80%

The full scale data is plotted along with the results from the laboratory jar tests in Figure 27. The data for the pre- and mid-softening locations correlates well with the exception of two points from the full-scale experiments. On 6/28/11 and 7/11/11, 5 mg/L PAC was dosed at the mid-softening location and removal efficiencies of 81% and 85%, respectively, were observed. Results from the jar tests suggest that approximately 40% removal efficiency would be expected. The other ten data points from the full-scale pre- and mid-softening locations were within 10% of the values predicted by the laboratory jar tests.

There is a large difference between the data sets for the post-softening location. At a PAC dose of 20 mg/L, the laboratory experiments suggest a removal efficiency of

approximately 65%. At the treatment plant, however, no geosmin was detected in any of the finished water samples, resulting in removal efficiencies between 81-93%.

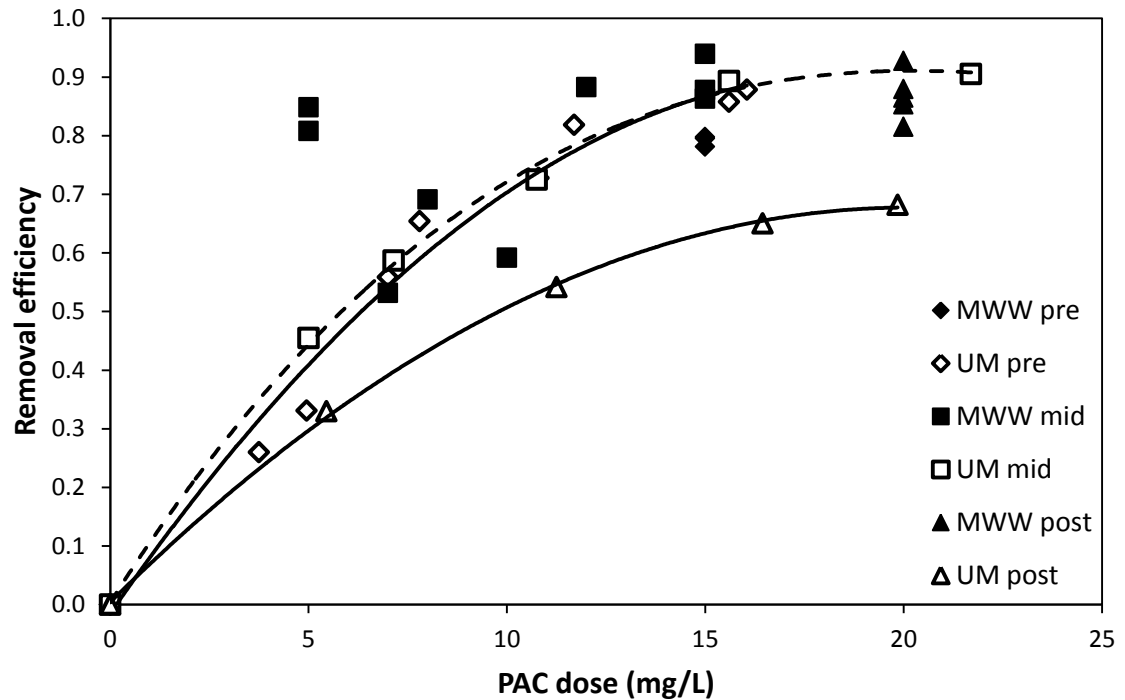


Figure 27: Comparison of full-scale results (MWW) and laboratory results (UM) using Norit PAC 20BF

Discussion

There are a number of reasons for the discrepancy between the full-scale and laboratory results. The first possibility is that the PAC stays in suspension past the recarbonation tanks and the additional contact time allows for additional removal. The data used for these plots was based on the geosmin concentrations of the river water (initial concentration) and the finished water (final concentration), taken at the entry point to the distribution system. When geosmin concentrations at the end of the recarbonation tanks are evaluated, however, it is apparent that nearly all of the removal occurs by the recarbonation tank effluent (Table 25).

There are three other factors that could contribute to the difference between full-scale and bench-scale results: potassium permanganate dose, differences in water quality between full-scale and the laboratory-prepared recarbonated water (most notably DOC levels), and differences in PAC contact time between the full-scale plant and jar tests. The potassium permanganate dose varied between 0-4 mg/L throughout the experiment. On all five dates in which 20 mg/L PAC was dosed at the post-softening addition point, the potassium permanganate dose was 4 mg/L. It is possible that potassium permanganate enhances geosmin removal by oxidation. It is also possible that the discrepancy in results is due to differences in water quality between the jar tests and treatment plant. The DOC levels in the water used in jar tests was 11.5 mg/L while the DOC of the water in the recarb tanks on the post-softening dates was between 5-8 mg/L. Part of the discrepancy between full-scale and jar test results is likely due to this difference in DOC concentration. Lastly, if the retention time in the full-scale recarbonation tanks was longer between 4/5/2011-4/20/2011 than in the jar tests, higher removal efficiencies would be expected at the full-scale plant.

Table 25: Geosmin concentrations when the post-softening addition point was used (Recarb water = concentration of water taken at the end of the recarbonation tanks)

Date	River water	Recarb water	Distribution water	Post- PAC dose	KMnO ₄
	(ng/L)	(ng/L)	(ng/L)	(mg/L)	(mg/L)
4/5/2011	13.8	ND	ND	20	4
4/11/2011	8.3	ND	ND	20	4
4/14/2011	7.4	ND	ND	20	4
4/18/2011	5.4	ND	ND	20	4
4/20/2011	6.8	ND	ND	20	4

4.4. Kinetics

The results for the kinetic experiments with PAC are shown in Figure 28. With a Norit PAC 20BF dose of 7.5 mg/L, 52% and 59% removal was achieved within 150

minutes in two separate beakers. In the remaining 330 minutes (5.5 hours), only 16% and 18% of additional removal was observed, for a total of 70% and 75% removal.

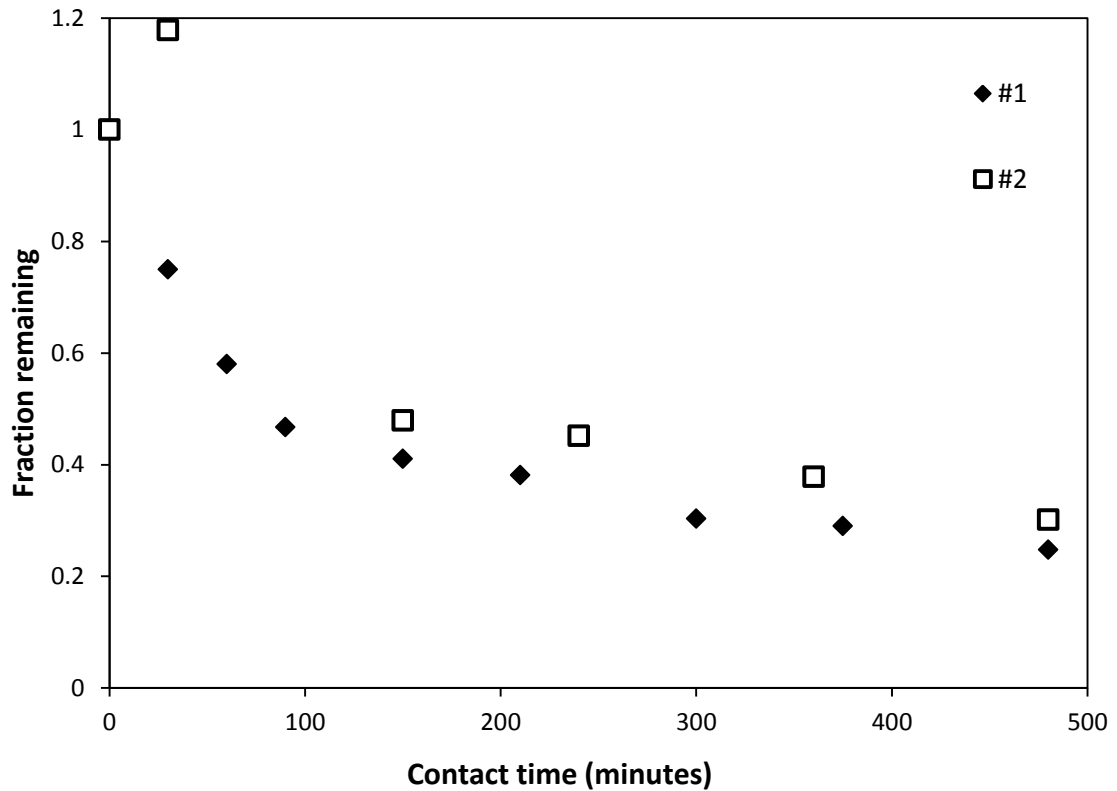


Figure 28: Geosmin removal over time by 7.5 mg/L Norit PAC 20BF

Experiment #1: $C_0=58.8$ ng/L, $T=21.5^\circ\text{C}$, $\text{DOC}=7.1$ mg/L

Experiment #2: $C_0=68.0$ ng/L, $T=21.0^\circ\text{C}$, $\text{DOC}=7.1$ mg/L

For Experiment #2, there was a problem with the analysis of the $t=60$ min and $t=90$ min samples.

To determine volatilization rates, three experiments were conducted with no PAC added. Results are shown in Figure 29. The data for all three volatilization experiments was regressed together in Figure 30. A linear regression of the compiled data gives a slope of -0.00039 , with units of percent/minute, which indicates a volatilization rate of 2.3% per hour (95% confidence interval: 0.3%, 4.3%). Figure 31 displays the data in terms of the natural log of fraction remaining ($\ln [C/C_0]$). The slope gives a first order rate constant of 0.00046 min^{-1} .

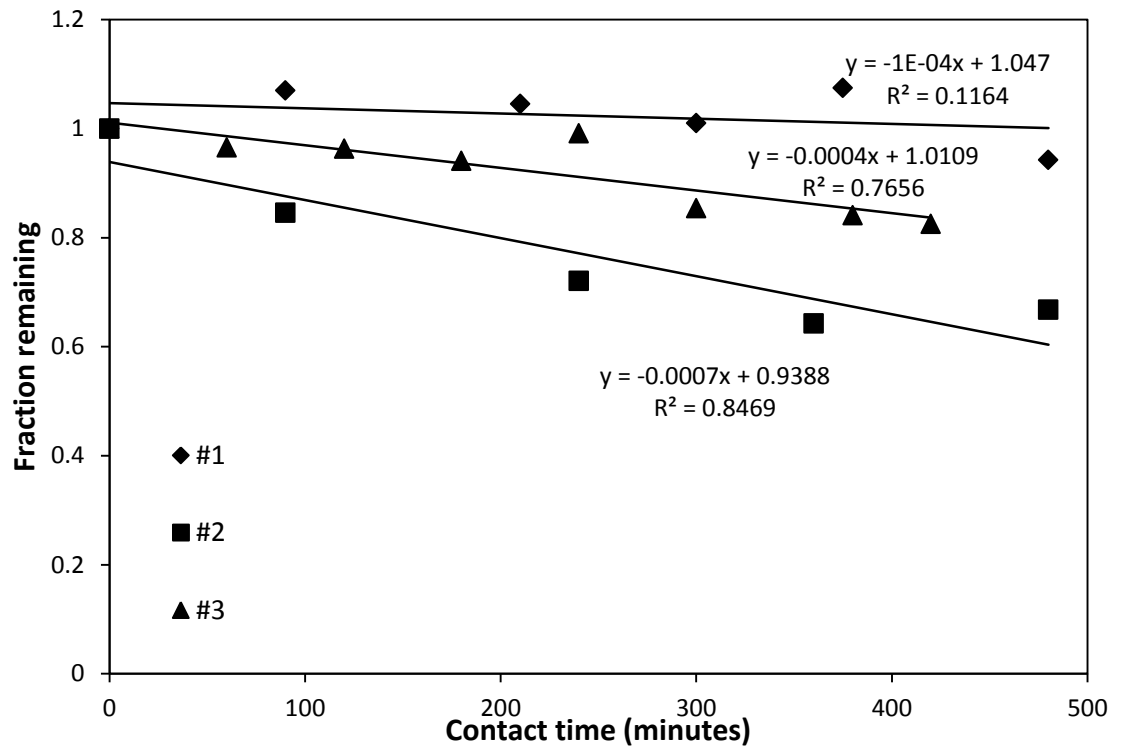


Figure 29: Geosmin volatilization data from three 8-hour jar tests (no PAC added)

Experiment #1: $C_0=56.3$ ng/L, $T=21.5^\circ\text{C}$, $\text{DOC}=7.1$ mg/L

Experiment #2: $C_0=77.8$ ng/L, $T=21.0^\circ\text{C}$, $\text{DOC}=7.1$ mg/L

Experiment #3: $C_0=73.4$ ng/L, $T=22.0^\circ\text{C}$, $\text{DOC}=7.1$ mg/L

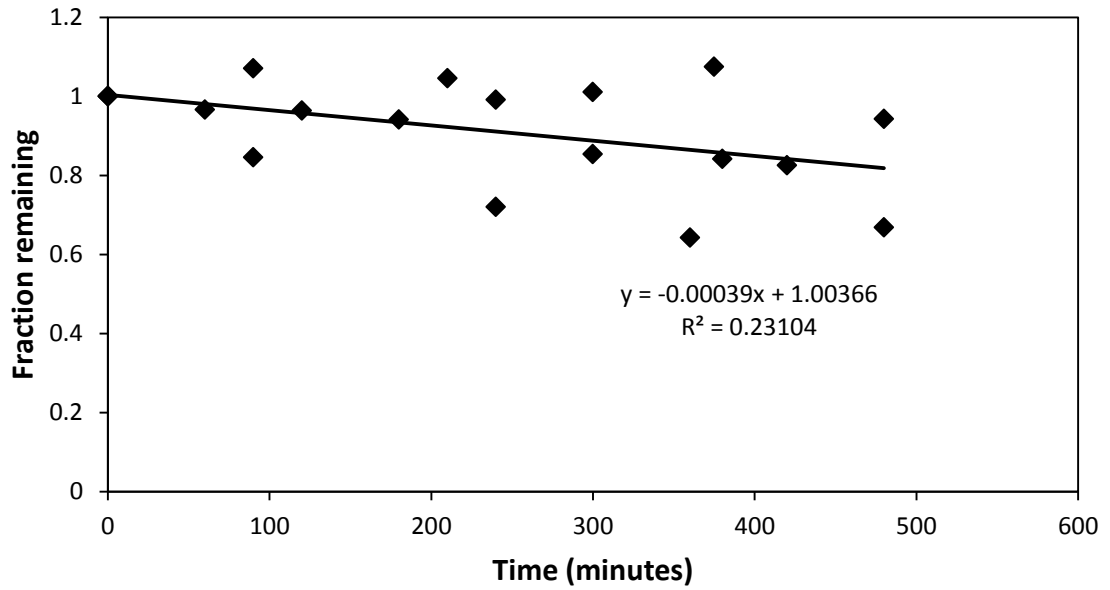


Figure 30: Geosmin volatilization data from three experiments compiled and regressed

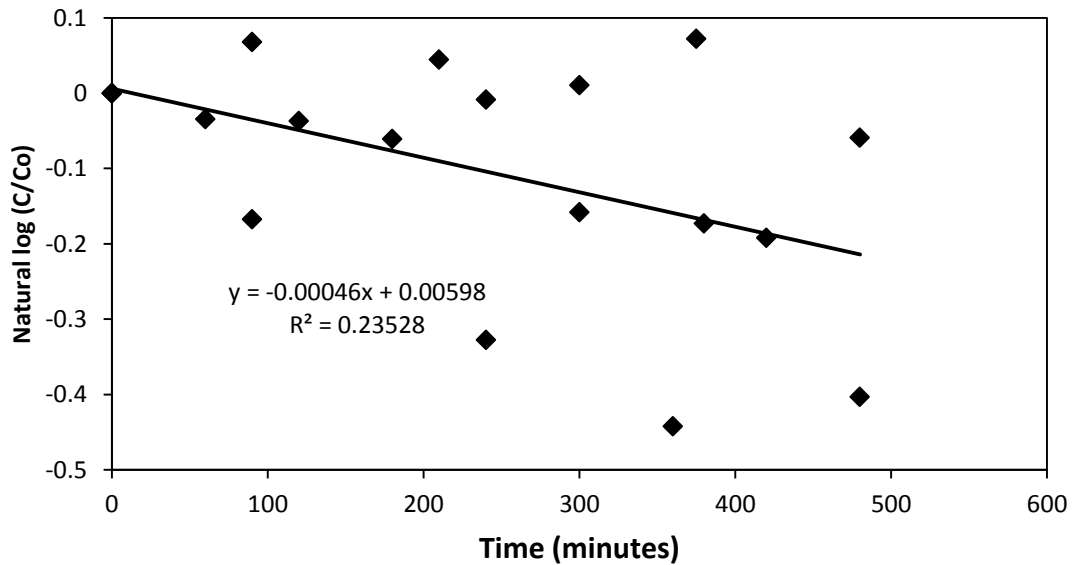


Figure 31: Volatilization data yields a first order rate constant of 0.00046 min^{-1}

Discussion

The results from the volatilization experiments suggest that over a standard 190 minute jar test, 7.4% of the geosmin would be expected to volatilize. Thus, the

volatilization is small but not insignificant. The rate of volatilization, however, is dependent on concentration. The initial concentration in the experiments ranged from 56 to 78 ng/L. At higher geosmin concentrations, the increased mass transfer driving force would result in a faster rate of volatilization. Similarly, the rate of volatilization would be slower at lower geosmin concentrations.

5. Implications for Minneapolis Water Works

The results from the jar tests simulating the full-scale plant suggest that adding PAC simultaneously with lime and alum does not negatively affect PAC performance (section 4.2.2). Therefore, contact time is the most important parameter and PAC should generally be added at the point which maximizes contact time. At MWW, the pre-softening or mid-softening PAC addition point most likely offers the highest contact time.

Results from experiments investigating the effect of NOM (section 4.2.3) indicate that NOM levels have a significant effect on PAC performance. This has important implications for full-scale water treatment plants. If two PAC dose points are available that provide similar contact times, yet the DOC level is lower at one location compared to the other, then PAC should be added to the water with a lower DOC concentration. At MWW, the DOC concentration of the softened water is 35 to 60% less than the DOC of the raw water. If PAC added at the post-softening location has similar contact time as PAC added at the pre- or mid-softening location, then the post-softening location should be used for PAC addition.

Additionally, assuming that the contact times used in jar tests are correct and incorporating results from the experiments with whole SR NOM, then the post-softening dose point may offer higher removal efficiencies under certain DOC conditions. For example, at a PAC dose of 7.5 mg/L, adding PAC at the post-softening dose point would be beneficial if the difference in DOC concentration between the river water and softened water is greater than 7 mg/L. At that difference in DOC level, the benefit of additional contact time at the pre- or mid-softening locations is offset by the benefit of lower DOC levels at the post-softening location. At a PAC dose of 15 mg/L, the post-softening dose point would offer a higher removal efficiency if the softened water had a DOC level 18 mg/L lower than the river water. Because the difference in DOC level between river and softened water is never 18 mg/L, perhaps the post-softening addition point is only potentially beneficial at low PAC doses.

The solids recycle process likely has minimal effect on PAC performance (section 4.2.4). Fresh PAC was not adversely affected by the addition of solids recycle, and PAC contained in recycled solids had reduced sorption capacity compared to fresh PAC. This is likely due to the extended PAC exposure to NOM and lime solids. The process of recycled solids, therefore, should not be an important factor when considering PAC addition locations.

Results from 2011 at the lime softening plant suggest that the three PAC addition points offer similar geosmin removals (section 4.3). Due to the limited sample size (n=16) and low river water geosmin concentrations, further full-scale testing should be conducted to conclusively determine the optimum PAC addition location at MWW. Because the pre- or mid-softening addition locations likely offer more PAC contact time, those locations should generally offer the highest geosmin removal efficiency. Adding the PAC to the softened water may be beneficial at low PAC doses (<10 mg/L) and when there is a large difference between river and softened water DOC levels (>7 mg/L) because of the reduced competition from NOM.

6. Summary and Conclusions

Results from the equilibrium experiments and two hour jar tests indicate that Norit PAC 20BF and Carbon Resources 325AA are the most effective PAC types for removing geosmin from Mississippi River water. Both of these PAC types are coal-based; two wood-based PAC types did not perform nearly as well as coal-based PAC's.

The results from jar tests that simulate the full-scale plant suggest that lime and alum do not affect sorption when added simultaneously with PAC. The most important parameter in regards to geosmin sorption via PAC was contact time, indicating that PAC should be added to the water at the point which maximizes contact time.

PAC contained in recycled lime solids has reduced sorption capacity compared to fresh PAC. This is likely because additional contact time between the PAC and NOM allows more NOM to adsorb to the PAC and thus inhibit sorption of geosmin. Extended interaction between PAC and lime solids could also result in pore blockage. Furthermore, recycled PAC that has been pre-exposed to geosmin, as would be the case in the full-scale plant, has even further reduced sorption capacity. These results indicate that PAC contained in recycled solids likely plays a small role in geosmin removal.

The presence of NOM inhibited the sorption of geosmin to PAC, and four NOM types had significantly different effects on geosmin sorption. When Suwanee River NOM was added to ultrapure water, an increase of 1 mg/L DOC resulted in a decrease of 2.7% in geosmin removal efficiency at a PAC dose of 7.5 mg/L. Suwanee River fulvic acid, Suwanee River humic acid, and Pony Lake fulvic acid also inhibited the sorption of geosmin, but the effect was less significant than that of whole Suwanee River NOM. For the three Suwanee River NOM types, the inhibitive effect increased as the average molecular weight decreased. This is likely because smaller NOM molecules more readily adsorb to PAC and thus block PAC pores or compete with geosmin for sorption sites. Pony Lake fulvic acid did not follow this trend, perhaps because with respect to Suwanee River NOM, Pony Lake fulvic acid has fewer aromatic groups and more aliphatic groups, which could lead to decreased hydrophobicity.

At a full-scale lime softening plant, PAC should generally be added at the point which maximizes contact time, irrespective of lime or coagulant addition (since the presence of lime and alum did not affect PAC performance). NOM levels, however, must also be considered. If there are two available locations for PAC addition that offer similar contact times but one location has a lower DOC concentration (such as softened water), then the PAC should be added to the water with a lower DOC level.

In the past, as geosmin concentrations were difficult to determine in a timely manner, it was challenging for a water utility to determine an appropriate PAC dose to remove geosmin (or other known T&O compounds). Now, as SPME autosamplers become more common, it is becoming easier for water utilities to have near real-time geosmin or MIB concentrations. It is important that a water utility have the ability to determine the correct PAC dose given influent concentration and DOC level in order to minimize PAC cost while maximizing compound removal, and thus maintaining high consumer confidence.

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Appendix A: Selection of mixing speeds, contact times, and chemical doses for jar tests with lime and alum

A flow rate of 60 MGD was assumed to calculate retention times for the mixing chambers, softening cones, and recarbonation tanks. Calculations for retention times for the mixing chambers, softening cones, and recarbonation tanks are shown below: The mixing time of 10 seconds (0.17 minute) after alum addition was selected to allow adequate alum mixing in the jar tests.

$$(1) \text{ time}_{\text{mixing chambers}} = \frac{V}{Q} = \frac{22300 \frac{\text{gal}}{\text{chamber}} * 2 \text{ chambers}}{60 * 10^6 \frac{\text{gal}}{\text{day}}} = 0.0007 \text{ days} = 1.07 \text{ minutes}$$

$$(2) \text{ time}_{\text{softening cones}} = \frac{661000 \frac{\text{gal}}{\text{cone}} * 9 \text{ cone}}{60 * 10^6 \frac{\text{gal}}{\text{day}}} = 0.099 \text{ days} = 142.8 \text{ minutes}$$

$$(3) \text{ time}_{\text{recarbonation tanks}} = \frac{1.1 * 10^6 \frac{\text{gal}}{\text{tank}} * 2 \text{ tanks}}{60 * 10^6 \frac{\text{gal}}{\text{day}}} = 0.037 \text{ days} = 52.8 \text{ minutes}$$

Similarly, the mixing speeds were chosen to simulate full-scale plant conditions. The 120 rpm value was chosen to mimic the jet-mixing injection of alum. The 65 rpm value for the mixing chamber portion of the jar test corresponds to a G value of approximately 163 sec⁻¹ (Table A1). This matches well with the G value in the full-scale mixing chambers, which is approximately 156 sec⁻¹ (Table A2). The 50 rpm value was selected for the softening cone portion because it is the minimum mixing speed that keeps all but the largest solids in suspension. The 10 rpm value was intended to mimic the recarbonation tank. At that mixing speed, most solids settle but the water does not completely clarify, as is the case in the full scale recarbonation tank.

The alum and lime doses correspond to typical doses used at the full-scale plant. The aluminum sulfate dose of 8 mg/L was chosen to match the full scale plant's alum dose in terms of mM/L of Al³⁺. At the full-scale level, a 48.5% strength solution of Al₂(SO₄)₃*14H₂O is dosed at varying levels depending on influent water quality; a typical dose of 15 mg/L of the alum solution is equivalent to 0.0245 mM/L of Al³⁺. The dose of

8 mg/L aluminum sulfate chosen in the jar tests is equivalent to 0.0240 mM/L of Al^{3+} . MWW uses calcium oxide for lime. The calcium hydroxide dose of 190 mg/L used in the jar tests is equivalent to a calcium oxide dose of 146 mg/L, which is within the typical range used at the treatment plant.

G calculation for the mixing chamber portion of the jar test

Table A1: G calculation for the mixing chamber portion of the jar test

n	63	rpm (mixing speed)
r	0.125	feet, radius of paddle
b	0.0833	feet, width of paddle
C_D	1.8	constant
k	0.25	constant
ρ	62.4	lb/ft ³ , density of water
P	0.0345918	ft·lb/sec, Power ¹
μ	0.0000203	lb·s/ft ² , dynamic viscosity (at 20°C)
V	0.0706	ft ³ , tank volume
G	155.36	1/sec, velocity gradient²

$${}^1Power = 5.74 * 10^{-4} * C_D * \rho * \{n * (1 - k)\}^3 * \frac{b}{4} * r^2$$

$${}^2G = \sqrt{\frac{P}{\mu * V}}$$

G value for mixing chambers (from Dr. Michael Semmens)

Table A2: G value calculation for the full-scale mixing chambers

Flocculator calculations					
Total Flowrate	60	MGD			
Flowrate =	30	MGD	Per channel flocculator		
	1.314	m ³ /s			
	46.41	ft ³ /s			
Channel Info and calculation of velocity between baffles					
<i>(Channel Dimensions supplied by Annika Bankston)</i>					
Channel 1			Channels 2--5		
Height	12	Feet	Height	12	Feet
Width	4.5	Feet	Width	2.75	Feet
Length	13.5	Feet	Length	13.5	Feet
Velocity =	0.763950617	Ft/sec	Velocity =	1.25010101	Ft/sec
	0.232852148	m/sec	Velocity =	0.38103079	m/sec
Headloss in channels based on Chezy Equation					
$\Delta H = L \cdot V^2 / C^2 \cdot R$					
Where	L =	Channel length		m	
	V =	Velocity		m/s	
	C =	Chezy Coefficient		m ^{0.5} /s	
	R =	Hydraulic radius		m	
	n =	Manning friction factor		s · m ^{-0.33}	
	$C = ((R^{1/6})/n)$				
conversion ft to m =		0.3048			
For concrete n =		0.015			
Channel 1					
L =	3.6576	m			
V =	0.232852148	m/s			
C =	62.60647346	m ^{0.5} /s			
R =	0.6858	m			
n =	0.015	s · m ^{-0.33}			
$\Delta H =$	7.3777E-05	m			
Channels 2-5					
L =	3.6576	m			
V =	0.381030788	m/s			
C =	57.67189241	m ^{0.5} /s			
R =	0.4191	m			
n =	0.015	s · m ^{-0.33}			
$\Delta H =$	0.001523808	m			

Calculation for flow around ends of baffles			
$\Delta H =$	$(k \cdot V^2) / (2 \cdot g)$		
Where $k = 3.3$ for 180° turns around baffles			
Height of water in turns = 2 ft at the top of submerged baffles and 3 ft below baffles			
Number of turns =	4		
For 2 turns $V =$	0.52391733	m/sec	
For 2 turns $V =$	0.34927822	m/sec	
$\Delta H =$	0.133374041	m	
Total headloss =	0.13497163	m	sum of headlosses for Channel 1, Channel 2-5, and flow around baffles
Assume temp = 20°C			
Calculation of G value:			
G =	156	1/sec	

Appendix B: Determination of correct solids recycle rate for jar tests

The correct mass of lime solids that should be dosed in the jar tests to accurately simulate the solids recycle process at treatment plant was determined (a schematic is shown in Figure B1). Typical flow rates of 3500 GPM and 4000 GPM were chosen for the recycle pumps and waste pumps. For simplification, C_{out} is assumed to equal zero. Thus, the mass of solids entering the system must equal the mass of solids exiting the system. Given this, the rate of recycled solids to influent solids is the same as the rate of recycled solids to wasted solids, or 3500 to 4000 (0.875). In other words, 87.5% of the influent solids are recycled. To collect the appropriate amount of recycled solids in a jar test, a 2 L jar test was conducted and solids were collected from 1.75 L (87.5%) of the water.

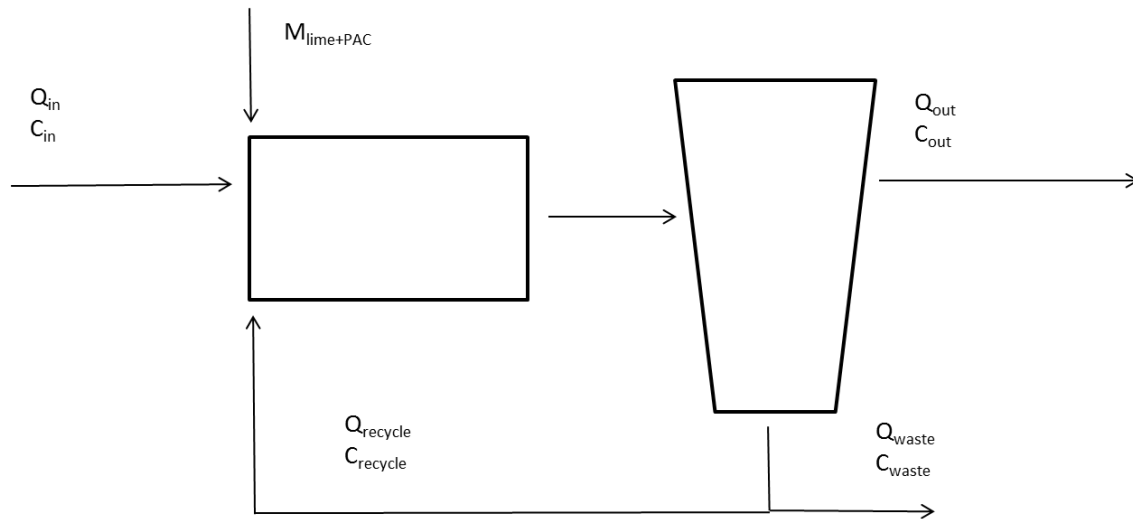


Figure B1: Schematic of solids in the lime softening plant (Q= flow rate, C= concentration of solids, M=mass flow rate)

Appendix C: NOM experiments excluded from results

A total of six experiments were conducted with Suwannee River NOM (shown in the order that they were conducted in

Figure C1). The results from experiments #3 and #4 were very different than for the other four experiments and were not included in the regression in section 4.2.3. For experiment #3, the fraction remaining was higher at a given DOC level than all other experiments. For experiment #4, the fraction remaining was similar at all four DOC levels, including in the control beaker to which no NOM was added. One explanation is that less PAC was added in these experiments, and thus less geosmin was removed. This fact, however, would not explain why the slopes for experiment #3 and #4 is significantly lower ($p\text{-value} < 0.05$) than for the other four experiments.

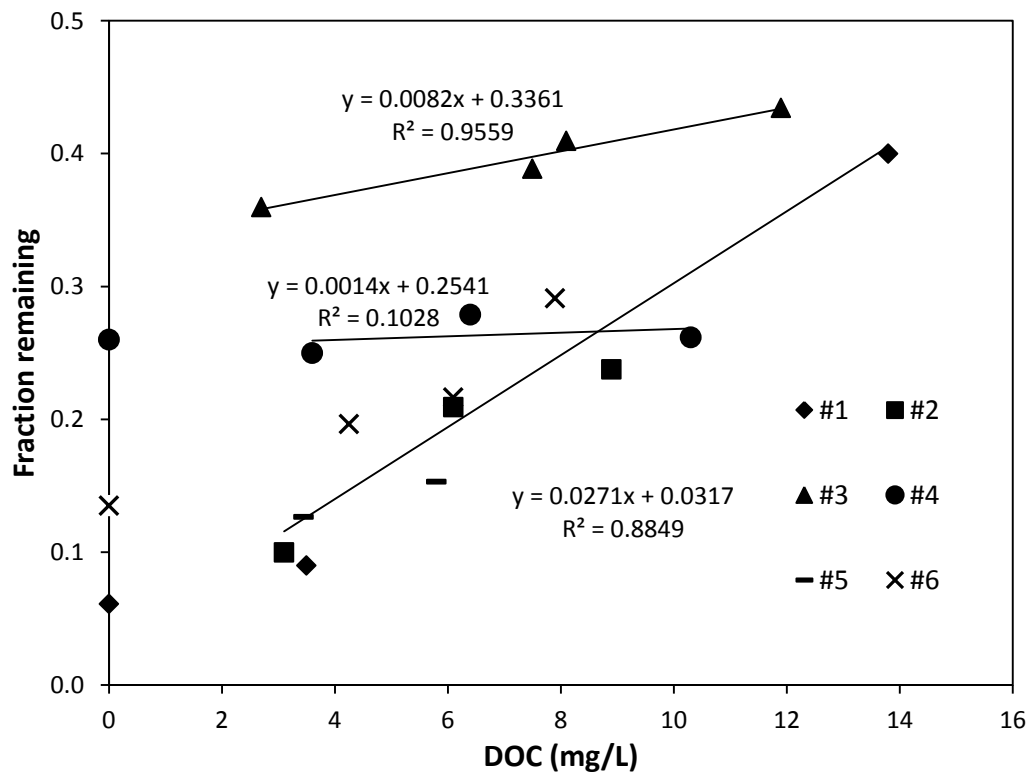


Figure C1: Effect of whole Suwannee River NOM on geosmin removal from ultrapure water at a Norit PAC 20BF dose of 7.5 mg/L

Appendix D: Determination of the effective PAC dose for section 4.2.4.4 (sorption of geosmin to full-scale recycled solids containing PAC)

It was necessary to determine the PAC dose when recycled solids were collected from the full-scale plant and dosed into laboratory jar tests. The recycled solids were collected on June 5, 2012. On that day, water production was approximately 60 MGD, the solids recycle pumps were operating at 3300 gpm, and the solids waste pumps were operating at 3800 gpm. The PAC dose was 12 mg/L and had been constant for several days. If complete recovery is assumed (all PAC is recovered in the solids), then the PAC concentration in the recycled solids is 132 mg/L. In this experiment, 0.2 L of solids were added to 2 L of river water. This equates to 26.2 mg of PAC added to 2.2 L of water, which results in a PAC dose of 11.9 mg/L. Calculations are shown below.

$$\dot{m}_{PAC \text{ dosed}} = \frac{12 \text{ mg PAC}}{\text{L water}} * \frac{60 * 10^6 \text{ gal}}{\text{day}} = 2.73 * 10^9 \frac{\text{mg PAC}}{\text{day}}$$

$\dot{m}_{PAC \text{ in waste stream}} = \dot{m}_{PAC \text{ dosed}}$ (since all PAC is recovered in the waste/recycle stream)

$$C_{PAC \text{ in wasted solids}} = \frac{\dot{m}_{PAC \text{ in waste stream}} \left(\frac{\text{mg}}{\text{day}} \right)}{\dot{m}_{\text{waste stream}} \left(\frac{\text{gal}}{\text{min}} \right)} = \frac{2.73 * 10^9 \frac{\text{mg PAC}}{\text{day}}}{3800 \frac{\text{gal}}{\text{min}}} = 132 \frac{\text{mg PAC}}{\text{L waste}}$$

$C_{PAC \text{ in recycle stream}} = C_{PAC \text{ in waste stream}}$ (since the recycle and waste streams are the same)

$$\begin{aligned} C_{PAC \text{ in jar test}} &= \frac{C_{PAC \text{ in recycle stream}} * V_{\text{recycled solids added}}}{V_{\text{water in jar test}}} \\ &= \frac{132 \frac{\text{mg PAC}}{\text{L recycled solids}} * 0.2 \text{ L recycled solids}}{2.2 \text{ L water}} = 11.9 \frac{\text{mg PAC}}{\text{L}} \end{aligned}$$

Appendix E: Geosmin sorption capacity in DI water compared to Mississippi River water

As shown in Figure E1 and Figure E2, sorption capacity for geosmin was significantly higher in DI water than in Mississippi River water. This is due to the presence of background organic matter in the river water.

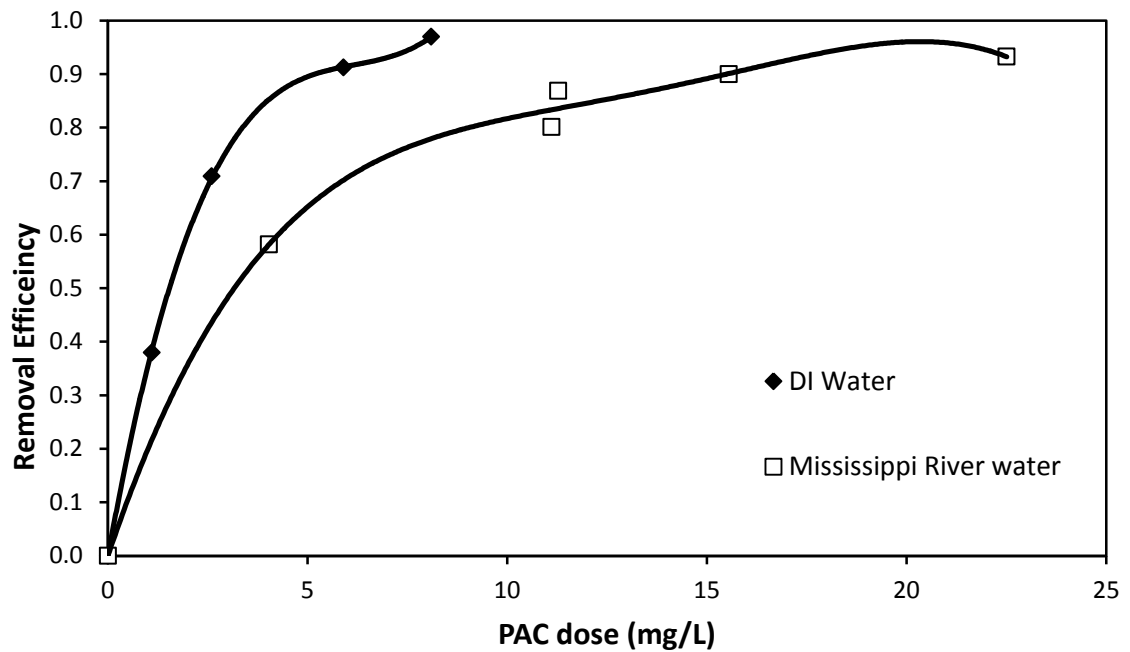


Figure E1: Comparison of equilibrium geosmin removal efficiency with Norit PAC 20BF in DI water and Mississippi River water

DI water: $C_0 = 100.8$ ng/L, $T = 22.0^\circ\text{C}$, $\text{pH} = \text{NA}$, $\text{DOC} = \text{NA}$

Mississippi River water: $C_0 = 83.9$ ng/L, $T = 22.0^\circ\text{C}$, $\text{pH} = 7.54$, $\text{DOC} = 11.69$ mg/L

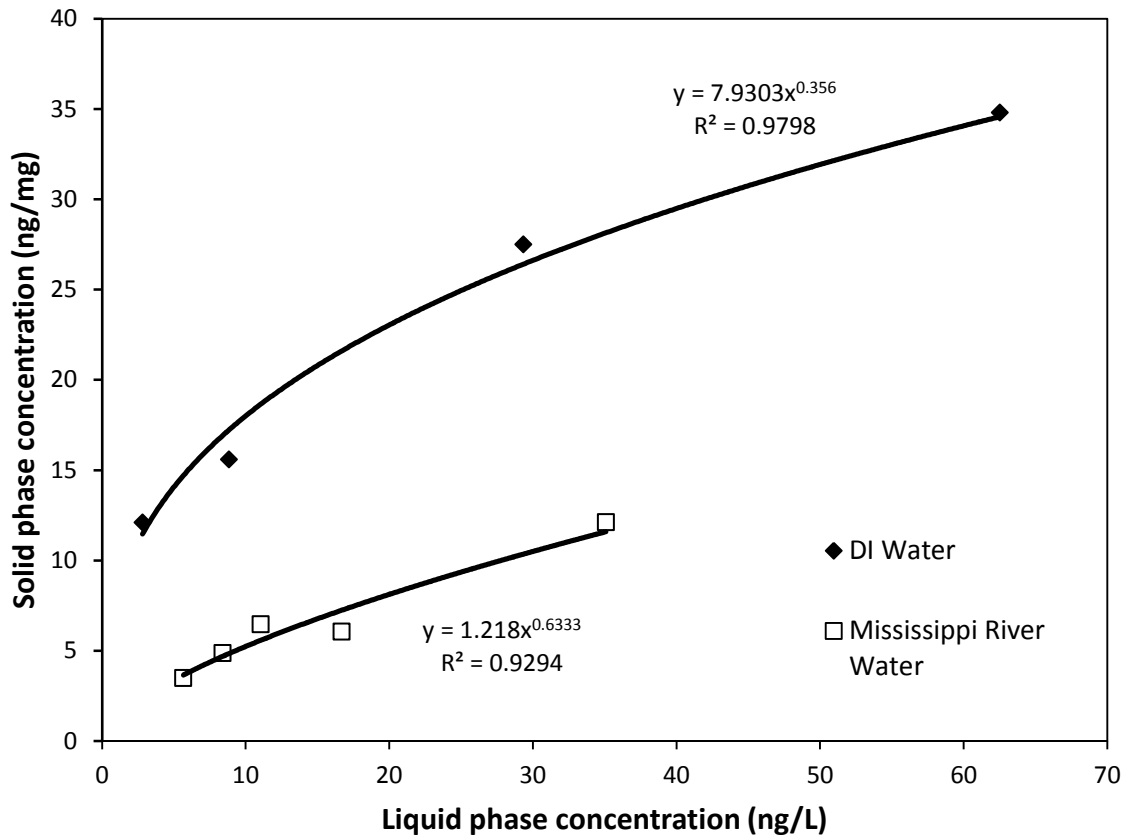


Figure E2: Isotherm plots for the geosmin sorption results shown in Figure E1

Appendix F: Effect of initial geosmin concentration on jar test results

Two identical jar tests were conducted following the procedure given in section 3.3.2. Norit PAC 20BF was dosed at a range between 0-25 mg/L. In one experiment, geosmin was spiked into the river water at a concentration of 62 ng/L. In the second experiment, the initial concentration was 259 ng/L. The removal efficiencies at a given PAC dose were similar (Figure F1). The isotherms for the two experiments, shown in Figure F2, are very different. For the experiment with a higher initial geosmin concentration, solid phase concentrations are much higher at a given liquid phase concentration. This must be considered when evaluating other isotherm plots.

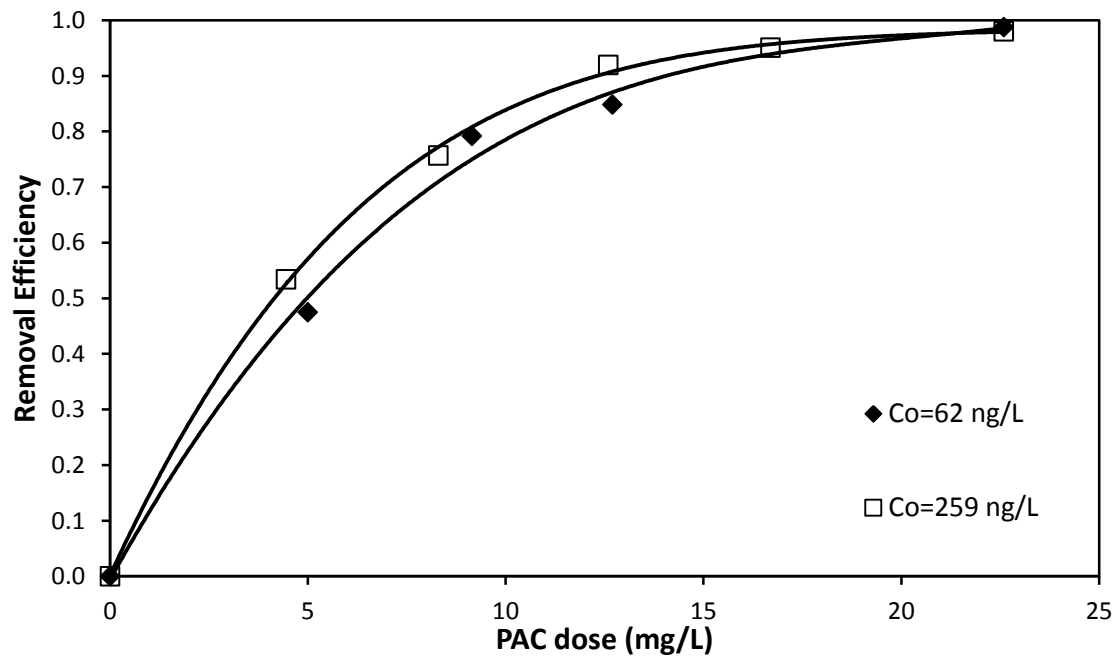


Figure F1: Effect of initial concentration on geosmin removal efficiency in 195 minute jar tests simulating the pre-softening PAC addition point with Norit PAC 20BF

Co=61.7 ng/L: DOC=7.43 mg/L, T=19.5°C, pH=8.3

Co=258.6 ng/L: DOC=7.43 mg/L, T=18.0°C, pH=8.2

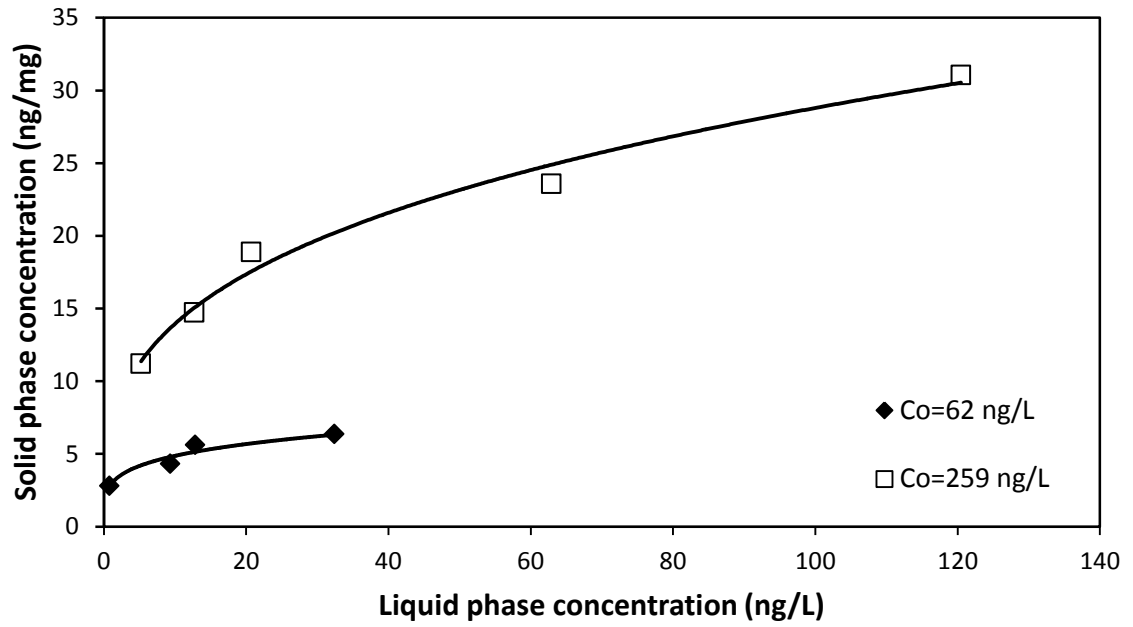


Figure F2: Isotherm plots for the geosmin sorption results shown in Figure F1

Appendix G: Effect of using geosmin standards in methanol versus geosmin standards in water

For the majority of experiments, a geosmin standard in methanol was added to the water to achieve the desired concentration. The following experiment was conducted to determine if the methanol affected sorption. Two separate jar tests were conducted, one in which geosmin was added in the typical manner (geosmin in methanol standard). In the second experiment, a geosmin standard in water was used. In Figure G1, it is apparent that removal efficiencies are very similar for the two experiments. The isotherm plot, in Figure G2, is slightly different, though the difference can be attributed to the difference in initial concentration.

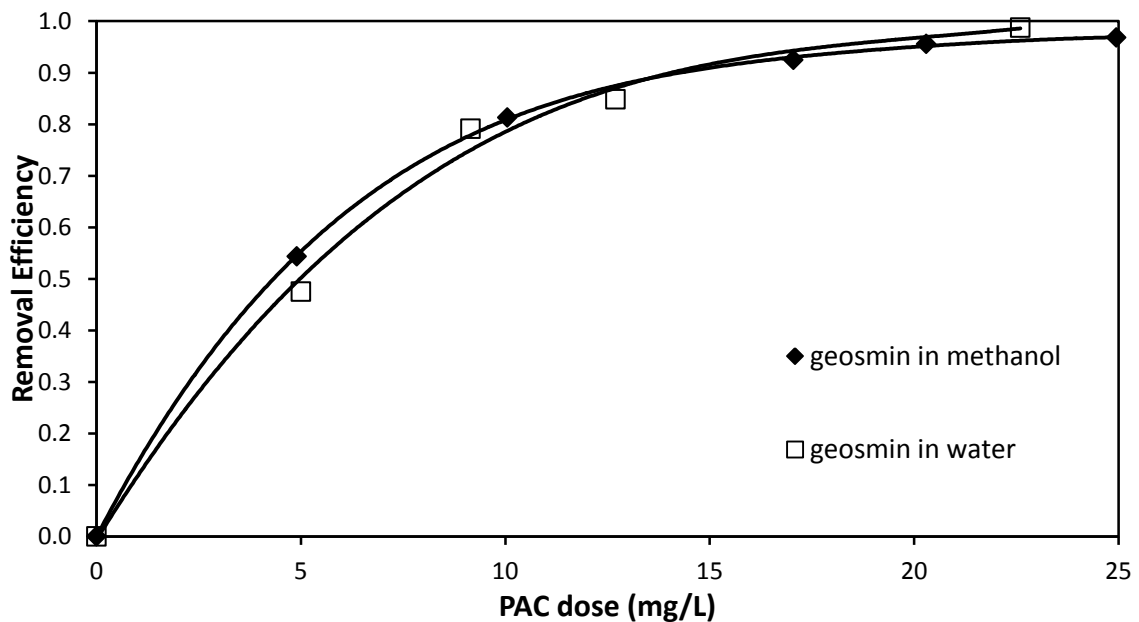


Figure G1: Effect of geosmin standard type on geosmin removal efficiency in 195 minute jar tests simulating the pre-softening PAC addition point with Norit PAC 20BF
 Geosmin in methanol: $C_o=118.0$ ng/L, DOC=7.43 mg/L, $T=21.0^\circ\text{C}$, pH=8.1
 Geosmin in water: $C_o=61.7$ ng/L, DOC=7.43 mg/L, $T=19.5^\circ\text{C}$, pH=8.3

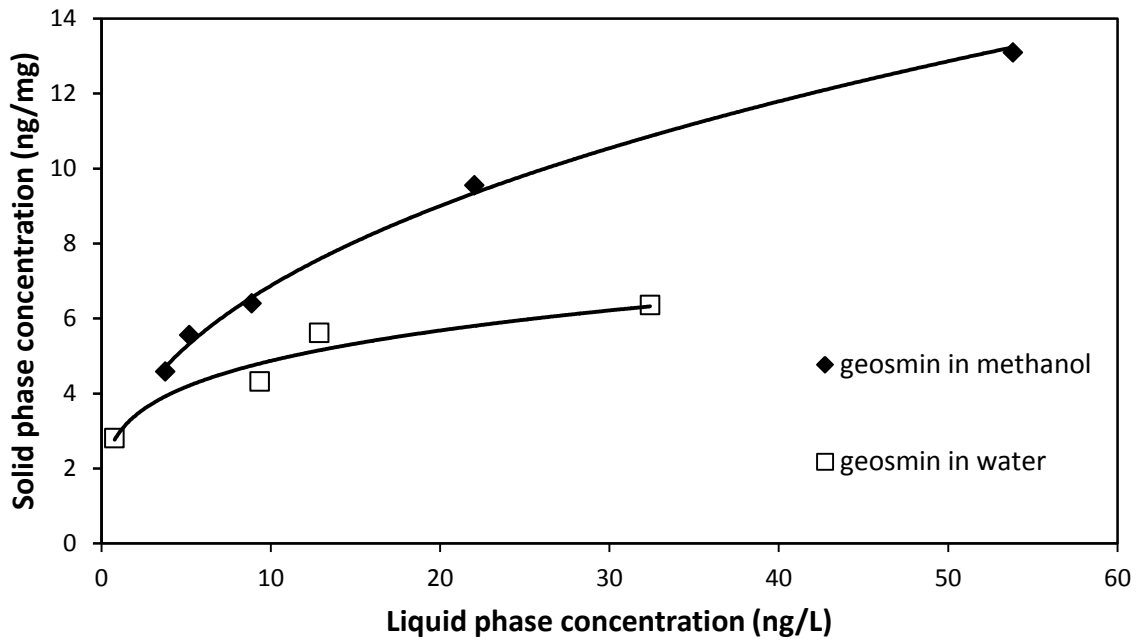


Figure G2: Isotherm plots for the geosmin sorption results shown in Figure G1

Appendix H: Effect of different chemical doses

Several experiments were conducted with the following chemical doses: 160 mg/L calcium hydroxide and 25 mg/L hydrated potassium aluminum sulfate, a chemical commonly referred to as alum. This alum dose is equivalent to .0541 mmol/L as Al^{3+} . These doses are referred to as “Old lime/alum doses” in the Figure H1 and Figure H2. “New lime/alum doses” are those discussed in section 3.3.2 and Appendix A: 190 mg/L calcium hydroxide and 0.024 mmol/L as Al^{3+} . Two experiments were conducted to compare PAC performance at each of the two chemical doses using the same batch of river water. There appears to be no difference in sorption of geosmin to PAC between the two lime and alum doses.

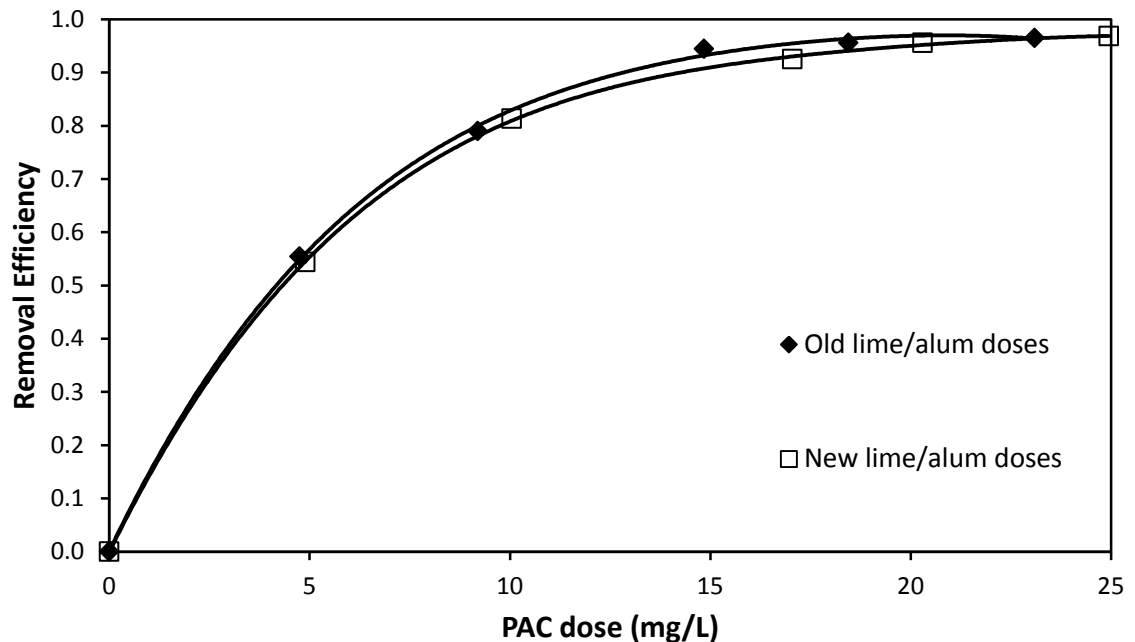


Figure H1: Effect of lime and alum dose on geosmin removal efficiency in 195 minute jar tests simulating the pre-softening PAC addition point with Norit PAC

Old dose: $C_0=88.3$ ng/L, DOC=7.4 mg/L, $T=19.5$ °C, pH=8.3

New doses: $C_0=118.0$ ng/L, DOC=7.4 mg/L, $T=21.0$ °C, pH=8.1

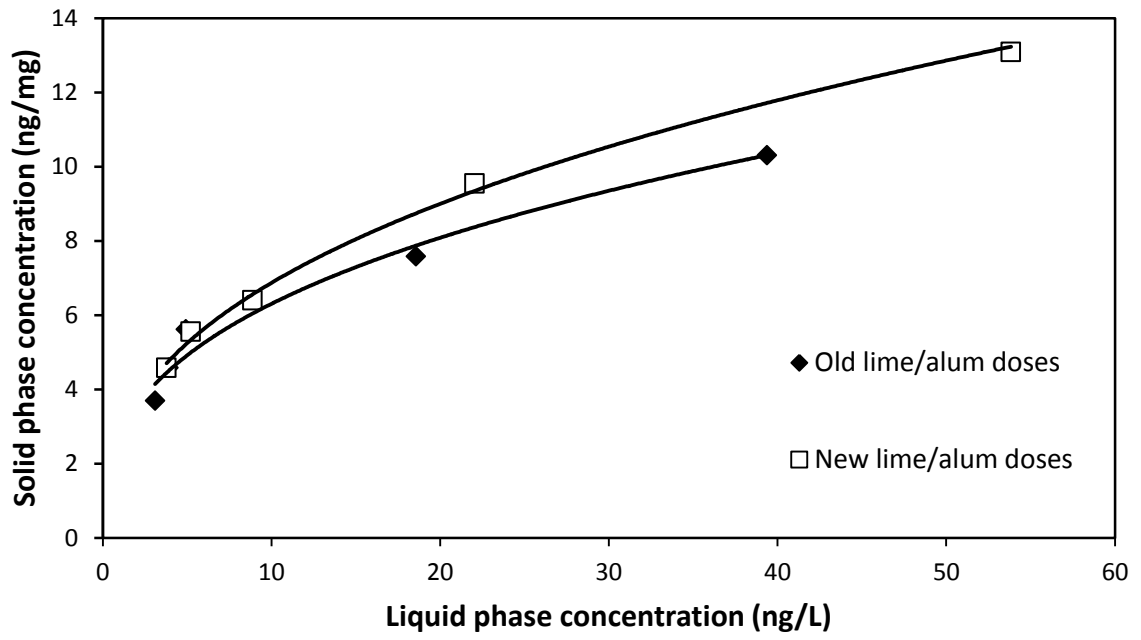


Figure H2: Isotherm plots for the geosmin sorption results shown in Figure H1

Appendix I: Effect of DOC on jar test results

A total of four jar tests were performed with two different water batches, and thus two different DOC levels. In all four jar tests, Norit PAC 20BF was added at the pre-softening location. These results confirm the findings of the NOM experiments in section 4.2.3. Inferring from the Suwannee River NOM experiments, a difference of 4.1 mg/L DOC would result in a difference of 11% in removal efficiency at a PAC dose of 7.5 mg/L. Evaluating Figure I1 at a PAC dose of 7.5 mg/L, the difference in removal efficiencies is approximately 15%.

Table II: Experimental conditions for four experiments evaluating the effect of DOC on PAC performance

Experiment	C _o	T	pH
	ng/L	°C	
DOC=7.4 mg/L #1	118.0	21.0	8.11
DOC=7.4 mg/L #2	88.3	19.5	8.25
DOC=11.5 mg/L #1	80.7	18.5	7.70
DOC=11.5 mg/L #2	93.7	19.5	7.90

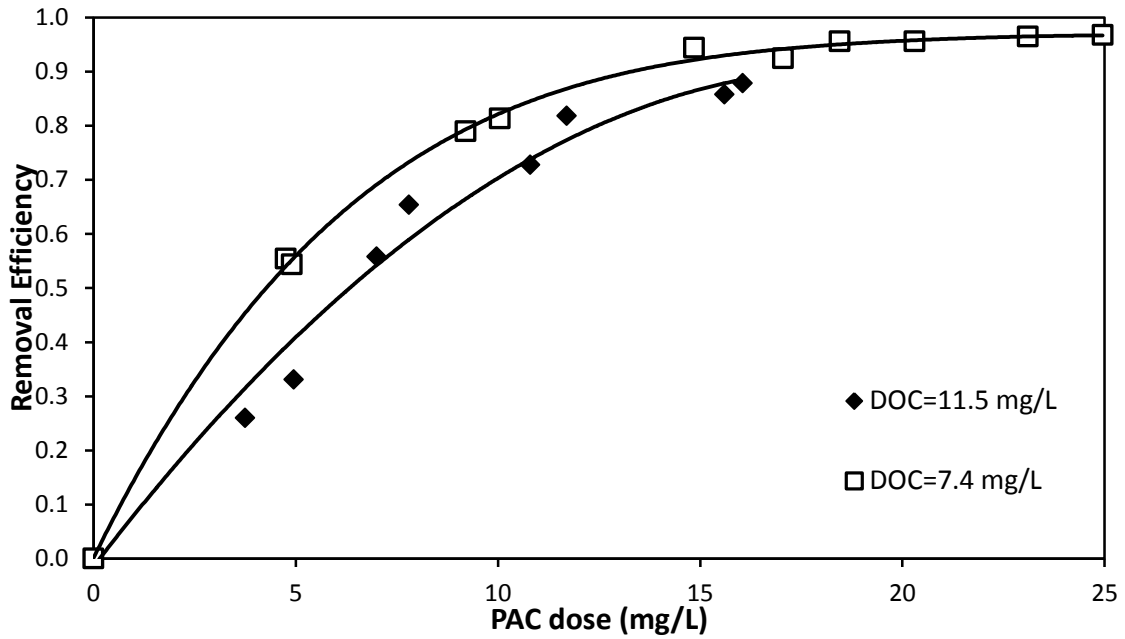


Figure I1- Effect of Mississippi River water DOC on geosmin removal efficiency in 195 minute jar tests simulating the pre-softening PAC addition point with Norit PAC 20BF

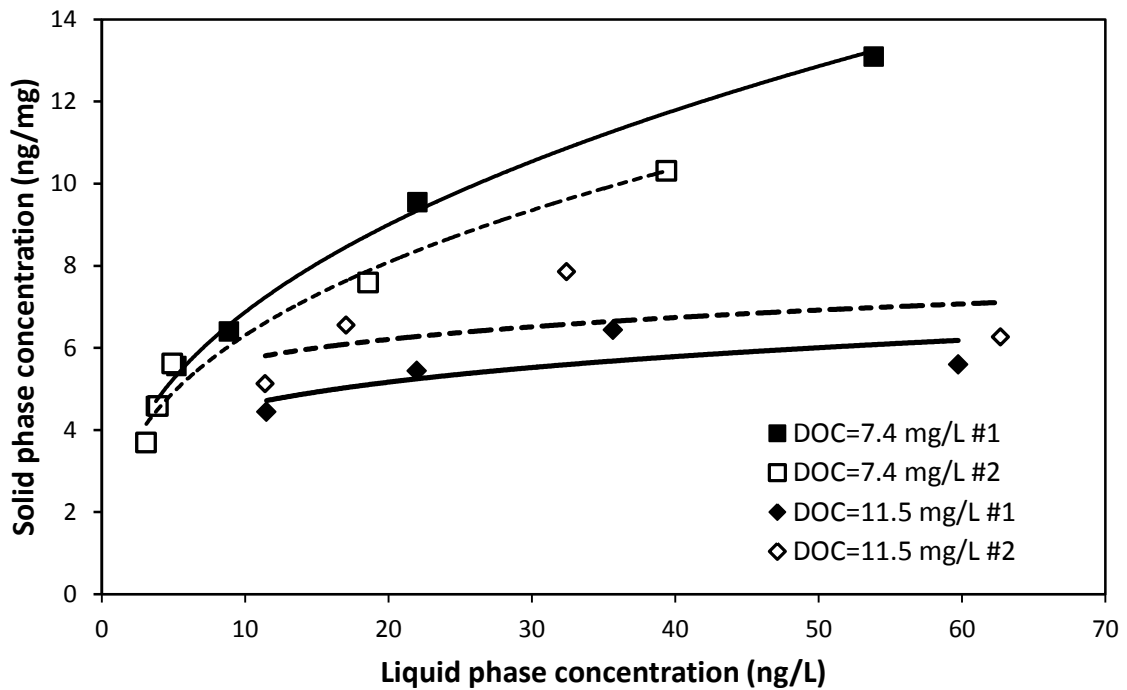


Figure I2: Isotherm plots for the geosmin sorption results shown in Figure I1

Appendix J: Repeatability of jar tests

Repeatability of two hour jar tests without lime

To help determine the repeatability of jar tests, duplicates for two experiments were performed. Results from duplicate jar tests performed without lime are shown in Table J1, Figure J1, and Figure J2. In these experiments, all variables were held constant (water batch, chemical doses, geosmin standard type). This data suggests that data sets are very similar for repeated duplicate experiments.

Table J1: Experimental conditions for two 2-hour jar tests with Carbon Resources 325AA

Experiment	C_0	T	pH	DOC
	ng/L	°C		mg/L
Carbon Resources 325AA #1	100.5	20.8	7.70	13.65
Carbon Resources 325AA #2	112.1	21.5	7.63	13.65

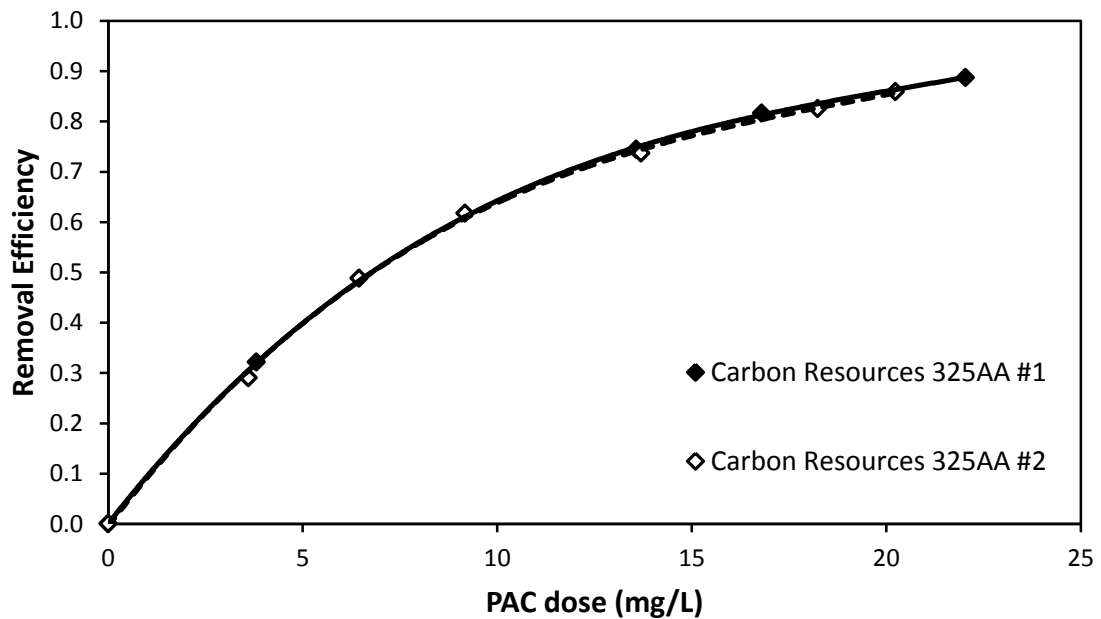


Figure J1: Repeatability of two-hour jar tests conducted Mississippi River water with Carbon Resources 325AA

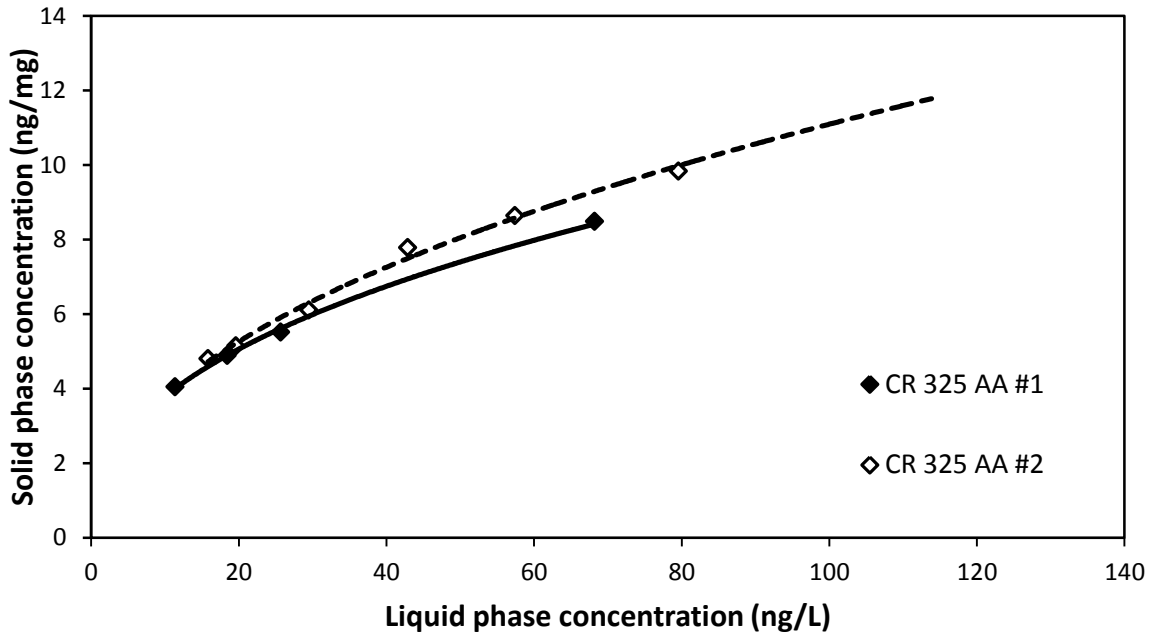


Figure J2: Isotherm plots for the geosmin sorption results shown in Figure J1

Repeatability of jar tests with lime and alum

Duplicate jar tests with lime and alum yield very similar data as shown in Figure J3. This data was previously shown in Appendix H. Experimental conditions and an isotherm comparison are shown in Table I1 and Figure I2. For the data at DOC=11.5 mg/L, two trendlines are plotted on Figure J3, but they overlap entirely.

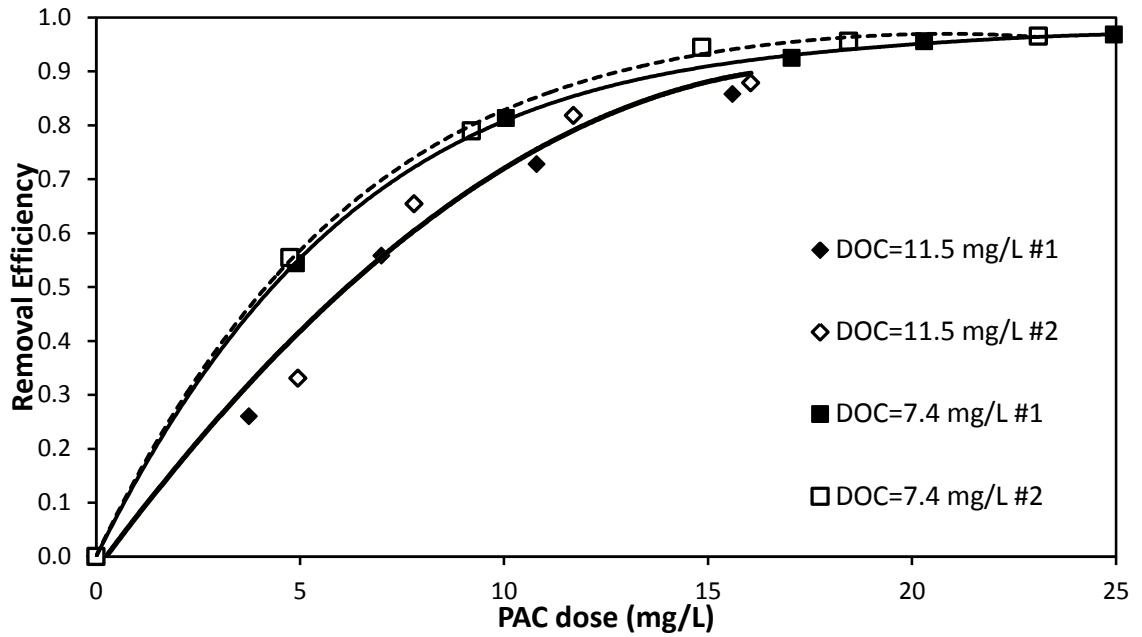


Figure J3: Repeatability of 195-minute jar tests with Mississippi River water simulating the pre-softening PAC addition point with Norit PAC 20BF

Appendix K: Additional experiments to determine the effect of lime and alum on PAC performance

Two hour jar tests were conducted to determine if the addition of lime and alum impacted the performance of freshly added PAC. In the first set of jar tests, 5 mg/L Norit PAC20BF was added to geosmin-spiked Mississippi River water and the water was mixed at 50 rpm for 120 minutes. In the second set of jar tests, lime and alum were added immediately following PAC addition, and the PAC dose, contact time, and mixing speed were the same as the first set. Results are shown in Table K1. When PAC was added alone, the mean removal efficiency was $38.0 \pm 8.7\%$ and when PAC was added with lime and alum, the mean removal efficiency was $39.8 \pm 4.8\%$. The results confirm the findings from section 4.2.2 that lime and alum do not inhibit sorption.

Table K1: Effect of lime and alum on geosmin removal from Mississippi River water by 5 mg/L Norit PAC 20BF in two hour jar tests

Experiment	C_o	C_{final}	Fraction removed	T	pH	DOC
	ng/L	ng/L		°C		mg/L
No lime #1	93	65.9	29.1	18.6	7.9	14.8
No lime #2	80.8	54.8	32.1	18.6	7.9	14.8
No lime #3	93.8	52.4	44.1	22.0	8.0	14.8
No lime #4	93.8	50.1	46.6	22.0	8.0	14.8
Lime/alum #1	98.4	65.3	33.7	18.6	7.9	14.8
Lime/alum #2	106.8	64.7	39.4	18.6	7.9	14.8
Lime/alum #3	93.8	51.3	45.4	22.0	8.0	14.8
Lime/alum #4	93.8	55.7	40.6	22.0	8.0	14.8

Appendix L



Figure L1: Image of HTA autosampler (top) and HP GC-MS (bottom)



Figure L2: Phipps and Bird jar test apparatus used for all jar test experiments