Organic Matter Occurrence in Arizona and Innovative Treatment by Granular Activated Carbon

by

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ABSTRACT

Population growth and fresh water depletion challenge drinking water utilities. Surface water quality is impacted significantly by climate variability, human activities, and extreme events like natural disasters. Dissolved organic carbon (DOC) is an important water quality index and the precursor of disinfection by-products (DBPs) that varies with both hydrologic and anthropogenic factors. Granular activated carbon (GAC) is a best available technology for utilities to meet Stage 2 D/DBP rule compliance and to remove contaminants of emerging concern (CECs) (e.g., pharmaceutical, personal care products (PCPs), etc.). Utilities can operate GAC with more efficient and flexible strategies with the understanding of organic occurrence in source water and a model capable predicting DOC occurrence. In this dissertation, it was found that DOC loading significantly correlated with spring runoff and was intensified by dry-duration antecedent to first flush. Dynamic modeling based on reservoir management (e.g., pump-back operation) was established to simulate the DOC transport in the reservoir system. Additionally, summer water recreational activities were found to raise the level of PCPs, especially skin-applied products, in raw waters.

GAC was examined in this dissertation for both carbonaceous and emerging nitrogenous DBP (N-DBP) precursors (i.e., dissolved organic nitrogen (DON)) removal. Based on the experimental findings, GAC preferentially removes UV254-absorbing material, and DOC is preferentially removed over

DON which may be composed primarily of hydrophilic organic and results in the low affinity for adsorption by GAC. The presence of organic nitrogen can elevate the toxicity of DBPs by forming N-DBPs, and this could be a major drawback for facilities considering installation of a GAC adsorber owing to the poor removal efficiency of DON by GAC. A modeling approach was established for predicting DOC and DON breakthrough during GAC operation.

However, installation of GAC adsorber is a burden for utilities with respect to operational and maintenance cost. It is common for utilities to regenerate saturated GAC in order to save the cost of purchasing fresh GAC. The traditional thermal regeneration technology for saturated GAC is an energy intensive process requiring high temperature of incineration. Additionally, small water treatment sites usually ship saturated GAC to specialized facilities for regeneration increasing the already significant carbon footprint of thermal regeneration. An innovative GAC regeneration technique was investigated in this dissertation for the feasibility as on-site water treatment process. Virgin GAC was first saturated by organic contaminant then regenerated in-situ by iron oxide nanocatalysts mixed with hydrogen peroxide. At least 70 % of adsorption capacity of GAC can be regenerated repeatedly for experiments using modeling compound (phenol) or natural organic matter (Suwannee River humic acid). The regeneration efficiency increases with increasing adsorbate concentration. Used-iron nanocatalysts can be recovered repeatedly without significant loss of catalytic

ability. This in-situ regeneration technique provides cost and energy efficient solution for water utilities considering GAC installation.

Overall, patterns were found for DOC and CEC variations in drinking water sources. Increasing concentrations of bulk (DOC and DON) and/or trace organics challenge GAC operation in utilities that have limited numbers of bed-volume treated before regeneration is required. In-situ regeneration using iron nanocatalysts and hydrogen peroxide provides utilities an alternative energy-efficient operation mode when considering installation of GAC adsorber.

To my beloved Mom and Dad.

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CHAPTER 1

INTRODUCTION

1.1 Background

Dissolved organic matter (DOM) affects water treatment processes (Alarconherrera et al, 1994) and plays an important role in the global carbon cycle by transferring carbon from terrestrial to aquatic and marine ecosystems (Hope et al, 1994). In most studies concerning DOM, dissolved organic carbon (DOC) is usually used as the surrogate for quantification. While controls on spatial DOC variations among freshwaters can be considered reasonably well understood (Hope et al, 1997), the causes of temporal change in DOC or other organic compounds at a particular site remain more uncertain. Drinking water has received considerable attention recently and many of the developed countries take safe drinking water for granted. In the last hundred years, safe water has been widely accessible after the introduction of chemical disinfectants. Subsequently, safe drinking water has become increasingly dependent on the widespread use of disinfection treatment and the importance of source water integrity is barely emphasized. This treatment-based approach leaves consumers highly vulnerable to process failure.

Safe Drinking Water

A multi-barrier approach was proposed by Watson & Lawrence begins with source protection, followed by a systematic development, installation and evaluation of treatment technologies for contaminant removal and monitoring. The multi-barrier approach is schematically described in lower part of Figure 1.1 as “Water Sources”, “Treatment”, and “Management”. Water sources represent clean freshwater resources from lakes, streams, and groundwater.

Drinking water is part of the global water cycle, which is a function of many abiotic and biotic processes. Three compartments which contribute to water source exacerbation prior to utilities are schematically described in the upper part of Figure 1.1, which are: i) climate variability, ii) anthropogenic activities, and iii) contaminants. Climate warming can lead to disturbances in the global water cycle by rising temperatures and hydrologic processes, with changing precipitation and runoff frequency and occurrence of extreme meteorological events (Milly et al, 2005; Zhang et al, 2007). Climate-induced disturbances represent an emerging challenge for integral water resources management giving the high demands from population growth and water pollution (Park et al, 2010). Extreme hydrologic have been observed in the recent decades and projected to increase in the future (Manton et al, 2001; Min et al, 2006). To date, there have been few efforts to assess the environmental impacts of climate variability on the freshwater resources in development world.

Climate Variability and Anthropogenic Activities

Increased climate variability, including extreme events such as floods and droughts, have been suggested to have significant impacts on water quality around the world (Murdoch et al, 2000; Worrall et al, 2003; Senhorst and Zwolsman, 2005; Park et al, 2010). Climate variability can impact human health and aquatic ecosystems through water quality deterioration caused by higher water temperatures, increased precipitation intensity, and longer periods of low flow (Park et al, 2010). In prior study, water quality deterioration and water facility failures due to recent extreme weather events across East Asia have clearly illustrated how climate event poses a major threat to both the quantity and quality of freshwater resources (e.g., Kim et al, 2000).

The climate variability impacts on surface water quality are summarized in upper part of Figure 1.1. Increasing concentration of these organics in drinking water sources due to direct/indirect impact of extreme weather or warming has been investigated in previous studies in Europe and North America (Park et al, 2010; Delpla et al, 2009; Monteith et al, 2007; Hongve et al, 2004; Worrall et al, 2004; Oppel et al; 2004; Hejzlar et al, 2003; Petterson et al, 2003; Mooij et al, 2003; Hunter, 2003). Additionally, these environmental factors and water parameters could interact to enhance water quality deterioration (e.g. increase temperature and nutrient concentration causes massive cyanobacteria bloom in lakes). As a consequence, water treatment cost will increase for regulation compliance and public health risk will also increase due to exacerbation of source water quality. For example, rainstorm events could lead to elevated levels of turbidity and organic matter found in surface waters, having a direct impact on coagulant demand during water treatment and on disinfection by-products (DBPs) formation (Shin et al, 2008).

Disinfection By-Product

The study on the occurrence of DBPs in drinking water system has increased in the recent years. Studies have showed that dissolved organic carbon (DOC) concentration in alum or iron treated water was directly related to the DBP formation potential (Uyak &Toroz, 2007; van Leeuwen et al, 2005). Except regulated DBPs (THM and HAA), non-regulated nitrogenous DBP (N-DBP) precursors is likely to increase in surface water due to impact of environmental change. Concerning the occurrence of trace organics (e.g. pharmaceutical) with respect to drinking water treatment, the efficiency of wastewater treatment could affect the quality of water resources downstream a treated effluent discharge. Anthropogenic activities are main sources of these organics in waters while extreme weather can increase the load by urban or agricultural runoff.

Dissolved organic nitrogen (DON) is commonly the dominant form of the total dissolved nitrogen (TDN) in pristine waters, but shows a lower proportion of TDN in human-impacted water (Perakis et al, 2002). Primary sources of DON in watersheds include forest litter, excretion of algal products in eutrophic waters, infiltration or runoff of organic fertilizers from agricultural areas, urban runoff, and upstream wastewater discharge (Tuschall & Brezonik, 1980; Bronk et al, 1971; Seitzinger & Sanders, 1997; Alberts & Takacs, 1999; Westerhoff & Mash, 2002). These impacted source waters can react with disinfectants to form greater concentrations of emerging nitrogenous disinfection by-products (N-DBPs) (e.g., haloacetonitriles (HANs), halonitromethanes, and nitrosamines) and affect the speciation of currently regulated disinfection by-products (e.g., trihalomethanes (THMs) and haloacetic acids (HAAs)) (Krasner et al, 2008; Mitch et al, 2008; Choi & Valentine, 2002; Najm & Truschall, 2001; Richardson et al, 1999).

Nitrogenous disinfection by-product (N-DBP) species occur in treated drinking waters at concentrations less than those of regulated carbonaceous DBPs (C-DBPs) (e.g., trihalomethanes (THMs) and haloacetic acids (HAAs)) (Krasner et al., 1989; Caughran et al., 1999; Krasner et al., 2006; Kemper et al., 2008). N-DBPs are important because they may exert greater mutagenic or carcinogenic risk than currently regulated DBPs (Plewa et al., 2004; Richardson et al., 2007; Muellner et al, 2007; Plewa et al., 2008). Increasing dissolved organic nitrogen (DON) concentrations in surface water resulting from upstream wastewater discharges, agriculture runoff and/or algal activity can lead to N-DBP formation upon application of disinfectants (Reckhow et al., 1990; Lee et al., 2007; Nam et al., 2008).

Granular Activated Carbon (GAC) for Organic removal

Granular activated carbon (GAC) is widely used in water treatment facilities to remove natural organic matter (NOM), taste and odor compounds, and contaminants of emerging concern (CECs) from drinking water (Ridal et al., 2001; Newcombe et al., 2002; Quinlivan et al., 2005). To design a full-scale column for a treatment process, information on the breakthrough of these compounds is often required; fortunately, laboratory column tests can be conducted to assess design parameters and performance. Rapid small-scale column tests (RSSCT) conducted over a period of days can simulate months of full-scale GAC operations data (Crittenden et al., 1986, 1987, 1999; Vidic et al., 1992; Knappe et al., 1997; Matsui et al., 2002; Westerhoff et al., 2005; Patni et al., 2008). As GAC usage becomes more widespread, its ability to aid in compliance with regulations on emerging DBPs is becoming a central justification for its usage. While GAC is an excellent treatment process for controlling currently regulated C-DBPs, no information is available on the use of GAC to control unregulated N-DBPs.

Catalytic Regeneration of Saturated-GAC

A Fenton-driven mechanism for regeneration spent granular activated carbon (GAC) was recently proposed and tested (Huling et al., 2007; Kommineni et al., 2003). Fenton (ferrous iron and hydrogen peroxide) and Fenton-like (ferric iron and hydrogen peroxide) processes are known to degrade a wide range of organic contaminants in soil and water by producing highly reactive and nonspecific free hydroxyl radical (·OH) (DeLaat and Gallard, 1999; Huling et al., 2000). It reacts with most organic compounds by adding to a double bound or by abstracting hydrogen atoms from organic molecules (Buxton et al., 1998).

The mechanism for producing free hydroxyl radicals in Fenton process is very complex and thought to occur in the following stages (Neyens and Baeyens, 2003):

$$Fe^{+3} + H_2O_2 \rightarrow Fe\text{-}OOH^{+2} + H^{+} \qquad (1)$$

$$Fe\text{-}OOH^{+2} \rightarrow Fe^{+2} + HO_2\cdot \qquad (2)$$

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH\cdot + OH^{-} \qquad (3)$$

$$Fe^{+2} + OH\cdot \rightarrow Fe^{+3} + OH^{-} \quad (4)$$

$$H_2O_2 + OH\cdot \rightarrow HO_2\cdot + H_2O \quad (5)$$

$$2Fe^{+2} + H_2O_2 + 2H^{+} \rightarrow 2Fe^{+3} + 2H_2O \quad (6)$$

The first three equations are responsible for the continuous production of the active hydroxyl radical. Equation (4) and (5) represent for the decay of this radical (scavenging) and the final one is for reducing the peroxide concentration.

As a summary, Fenton- and Fenton-like-driven regeneration of granular activated carbon shared several benefits:

(1) the oxidation process caused less carbon mass loss (< 0% AC loss) compared with thermal regeneration (5-15% AC loss);
(2) high regeneration efficiency (97-99%) in scale of hour;
(3) occurred at room temperature (Bach et al., 2008);
(4) no UV or visible light was needed (Bach et al., 2008);
(5) large number of adsorption-recovery cycles (5~10 cycles);
(6) without a reduction in the adsorptive properties of the virgin activated carbon;
(7) insignificant total surface area decline (2%);
(8) iron impregnated after oxidation process;
(9) high recovery of adsorption capacity (>90%) and destruction efficiency of contaminants after treatment;
(10) reasonable cost for H_2O_2 (Kommineni et al., 2003);

The use of GAC is a delimma for many utilities because of its high cost, long down-time and CO_2 production during regeneration. A low maintenance and energy cost of on-site GAC regeneration technique could provide better solution for facilities consider installing GAC adsorber.

1.2 Aim of Research

The aim of this dissertation is to investigate the water quality response in rivers and reservoirs under variable climate conditions in Arizona and evaluate virgin-GAC and a novel GAC regeneration process to control organic nitrogen, DBP and DBP precursors. Bulk and CECs organic concentration and loading patterns are examined for the three primary raw water supply reservoirs serving more than 3.5 million inhabitants in the Phoenix, Arizona metropolitan area. The reservoirs are on different river systems - Verde, Salt, and Colorado / Agua Fria Rivers - and operate differently. The results of these analyses provide a better understanding of long-term water quality response under climate change and lead to improved source water quality prediction and management. Understanding GAC performance on removal of emerging nitrogenous DBP precursors along with bulk organic matter and subsequent regeneration helps to assess the feasibility of GAC installation at water treatment plants.

As part of a long term water quality monitoring project, significant amounts of background organics data (1999 to 2007) in three surface water sources for metro-Phoenix area, along with new data I collected is used in this research. DOC and hydrologic data are used to determine DOC mass fluxes through the Salt and Verde River systems and to parameterize a predictive DOC concentration model for the Salt River. I evaluate wet season, prolonged drought, forest fire, and seasonal impacts on DOC in these reservoirs. Investigation of emerging contaminant was conducted (September 2007 to July 2009) by collecting samples from watersheds, canals, groundwater near recharging site, wastewater plants and one water treatment plant. Correlation between wastewater impacts, recreation and location within the water supply system provide insight into previously undocumented levels of CECs in Arizona.

Laboratory tests evaluated GAC adsorption capacity for C-DBP and N-DBP precursors. This is the first study of DON removal by GAC. Waters collected from water treatment plants and their source waters were evaluated using rapid small-scale column tests (RSSCTs) with GAC to establish DON breakthrough profiles. The formation of C-DBPs (THM and HAA) and N-DBPs (HAN) after GAC treatment were measured as a function of RSSCT operation time. A predictive model for DOC and DON removal by GAC was developed as part of an overall DBP control strategy.

Additional lab tests evaluated a new in-situ iron-nanoparticle-based catalytic regeneration for spent-GAC to provide alternative non-thermal, in-situ approach. In order to reproduce iron nanoparticles (NPs) with consistent size, the impact of temperature and reaction time on hematite nanoparticle during hydrolysis was investigated. An empirical model was developed by synthesizing hematite NPs at different temperatures and hydrolysis times, and correlating them to the obtained nanoparticle sizes. Phenol was selected as model contaminant to examine the efficiency of in-situ catalytic regeneration of GAC by iron NPs. The relative small molecular size of phenol allows it to penetrate into GAC pores which challenges the in-situ regeneration process. Variable phenol concentrations in feed water to GAC columns allowed examination of the in-situ regeneration efficiency on different GAC solid phase phenol concentrations. Swannee River NOM was used to determine the regeneration efficiency of GAC adsorbed with natural organics rather than phenol.

Overall my dissertation attempts to answer the following questions:

1) Given the extreme variability in hydrologic conditions typical of arid climates, how much variation in reservoir DOC concentrations and loadings occur? What is the impact of anthropogenic activities on emerging contaminants occurrence in urban water system?
2) How efficiently is DON removal relative to DOC removal by GAC? How can predictive empirical DOC breakthrough models be extended to simulate DON breakthrough?
3) How can iron NPs be applied for in-situ catalytic regeneration of exhausted-GAC? What are the benefits and limitations for adopting this in-situ regeneration process?

1.3 Description of Chapters

Chapter 2 (Hypotheses) presents the development of the hypotheses that will serve as the basis for this research.

Chapter 3 describes the variation of dissolved organic carbon in three arid-region water supply reservoirs in Arizona. The effect of hydrologic variability on water quality response was investigated by comparison between different hydrologic years. This chapter addresses part of *Hypothesis 1*: The variability of bulk and CECs organic concentration in reservoirs and/or urban water systems has been impacted by meteorological factors, reservoir operations, and/or anthropogenic activities.

Chapter 4 evaluates the DOC occurrence and transport in Salt River multiple-lake system impacted by hydrology and reservoir operation by modeling approach. This chapter addresses part of Hypothesis 1.

Chapter 5 investigates emerging contaminant occurrence in urban water system in Arizona. This chapter addresses part of *Hypothesis 1* and provides a case of anthropogenic activities impact on CEC occurrence in surface water.

Chapter 6 examines GAC breakthrough patterns of organic nitrogen and bulk organics, as precursors for C-DBP and N-DBP formation. Models are developed for both DOC and DON breakthrough prediction. This chapter answers *Hypothesis 2*: GAC removes carbonaceous-DBP precursors better than N-DBP precursors.

Chapter 7 builds up an empirical model for synthesis of hematite iron-NPs using forced hydrolysis method. The effect of temperature and aging time on the particle size was examined. This chapter was designed to synthesize hematite NPs which might be able to serve for in-situ GAC regeneration.

Chapter 8 compares hematite NPs to another synthesized iron (hydr)oxide NPs in the ability to serve as catalyst in catalytic oxidation process. The one which shows faster organic removal rate is selected for the test of in-situ GAC regeneration in *Chapter 9*.

Chapter 9 establishes in-situ GAC regeneration method and examines multiple adsorption-regeneration cycles and the effect of adsorbate concentration. This chapter addresses the first part of *Hypothesis 3*: Iron-NPs plus H_2O_2 can regenerate GAC in-situ for control of dissolved organics.

Chapter 10 integrates findings from the hypotheses (*1, 2, and 3*) and provides a synthesis for the research.

Chapter 11 provides the summary and conclusion of the search, and future research needs.

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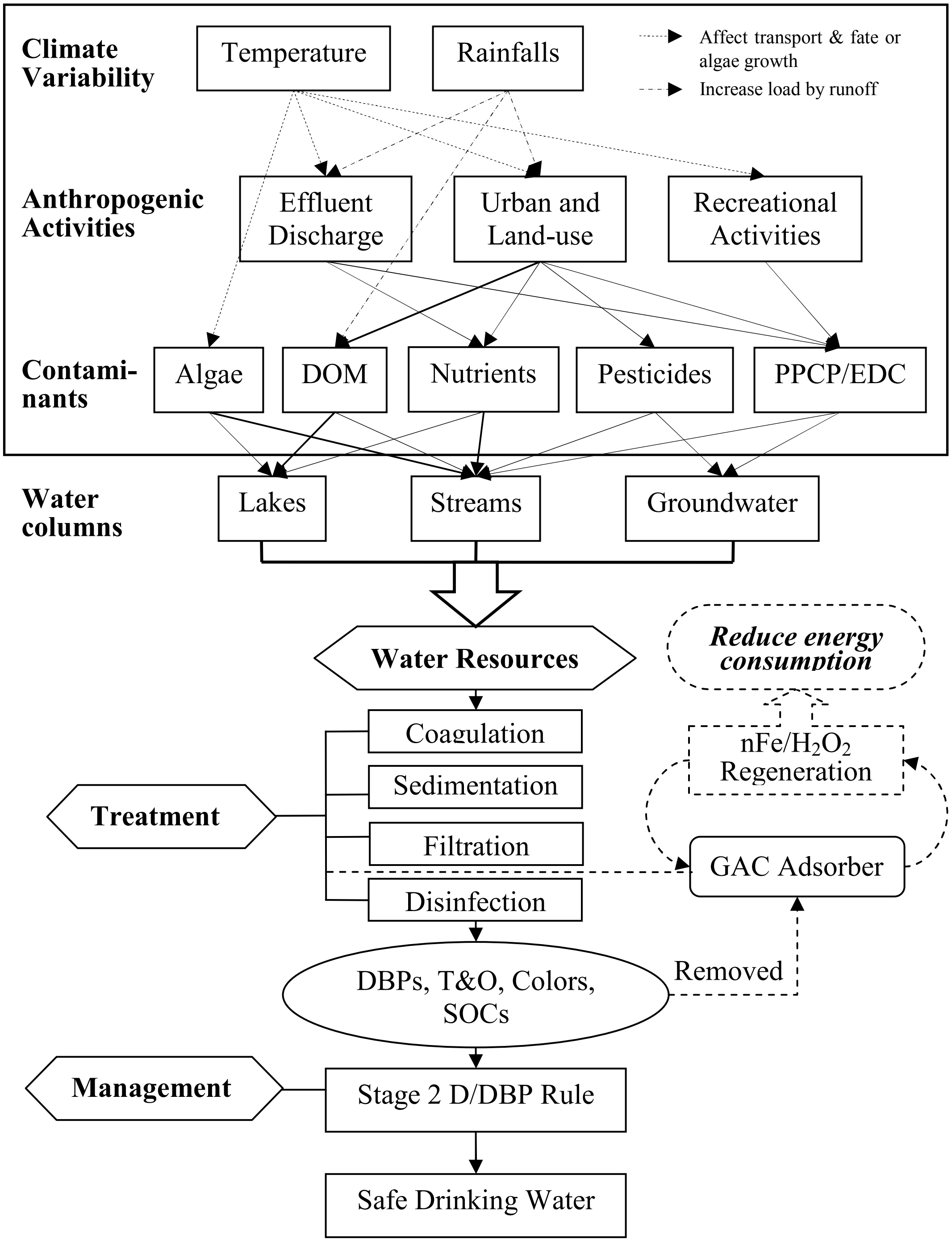

Figure 1. 1 Environmental change impacts and multi-barrier approach to safe drinking water with novel GAC regeneration technique. The dash line represents the innovative technique of on-site regeneration for spnet-GAC.

CHAPTER 2

RESEARCH HYPOTHESES

This research focuses on using in-situ regenerable GAC as a sustainable strategy of unregulated N-DBP and regulated C-DBP formation control for water facilities facing climate variability and increasing anthropogenic activities. This research provides insight into overall management of regulated and unregulated DBP formed from climate-impacted NOM occurrence and cost assessment as facilities consider installing GAC coupled with in-situ regeneration technique for spent-GAC. **The goal of this dissertation is to investigate the water quality response in rivers and reservoirs under variable climate conditions in Arizona and evaluate virgin-GAC and a novel GAC regeneration process to control organic nitrogen, DBP and DBP precursors.** To achieve this goal, the research approach is divided into three components. First, I collected samples and analyzed historical data to understand and predict the impact of climate change on bulk and CECs organic occurrence in drinking water sources. Second, because of increasing stringent DBP regulations and recognition of decadonal variation in DBP precursors due to climate variability, for the first time I provide data on DON removal by GAC compared against DOC removal as a means of removing N-DBP precursors. Third, I present a novel in-situ regeneration technique to increase the inclination for facilities to install GAC for DBP mitigations. The research addresses the following three hypotheses:

2.1 Hypothesis # 1: The variability of bulk and CECs organic concentration in reservoirs and/or urban water systems has been impacted by meteorological factors, reservoir operations, and/or anthropogenic activities.

In semi-arid regions of the southwestern US, environmental conditions (e.g., intermittent runoff, spring storm, snowmelt, wildfire, etc.) may result in pulses of DOC into reservoirs. Reservoir management (e.g., increased hydraulic retention time) may be able to attenuate DOC concentration in water treatment plants downstream. As a consequence, DOC loading from terrestrial sources, especially after extreme events (e.g., drought) would be impacted significantly by meteorological factors and reservoir operations. Additionally, anthropogenic activity may lead to detectable levels of CECs in the Phoenix urban water system. A case study was conducted to examine the significance of emerging contaminants occurrence from human recreational activities.

2.2 Hypothesis # 2: GAC removes carbonaceous-DBP precursors better than N-DBP precursors.

GAC is considered as barrier to handle broad range of bulk organics and CECs with variable concentration. While granular activated carbon is an excellent treatment technique for controlling currently regulated carbonaceous DBPs, little information is available on the use of GAC to control unregulated nitrogenous DBPs, and none for DON specifically. GAC breakthrough profiles are developed for DOC, DON, UV254 absorbance material and bromide, as well as subsequent formation and speciation of regulated DBP (THM and HAA5) and unregulated DBP (e.g., haloacetonitriles). Three river waters and three water treatment plant treated waters are used to consider the breakthrough of potential water sources which could be treated by GAC. A unique aspect of this work is use of coagulated surface waters, rather than source waters, because coagulation tends to remove similar NOM fractions as GAC. Rapid small-scale column tests (RSSCTs) are used to simulate full-scale GAC adsorption to demonstrate the removal of bulk organic materials and potential DBP precursors.

Models capable of simulating DOC breakthrough are developed to aid in understanding how GAC reacts under a range of influent NOM and operating conditions (EBCT). These include climatic variations that could lead to DOC levels from 2 to 7 mg/L. A modeling approach developed previously (Zachman et al., 2007) is modified for coagulated waters and expanded to include DON removal.

2.3 Hypothesis # 3: Synthesized iron NPs plus H_2O_2 can regenerate GAC in-situ for control of dissolved organics.

GAC is very effective in removing organics from liquid and gas streams in facilities for compliance of more stringent USEPA regulations on DBPs and presence of CECs, taste and odor compounds, etc. in drinking waters which pose aesthetic and/or perceived/actual human health risks. However, operational costs for GAC can be extremely high in cases when NOM breakthrough occurs rapidly with limited number of bed volumes treated. Once saturated with organics, GAC adsorber must be removed from the contactors, once saturated, and thermally re-activated, because it is roughly half the cost of purchasing virgin GAC, and then replaced in the contactor. Thermal regeneration is very capital intensive and requires a significant investment in equipment, operation, and maintenance and up to 10% of GAC is destroyed during this process. The carbon dioxide footprint and associated energy costs of thermal reactivation pose significant burdens on water facilities. An iron NPs-based catalytic regeneration technique was investigated to enable in-situ regeneration of GAC without removing it from the contactors and mineralizes contaminants in the same reactors which could reduce the cost and carbon dioxide footprints as a measure of sustainability.

In order to reproduce iron nanoparticles (NPs) with consistent size, the impact of temperature and reaction time on hematite nanoparticle during hydrolysis was investigated. An empirical model was developed by synthesizing hematite NPs at different temperatures and hydrolysis times, and correlating them to the obtained nanoparticle sizes. Based on the systematical synthesis method, hematite NPs were prepared in comparable size to another synthesized iron (hydr)oxide NPs according to method developed by research group of Dr. Semiat in Israel Institute of Technology. These two synthesized iron NPs with similar particle size were tested for catalytic ability during Fenton-like reaction; the one showed better organic oxidation rate was used to serve as catalyst for in-situ GAC regeneration.

Multiple cycles of phenol adsorption and iron nanoparticle regeneration are performed to investigate this unique regeneration process. My work varies from an initial study of iron nanoparticle regeneration of GAC by varying phenol concentration to more relevant levels, evaluating regeneration of GAC loaded with NOM. Iron NPs are shown to be catalysts and as such could be recovered and reused for multiple regeneration cycles for saving operation cost further. The iron NPs synthesized from ferric chloride, a chemical already having NSF certification for use in WTPs, can be produced on-situ. Thus, adaption of this technology may be quite rapid.

CHAPTER 3

DISSOLVED ORGANIC OCCURRENCE IN SOUTHWESTERN US WATERSHEDS AND RESERVOIRS

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Abstract

Climate variability in the southwestern USA impacts the frequency and severity of extremes such as storms, floods, droughts and forest fires. Understanding vulnerabilities to such changes is important in understand future impacts on human health, society and the environment, namely in terms of water quality in drinking water supplies. Dissolved organic carbon (DOC) concentrations in drinking water sources vary during abrupt extreme events, resulting in increasing treatment costs and public health risk. DOC concentration trends from three freshwater reservoirs (Saguaro Lake, Bartlett Lake and Lake Pleasant) in adjacent watersheds are investigated to determine the water quality responses under climate changes. DOC loading from watershed in early spring is associated with surface runoff exhibits strong variability. The impact of spring flush could be delayed and attenuated in multiple-lake system (Salt River). Single lake system (Bartlett Lake) is more vulnerable to extremes such as winter storm and the dry duration antecedent to first flush will enhance the severity of the scenarios.

Key words: Organic carbon; Hydrology; Reservoir; Climate variability

3.1 Introduction

Dissolved organic carbon (DOC) is a material in freshwater that can be transported and transformed through natural biogeochemical processes (biodegradation, photolysis, hydrolysis, adsorption, precipitation, sedimentation) (Hertkorn et al., 2002; Barber et al., 2001). Aquatic DOC concentration and structural composition in many surface water ecosystems depends on characteristics of the watershed (Aiken and Cotsaris, 1995). Organic matter is produced by soils and plants of the terrestrial water shed (allochthonous DOC) or from biological growth and decomposition of algae and macrophytes within lakes or reservoirs (autochthonous DOC) (Baron et al., 1991; Tate & Meyer, 1983). Terrestrial plant and soil sources contribute allochthonous organic matter to a stream mainly during runoff from overland water flow during rainfall events (McKnight et al., 1994; Onstad et al., 2000). Algae and bacteria (autochthonous sources) produce and consume or alter the concentration and composition of organic matter (McDowell and Likens, 1988; Leff and Meyer, 1991). Hydrologic flow paths and quantities of runoff water impact the relative importance of these DOC flux processes to impact DOC levels in drinking water supplies.

DOC is a precursor in the formation of carcinogenic by-products during drinking-water treatment when chemical disinfectants (e.g., chlorine) react with DOC to form disinfection by products (DBPs) (Reckhow et al, 1990, Amy et al, 1987). The amount and chemical nature of DOC are important to influence DBP formation. Previous studies have shown that humic substances with high aromatic content and molecular weight yield more DBPs upon chlorination (Reckhow et al., 1990). Amy et al. (1987) showed that the parameter of untraviolet absorbance (UVA) × DOC was a good predictor of DBP formation potential. Specific UVA (SUVA = UVA/DOC) correlates with aromatic content and is also a good surrogate of DBP precursors, (Weishaar et al., 2003; Traina et al., 1990). Allochthonous sources of natural organic matter (NOM) have higher SUVA than from autochthonous sources.

Temperate weather conditions prevail through most of the USA and Western Europe and contribute to maintaining a constant source of terrestrial organic material for surface waters and soils. These allochthonous carbon inputs contribute significantly to the global carbon cycle (Malcolm et al., 1990). The transportation of DOC originating in temperate climates has been intensively studied and the processes involved are reasonably well understood. Arid regions throughout the world are experiencing rapid population growth and areal expansion, necessitating development of large urban areas requiring extensive water infrastructure systems (e.g., reservoirs, water treatment plants, distribution systems). In these regions, higher air and water temperatures, greater seasonal hydrologic variations, and widespread impoundment of rivers suggests that DOC sources and transportations could be different from that found in terrestrial system. Water storage reservoirs in arid and semi-arid regions, like Arizona, are implemented with longer hydraulic residence times (HRT) and most likely altered the DOC characteristics in these freshwater systems (Nguyen et al., 2002; Westerhoff and Anning, 2000; Parks and Baker, 1997).

Whereas autochthonous DOC and other algal extracellular by-products (methylisoborneol (MIB) and geosmin) originating in US Southwestern reservoirs has been discussed in literatures (Westerhoff et al., 2005; Mash et al., 2004), little is known about the impact of extreme meteorological events on the DOC responses in downstream reservoirs and utility water sources. In arid and semi-arid regions of the southwestern USA, a typical annual hydrologic sequence for major rivers includes a major hydrologic pulse associated with upland snowmelt, followed by a prolonged dry period with low stream flow. DOC loading and characteristic in Southwestern US reservoirs reflect the hydrologic inputs, dominated by early spring snowmelt, with low DOC loading during the dry season. A small but significant DOC pulse during the first monsoon events in the early summer months was reported (Nguyen et al., 2002; Westerhoff and Anning, 2000; Parks and Baker, 1997). The Intergovernmental Panel on Climate Change (IPCC) projects the likely to virtually certain changes in different extreme events globally (e.g., heavy precipitations, droughts, and heat waves) between now to 2100 (IPCC, 2007). According to The Flood Control District of Maricopa County, more extreme weather events such as winter storms and summer droughts were observed in Arizona over the last ten years (website of Flood Control District of Maricopa County). Consequently, these events would result in variability of DOC concentration and cause challenge for utilities to meet regulation compliance. A limiting factor to assessing variability of DOC in southwestern USA watersheds has been a plausity of consistently collected water quality data at key locations, superimposed by major changes on water infrastructure operations. Over the past decade our group has developed a comprehensive database spanning drought, flood and "normal" climate periods.

Differing hydrology and water management practices of three surface water sources serving the metropolitan Phoenix in Arizona of 3.5 million peoples off the opportunity to study climate variability on a key water quality parameter for drinking water sources, namely DOC. The objectives of this study are to 1) analyze the long-term DOC occurrences and characteristics in three major reservoirs in Arizona, 2) determine the impact of climate variability on DOC loading, and 3) develop a dynamic model for understanding of DOC transportation in multiple-lake system. The findings are interpreted in light of potential future impacts of droughts, forest fires and floods on drinking water utilities. While climate variability impacts water availability (quantity), many cities have multiple sources in their water portfolios, and thus our analysis focus on water quality rather than quantity for each source.

3.2 Materials and Methods

3.2.1 Site Descriptions

The drinking water supply to nearly 3.5 million people of the Phoenix metropolitan area is provided by the Salt River watershed, which originates in the White Mountains of eastern Arizona and New Mexico, and the Central Arizona

Project (CAP), which delivers water from the Colorado River (below Lake Havasu) via a 150 miles canal system. Lake Pleasant is a fill-and-drain reservoir in central Arizona on the Agua Fria River which is used for seasonal storage of Colorado River water via the CAP canal system. There are four reservoirs on the main Salt River (Roosevelt Lake, Apach Lake, Canyon Lake, and Saguaro Lake) and two on the Verde River (Horseshoe Lake and Bartlett Lake), which joins the Salt River below the lowermost mainstream reservoir. These reservoirs store water derived mainly from snowmelt at higher elevations. Precipitation during the winter months in Arizona is generally from broad regional storms and falls as rain at lower elevations or as snow at higher elevations, or during the summer as thunderstorms (i.e. monsoons) (Mash et al, 2004). A site location map for the reservoirs and rivers is shown in Figure 3.1.

Saguaro Lake is the lowest of four reservoirs on the Salt River, and used for water storage and flood control. Three of the upstream Salt River reservoirs have hydropower generation facilities, and water is pumped back from Saguaro Lake to Canyon Lake and Apach Lake during summer months through pump-back piping to increase hydropower revenue. Saguaro Lake also has single outlet located near the bottom of the dam. Most releases occur in the summer (> 8.5 m^3/s) with minimal release (~0.1 m^3/s) between October and April. Water levels of Saguaro Lake fluctuate by less than five meters throughout the year.

Bartlett Lake is an on-stream reservoir on the Verde River located 3 km downstream of Horseshoe Lake. Horseshoe Lake is small and was less than 30%

capacity during most of the study period. Most water enters the reservoir following snowmelt at higher elevations between February and May and is stored throughout the summer, with minimal release to maintain channel flow in the Verde River. Water levels fluctuated between 10 to 20 meters for Bartlett Lake during the current study. Further information on the limnology of Bartlett Reservoir is available elsewhere (Nguyen et al., 2002; Parks and Baker, 1997).

Lake Pleasant is an off-stream water supply reservoir near the Central Arizona Project canal (CAP) located on the Agua Fria River. It is filled with water pumped from Colorado River through an open, concrete-lined CAP Canal approximately 200 km in length between October to April. Water is released from Lake Pleasant between April and October through two dual inflow/outflow release gates near the dam. Natural drainage from the Agua Fria River supplies a small amount of inflow (< 10% of the reservoir inflow during this study period) to Lake Pleasant. Water levels fluctuated considerably (> 30m) throughout the year.

3.2.2 Dissolved Organic Carbon Mass Balance

Annual reservoir hydrological data (1999 to 2011) obtained from US Geological Survey (USGS), Salt River Project (SRP) and CAP was used to develop DOC mass balances. Continuous flow records (daily average) were used to compute river inflow and reservoir outflow volumes and were taken at three locations: 1) Salt River below Steward Mountain Dam (USGS station 09502000), 2) Verde River below Bartlett Dam (USGS station 09510000), and 3) Agua Fria River near Rock Spring (USGS station 09512800). Monthly reservoir storage for four lakes along Salt River and Bartlett Lake and Lake Pleasant were obtained from SRP or CAP and used to complete the DOC mass balances. Based on the conservation of mass, the DOC mass loading exported from watershed and/or reservoirs upstream was calculated as follows:

$$\begin{aligned}&\text{Inflow loading of DOC mass (kg)}\\&=(\text{Storage}_{final}-\text{Storage}_{initial})+\text{Outflow loading}\ \pm\ \text{Reaction}\end{aligned} \qquad \textbf{Eq.1}$$

where $\text{Storage}_{\text{initial}}$ and $\text{Storage}_{\text{final}}$ are the DOC mass stored in reservoir at the beginning and the end of a month; Outflow loading represents the total DOC mass that outflows from reservoir; Reaction represents the source/sink of DOC.

3.2.3 Field Sampling

Monthly grab samples were collected at a depth of 1m below the water surface from three main reservoirs (Saguaro Lake, Bartlett Lake, and Lake Pleasant) during the study period. Hypolimnion samples (~ 15 m) were also collected and analyzed which showed less than 10% difference from surface concentration during most of study period. In addition, samples were also collected from Salt River near the inlet to Roosevelt Lake during 2002 to 2004 to investigate the impact of Rodeo-Chediski wild fire during early summer in 2002 on downstream water quality. Reservoir samples were collected from a boat with a Kemmerer sampler and the river water was collected by grab samples taken from the bank. The USGS collected samples from the site of upstream Salt River near Roosevelt inlet (USGS station 09498500) between 2002 and 2004. All DOC-related samples were collected in acid-washed, oven-ashed (550ºC) 1-L amber glass bottles. Samples were filtered through an ashed (550ºC) 0.7 µm filter

(Whatman glass fiber filters, GF/F) and stored in acid-washed, pre-ached (550ºC) 40mL amber glass vials. DOC and UV absorbance at 254 nm wavelength (UVA254) analyses were conducted within one week of sample collection.

3.2.4 Laboratory Analyses

DOC was measured using a Shimadzu TOC-V_{CSH} analyzer (high temperature combustion at 720°**C** non-dispersive infrared detection with TNM-1 unit chemiluminescence detection) (Shimadzu Corp., Tokyo, Japan). Before analysis, water samples were acidified with hydrochloric acid to pH 2~3 to remove inorganic carbon during purging by nitrogen gas. Blank samples (prepared from Nanopure water) and quality control (QC) samples are inserted between every 10 samples. UVA was measured with a Shimadzu UV-1601 variable wavelength spectrophotometer and a 1-cm path length quartz cuvette. Blank sample prepared from Nanopure water is run for each experimental set as quality control sample. Specific UVA (SUVA) was determined by normalizing UVA to DOC concentration (UVA/DOC). Increasing SUVA values indicate a higher density of sp^2-hybridized carbon-carbon double bonds and a larger degree of humification (Chin et al., 1994; Westerhoff et al., 1999).

3.3 Results and Discussion

3.3.1 Reservoir Hydrology

Saguaro Lake remained near full capacity typically with very little (2-4 m) variation in surface elevation) for hydropower generation through the study period (1999 to 2010) (Table 3.1). During summer, the pump-back piping from Saguaro

Lake to upstream reservoirs pumped the water released from upstream during peak demand time (daytime) back to the reservoirs upstream during off-peak time (nighttime). This operational mode resulted in a very short reservoir hydraulic residence time (HRT = outflow/volume = ~70 days) (Table1). During this period, the inflow ranged from 0.2 to 0.7 × 10^5 acre-ft (2.3 to 8.3 × 10^7 m^3) during May to October, and ranged from 0.05 to 4.5 × 10^5 acre-ft (0.7 to 5.5 × 10^7 m^3) during November to April. Most of the water entering the reservoirs system occurred during May to August in each year (> 50%).

Bartlett Lake is located on the lower end of the Verde River and is an on-stream reservoir 3 km downstream of Horseshoe Lake. Bartlett Lake was at less than 30% capacity during the study period (Table 3.1). Water from Verde River entered the Horseshoes Lake following snowmelt at higher elevations between February and May and was stored throughout the summer and release from October to April. The inflow ranged from 0.1 to 0.2 × 10^5 acre-ft (1.3 to 2.2 × 10^7 m^3) during May to October, and ranged from 0.2 to 0.7 × 10^5 acre-ft (0.2 to 8.4 × 10^7 m^3) during November to April. This operational mode resulted in an increase in storage volume (+9000 acre-ft [1.1 × 10^7 m^3] in average) during summer and a decrease in storage volume (-9000 acre-ft [1.1 × 10^7 m^3] in average) during the rest of seasons (Table 3.1).

Lake Pleasant is an off-stream reservoir located on the Agua Fria River near the Central Arizona Project and was at less than 60% capacity from 1999 to 2010 (Table 3.1). Water pumped from Lake Havasu on the Colorado River was pumped from the CAP canal to fills Lake Pleasant from October to April and the Lake Pleasant water was released into the CAP canal between May to September during the study period. The operational mode resulted in lower inflow (0.07 × 10^5 acre-ft [0.8 × 10^7 m^3] in average) between May to October than the rest of months (0.7 × 10^5 acre-ft [9.0 × 10^7 m^3] in average). Natural drainage from the Agua Fria River released a small amount of additional inflow (0.01 to 0.8 × 10^5 acre-ft [0.1 to 9.2 × 10^7 m^3] per year) to Lake Pleasant during the study period except for 2005 (2.2 × 10^5 acre-ft [27 × 10^7 m^3]) per year and 2010 (1.2× 10^5 acre-ft [16 × 10^7 m^3]). As a result, the reservoir storage decreased (-29000 acre-ft [3.3 × 10^7 m^3] in average) between May to October and increased (+29000 acre-ft [3.3 × 10^7 m^3] in average) during other months (Table 3.1).

3.3.2 Organic Matter Trends in Major Reservoirs of Arizona

Long term trends of DOC concentration in three major reservoirs showed different patterns during the last ten years. The variations of DOC concentrations are plotted against time in Figure 3.2.

From 1999 to 2010, the yearly average DOC in Saguaro Lake increased from 3 mg/L to 5 mg/L with two higher levels observed in 2005 and 2008 (yearly average DOC = 5.7 and 5.5 mg/L, respectively). In terms of seasonal variation, the average DOC concentration was 5.0 ± 0.4 mg/L during May to October and was 4.5 ± 0.2 mg/L during November to April. UVA254 absorbance varied from 0.084 to 0.099 within a year. The yearly variation of DOC in Saguaro Lake was less than observed in other reservoirs (Figure 3.2a) which can be attributed to the hydrological management and operational mode of multiple-lake system for Salt River.

The long-term DOC trend in Bartlett Lake showed a strong variation and tended to increase (from 2 mg/L to 4 mg/L) over the last ten years (Figure 3.2b). With respect to seasonal variation, the average DOC concentration was 3.6 ± 0.3 mg/L during May to October and was 3.3 ± 0.4 mg/L during November to April. UVA254 absorbance varied from 0.07 to 0.13 within a year. In 2003, 3005, 3008, and 2010, high DOC concentration and variation were observed. Although Bartlett Lake is the lower reservoir of the two reservoirs system on Verde River, the upper reservoir – Horseshoe Lake – is operated with short hydraulic residence time (~60 days) (Table 3.1) and is completely drawn down during the summer.

For Lake Pleasant, the yearly averaged DOC showed a little increase from 3 to 3.8 mg/L during the study period with medium yearly variation compared with other reservoirs (Figure 3.2c). The average DOC concentration was 3.8 ± 0.2 mg/L during May to October and was 3.4 ± 0.1 mg/L during November to April. UVA254 absorbance varied from 0.05 to 0.06 within a year. High DOC responses only occurred in 2003 and 2005. The stable DOC in Lake Pleasant might result from the relative long hydraulic residence time (400 days) (Table 3.1) and water management and operation as off-stream reservoir.

The temporal pattern of inflows and DOC concentrations into each reservoir differ within a year (Figure 3.4.3). The highest inflow to Bartlett Lake occurred during January to March of each year and it accounted for 55% of yearly inflow. The highest DOC concentrations were observed in March and June (~ 4 mg/L) in Bartlett Lake (Figure 3.3a). For Saguaro Lake, the main inflow during a year was occurred during late spring to early fall especially from June to August and the highest DOC concentration was 5.5 mg/L in June (Figure 3.3b). There was very low inflow to Lake Pleasant during summer and the highest inflows were occurred from November to February. The highest DOC concentrations were observed during summer (Figure 3.3c) in Lake Pleasant. Close examination of temporal trends in DOC and inflow suggest that the DOC concentrations increased during summer in all three reservoirs. In contrast, the UVA254 absorbance and SUVA values were low during summer and tended to increase at the beginning of the year; this was true in all reservoirs. Regression analyses using DOC, UVA254, or SUVA values as a function of logarithmic transformed inflow for three reservoirs showed poor relationship between most of the combinations. However, for Bartlett Lake, a strong correlation ($R^2 = 0.74$; slope = 1.3) was found between SUVA value and log inflow) which indicates that Bartlett Lake inflows during spring runoff bring in significant amount of terrestrial DOM, and the impact of the spring flush on DOC variability is strong due to short HRT.

3.3.3 Organic Carbon Mass Balance in Bartlett Lake

Bartlett Lake with a shorter average HRT served as a good location to investigate the correlation between spring runoff and DOC loading in reservoir. Figure 3.4 shows the monthly variation of inflow to (Figure 3.4a) and the monthly variation of SUVA values (Figure 3.4b) in Bartlett Lake. Between January and

March, the inflow to Bartlett Lake showed a largest variation (Figure 3.4a). Simultaneously, SUVA values were higher and had greater variability between January and March (Figure 3.4b). Previous research has shown that DOM from water with greater autochthonous production has lower SUVA values in comparison with more terrestrially influenced water (Barber et al., 2001; Chin et al., 1994; Westerhoff & Anning, 2000). Mash et al. (2004) suggested that DOC production found in western US reservoirs in arid climates was attributed to in-lake sources during summer. For reservoirs in series, like Salt River system, autochthonous DOC associated with taste and odor compounds (e.g., MIB and Geosmin) contributions from upstream was mentioned to be important DOC sources in lake downstream (Westerhoff et al., 2005). Due to long total retention time for water in Saguaro Lake and Lake Pleasant and in upstream reservoirs (2.5 and 4.5 years, respectively) (Table 3.1), extracellular release of DOC from algae and macrophytes contributed to the major production of DOC within reservoirs. Although DOC concentrations are high due to biological activities during summer, little variation and autochthonous signature reduce the difficulty and unpredictability for facilities to meet regulation compliance.

Figure 3.5 shows upstream flow rate and DOC trend for Bartlett Lake during the study period. High DOC concentrations occurred during high surface runoff, especially spring snowmelt. Smaller pulses of DOC were observed during monsoons in July and August with DOC concentrations ranged from 3 to 4 mg/L (Figure 3.5). The high DOC concentrations observed in 2008 last longer and declined from about 6 mg/L during spring runoff to 3 mg/L during the base flow period after July, which can be attributed to the river-reservoir operation with longer retention time of water residing in the lake. For the remainder of the years, DOC pulses declined sharply when spring runoff receded. These DOC pulses probably represent a “first flush” phenomenon. Parks and Baker (1997) postulated that organic matter builds up on the soil surface of desert watersheds due to annual vegetation which grows in the spring dies and starts to decay during the dry summer. After several months with no precipitation, the first monsoon rains flush this accumulated material from the watershed. If the precipitation during monsoon season was small, the consequent longer dry season antecedent to first flush (spring snowmelt) would result in exporting more DOM from watershed to reservoir.

To examine the relationship between early spring (February to April) runoff and DOC loading and the impact of dry season antecedent to first flush, three assumptions need to be addressed. First, biological activity (microbial degradation and algal production) increases with higher water temperature, and preferentially utilizing more labile DOC compounds, e.g., structural carbohydrates (Wilen et al., 2000). During winter and spring, lower water temperature and less bio degradable compounds contribute to the decrease of microbial activity (Hung et al., 2005; Findlay et al., 1991; Leff and Meyer, 1991; Sweet & Perdue,1982). Consequently, biological processes as DOC source/sink could be negligible compared with DOC mass inflow from a spring flush; term of “reaction” was assumed to be zero in Equation 1. Second, the total evaporation volume from February to April accounted for less than 0.5% of inflow during the study period. Third, water column in reservoirs was well mixed due to thermal convection between epilimnion and hypolimnion, while stratification was only observed through June to September.

Using Equation 1, the data of DOC mass loading and inflow to Bartlett Lake during the spring runoff period from February to April is plotted in Figure 3.6. The regression analysis shows that DOC mass loading in Bartlett Lake during early spring was strongly correlated with inflow data (R^2 = 0.87, solid line, open symbols) (Figure 3.6). DOC mass loading during spring runoff (basically snowmelt) followed a predictable pattern that was related to upstream inflow. For Bartlett Lake with relative shorter HRT, DOC loading was fairly constant and nearly always less than 5×10^8 kg when total inflows were less than 10^5 acre-ft. DOC mass loading during early spring increased to greater than 10^9 kg when total inflows increased due to extreme early storms. Much of the Verde River watershed region received 3 to 5 inches of total rainfall within a day during the spring of 2003, 2005, 2008, and 2010 (inset of Figure 3.5). Consequently, the pulses of DOC discharge from spring runoff in Verde River watershed impact directly on water quality in Bartlett Lake. However, the data of 2008 followed a different trend which might result from higher DOC content accumulated in watershed soil with longer dry duration. To examine the dry duration impact on DOC mass loading discussed previously, a factor of “dry duration (DD)” antecedent to first flush is introduced. To evaluate the intensity of DD factor, a criterion of average of moderate inflow is used to judge if the month is dry month. The average of moderate inflow, which is calculated to be 16000 acre-ft, is the average of the monthly inflow which is less than 50% of reservoir average volume (1.2×10^5 acre-ft) during 1999 to 2010, while he inflow is extreme if the volume exceeds half of the reservoir volume and might cause rapid flush to lake. With the criterion of average of moderate inflow (shown as dash line in Figure 3.5) the intensity of DD factors before early spring runoff of each year are calculated and shown in Table 3.2. The total inflow from February to April is now adjusted ($\text{inflow}_{\text{adj}}$) by DD factor with an empirical equation as:

$$Inflow_{adj} = inflow(\text{acre-ft}) \times \log_{10}(DD) \quad \textbf{Eq.4}$$

After adjustment of inflow by DD factor, the regression analysis between DOC mass loading in Bartlett Lake and inflow shows better correlation ($R^2 = 0.99$) (Figure 3.6b) than that without adjustment. With the longer dry duration antecedent to first flush occurred in 2008, DOC mass loading was higher than expected with 2×10^5 acre-ft of inflow intensity. The DD factor could be applied for water facilities to plan operational strategy ahead when longer dry duration is observed. The logarithmic transformation of DD factor based on 10 also indicate that dry duration antecedent to first flush longer than 10 months can result in more organic matter flushed from watershed.

3.3.4 Organic Carbon in Lakes with Longer Hydraulic Retention Time

Based on the observation, reservoirs with more upstream residence time tend to dampen in-reservoir DOC variability. Figure 3.7 shows long-term inflow and DOC trends for Saguaro Lake (Figure 3.7a) and Lake pleasant (Figure 3.7b) during the study period. In both lakes, high DOC concentrations occurred during the summer; DOC concentration tended to increase over the last 10 years in Saguaro Lake. In comparison Bartlett Lake (Figure 3.5), both Saguaro Lake and Lake Pleasant showed small seasonal variations in the concentration of DOC (within 2 mg/L). The long-term inflow patterns were consistent annually in these two lakes. Inflows to Saguaro Lake increased from April and declined to base levels by late October consistently because Saguaro Lake is primarily operated for hydropower generation considerations. In contrast, water is releasing into Lake Pleasant in October and lasted until May of next year. Although the natural drainage from the Agua Fria River supplied an additional inflow to Lake Pleasant, it only accounted for less than 10% of the total reservoir inflow during this study (Figure 3.7b). The major storage is Lake Havasu, Lake Mead, and Lake Powell on upstream Colorado River.

The DOC mass loadings and total early spring inflows of Saguaro Lake and Lake Pleasant were calculated in the same manner as for Bartlett Lake. For Saguaro Lake, DOC mass loading was fairly constant and nearly always less than 10^9 kg when flows were less than 10^5 acre-ft. When total inflows were higher than 10^5 acre-ft, DOC loading increased and varied enormously, from 5 to 9×10^9 kg. The relationships between DOC mass loadings and early spring inflows in

Saguaro Lake and Lake Pleasant were calculated but showed no apparent correlation ($R^2 < 0.4$) (shown in Appendix 3.A); even accounting for dry duration did not improve R^2 values. For Lake Pleasant, DOC mass loadings were poorly correlated with total early spring inflows and had a very low R^2 value (0.05).

3.4 Conclusions

The quality of surface water served as drinking water sources in southwestern USA varies significantly upon the impact of climate variability and depends largely on hydrologic conditions and reservoir management. The following points summarize the key aspects of this study:

- The characteristic and temporal pattern of DOC concentrations in reservoirs served for Metro-Phoenix area varied significantly within each year and among years. In general, DOC concentrations tended to increase over the last ten years. Bartlett Lake exhibited largest water quality variability while Saguaro Lake and Lake Pleasant showed less variation.
- Depending on climate, spring runoff contributed 50 to 90% of the total annual DOC input to Bartlett Lake which was operated with shorter upstream HRT. The strong variation in DOC loading during early spring with allochthonous material can cause vulnerability to safe drinking water supply which will result in failure to operation of water treatment processes with respect to DBP control.
- Mass loading of DOC in the Bartlett Lake during early spring followed a predicted flow pattern. During the period of extreme events, like spring

storms, DOC concentrations ranged from 3 to 7 mg/L and DOC mass exported from watershed was elevated to 50 times higher than in regular years. Longer dry seasons antecedent to first flush resulted in higher abundance of DOC in runoff water.

- Reservoir operated with longer upstream HRT, e.g. multiple-lake system on Salt River, showed the capacity to attenuate DOC pulses occurred during extreme events.
- Understanding the DOC response in the reservoirs after extreme climate events (e.g., winter storm followed by long duration of dry season) can assist in operational changes to avoid high DOC concentration in water delivered to downstream water facilities.

Acknowledgements

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Table 3. 1 Hydrologic and physical characteristics of three reservoirs and hydrologic data during study period (1999 to 2010).

1999 to 2010		**Saguaro Lake**	**Bartlett Lake**	**Lake Pleasant**
Maximum Reservoir capacity (acre-ft)		0.7×10^5	1.8×10^5	11×10^5
Average in Storage (acre-ft)		0.7×10^5	1.2×10^5	6×10^5
Hydraulic Retention Time (day)		70	150	400
Combined Hydraulic Residence Time (years)		2.5	0.6	4.5
May to October	Monthly Inflow (acre-ft)	0.2×10^5	0.2×10^5	0.07×10^5
	Change in Storage (acre-ft)	-200	9000	-29000
November To April	Monthly Inflow (acre-ft)	0.5×10^5	0.4×10^5	0.7×10^5
	Change in Storage (acre-ft)	200	-9000	29000

Table 3. 2 Inflow and DOC loading data between February and April from upstream Bartlett Lake and the estimate of dry duration factors during study period.

Year	Total inflow from Feb to Apr (acre-ft)	Inflow DOC loading from Feb to Apr (kg)	Dry duration antecedent to February (month)
2000	5.3E+04	4.7E+07	2
2001	1.0E+05	5.8E+08	7
2002	3.1E+04	5.6E+07	10
2003	1.5E+05	1.1E+09	5
2004	3.5E+04	4.8E+07	7
2005	5.7E+05	3.7E+09	5
2006	3.7E+04	-2.4E+07	6
2007	2.3E+04	-4.9E+05	18
2008	2.0E+05	2.7E+09	27
2009	7.1E+04	5.7E+08	4
2010	3.0E+05	2.3E+09	7

*Note: the negative number of DOC mass loading observed for 2006 and 2007 could be attributed to precipitation of DOC in lake caused by low inflow throughout these years.

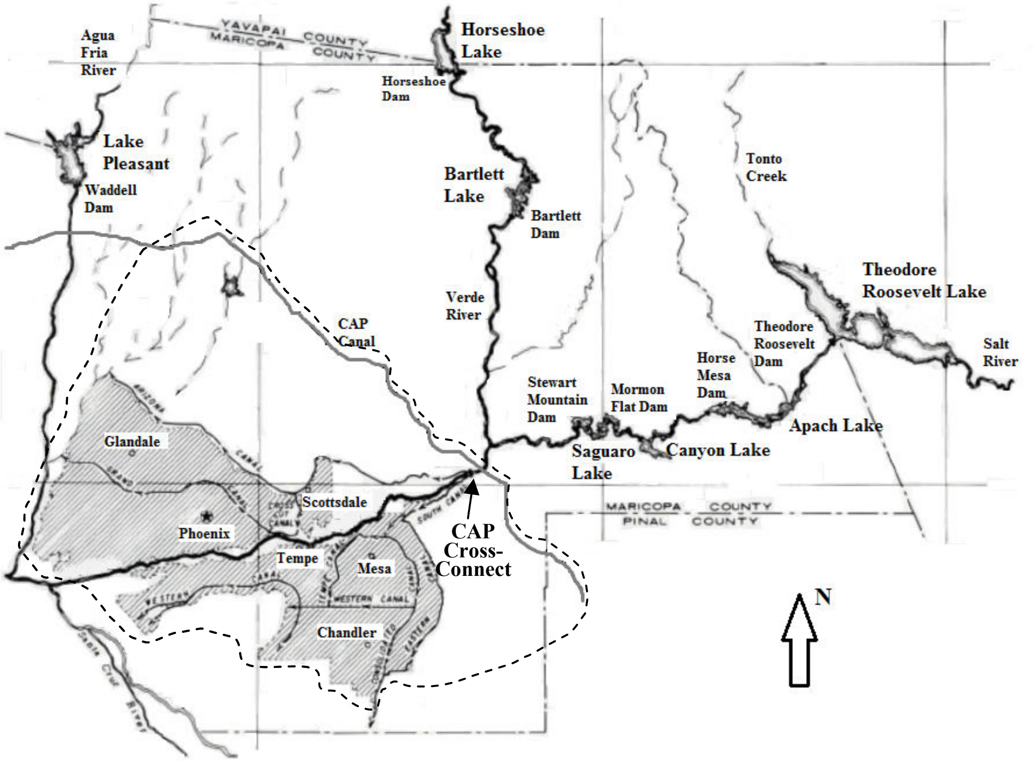

Figure 3. 1 Location of the reservoirs around Phoenix, Arizona. Concrete canals convey surface waters to water treatment plants (n ≈ 15) within the urban area. Shaded area shows the SRP water service area. Dash line represents the Metro-Phoenix region reserved by canal system.

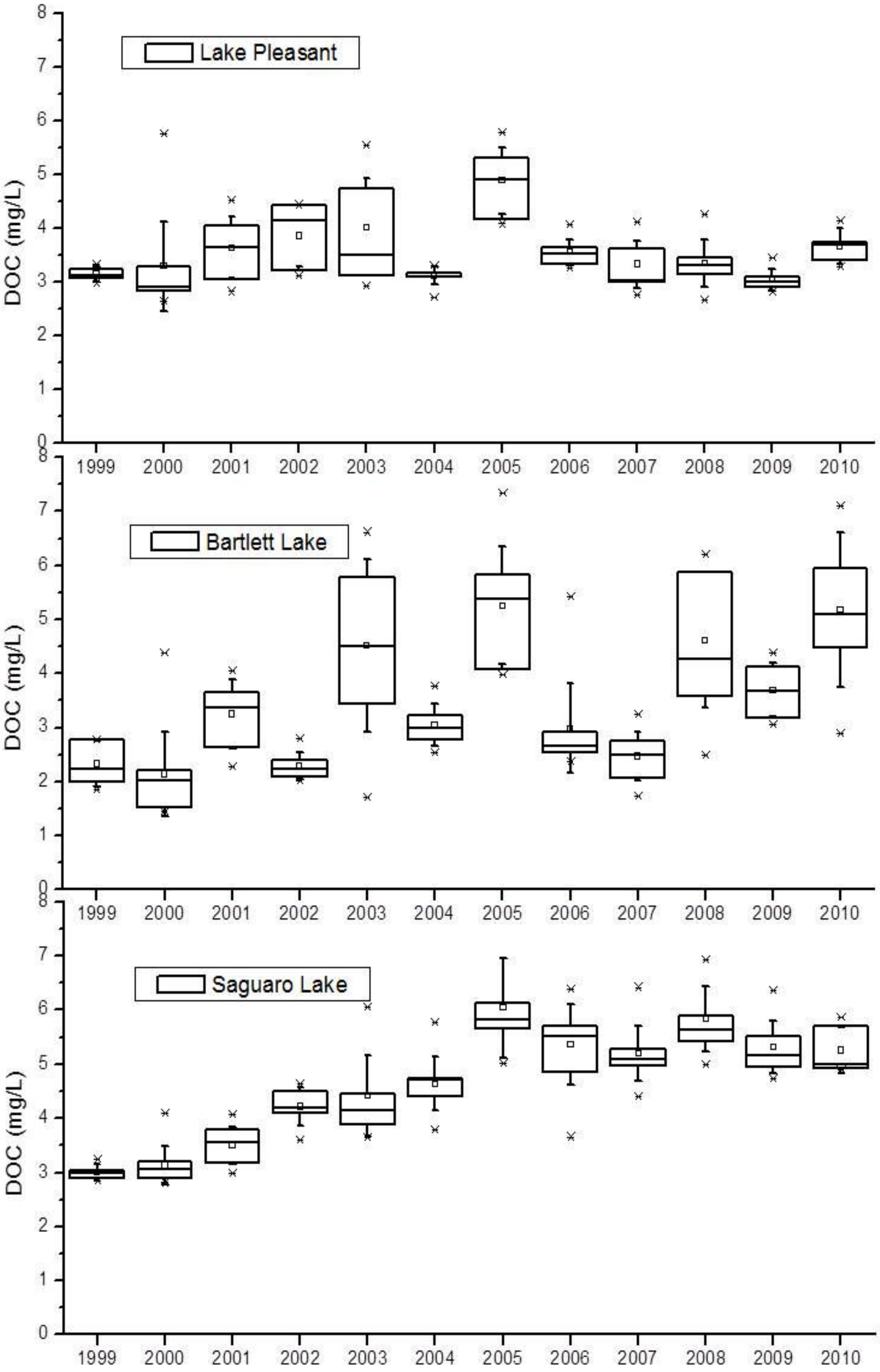

Figure 3. 2 Long-term DOC concentration variations of three reservoirs during study period (1999 to 2010).

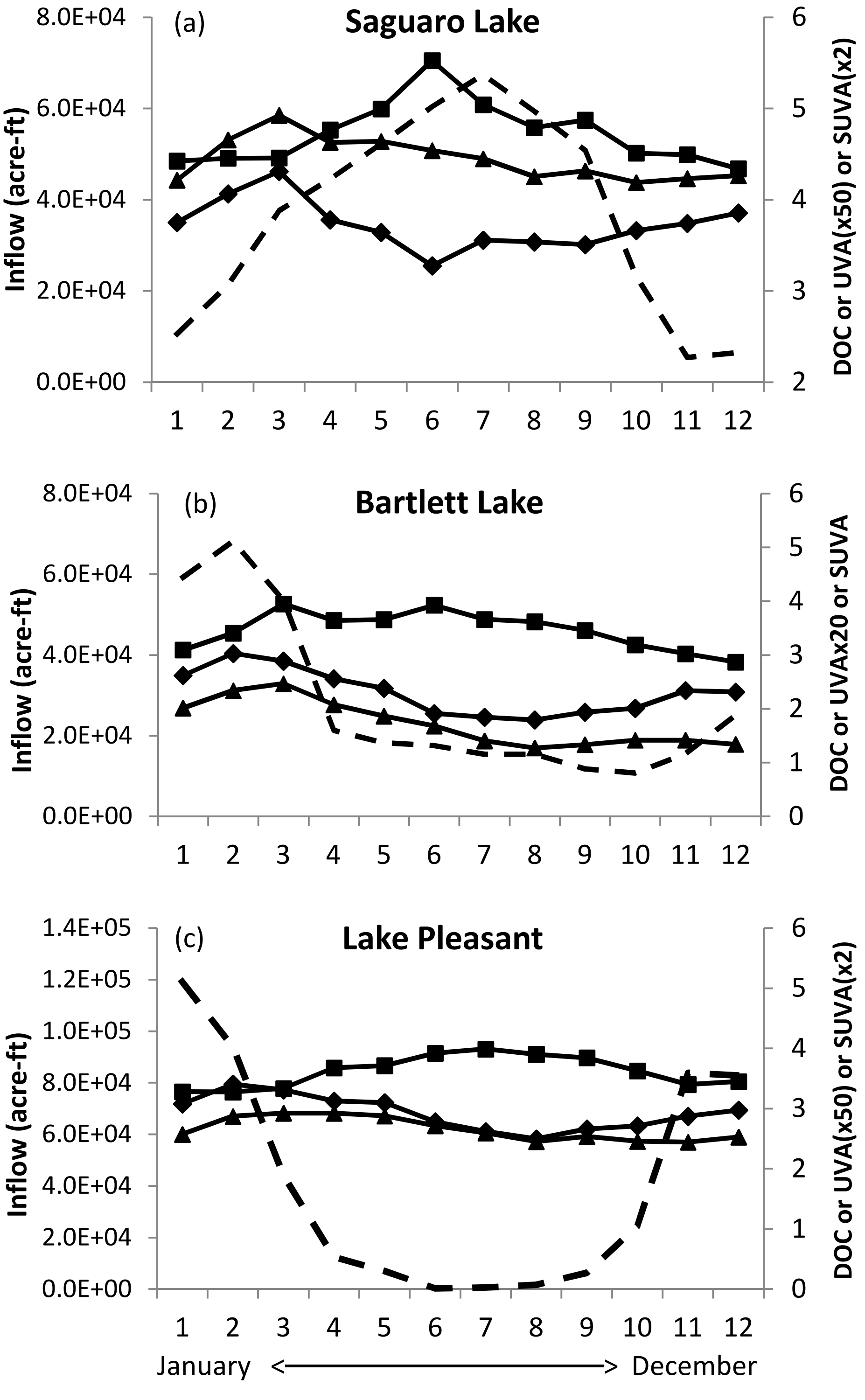

Figure 3. 3 Averages of inflow and other organic parameters of three reservoirs in each month during study period (1999 to 2010). Dash line: inflow (acre-ft); Square: DOC (mg/L); Triangle: UVA (1/cm); Diamond: SUVA (L/mg-m).

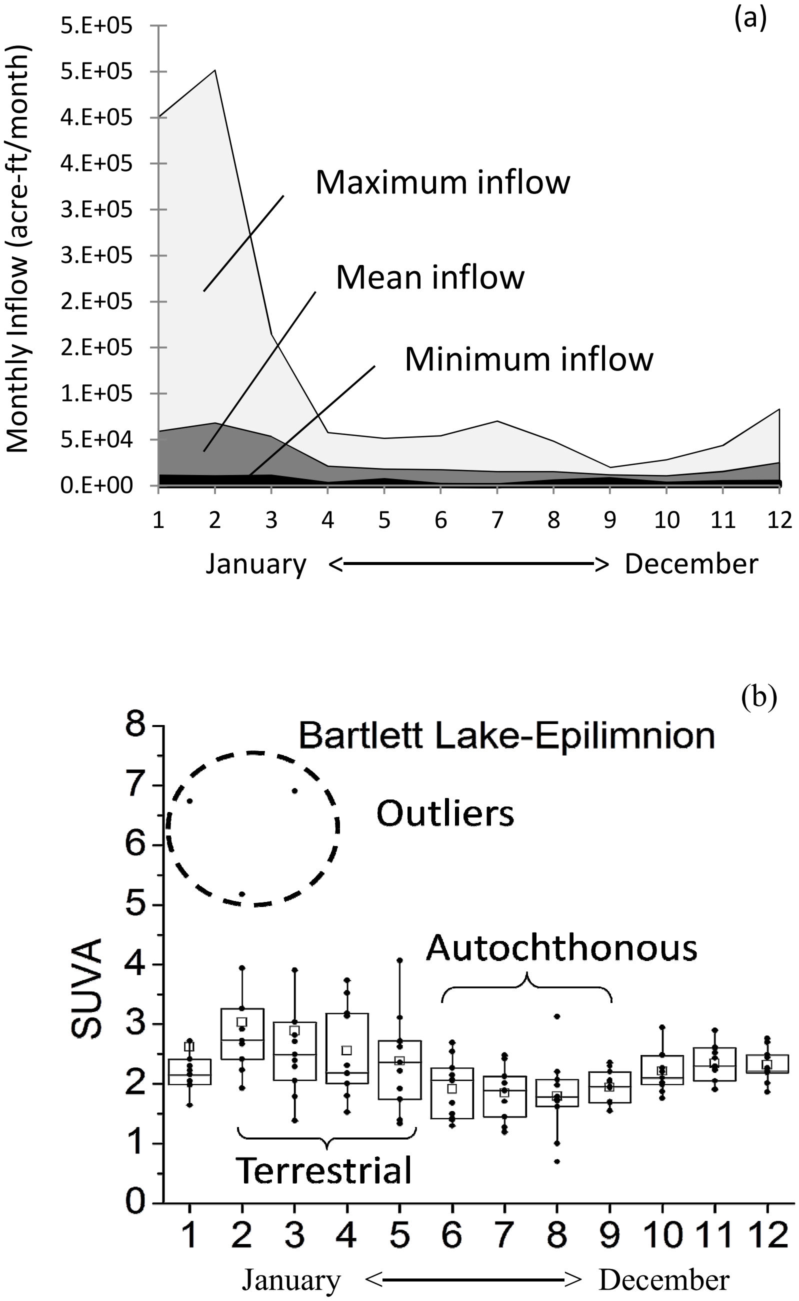

Figure 3. 4 (a) Variation of inflow to Bartlett Lake in each month and (b) variation of SUVA values in Bartlett in each month during study period (1999 to 2010).

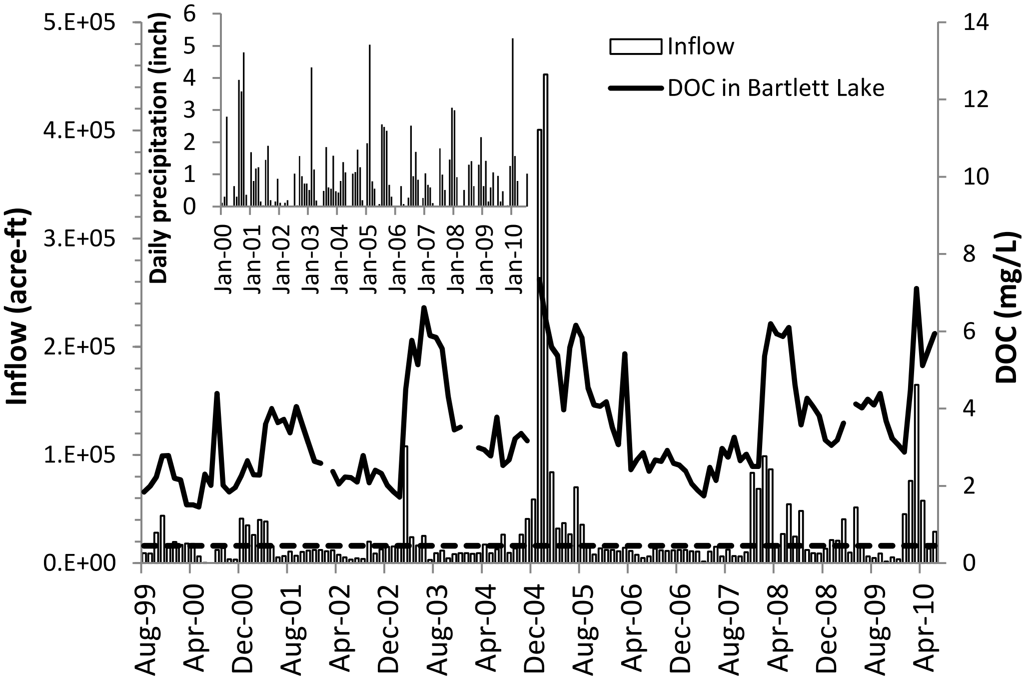

Figure 3. 5 Monthly inflow and DOC concentration trends for Bartlett Lake during study period (1999 to 2010). Inset shows the precipitation data of Bartlett Lake watershed during obtained from The Flood Control District of Maricopa County, Arizona.

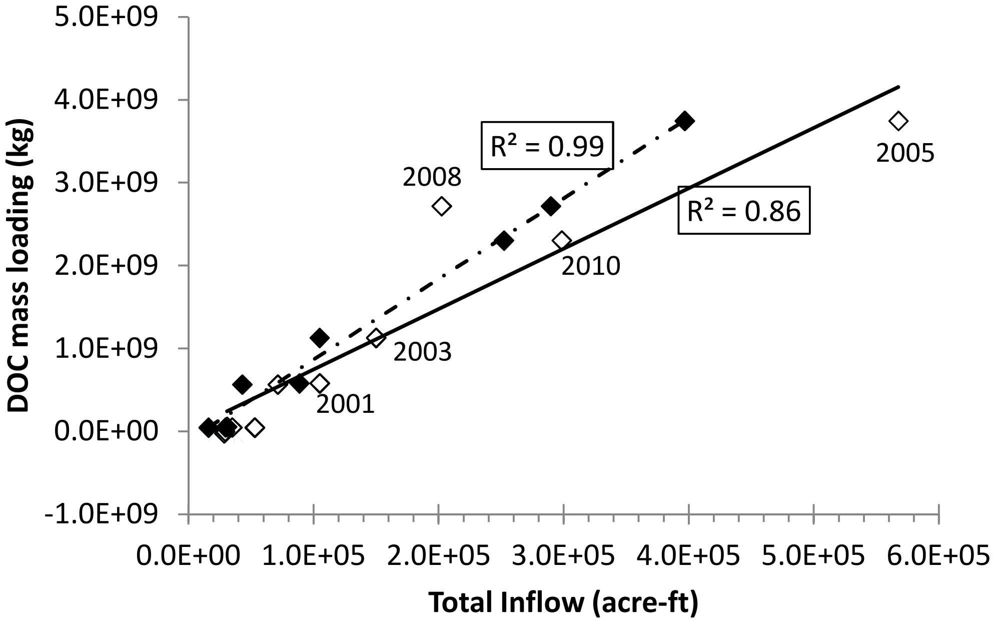

Figure 3. 6 Linear regression result for DOC mass loading as a function of inflow (solid line) and the result with dry duration factors modification (dash line) of Bartlett Lake during early spring.

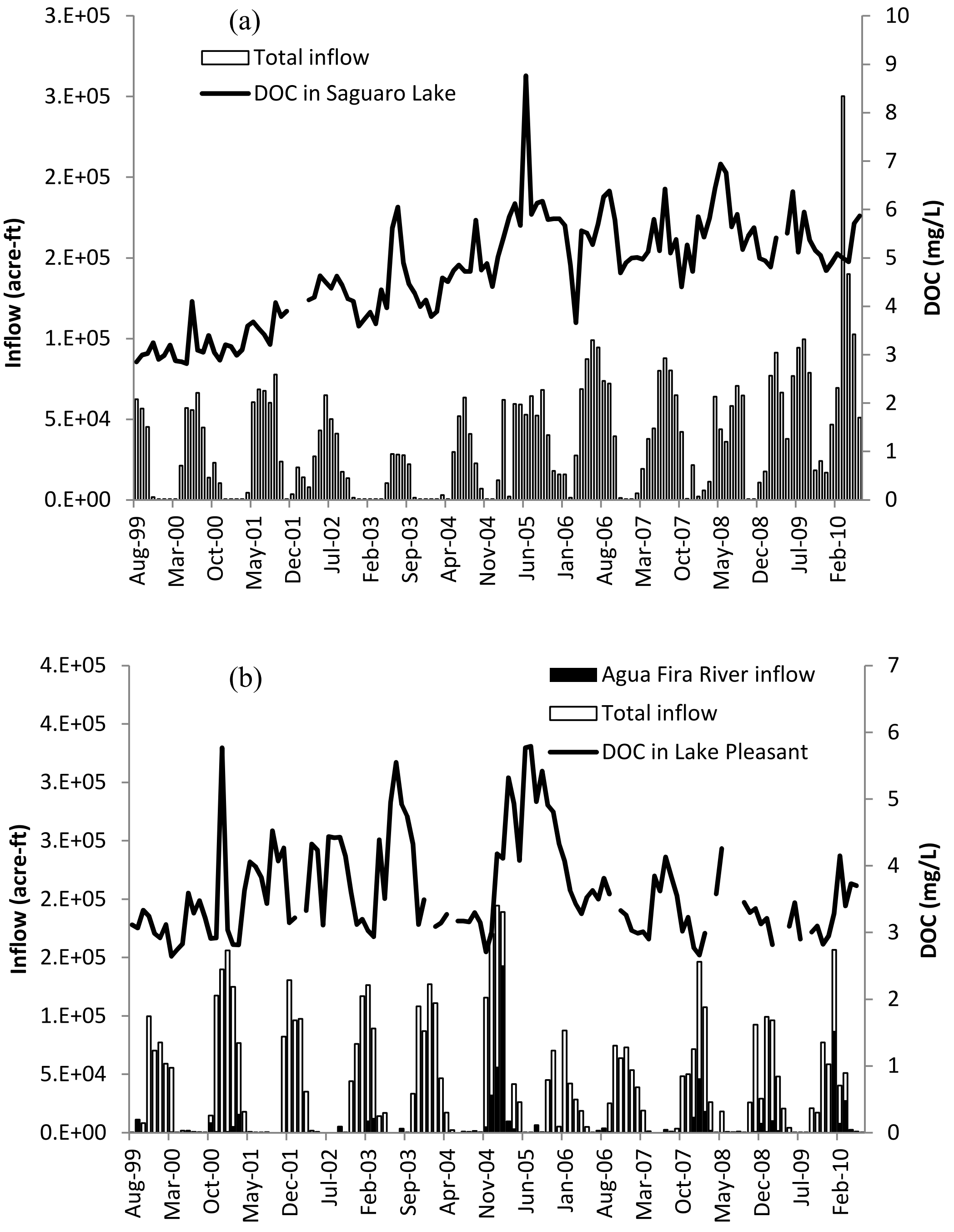

Figure 3. 7 Monthly inflow and DOC concentration trends for Saguaro Lake (a) and Lake Pleasant (a) during study period (1999 to 2010).

CHAPTER 4

MODELING OF ORGANIC MATTER OCCURRENCE AND TRASNPORT IN SALT RIVER MULTIPLE-LAKE SYSTEM

Prepared for peer-reviewed submission to *Water Research*

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Abstract

Dissolved organic carbon (DOC) concentrations in drinking water sources vary during abrupt extreme events, resulting in increasing treatment costs and public health risk. DOC concentration trends and transport in a multiple-lake Salt River system are investigated to determine the water quality responses under the impacts of hydrology and reservoir management. DOC loading from watershed in early spring is associated with surface runoff exhibits strong variability. The discharge of DOC pulses from watershed can be delayed and attenuated in multiple-lake system of Salt River. The reservoir operations, e.g., pump-back and hydraulic retention time (HRT), demonstrate significant impact on DOC occurrence between lakes and in the raw water of downstream water treatment facilities. Roosevelt Lake serves as the major reactor for DOC degradation/production with longest HRT; operation of pump-back for lakes with short HRT creates longer water residence time which results in further in-lake DOC degradation.

Key words: Organic carbon; Hydrology; Reservoir operation; Modeling

4.1 Introduction

Dissolved organic carbon (DOC) is a material in freshwater that can be transported and transformed through natural biogeochemical processes (biodegradation, photolysis, hydrolysis, adsorption, precipitation, sedimentation) (Hertkorn et al., 2002; Barber et al., 2001). Aquatic DOC concentration and structural composition in many surface water ecosystems depends on characteristics of the watershed (Aiken and Cotsaris, 1995). Organic matter is produced by soils and plants of the terrestrial watershed (allochthonous DOC) or from biological growth and decomposition of algae and macrophytes within lakes or reservoirs (autochthonous DOC) (Baron et al., 1991; Tate & Meyer, 1983). Terrestrial plant and soil sources contribute allochthonous organic matter to a stream mainly during runoff from overland water flow during rainfall events (McKnight et al., 1994; Onstad et al., 2000). Algae and bacteria (autochthonous sources) produce and consume or alter the concentration and composition of organic matter (McDowell and Likens, 1988; Leff and Meyer, 1991). Hydrologic flow paths and quantities of runoff water impact the relative importance of these DOC flux processes to impact DOC levels in drinking water supplies.

DOC is a precursor in the formation of carcinogenic by-products during drinking-water treatment when chemical disinfectants (e.g., chlorine) react with DOC to form disinfection by products (DBPs) (Reckhow et al, 1990, Amy et al, 1987). The amount and chemical nature of DOC are important to influence DBP formation. Previous studies have shown that humic substances with high aromatic content and molecular weight yield more DBPs upon chlorination (Reckhow et al., 1990). Amy et al. (1987) showed that the parameter of untraviolet absorbance (UVA) × DOC was a good predictor of DBP formation potential. Specific UVA (SUVA = UVA/DOC) correlates with aromatic content and is also a good surrogate of DBP precursors, (Weishaar et al., 2003; Traina et al., 1990). Allochthonous sources of natural organic matter (NOM) have higher SUVA than from autochthonous sources.

In arid and semi-arid regions of the southwestern USA, a typical annual hydrologic sequence for major rivers includes a major hydrologic pulse associated with upland snowmelt, followed by a prolonged dry period with low stream flow. DOC loading and characteristic in Southwestern US reservoirs reflect the hydrologic inputs, dominated by early spring snowmelt, with low DOC loading during the dry season. Differing hydrology and water management practices of three surface water sources serving the metropolitan Phoenix in Arizona of 3.5 million peoples off the opportunity to study climate variability on a key water quality parameter for drinking water sources, namely DOC. The objective of this study is to develop a dynamic model for understanding of DOC occurrence and transport in Salt River multiple-lake system. The findings are interpreted in light of potential future impacts of hydrology and reservoir management on drinking water utilities.

4.2 Materials and Methods

4.2.1 Site Descriptions

The drinking water supply to nearly 3.5 million people of the Phoenix metropolitan area is provided by the Salt River watershed, which originates in the White Mountains of eastern Arizona and New Mexico. There are four reservoirs on the main Salt River (Roosevelt Lake, Apach Lake, Canyon Lake, and Saguaro Lake) which joins the Verde River below the lowermost mainstream reservoir. These reservoirs store water derived mainly from snowmelt at higher elevations. Precipitation during the winter months in Arizona is generally from broad regional storms and falls as rain at lower elevations or as snow at higher elevations, or during the summer as thunderstorms (i.e. monsoons) (Mash et al, 2004). A site location map for the reservoirs and rivers is shown in Figure 4.1.

Saguaro Lake is the lowest of four reservoirs on the Salt River, and used for water storage and flood control. Three of the upstream Salt River reservoirs have hydropower generation facilities, and water is pumped back from Saguaro Lake to Canyon Lake and Apach Lake during summer months through pump-back piping to increase hydropower revenue. Saguaro Lake also has single outlet located near the bottom of the dam. Most releases occur in the summer (> 8.5 m^3/s) with minimal release (~0.1 m^3/s) between October and April. Water levels of Saguaro Lake fluctuate by less than five meters throughout the year.

4.2.2 Modeling of Dissolved Organic Carbon occurrence and transport

A continuous flow dynamic model with recycle derived from material mass balance model for continuous stirred-tank reactor (CSTR) was utilized to compute DOC transport in four-lake system on Salt River main stem. The derived equation of single continuous stirred-tank reactor (CSTR) with recycling can be expressed as:

$$C_{out} = \left(\frac{Q_{in} C_{in}}{Q_{out} + kV - q_R} \right) - \left[\left(\frac{Q_{in} C_{in}}{Q_{out} + kV - q_R} \right) e^{-\frac{t}{V}\left(Q_{out} + kV - q_R\right)} \right] + \left(C^{*}_{out} e^{-\frac{t}{V}\left(Q_{out} + kV - q_R\right)} \right) \quad \textbf{Eq.1}$$

where bulk concentration, C_{out}, is the DOC concentration in water leaving the lake at time = t; V is the tank volume; C_{in} is the concentration in influent; Q_{in} is the inflow rate; Q_{out} is the outflow rate; k is the reaction constant; q_R is the recycle flow rate; C^{*}_{out} is the initial bulk concentration in reactor at t = 0. Monthly reservoir storage and annual reservoir hydrological data for four lakes along Salt River (1999 to 2011) were obtained from US Geological Survey (USGS) and Salt River Project (SRP). Continuous flow records (daily average) were used to compute river inflow and reservoir outflow volumes (USGS station 09502000). Monthly inflow to Roosevelt Lake from Salt River and Tonto Creek obtained from SRP were used to complete the dynamic model for multiple-lake system.

4.2.3 Field Sampling

Monthly grab samples were collected at a depth of 1m below the water surface from Saguaro Lake during the study period. Hypolimnion samples (~ 15

m) were also collected and analyzed which showed less than 10% difference from surface concentration during most of study period. Temperature and dissolved oxygen were measured every 5 meters from surface to bottom. In addition, samples were also collected from Salt River near the inlet to Roosevelt Lake during 2002 to 2004 to investigate the impact of Rodeo-Chediski wild fire during early summer in 2002 on downstream water quality. Reservoir samples were collected from a boat with a Kemmerer sampler and the river water was collected by grab samples taken from the bank. The USGS collected samples from the site of upstream Salt River near Roosevelt inlet (USGS station 09498500) between 2002 and 2004. All DOC-related samples were collected in acid-washed, oven-ashed (550ºC) 1-L amber glass bottles. Samples were filtered through an ashed (550ºC) 0.7 µm filter (Whatman glass fiber filters, GF/F) and stored in acid-washed, pre-ached (550ºC) 40mL amber glass vials. DOC and UV absorbance at 254 nm wavelength (UVA254) analyses were conducted within one week of sample collection.

4.2.4 Laboratory Analyses

DOC was measured using a Shimadzu TOC-V_{CSH} analyzer (high temperature combustion at 720°**C** non-dispersive infrared detection with TNM-1 unit chemiluminescence detection) (Shimadzu Corp., Tokyo, Japan). Before analysis, water samples were acidified with hydrochloric acid to pH 2~3 to remove inorganic carbon during purging by nitrogen gas. Blank samples (prepared from Nanopure water) and quality control (QC) samples are inserted between every 10 samples. UVA was measured with a Shimadzu UV-1601 variable wavelength spectrophotometer and a 1-cm path length quartz cuvette. Blank sample prepared from Nanopure water is run for each experimental set as quality control sample. Specific UVA (SUVA) was determined by normalizing UVA to DOC concentration (UVA/DOC). Increasing SUVA values indicate a higher density of sp^2-hybridized carbon-carbon double bonds and a larger degree of humification (Chin et al., 1994; Westerhoff et al., 1999).

4.3 Results and Discussion

4.3.1 Estimation of DOC reaction rate constants for dynamic model

To evaluate the phenomena of attenuation of abrupt DOC pulses, a dynamic model based on mass balance equation for Salt River four lakes system was established in this study. In this continuous time dynamic model, changes in inflows and DOC loadings over time were considered as independent variables. Equation 1 is used for prediction of DOC concentration in water leaving Saguaro Lake. CSTR model is selected for simulation because lake water was destratified for most of the months, and DOC concentrations in epilimnion and hypolimnion were similar (<10% difference) for most of the time during the study. To apply this CSTR model for lakes (reactors) in series, C_{out} is used as the DOC concentration in water flowed into followed lake and as the initial bulk concentration (C^*_{out}) in lake for next time interval.

Assuming first order kinetic reaction, the estimated net reaction rate constant of DOC degradation during destratified seasons (Figure 4.2a) was 0.002

d^{-1} based on the observation of DOC decreasing from 4.6 to 4.3 mg/L per month. This value is comparable to the 0.001 d^{-1} to 0.05 d^{-1} decomposition rate of allochthonous (refractory) DOC reported by Hanson (2011) and Schlickeisen (2003). The lower rate of apparent DOC degradation observed in this study may have resulted from new inputs of fresh autochthonous (algal) DOC to the lake. During the stratified seasons (Figure 4.2a), rate constant (0.0023 d^{-1}) for epilimnion (from the surface to 10 m depth) was estimated based on the observation of DOC increasing from 4.5 to 4.8 mg/L per month due to strong algal activities; rate constant (0.001 d^{-1}) for hypolimnion (10 m below the surface to bottom, Figure 4.2b) was estimated based on the observation of slower DOC increasing from 4.5 to 4.6 mg/L per month. These values are comparable to the 0.0022 ± 0.0018 d^{-1} production rate of algal excretion organic carbon reported by Laird et al. (1986).

Monthly average storage and releasing data of each reservoir and the monthly inflows to Roosevelt Lake (highest end of four lakes system) from Salt River upstream were provided by Salt River Project. Operation of pump-back water between three lower end lakes for the purpose of increasing hydropower revenue were computed based on the hydropower generation data provided by SRP (Appendix 4.A).

4.3.2 Attenuation and delay of DOC pulses

Figure 4.3 shows the model fitted results for the DOC variation in the Saguaro Lake based on measured DOC concentration in inflow to Roosevelt Lake during 2002 to 2004. The measured DOC concentration in inflow to Roosevelt Lake showed two pulses occurred in August of 2002 and 2003 (Figure 4.3, open symbol). These two DOC peaks occurred during the summer runoff (i.e. monsoon impacted) were observed with high DOC concentration (30 mg/L and 25 mg/L, respectively), which was attributed to wild fire (Rodeo-Chediski Fire) occurred in Salt River watershed beginning in June, 2002. The post-fire storm events elevate the DOC concentrations in runoff water. With long combined HRT of Salt River four-reservoir system (2.5 to 3 years), the impact of extreme DOC concentrations exported from watershed was mitigated and the DOC concentrations in lower end Saguaro Lake shown less variations (2 to 5 mg/L). The impact of DOC pulses was delayed for about 1 year to elevate DOC concentrations in Saguaro Lake (arrows in Figure 4.3).

Observed DOC concentrations in Saguaro Lake outflow were plotted in comparison to fitted values. The DOC variation of observed data exhibited an agreement with the predicted results derived from the continuous time dynamic model in this study. The slight underestimated DOC concentrations during the summers may have resulted from inputs of fresh autochthonous DOC derived from strong algal activities. For the reservoirs in this study, the long HRT of first reservoir (Roosevelt Lake) served as major sink for DOC attenuation and can serve to buffer the abrupt DOC pulses exported from watershed. Local utilities wanted to know how long the DOC pulses observed in Salt River upstream would impact the water quality of water treatment plant downstream, and based upon the continuous time dynamic model a delay of DOC responses of 300 to 400 days was estimated; DOC concentration was dampened from 30 to 5 mg/L. This estimation allowed water facilities to adjust chemical dosage at corresponding time.

4.3.3 Evaluation of DOC occurrence and transport between four lakes

By using this dynamic model for multi-lake system, the long term DOC transport between each lake and the contribution of pump-back operation can be identified. Figure 4.4 shows the simulated DOC transport and the observed DOC concentrations in each lake on Salt River system. Except for data between 2002 and 2004, simulated DOC concentrations in each lake were calculated based on the relationship between Roosevelt Lake inflows and DOC concentrations observed during 2002 to 2004 (Figure 4.4a).

Figure 4.4b shows a good fitness between fitted data and observed data. The DOC variation between each lake suggests that 50 to 70 % of DOC degradation occurred in Roosevelt Lake (2.5 years of HRT), around 10 % occurred in Apach Lake (0.6 years of HRT), and less than 2 % occurred in Canyon and Saguaro Lake (0.2 years of combined HRT). For the reservoirs system along Salt River, the long HRT of the highest end reservoir (Roosevelt Lake) served as major sink for DOC attenuation and can serve to buffer the abrupt DOC pulses exported from watershed. Local utilities wanted to know for how long the DOC pulses observed in Salt River upstream would impact the water quality of water treatment plant downstream, and based upon the continuous time dynamic model a delay of DOC responses of 300 to 400 days was estimated.

The operation of water release and pump-back (Appendix 4.A) were also considered in this model which represents the real water management practices. During July 2002 to July 2005, the Apach Lake was operated with less inflow from Roosevelt Lake and more pump-back from Canyon Lake. This reservoir operation created longer water residence time in Apach Lake and resulted in significant in-lake degradation of DOC (30% to 40% reduction, Figure 4.4). This observation indicates that reservoir management can aid in DOC removal when discharge of DOC pulses occurs. Modeling approach provides useful information for understanding the DOC transport between lakes and could be applied for prediction of future DOC occurrence in raw water of downstream drinking water utilities.

4.4 Conclusions

Hydrologic conditions and reservoir management impact the quality of surface water served as drinking water sources. Multiple-lake system on Salt River provides practical information regarding DOC occurrence and transport between lakes upon influences of hydrology and reservoir operation. Reservoir operated with longer upstream HRT, e.g. multiple-lake system on Salt River, showed the capacity to attenuate DOC pulses occurred during discharge of DOC pulses. In this study, DOC concentrations decreased significantly through the four-lake system and the pulses were also delayed by around one year. Roosevelt

Lake with the longest HRT served as the major DOC reactor; the study of thermal structure and DOC cycle in Roosevelt Lake is important which can assist in better

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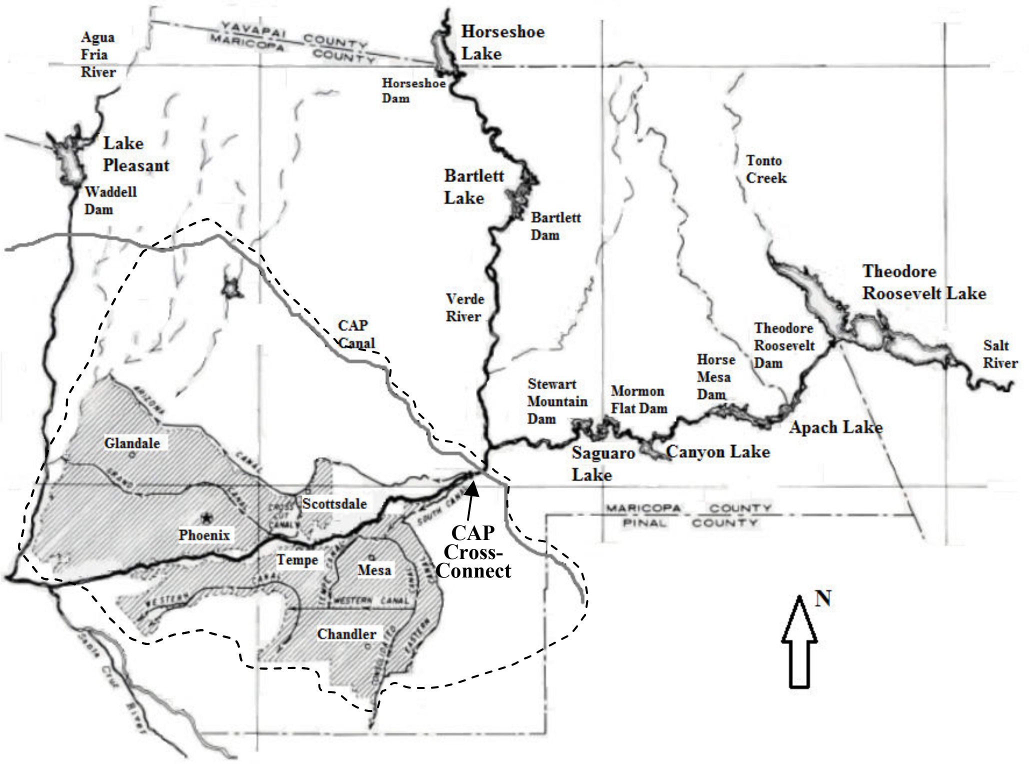

Figure 4. 1 Location of the reservoirs around Phoenix, Arizona. Concrete canals convey surface waters to water treatment plants (n ≈ 15) within the urban area. Shaded area shows the SRP water service area. Dash line represents the Metro-Phoenix region reserved by canal system.

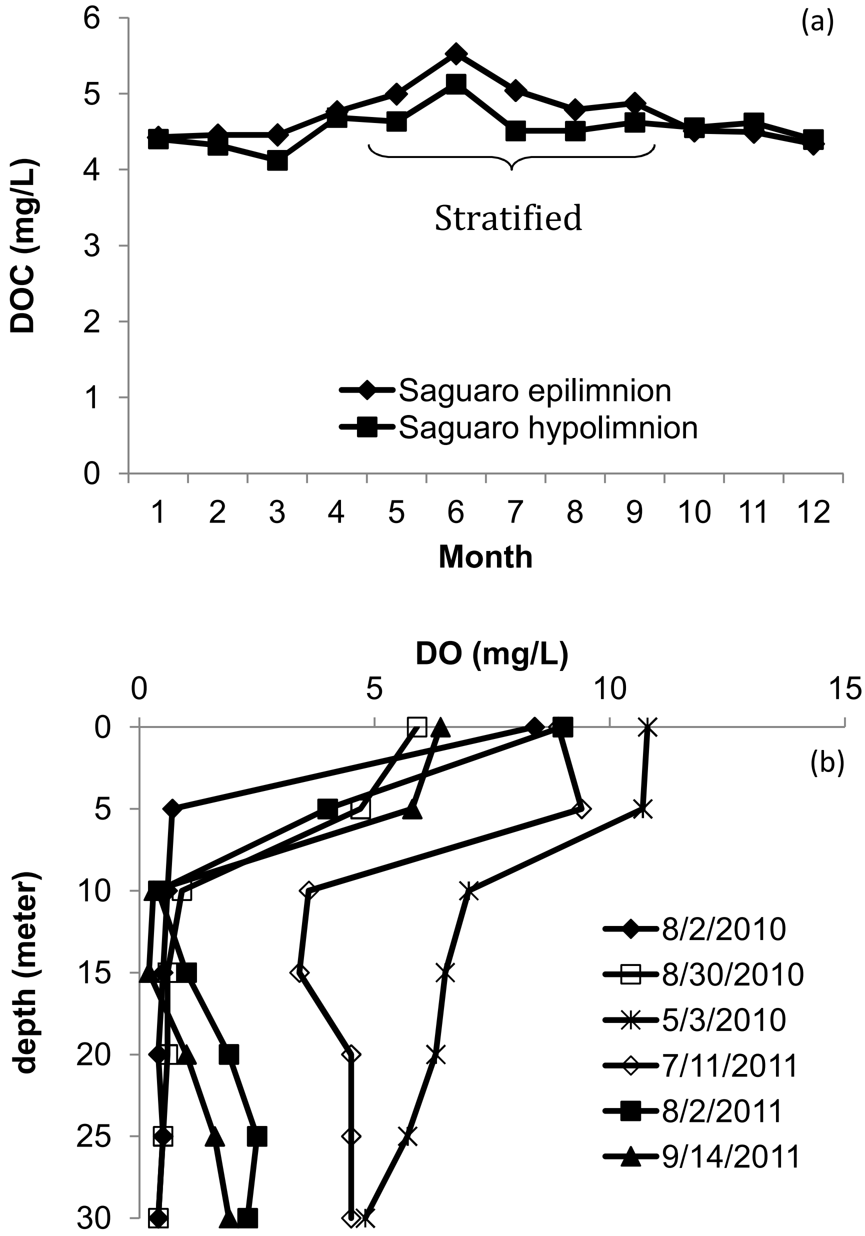

Figure 4. 2 (a) Temperal DOC concentration in Saguaro Lake epilimnion and hypolimnion, (b) spatial dissolved oxygen (DO) in Saguaro Lake during stratified seasons.

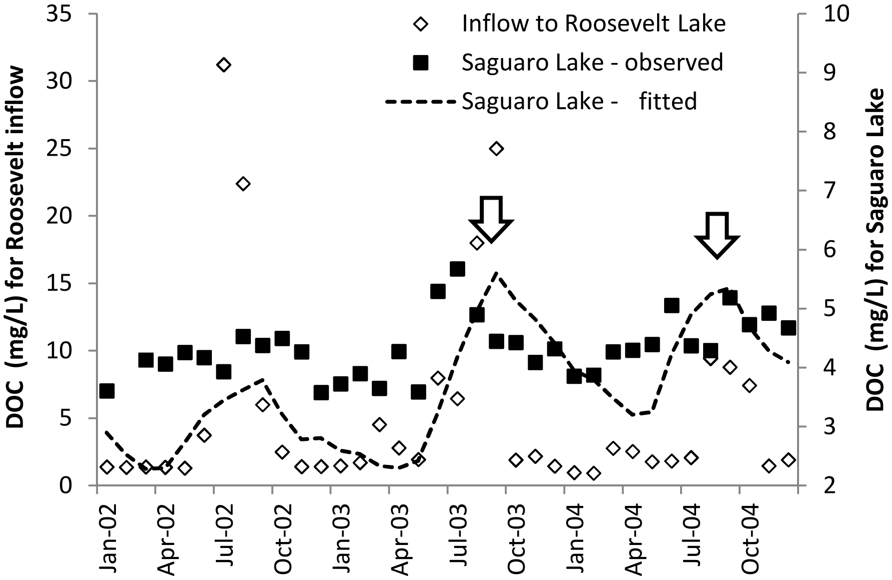

Figure 4. 3 The comparison between fitted and observed DOC concentrations in lowest end Saguaro Lake (2002 to 2004).

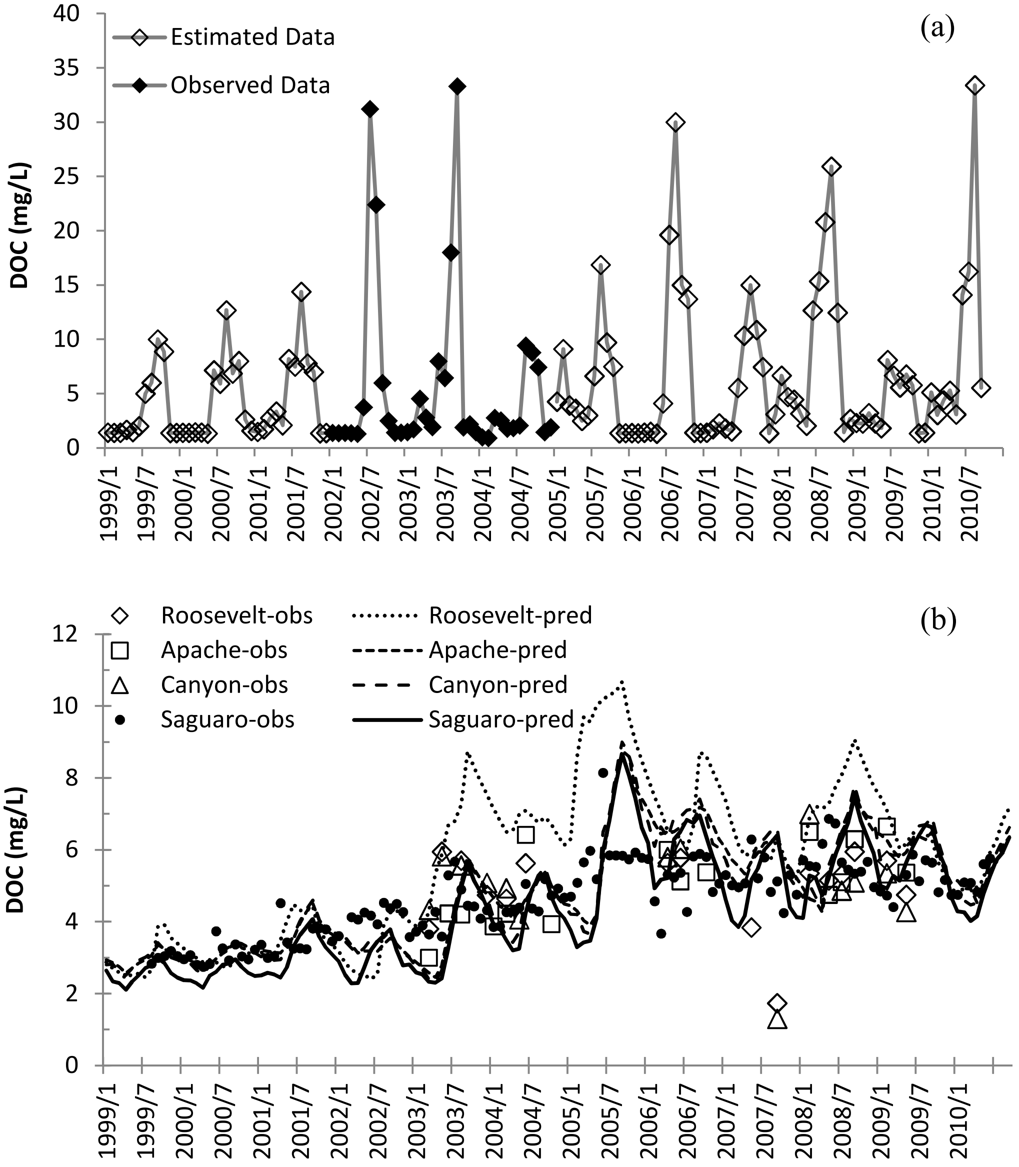

Figure 4. 4 (a) Observed (solid symbol) and estimated (open symbol) DOC concentrations in Roosevelt Lake inflow, (b) Comparison between fitted (lines) and observed (symbols) DOC trends in each lake on Salt River.

CHAPTER 5

CONTAMINANTS OF EMERGING CONCERN IN ARIZONA SURFACE AND WATERWATERS

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Abstract

To investigate the occurrence of contaminants of emerging concern (CECs) in waters throughout Arizona, 26 compounds (pharmaceuticals and personal care products (PPCPs), endocrine disrupting compounds (EDCs), and artificial sweetener) were analyzed in samples from surface waters, drinking water treatment plants (WTPs), wastewater treatment plants (WWTPs), and a groundwater recharge site during September 2007 to July 2009. Samples were analyzed using liquid chromatography/tandem mass spectrometry (LC/MS/MS). CECs were prevalent during this study, as they were found in 95% of the samples collected (n>100). The most frequently detected compounds in surface waters were oxybenzone, caffeine, and sucralose. The total concentration of CECs varied seasonally with the highest concentration detected during summer. For WTPs, the majority of CECs detected in surface water were also identified in WTP raw waters and sedimentation effluent. High CEC concentrations were detected in raw wastewater, and certain compounds (e.g. oxybenzone, ibuprofen, DEET, etc.) exhibited an increasing trend during summer. WWTP processes were shown to remove 11 of 26 compounds with up to 98% efficiency. Sucralose and sulfamethoxazole were dominant compounds (>60%) in WWTP effluent. Pharmaceuticals were also present in the ground water system of the Phoenix water supply area (<5 ng/L). Overall, the top six compounds detected were a) by frequency: oxybenzone, caffeine, sucralose, DEET, sulfamethoxazole, and acetaminophen; and b) by concentration: oxybenzone, caffeine, sucralose, DEET,

sulfamethoxazole, and dilantin. Results of this study demonstrate the occurrence of CECs in the Phoenix drinking water system. Other sources of CECs that might impact drinking water, such as lakes, WWTP recharging sites, and landfill sites, need to be investigated for overall water resource management in Arizona.

5.1 Introduction

Contaminants of emerging concern (CECs) like endocrine disrupting compounds (EDCs), pharmaceuticals and personal care products (PPCPs), and artificial additives (e.g., sucralose) have been detected in water supplies and wastewater effluents around the world (1-4). Some CECs exhibit adverse ecological impacts that have raised concern among public and regulatory groups about the fate of such compounds during potable water treatment and human exposure from drinking water (3,5-13). The impacts of EDCs on the environment are not entirely known, but undesirable effects on non-target aquatic organisms and damage to sensitive ecosystems are possible. Although pharmaceuticals are not considered to pose an appreciable risk to human health through drinking water and the food chain (14), a previous study that applied a life cycle impact assessment to a Spanish wastewater treatment plant located on the Mediterranean coast revealed that PPCPs, rather than the priority pollutants, contributed most to water toxicity (15). However, not only the persistence in the environment but also the biological activity of degradation by-products will exert the impact of these chemicals on the environment. Despite all the drawbacks related to the presence of CECs in the environment, most people are not aware of the importance of this growing issue. A survey conducted in the United States showed that unused or expired medicines are generally disposed of through trash, toilet, and sink rather than by return to pharmacies (16). Recent studies reported the occurrence of numerous CECs in both groundwater and surface waters throughout the world.

The greatest amount of data was available for Italy, Spain, Sweden, Switzerland, Netherlands, UK, Israel, USA, China, Canada, and Germany (17-24). According to the United States Geological Survey (USGS), the most frequently detected CECs in water streams are nonprescription and prescription drugs, insect repellents, detergent metabolites, plasticizers, fire retardants, antibiotics, herbicides, hormones, and solvents (25,26).

CECs enter in the environment from several sources such as: (i) effluents from wastewater treatment plants (WWTPs), (ii) leakage from septic tanks or landfill sites, (iii) surface water run-off, and (iv) direct discharge into waters. The major sources of such chemicals are WWTP effluents and secondary terrestrial run-offs. Run-off and leaching from livestock are the main paths for transport of veterinary drugs to groundwater. Human pharmaceuticals enter the aquatic system by ingestion followed by excretion in the form of non-metabolized parent compounds or as metabolites. Personal care products are discharged in particular through shower waste and water activities. All these contaminants can pass through WWTPs and enter into water streams because they may not be completely degraded (27). A study conducted in Taiwan showed that the highest drug concentrations were found in waste streams (37.5%), followed by animal husbandries (27.9%) and drug production facilities (23.4%) (28).

The majority of CECs are polar and hydrophilic, They have low octanol/water partition coefficients (log K_{ow}), which result in less binding to organic fractions of sludge or suspended sediments compared to other persistent organic compounds that are capable of bioaccumulation (polycyclic aromatic hydrocarbons, polychlorinated biphenyls, or organochlorine pesticides). The low volatility of CECs suggests that their distribution through the environment will mainly occur through aqueous transport and food chain dispersal (29). Moreover, pharmaceuticals have shown a greater resistance to microbial degradation in estuarine and coastal waters than many other similarly sized naturally occurring biogenic molecules, which are abundant in seawater (30). Batch experiments also indicated that the removal of these soluble pharmaceuticals from water columns to sediments was insignificant (30). Although the scientific literature about the fate of many of these substances is extensive, limited knowledge is available on the effects of these CECs on the environment, especially in the case of exposure to mixtures of these compounds.

Some CECs are more polar than current USEPA regulated polyaromatic contaminants. This, coupled with occurrence at trace levels (parts per trillion), creates unique challenges for analytical detection and assessment of removal performance by drinking water treatment plant (WTP) processes (3,12). Drinking water treatment relies primarily upon adsorptive and oxidative processes to remove or transform organic materials. Recent studies on selected groups of CECs, pesticides, and herbicides indicate that coagulation, sedimentation, and filtration achieve minimal levels of removal (13, 31-33). However, addition of common disinfectants (e.g., chlorine or ozone) can result in reaction and transformation of these compounds (34-43). Chemical coagulation and softening aid in removing suspended solids (i.e., turbidity) from the water and aid in removing dissolved organic carbon (DOC). Coagulation alone is generally not effective at removing trace-level organic pollutants (44,45).

Activated carbon adsorbs many organic pollutants (46). The USEPA identifies packed-bed granular activated carbon (GAC) as a “Best Available Technology” for treating numerous regulated organic pollutants. Powdered activated carbon (PAC) effectively removes many problematic organic pollutants (e.g., taste and odor compounds, some pesticides and herbicides) (47). For some organic compounds, adsorptive removal by PAC may not be effective, but the compounds may react with oxidants (48,49). The formation, fate, detection, and toxicity of oxidative by-products from pesticides and EDCs/PPCPs is of potential concern (34,50).

Several studies have investigated EDC or PPCP removal by ozone or chlorine (31,38,41,51,52), but direct comparisons are lacking between these two oxidants and a broad range of EDCs/PPCPs under the typical conditions of drinking water treatment facilities. Molecular ozone is a selective electrophile that reacts with amines, phenols, and double bonds, whereas $HO^{\bullet}$ reacts less selectively with organic compounds (42,53,54). Due to the selective nature of ozone, micropollutant transformation may require the use of advanced oxidation processes (AOPs), such as O_3/H_2O_2 (49,55).

Many municipalities are concerned about the potential for EDCs/PPCPs to occur in their water supplies, and the presence of these compounds may affect future treatment decisions. Collecting data over a watershed scale will provide useful information to address public questions or concern from advocacy groups, and this locally funded investigation demonstrates the proactive nature of local government for monitoring water quality. The key benefit will be providing a set of baseline data for trace organic occurrence from which future decisions regarding the need for additional monitoring can be rationally developed. The objectives of this article are to provide baseline data for EDCs/PPCPs in the Salt River watershed, including canals and recharge systems, as a state-wide view of these trace organics present in Arizona waters. Arizona is known for its limited water sources, and the water is used for many purposes such as irrigating and drinking. These data provide information on the occurrence of CECs as well as their natural attenuation in the environment. To accomplish the objectives, samples were collected from multiple water sources (such as watersheds, canals, groundwater, drinking water treatment facilities, etc.), as will be described in the next section.

5.2 Methods

5.2.1 Site Selection and Sampling

To provide a metro-Phoenix-wide view of CECs present in Arizona waters, samples were collected from three main water sources and from a selected drinking water treatment plant, wastewater treatment plants, and groundwater near a recharging site. Surface waters were collected from three different water sources for the Phoenix area water supply: Verde River (Verde River at Beeline

Highway), Waddell Canal (near Lake Pleasant Road), and Salt River (Blue Point Bridge); these samples were collected bi-monthly (see Appendix 5.A). Samples were also collected bi-monthly from one drinking water treatment plant (WTP A, see Appendix 5.A) to represent drinking water samples including raw water, sedimentation effluent, and finished waters (after chlorination). Wastewater samples were collected once during this investigation from eight wastewater treatment plant (see Appendix 5.A&B) effluents; a full investigation (samples from raw wastewater, tertiary effluent, and effluent) was conducted for WWTP A. Three measuring wells of the GRUSP (Granite Reef Underground Storage Project) recharging project (see Appendix 5.C) were selected as groundwater sampling sites that were visited three times during this investigation. In addition, two water recreation sites (see Appendix 5.D) were selected to testify to the occurrence of CECs in surface waters as a result of human activities. Moreover, an investigation of natural attenuation of CECs was conducted by collecting samples from the Santa Cruz River, which receives treated wastewater from Nogales WWTP directly. All these samples were collected during September 2007 to July 2009.

All samples were collected by ASU using 1-L ashed amber bottles and stored on ice. One hundred mg/L of sodium azide and 50 mg/L of ascorbic acid were added right after return to the laboratory to prevent biodegradation. Samples were filtered using 0.7 μm filter paper (GF/F, Whatman) before analysis. For the purpose of recovery correction for analyte loss during solid phase extraction (based on EPA Method 1694: Pharmaceuticals and Personal Care Products in

Water, Soil, Sediment, and Biosolids by HPLC/MS/MS), all standard and field samples were spiked with the same amount (50 ng/L) of internal standard (IS) (Acetaminophen-D_4, Caffeine-$^{13}C_3$, ^{13}C-Naproxen-D_3, Carboamazepine-D_{10}, Estradiol-$^{13}C_2$) after filtration. However, the filtration might lead to underestimated total concentrations, particularly for more hydrophobic compounds in raw wastewater. All the data that reported in this study are dissolved concentrations detected in filtered water samples.

5.2.2 Analytical Methods

Solid phase extraction was performed for each of the filtered water samples taken from the WWTPs and surface water samples using a Caliper Life Sciences Auto Trace extraction manifold. Methanol (HPLC grade, Fisher Chemical), MTBE (HPLC grade, Fisher Chemical), toluene (HPLC grade, Fisher Chemical), and water (HPLC grade, Honeywell, B&J) were used as solvents with Waters Oasis HLB extraction cartridges. PPCP analysis was performed with cooperation from the Arizona Department of Health Services using an Applied Biosystems API4000 triple quadrupole mass spectrometer and an Agilent 1100 Series HPLC system. A Phenomenex Synergi 4 micron Max RP 80A column was used for analyte separation. An LC gradient of water with 0.01% formic acid (A) and methanol with 0.01% formic acid (B) at a flow rate of 700 µL/min was used. The gradient was as follows: 5% (B) held for 3.5 min, increased linearly to 80% (B) at 10 min. and held for 3 min., at 13.5 min ramped to 100% (B) and held until 21.0 min., at 21.5 min ramped back down to 5% (B) and held until 30.0 min.

Twenty-two prescription drugs, artificial sweetener, and personal care products as well as four steroids were selected as target compounds because of their high frequency of household application and identification in previous research (55) as being prevalent in the environment. None of the 26 CEC compounds have the regulated criteria of guidelines in the form of maximum contaminant level (MCL). The effects of short term, high dose exposure conducted on aquatic life are summarized in Table 5.1, and the detected concentrations of these compounds in the surface waters were much lower than the aquatic life criteria. However, chronic effects from long term, low level environmental exposure to select CECs appear to be of much greater concern, and sufficient data collection will be required for further study. Table 5.1 also lists the K_{ow} (octanol-water partition coefficient) values and functions of these target compounds. Standards for these compounds were supplied by ADHS, and the LC/MS/MS operating conditions are shown in Appendix 5.E. Internal standards including Acetaminophen-D_4 (Cerilliant), ^{13}C-Naproxen-D_3 (Cambridge Isotope), Estradiol-$^{13}C_2$ (Cambridge Isotope), Caffeine-$^{13}C_3$ (Cambridge Isotope), and Carboamazepine-D_{10} (Cambridge Isotope) were spiked before solid phase extraction for recovery correction.

5.2.3 Quality Assurance Protocol

Laboratory blanks were used to assess potential sample contamination. These blanks were prepared using nanopure water in the laboratory. Field blanks were also used to determine the effect, if any, of field equipment and procedures on the concentrations of CECs during water sampling. These field blanks were also prepared using nanopure water and transferred into another clean, ashed bottle during water sampling. All blanks were subject to the same sample processing, handling, and equipment as the real samples. Concentrations obtained from blanks were not subtracted from environmental results. Environmental concentrations within the values observed in the set of blanks plus two times the standard deviation were reported as insignificant concentration or not detected. The measured concentrations in all blank samples and the statistical report are shown in Appendix 5.F. Furthermore, analyte loss might be occurred during solid phase extraction and the recovery varied between different water matrices. Fifty µg/L of 5 internal standards were spiked into calibration standards as well as all field samples and blanks (before solid phase extraction) for recovery calculation of the loss due to matrix effect. All data shown in this research are compared with blank results (average+2SD) for significance of detection and corrected with recovery efficiency (Appendix 5.G). In addition, no recovery test was performed for sucralose and steroids, and the results for these compounds shown in this article represent the minimum contamination level.

5.3 Results

5.3.1 Overview of CECs in Arizona Waters

The trace organics concentrations present in different water sources are varied. Table 5.2 summarizes the concentrations of CECs present in different waters during the investigation period.

The CEC levels were varied in different waters from less than 10 ng/L (most compounds in groundwater) to 100 μg/L (in raw wastewaters). In groundwater and surface waters (Salt River, Verde River, and CAP canal), about 13 compounds (including 4 steroids) were measured to be 2 ng/L or less than in blank samples. Some compounds were present in groundwater and surface waters consistently, like acetaminophen, caffeine, cotinine, dilantin, meprobamate, triclosan, DEET, and etc., with levels below 20 ng/L. Oxybenzone and sucralose concentrations in surface waters were higher (20 ng/L to 1 μg/L) but varied with seasons, which will be discussed later. CAP water is from the Colorado River which is located downstream of Lake Mead, which receives approximately 1% of its inflow from wastewater (56), and the observed sucralose concentrations are roughly 100x lower than observed in wastewater effluents. Sulfamethoxazole and sucralose were consistently present in one of the groundwater measuring well samples with a concentration of approximately 100 to 300 ng/L.

Most of the target compounds analyzed in WWTP effluents had concentrations in the range of 20 ng/L to 1 μg/L (WWTP adopted activated sludge and nitrification processes). The concentrations of acetaminophen, ibuprofen, and steroids (shown in Table 5.2) are relatively low, which means the treatment processes removed these compounds better than others. This result will be compared below with CEC concentrations in effluents from other treatment techniques. High CEC concentrations of 20 ng/L to 100 μg/L were detected in raw wastewaters. These high concentrations of emerging contaminants might accumulate in sludge or be transformed by microorganisms. The disposal of the wastewater sludge as well as the discharge of treated wastewater into natural water systems must be carefully managed.

5.3.2 Occurrences of CECs in Surface Waters

Three surface waters in the Phoenix metropolitan area serving as drinking water sources were investigated in this study: Waddell Canal, Salt River, and Verde River. From September 2007 to July 2009, 24 samples were collected from these three surface waters. One or more CECs were found in more than 95% of the 24 surface water samples during the investigation. The CEC results were compared with lab-blank and field-blank samples to make sure the measurements were significant and not due to artificial error.

Table 5.3 shows the CECs detected in the three surface waters during this study. Progesterone was not detected in any surface water samples. Measured concentrations were generally low (less than 50 ng/L); two compounds (oxybenzone and sucralose) exceeded 300 ng/L in some samples during the investigation. Fifteen of 26 target compounds were identified as prevalent anthropogenic contaminants in the surface waters (>50% occurrence); caffeine, DEET, sucralose, and oxybenzone were detected in most samples (>90% occurrence). The occurrence of estradiol was detected near and slightly above our reporting level of 2 ng/L in Arizona surface waters (not shown in Table 5.3). Although these values are lower than the suggested EC50 value (25 ng/L, conducted with fish) in previous study (57), the occurrence of estradiol is higher in this study than many surface waters reported in the United States (58,59). Our atypical estradiol detected in surface waters probably results from the detection method which is not suggested for drinking waters and which can show false positives in the analysis of steroid hormones in water. To obtain a broader view of the long-term variation for individual surface waters, the monthly results were divided into two groups, summer and other seasons. Figure 5.1 shows the monthly total CEC concentration for different surface waters and the diversified CEC content between summer and other seasons. Overall, the occurrence of CECs in the three surface waters was higher during summer than in other seasons. Salt River water was found to have the highest CEC concentration during summer (>350 ng/L, on average) but decreased sharply during other seasons (to 120 ng/L). CAP canal and Verde River samples exhibit less variance (30% difference) between summer and other seasons; the CAP canal had the highest total concentration during other seasons. From the point of view of content percentage, sucralose had the highest concentration in the CAP canal at any season (60% to 75%). For the Salt River, oxybenzone accounted for more than 80% of the total CECs measured during summer but decreased to 16% during other seasons. The Verde River had the lowest concentration of total CECs present, and oxybenzone had the highest concentration among the 26 compounds during summer.

These dramatic increases in oxybenzone, an ingredient in sunscreens, during summer suggest that water-based recreation (e.g., swimming and tubing) is popular upstream in the Salt River and Verde River. For example, the sampling site for Salt River was close to water recreational area which might be the direct contribution of oxybenzone during summer. The high proportion of sucralose present in the CAP canal might result from the discharge of treated wastewater into Colorado River. Artificial sweetener has been suggested as an ideal marker of domestic wastewater in drinking water sources (60), but further investigation is needed for verification. The total concentration of compounds other than oxybenzone and sucralose in surface waters was constant, which indicates a constant discharge into water column upstream of these three rivers/canal. The different patterns of CEC content between different water sources during different seasons could be important information for drinking water treatment plants planning to switch source waters throughout the year.

5.3.3 Occurrence and Fate of CECs in a Drinking Water Treatment Plant

Samples collected from drinking water treatment plant A (WTP A) were used for CEC analysis and examination of fate during drinking water treatment processes. WTP A is a utility on a Salt River Project canal with conventional coagulation/sedimentation/filtration treatment processes. Raw water, sedimentation effluent, and finished water from this drinking water treatment plant were collected for analysis. Finished water samples were collected after disinfection but before entering the distribution system. Thirty-one samples were collected from September 2007 to July 2009. Four out of 11 raw water samples were found to contain >100 ng/L of total CECs present. Eight out of nine finished water samples had a CEC residual (27 ng/L on average).

Table 5.4 shows the CECs detected in WTP A during the investigation. The measured concentrations for each compound were generally lower than 5 ng/L, and hydrocodone was not detected in any sample. For raw waters, five compounds (caffeine, cotinine, DEET, oxybenzone, and sucralose) were defined as prevalent emerging contaminants (>50% occurrences); 90% of raw waters contained DEET. Caffeine, DEET, oxybenzone, and sucralose concentrations greater than 10 ng/L were detected in some raw water samples; in one, oxybenzone was greater than 100 ng/L. The drinking water treatment processes achieved > 50% removal when concentrations of these compounds higher than 5 ng/L were present in raw waters. The remaining oxybenzone could be completely oxidized by chlorination, with no oxybenzone residual detected in the finished water. Nonetheless, the CEC residual remaining in the finished water are constant and significant. For long-term drinking water management, monitoring of source waters and the fate of CECs in drinking water systems is recommended. In addition, it is important to be addressed that the value of ethinyl estradiol in drinking water at 4 ng/L is high compared with values ever reported in literature (58,59,61). Considering the suggested EC50 value of 0.9 ng/L in previous study (57), the concentration of ethinyl estradiol would cause serious concern for the public health. However, the kinetics of reaction between chlorine and ethinyl estradiol are extremely efficient (~100% removal) according to the study of Westerhoff et al. (62). The atypical value of ethinyl estradiol detected in drinking water was probably resulted from the detection method which is not suggested for drinking waters and shows great errors in the analysis of steroid hormones in water.

Seasonal variations were observed for CECs in WTP waters. Figure 5.2 shows the summer and other seasons total CEC content. The highest concentration of oxybenzone (78 ng/L) was detected in raw waters in the summer, which is consistent to the result from surface water investigation. During the other three seasons, the concentration of oxybenzone decreased and sucralose increased in raw water, and the total concentration of CECs detected declined to only half of the summer level. This is because the Salt River is the major source (~66%) of raw water during summer; SRP (Salt River Project) switched its raw water source to the Verde River (>80%) mixed with CAP water (~10%) during winter. WTP processes prior to chlorination (coagulation, sedimentation, and filtration) exhibit similar capacity to remove oxybenzone during different seasons (16 ng/L for summer and 12 ng/L for the other seasons). However, >99% of the oxybenzone residual will be oxidized by chlorination in all seasons. The similar total CEC concentration in finished water in all seasons indicated that CEC residues remaining in the water phase were relatively stable, that is, they could resist most chemical, biological, and physical degradation throughout the environmental system and drinking water treatment processes. This 30 ng/L of CEC residual in the distribution system can serve as the baseline and worth of monitoring in the aspect of public health.

5.3.4 Occurrence and Fate of CECs in a Wastewater Treatment Plant

Wastewater samples were collected from wastewater treatment plant A. Raw wastewaters, tertiary effluent, and effluent after UV treatment were collected for investigation. Thirty samples were collected from September 2007 to July 2009. All 26 compounds were detected in more than one raw wastewater sample, and the highest measured concentration was that of acetaminophen (250 μg/L) and lowest that of diazepam (2 ng/L).

Table 5.5 shows the detected CECs in wastewater treatment plant A samples. In raw wastewaters, most compounds (16/26) were detected in the range of 0.1 to 10 μg/L, and acetaminophen, caffeine, ibuprofen, and naproxen concentrations higher than 10 μg/L were detected. Steroid concentrations were generally from 20 to 80 ng/L. In tertiary effluent and effluent after UV treatment, the total concentration of CECs declined significantly from 250 μg/L (in raw wastewaters) to 9 μg/L. The highest detected concentrations in treated wastewaters were those of sucralose and sulfamethoxzole (about 2.4 μg/L). Hormones and diazepam concentrations were found to be less than 5 ng/L. However, the removal efficiencies of the compounds by wastewater treatment processes are varied. Several compounds (acetaminophen, caffeine, naproxen, ibuprofen, oxybenzone, cotinine, triclosan, TBBA, testosterone, pentoxifylline, estradiol, ethinyl estradiol, and progesterone) were >90% removed in wastewater treatment units. For other compounds (sulfamethoxazole, carbamazepine, dilantin, and erythromycin) the removal efficiency was much lower (<20%). As observed by other researchers (63), K_{ow} (in Table 5.1) is not the only factor in the CEC removal for a wastewater treatment plant adopted activated sludge and nitrification techniques because the poor correlations were found (not shown here). However, the filtration process before analysis might lead to removal of hydrophobic compounds and underestimate the total concentration in wastewaters. Overall, the low removal sucralose and sulfamethoxazole suggested that these two compounds might serve as indicators of wastewater intrusion.

There also appears to be a seasonal effect on raw wastewaters. Of the 26 compounds detected in raw wastewaters, 73% were found at higher concentrations during the summer (May to September), and 46% had more than a 50% difference between summer and other seasons. Apparently, oxybenzone (sunscreen), DEET (insect repellent), and triclosan (sanitizer) were applied more frequently during summer. The average concentrations of hormones and fluoxetine (antidepressant) in summer samples were also higher than in the other seasons. These data on CECs in raw wastewaters reflect the Arizona household pharmaceutical application frequency during different seasons.

To provide a state-wide view of CECs in wastewater effluent, which could be potential source of trace organics in surface water, wastewater effluent samples were collected once during May 2009 from eight wastewater treatment plants (Table 5.6) (see Appendix 5.A & B for WWTP locations). Overall, three hormones (ethinyl estradiol, progesterone, and testosterone), diazepam, and TBBA were reported to be not detectable or in concentrations of less than 5 ng/L in treated wastewaters. Sucralose was found in all eight wastewater effluents (3±1.74 µg/L). Sulfamethoxazole was also present in all eight effluents with high concentration (2.3±0.95 µg/L) except for one sample with 12 ng/L of sulfamethoxazole detected (WWTP C using wetland with treated water ponds). This might result from different wastewater processes in different WWTPs. Generally, the total CEC concentration remaining in treated wastewaters varied from 3.5 µg/L to 1.2 µg/L depending on treatment technique (Figure 5.3). Wetland and membrane bioreactor WWTPs exhibited the lowest CEC residuals remaining in treated wastewaters (<5 µg/L), but wetland-based WWTPs had the highest caffeine and DEET concentrations remaining among the eight treated wastewaters. Compared with the other techniques, trickling filter led to the highest CEC residual in wastewater effluent. WWTP E with aerated lagoon treatment process shown highest estradiol concentration remaining in effluent (61 ng/L). Membrane bioreactor and wetland had the lowest trimethoprim (0 to 30 ng/L) concentration in effluent compared with other treatment techniques (0.6 to 2.5 µg/L). In addition to sucralose and sulfamethoxazole, caffeine (0.02 to 4 µg/L), carbamazepine (0.15 to 0.3 µg/L), DEET (0.03 to 0.5 µg/L), oxybenzone (0.04 to 0.3 µg/L), and primidone (0.03 to 0.2 µg/L) were also detected in all wastewater effluents. The efficiency comparison between different wastewater treatment techniques requires the inclusion of other parameters (such as removal percentage) to yield a more solid conclusion.

To understand the natural attenuation of trace organics, samples were collected from the Santa Cruz River, which receives treated wastewater (from WWTP E with aerated lagoon treatment) as its only water source during winter (shown in Table 5.7). Most of the CECs value were at the same magnitude as in Table 5.6, WWTP E. The extremely high value of trimethoprim might result from analytical error and could be referred to the value of 2.5 μg/L in Table 5.6. Concentrations of several compounds (e.g., acetaminophen, cotinine, diclofenac) declined along the stream, whereas others remained constant (e.g., caffeine, sucralose, sulfamethoxazole) in all samples. The results shown might not be able to represent real scenario of natural attenuation since the sampling time didn't match the stream flow rate. However, the trend of decline could serve as important information for understanding the fate of trace organics in the environment. Further research is necessary to clarify whether partitioning or biotransformation dominates the distribution and the potential impact on ecosystems.

5.3.5 Occurrence of CECs in Groundwater near Recharge Site

Groundwater samples were collected from three monitoring wells at a GRUSP recharge site during August 2008 and January and July 2009. Nine samples were collected, and three well volumes of groundwater were pumped out until pH and conductance were stable before sampling.

Table 5.8 shows the CEC results from the groundwater samples. Most of the compounds had concentrations lower than 5 ng/L in these three samplings.

Seven out of 26 compounds were not detected in significant concentrations in any of these samples. Erthromycin, meprobamate, and pentoxifylline were the most prevalent compounds in all nine samples but had low concentrations (<10 ng/L). Dilantin, oxybenzone, sucralose, and sulfamethoxzole concentrations higher than 10 ng/L were detected in some samples, whereas sucralose and sulfamethoxzole concentrations greater than 100 ng/L were found in samples from measuring well No. 3. As discussed in section on wastewaters, sucralose and sulfamethoxzole had the highest CEC residuals in wastewater effluent, and their high concentrations in groundwater might be correlated with Arizona household habits. However, these high-concentration compounds in groundwater need further investigation to clarify the possible sources, such as surface water discharge, wastewater discharge, or intrusion from landfill sewage. Groundwater hydrology is worth investigation for understanding the occurrence of CECs in groundwater systems as part of drinking water sources.

5.3.6 The Impact of CECs Occurrence in Surface Waters by Water Recreational Activities

To understand the human activities effect on CEC occurrence in surface water, two famous water recreation areas were selected for investigation in this study: Slide Rock Park and Salt River Tubing site. The Slide Rock Park is in Coconino National Forest and the water recreation park is on Oak Creek River (branch of Verde River) open from late May to early September every year. The Salt River Tubing is a water recreation site in Tonto National Park near Blue

Point Bridge on Salt River which is open from late May to early September. The sampling location of Slide Rock Park was at Manzanita Camp Ground (1.5 miles downstream Slide Rock Park) and the sampling location for Salt River was at 3 miles downstream Blue Point Bridge. Samples were collected from morning before site open until site closed in one day.

Figure 5.4 shows the total CECS detected from the three water recreation events. In the beginning of the event, water samples were collected 1 mile upstream the recreation site as background of the CECs present in water. The total CEC concentration as background was about 0.1 to 0.3 μg/L for Salt River and was about 0.15 μg/L for Oak Creek River. Along the time, total CECs detected in downstream Salt River increased to 0.8 μg/L at noon and increased up to 5 to 6 μg/L at 4:00 pm. The flow rate of Salt River during summer is about 1.2 miles per hour and the tubing area covered about 5 miles of Salt River. The increasing trend of CECs in river water indicates that these compounds might be released from tourists and flowed along river. Similar CEC trend was also found in Slide Rock water recreation event but the highest total CEC concentration detected was 2.4 μg/L at 5:00 pm. Of 26 compounds, only 6 compounds (acetaminophen, caffeine, cotinine, DEET, naproxen, oxybenzone, and sucralose) were detected in at least one sample from 2008 Salt River hourly sampling. Among 6 detected compounds (shown in Figure 5.4.a), continine and sucralose were detected constantly with low concentration (< 10 ng/L) while other compounds were detected to be increasing over time, especially oxybenzone (up to 6 μg/L). For 2009 Slide Rock hourly sampling (Figure 5.4.b) 6 compounds (acetaminophen, caffeine, cotinine, DEET, maprobamate, oxybenzone, and sucralose) were detected in at least one sample: continine, maprobamate, and sucralose tended to be constant (< 10 ng/L) and others tended to be increasing over time. The hourly sampling for water recreation areas shows that human activity exerted significant effect on CECs present in surface water even though wastewater was not discharged into river upstream directly. Most of the sources for these detected PPCPs were from skin-applied products, like sunscreen and insect-repellent.

To verify the trend of CECs in river after water recreation site closed, few more samples were collected for 2009 Salt River sampling (shown in Figure 5.4.c). Similar trend was shown for the same compounds as in Figure 5.4.a before 4:00 pm and a decreasing of these compounds was observed after 4:00 pm. This observation conformed to the closing time of this site at 3:00 pm and testified the increasing of CECs concentration in river was due to human activity.

5.4 Conclusions

Results of this study demonstrate that low levels of CECs are present throughout the surface water system in Arizona. Public recreation in rivers and lakes could be major sources of skin-applied PCPs present in the canal system of the Phoenix area, especially during summers. Seasonal effects on surface waters might influence raw water quality in WTPs during source water switches by SRP. The seasonal effects of CEC occurrence from different sources might cause pulses of higher concentration in the drinking water system. Overall, the top six CECs detected are a) by frequency: oxybenzone, caffeine, sucralose, DEET, sulfamethoxazole, and acetaminophen; and b) by concentration: oxybenzone, caffeine, sucralose, DEET, sulfamethoxazole, and dilantin. Tracking the occurrence and fate of these CECs in drinking water systems and establishing a database is important for water management of metropolitan Phoenix to control these unregulated organic compounds in case of emergent issue.

For future monitoring, other possible sources of CECs that might impact drinking water, such as lakes, WWTP recharging sites, and landfill sites, need to be investigated for overall water resource management and potential ecosystem impact in Arizona. Long term monitoring of CECs in drinking water systems is recommended in case of abrupt contamination from wastewater discharge or landfill. The monitoring should at least focus on the 10 compounds detected most frequently and with highest concentration, including oxybenzone, caffeine, sucralose, DEET, sulfamethoxazole, acetaminophen, and dilantin.

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Table 5. 1 Summary of CECs studied and their properties

Compound name	**CAS #**	**Use**	**Log K_{ow}**[a]	**LC50 or EC50**[b]	**Ionization mode**[c]
Acetaminophen*	103-90-2	NSAID[d]	0.27	41.5(D)[e]	ESI+
Caffeine*	58-08-2	stimulant	0.16	46.9(D)	ESI+
Carbamazepine*	298-46-4	anticonvulsant	2.25	6.4(D)	ESI+
Cotinine	486-56-6	metabolite of nicotine	0.34	112.5(D)	ESI+
DEET[f]	134-62-3	insect repellent	2.26	5.1(D)	ESI+
Diazepam	439-14-5	anxiolytic	2.7	2.3(D)	ESI+
Diclofenac	15307-86-5	NSAID[d]	4.02	4.2(D)	ESI-
Dilantin	57-41-0	antiepileptic	2.16	103.8(F)	ESI-
Erythromycin	114-07-8	antibiotic	2.48	7.8(D)	ESI+
Fluoxetine	54910-89-3	antidepressant	4.65	0.2(D)	ESI+
Hydrocodone	125-29-1	narcotic analgesic	2.16	4.9(D)	ESI+
Ibuprofen	15687-27-1	NSAID[d]	3.79	4.3(D)	ESI-
Meprobamate	57-53-4	anxiolytic	0.98	8.9(GA)	ESI+
Naproxen*	22204-53-1	NSAID[d]	3.1	15.1(D)	ESI-
Oxybenzone	131-57-7	sunscreens	3.52	2.9(D)	ESI+
Pentoxifylline	6493-05-6	antiplatelet drug	0.56	39.2(D)	ESI+
Primidone	125-33-7	anticonvulsant	0.73	73.0(D)	ESI+
Sucralose	56038-13-2	artificial sweetener	-1	2341.5(D)	ESI-
Sulfamethoxazole	723-46-6	antibiotic	0.48	4.5(D)	ESI+
TBBA[g]	79-94-7	flame retardant	7.2	0.007(GA)	ESI-
Triclosan	3380-34-5	antibiotic	4.66	0.6(GA)	ESI-
Trimethoprim	738-70-5	antibiotic	0.73	2.6(GA)	ESI+
Estradiol*	50-28-2	steroid hormone	3.94	2.4(D)	APCI
Ethinyl Estradiol	57-63-6	estrogen	4.12	2.0(GA)	APCI
Progesterone	57-83-0	steroid hormone	3.67	3.3(GA)	APCI
Testosterone	58-22-0	steroid hormone	3.27	6.1(GA)	APCI

[a] estimated data were acquired from ECOSAR.

[b] lowest predicted LC50 (lethal concentration, concentration in water having 50% chance of causing death to aquatic life) or EC50 (half maximal effective concentration) for the most sensitive indicator aquatic species (ppm).

[c] ionization mode for compounds during LC/MS/MS analysis (ESI+: electrospray ionization positive mode; ESI-: electrospray ionization negative mode; APCI: atmospheric pressure chemical positive mode).

[d] nonsteroidal anti-inflammatory drugs.

[e] indicator organism for LC50 or EC50 determination, D:daphid, F:fish, GA:green algae.

[f] N,N-Diethyl-meta-toluamide.

[g] Tetrabromobisphenol A.

*isotope labeled analog of these compounds were spiked before solid phase extraction for recovery correction.

Table 5. 2 Summary of CEC levels detected in different waters sampled across the state of Arizona

Source	Non-detected or < Blank	2 to 10 ng/L	10 to 20 ng/L	20 ng/L to 1 ug/L	> 1 ug/L
Groundwater at recharge site	Testosterone progesterone, ethinyl estradiol, estradiol and others	Acetaminophen, caffeine, DEET, erythromycin, meprobamate, oxybenzone, pentoxifylline	None	Sulfamethoxazole, sucralose (from one site)	None
Salt River Project waters (Verde River & Salt River)	Testosterone progesterone, ethinyl estradiol, estradiol and others	Sucralose, sulfamethoxazole,acetaminophen ,cotinine, dilantin,	Caffeine, DEET	Oxybenzone	None
Central Arizona Project Canal from Colorado River	Testosterone progesterone, ethinyl estradiol, and others	Sulfamethoxazole, oxybenzone, meprobamate, DEET, cotinine, dilantin, carbamazepine, acetaminophen, primidone, estradiol	Caffeine, triclosan	Sucralose	None
Activated sludge WWTP with nitrification	Testosterone progesterone, ethinyl estradiol, estradiol	Acetaminophen, ibuprofen, diazepam, pentoxifylline	Cotinine	Caffeine, naproxen, oxybenzone, carbamazepine, hydrocodone, meprobamate, sulfamethoxazole, TBBA, DEET, erythromycin, fluoxetine, trimethoprim, primidone, triclosan, sucralose, dilantin, diclofenac	None
Raw wastewater	None	None	Diazepam, Progestero, Ethinyl Estradiol, Estradiol	Testosterone, hydrocodone, pentoxifylline, erythromycin, trimethoprim, primidone, fluoxetine carbamazepine, dilantin, diclofenac	Ibuprofen, naproxen, triclosan, sucralose, acetaminophen, caffeine, cotinine, oxybenzone, meprobamate, DEET, TBBA, sulfamethoxazole

Table 5. 3 Summary of CECs detected in Arizona surface waters.

Concentration: (ng/L)*	CAP canal mean detected	 mean total	Salt River mean detected	 mean total	Verde River mean detected	 mean total
Acetaminophen	4	2	10	2	5	2
Caffeine	17	10	19	11	14	7
Carbamazepine	3	2	2	<MRL	2	<MRL
Cotinine	5	3	4	2	2	<2
DEET	6	4	17	8	10	5
Diazepam	<2	<MRL	2	<MRL	<2	<MRL
Diclofenac	2	<MRL	3	<MRL	3	<MRL
Dilantin	7	3	10	2	6	2
Erythromycin	2	<2	3	<2	2	<2
Fluoxetine	3	<2	6	<2	3	<2
Hydrocodone	2	<2	3	<2	2	<2
Ibuprofen	5	<2	3	<2	<MRL	<MRL
Meprobamate	11	6	5	<2	3	<2
Naproxen	3	<2	5	2	2	<2
Oxybenzone	10	6	230	130	36	21
Pentoxifylline	3	<2	3	<2	2	<2
Primidone	7	3	3	<MRL	2	<2
Sucralose	180	100	5	2	13	9
Sulfamethoxazole	17	8	6	2	5	2
TBBA	4	<MRL	6	<2	4	<MRL
Triclosan	13	<2	8	<2	7	<2
Trimethoprim	3	<2	6	<2	3	<2
Estradiol	-	-	-	-	-	-
Ethinyl Estradiol	<2	<MRL	<2	<MRL	<2	<MRL
Progesterone	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Testosterone	<2	<MRL	<MRL	<MRL	<MRL	<MRL

<2: concentration lower than 2 ng/L.
<MRL: concentration lower than method reporting limit which is indistinguishable from the blank sample (blank results are summarized in Appendix 5.F).
*the data reported are dissolved concentrations detected in filtered water samples.

Table 5. 4 Summary of CECs detected in WTP samples

	WTP influent		**Sedimentation effluent**		**Finished water**	
Concentration: (ng/L)*	mean detected	mean total	mean detected	mean total	mean detected	mean total
Acetaminophen	6	2	6	2	8	2
Caffeine	14	10	13	7	11	5
Carbamazepine	<2	<MRL	<2	<MRL	2	<MRL
Cotinine	2	<2	2	<2	2	<2
DEET	6	6	5	3	6	3
Diazepam	<2	<MRL	<2	<MRL	<2	<MRL
Diclofenac	2	<MRL	2	<MRL	2	<MRL
Dilantin	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Erythromycin	2	<2	2	<2	2	<2
Fluoxetine	5	<MRL	6	<2	6	<2
Hydrocodone	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Ibuprofen	<MRL	<MRL	<MRL	<MRL	5	<2
Meprobamate	3	<2	3	<2	4	<2
Naproxen	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Oxybenzone	78	43	93	25	<MRL	<MRL
Pentoxifylline	3	<2	3	<2	3	<2
Primidone	2	<MRL	2	<MRL	2	<2
Sucralose	15	10	8	4	11	4
Sulfamethoxazole	4	<2	4	<2	3	<MRL
TBBA	4	<2	4	<2	4	<MRL
Triclosan	<MRL	<MRL	<MRL	<MRL	9	<2
Trimethoprim	3	<2	4	<MRL	4	<MRL
Estradiol	<MRL	<MRL	3**	<MRL	<MRL	<MRL
Ethinyl Estradiol	2**	<MRL	<2	<MRL	4**	<2
Progesterone	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Testosterone	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL

<2: concentration lower than 2 ng/L.

<MRL: concentration lower than method reporting limit which is indistinguishable from the blank sample (blank results are summarized in Appendix 5.F).

*the data reported are dissolved concentrations detected in filtered water samples.

**steroid concentrations were at or near reporting levels

Table 5. 5 Summary of CECs detected in WWTP A

	Raw wastewater		**Tertiary effluent**		**Effluent after UV**	
Concentration: (ng/L)*	mean detected	mean total	mean detected	mean total	mean detected	mean total
Acetaminophen	140,000	140,000	13	4	20	8
Caffeine	51,000	51,000	32	26	47	37
Carbamazepine	480	480	440	440	450	450
Cotinine	2,200	2,200	11	11	14	14
DEET	1,200	1,200	210	210	200	200
Diazepam	11	6	5	3	4	3
Diclofenac	200	160	99	89	48	43
Dilantin	520	470	640	580	430	390
Erythromycin	160	160	180	160	190	170
Fluoxetine	120	72	63	63	48	48
Hydrocodone	99	89	61	61	53	53
Ibuprofen	10,000	9,200	17	8	14	8
Meprobamate	1,200	1,200	680	680	690	690
Naproxen	22,000	19,000	130	120	88	80
Oxybenzone	8,100	8,100	93	65	99	49
Pentoxifylline	46	32	7	3	8	3
Primidone	660	660	250	250	230	230
Sucralose	5,400	4,800	2,800	2,600	2,700	2,500
Sulfamethoxazole	2,500	2,500	3,000	3,000	2,300	2,300
TBBA	1,100	640	140	69	88	44
Triclosan	1,500	1,400	150	120	90	81
Trimethoprim	840	840	270	240	280	260
Estradiol	68	30	6	2	5	<2
Ethinyl Estradiol	25	17	2	<2	<2	<MRL
Progesterone	22	15	2	<2	<MRL	<MRL
Testosterone	75	67	3	<2	<MRL	<MRL

<2: concentration lower than 2 ng/L.

<MRL: concentration lower than method reporting limit which is indistinguishable from the blank sample (blank results are summarized in Appendix 5.F).

*the data reported are dissolved concentrations detected in filtered water samples.

Table 5. 6 Summary of CECs in effluent from eight WWTPs (one time sampling in May 2009)

	WWTP A	**WWTP B**	**WWTP C**	**WWTP D**
Concentration: (ng/L)*	Activated sludge	Membrane bioreactor	Wetland with treated water ponds	Activated sludge
Acetaminophen	<MRL	<MRL	<MRL	170
Caffeine	44	37	1,000	49
Carbamazepine	290	250	150	290
Cotinine	4	11	27	22
DEET	190	31	490	230
Diazepam	<MRL	<MRL	<MRL	2
Diclofenac	41	17	<MRL	20
Dilantin	470	150	<MRL	220
Erythromycin	<MRL	<MRL	<MRL	70
Estradiol	14	<MRL	10	<MRL
Ethinyl Estradiol	<MRL	<MRL	<MRL	<MRL
Fluoxetine	25	<MRL	<MRL	51
Hydrocodone	51	37	<MRL	38
Ibuprofen	<MRL	6	<MRL	39
Meprobamate	430	280	11	670
Naproxen	<MRL	<MRL	<MRL	270
Oxybenzone	35	64	59	130
Pentoxifylline	5	<MRL	<MRL	<MRL
Primidone	180	122	78	89
Progesterone	<MRL	<MRL	<MRL	<MRL
Sucralose	3,200	1,700	2,500	4,000
Sulfamethoxazole	3,200	780	12	2138
TBBA	<MRL	<MRL	<MRL	<MRL
Testosterone	<MRL	<MRL	<MRL	<MRL
Triclosan	<MRL	<MRL	<MRL	41
Trimethoprim	63	27	0	1,800

<2: concentration lower than 2 ng/L.
<MRL: concentration lower than method reporting limit which is indistinguishable from the blank sample (blank results are summarized in Appendix 5.F).
*the data reported are dissolved concentrations detected in filtered water samples.

Table 5.6 (continued)

Concentration: (ng/L)*	**WWTP E** Aerated lagoon	**WWTP F** Activated sludge	**WWTP G** Trickling filter	**WWTP H** Activated sludge
Acetaminophen	53	52	280	27
Caffeine	14	250	4,000	55
Carbamazepine	160	250	210	230
Cotinine	13	410	180	20
DEET	140	95	82	180
Diazepam	2	3	<2	3
Diclofenac	320	11	24	18
Dilantin	120	240	180	820
Erythromycin	64	60	<MRL	4
Estradiol	61	10	16	9
Ethinyl Estradiol	<MRL	<MRL	<MRL	2
Fluoxetine	<MRL	130	36	49
Hydrocodone	10	70	47	45
Ibuprofen	23	37	97	<MRL
Meprobamate	63	490	430	610
Naproxen	47	440	1,000	30
Oxybenzone	45	60	340	55
Pentoxifylline	27	21	33	4
Primidone	30	110	54	230
Progesterone	<MRL	<MRL	<MRL	<MRL
Sucralose	1,400	2,900	2,000	7,000
Sulfamethoxazole	3,100	1,600	1,500	2,800
TBBA	<MRL	<MRL	<MRL	<MRL
Testosterone	<MRL	<MRL	<MRL	<MRL
Triclosan	13	32	42	13
Trimethoprim	2,500	2,400	950	600

<2: concentration lower than 2 ng/L.
<MRL: concentration lower than method reporting limit which is indistinguishable from the blank sample (blank results are summarized in Appendix 5.F).
*the data reported are dissolved concentrations detected in filtered water samples.

Table 5. 7 CECs detected in the Santa Cruz River

	WWTP E effluent	**Santa Cruz River A**	**Santa Cruz River B**	**Santa Cruz River C**	**Santa Cruz River D**
Concentration: (ng/L)*	River start 0 mile	Downstream 2.5 mile	Downstream 5.4 mile	Downstream 7.5 mile	Downstream 10.5 mile
Acetaminophen	310	120	130	120	110
Caffeine	210	250	220	350	370
Carbamazepine	88	110	100	100	110
Cotinine	1,200	1,400	1,400	990	860
DEET	150	160	160	160	150
Diazepam	3	4	4	4	3
Diclofenac	510	490	500	320	300
Dilantin	270	92	92	98	97
Erythromycin	220	130	260	250	340
Fluoxetine	17	12	10	<MRL	<MRL
Hydrocodone	<MRL	4	<MRL	<MRL	5
Ibuprofen	280	270	320	400	330
Meprobamate	40	58	55	57	70
Naproxen	1,900	550	500	490	480
Oxybenzone	40	33	36	41	41
Pentoxifylline	110	67	63	80	92
Primidone	39	55	55	61	63
Sucralose	1,500	1,700	1,400	1,300	1,100
Sulfamethoxazole	4,900	2,900	2,600	2,700	2,700
TBBA	<MRL	<MRL	<MRL	<MRL	<MRL
Triclosan	210	98	99	88	78
Trimethoprim	(11,000)**	230	270	330	290
Estradiol	110	89	48	32	67
Ethinyl Estradiol	<MRL	<MRL	<MRL	<MRL	<MRL
Progesterone	<MRL	5	5	3	3
Testosterone	<MRL	<MRL	<MRL	<MRL	<MRL

<2: concentration lower than 2 ng/L.

<MRL: concentration lower than method reporting limit which is indistinguishable from the blank sample (blank results are summarized in Appendix 5.F).

*the data reported are dissolved concentrations detected in filtered water samples.

**this value might be wrong due to analytical error and could be referred to the value of 2.5 µg/L shown in Table 5.6, WWTP E.

Table 5. 8 Summary of CECs detected in groundwater

	GW MW1		GW MW2		GW MW3	
Concentration: (ng/L)*	mean detected	mean total	mean detected	mean total	mean detected	mean total
Acetaminophen	4	2	4	2	4	2
Caffeine	8	3	5	2	6	2
Carbamazepine	<2	<2	<2	<2	<2	<2
Cotinine	2	<2	2	<2	2	<2
DEET	4	<2	<MRL	<MRL	5	2
Diazepam	<2	<2	<2	<2	<2	<2
Diclofenac	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Dilantin	<MRL	<MRL	<MRL	2	<MRL	8
Erythromycin	2	2	2	2	2	2
Fluoxetine	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Hydrocodone	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Ibuprofen	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Meprobamate	3	3	3	3	3	3
Naproxen	7	2	<MRL	<MRL	<MRL	<MRL
Oxybenzone	17	6	24	8	<MRL	<MRL
Pentoxifylline	2	2	2	2	2	2
Primidone	<2	<MRL	<2	<MRL	2	2
Sucralose	3	2	3	2	92	92
Sulfamethoxazole	5	3	17	11	200	200
TBBA	<MRL	<MRL	<MRL	<2	3	<2
Triclosan	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Trimethoprim	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Estradiol	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Ethinyl Estradiol	<MRL	<MRL	<MRL	<MRL	<2	<MRL
Progesterone	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Testosterone	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL

<2: concentration lower than 2 ng/L.
<MRL: concentration lower than method reporting limit which is indistinguishable from the blank sample (blank results are summarized in Appendix 5.F).
*the data reported are dissolved concentrations detected in filtered water samples.

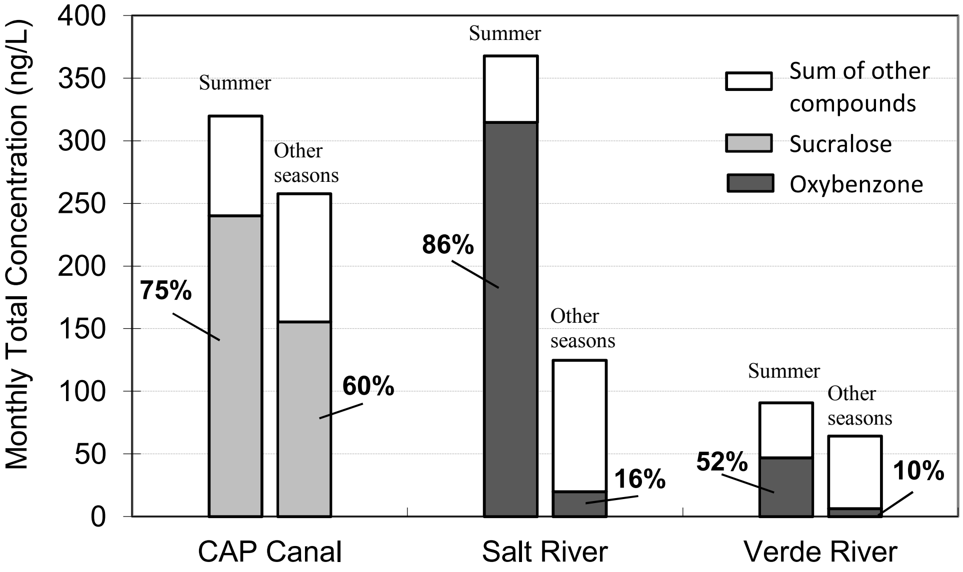


Figure 5. 1 Seasonal variation of CECs detected in surface waters.

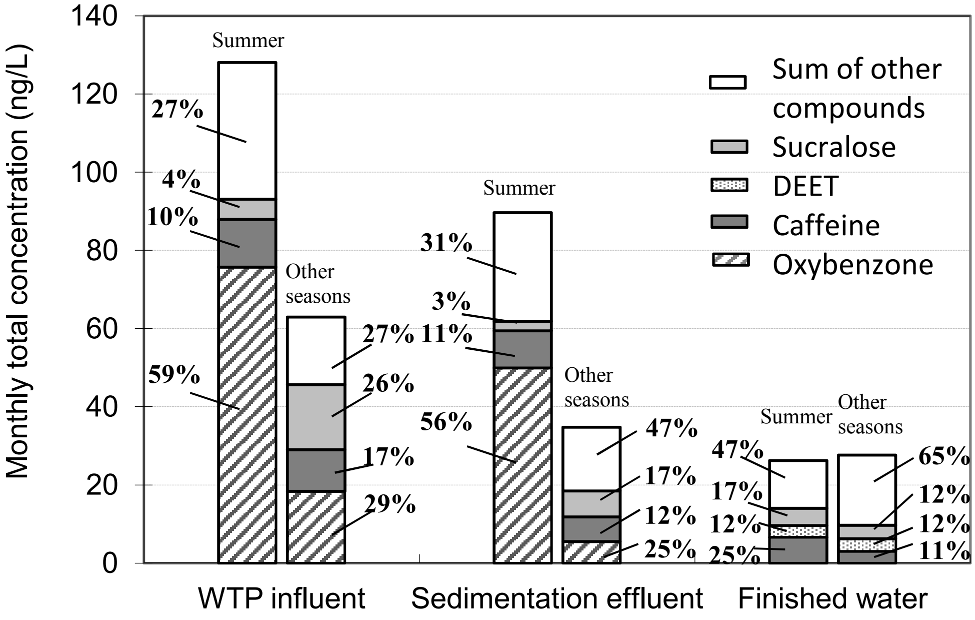


Figure 5. 2 Seasonal variations in CEC levels detected at three sampling locations of a Phoenix WTP

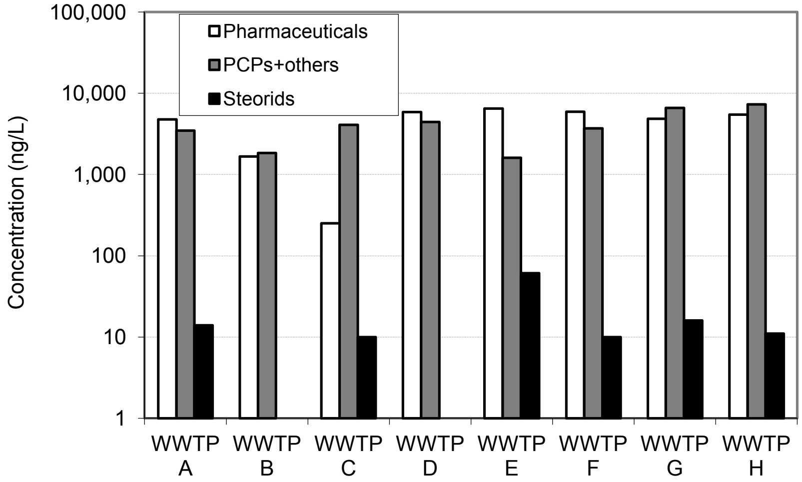
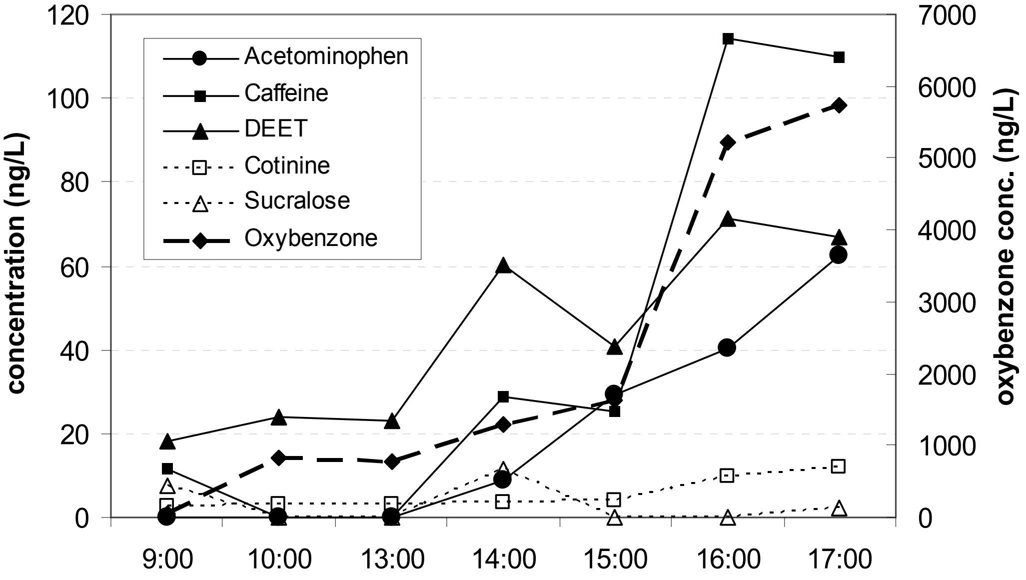
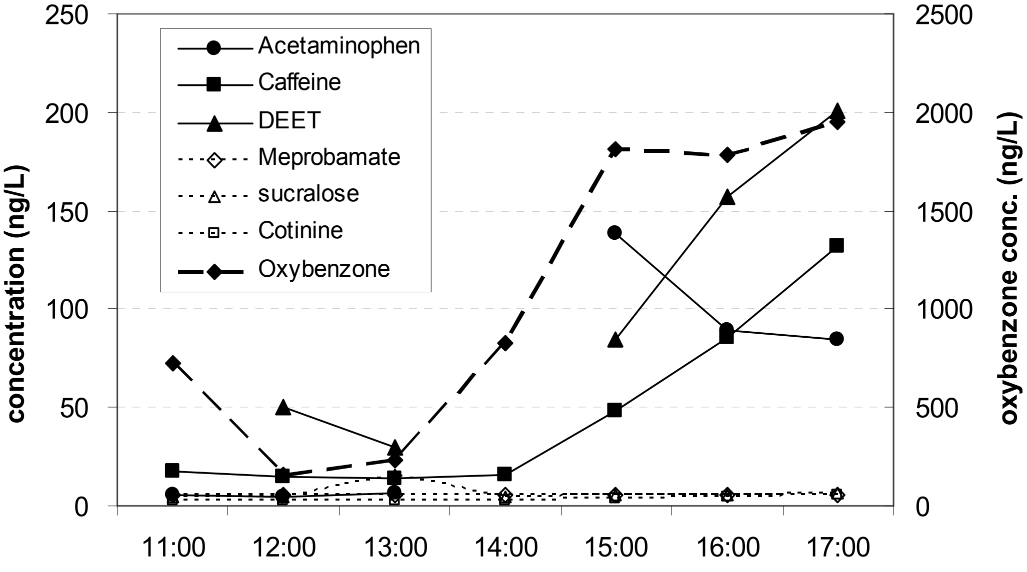


Figure 5. 3 Concentrations of different groups of CECs in each WWTP effluent.

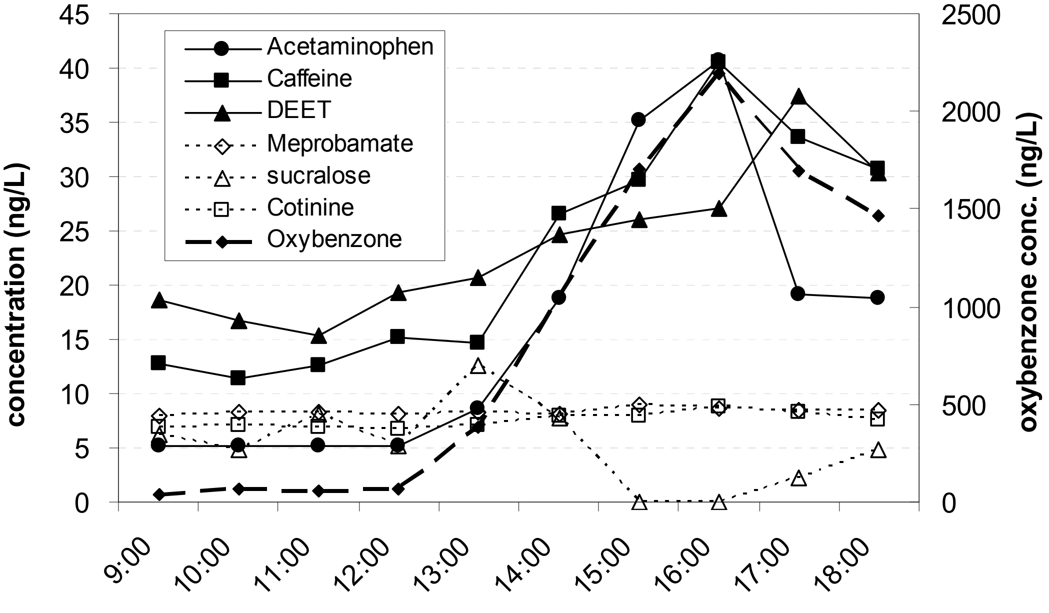


(a). PPCP/EDC detected over time in Salt River downstream of recreational site (September, 2008)



(b). PPCP/EDC detected over time in downstream of Slide Rock Park (July, 2009)

Figure 5. 4 PPCP/EDC detected over time downstream of recreational sites



(c). PPCP/EDC detected over time in Salt River downstream of recreational site (July, 2009)

Figure 5.4 (Continue).

CHAPTER 6

GAC REMOVAL OF ORGANIC NITROGEN AND OTHER DBP PRECURSORS

Submitted for peer-reviewed journal submission to *Journal of American Water Works Association*

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Abstract

The increased mutagenicity of bromide- and nitrogen-containing disinfection by-products (DBPs) requires a renewed evaluation of DBP control best available treatment technologies. The aim of this paper is to document the removal of organic nitrogen during granular activated carbon (GAC) treatment and to illustrate how GAC treatment alters DBP speciation. Rapid small-scale column tests (RSSCTs) with GAC were conducted on pretreated surface waters to evaluate the simultaneous removal of carbonaceous and nitrogenous DBP precursors (dissolved organic nitrogen (DON) and carbon (DOC), UV254-absorbing organics, and bromide). Simulated distribution system tests were conducted with RSSCTs effluent samples throughout NOM breakthrough using free chlorine to evaluate the formation of halogenated carbonaceous and nitrogenous DBPs. GAC preferentially removed UV254-absorbing material over DOC, which was removed better than DON. Bromide was not removed. Consequently, effluent Br/DOC and Br/DON ratios changed during GAC operation, and the ratio of brominated to chlorinated DBPs shifted during the GAC breakthrough cycle; brominated DBPs dominated earlier in the GAC breakthrough of DOC. DON as well as nitrogenous DBP precursors were not removed efficiently during GAC treatment.

Key words: activated carbon, rapid small-scale column test, disinfection by-product, dissolved organic nitrogen, DBP speciation

6.1 Introduction

Granular activated carbon (GAC) is widely used in water treatment facilities to remove natural organic matter (NOM), taste and odor compounds, and synthetic organic compounds (SOCs) from drinking water (Quinlivan et al, 2005; Pontius, 1990). To design a full-scale column for a treatment process, information on the breakthrough of these compounds is often required. Fortunately, laboratory column tests can be conducted to assess design parameters and performance. Rapid small-scale column tests (RSSCTs) conducted over a period of days can simulate months of full-scale GAC operations data for waters containing NOM or trace organics (Westerhoff et al, 2005; Cummings & Summers, 1994; Crittenden et al, 1991, 1987, 1986). As GAC usage becomes more widespread, its ability to aid in compliance with regulations on emerging DBPs is becoming a central justification for its use.

Dissolved organic carbon (DOC), organic nitrogen (DON), and bromide are source water precursors that control levels and speciation of disinfection by-products (DBPs) in finished water, and thus the management of their concentrations is an important compliance issue. This challenge becomes more difficult as the acceptable level of DBPs is lowered. The current maximum contaminant levels (MCLs) for carbonaceous DBPs (C-DBPs) are currently 0.080 mg L^{-1} TTHM (total trihalomethanes) and 0.060 mg L^{-1} HAA5 (sum of five haloacetic acids) in the Stage 2 DBP Rule (USEPA, 2006). Brominated DBPs, both regulated (THM, HAA5) and unregulated (haloacetonitriles (HANs)), have been suggested to exert greater mutagenic risk than chlorinated DBPs (Muellner et al, 2007).

Nitrogenous DBP (N-DBP) species (e.g., HANs, halonitromethanes, and nitrosamines) occur in treated drinking waters at concentrations less than those of regulated C-DBPs (e.g., THMs and HAAs) (Kemper et al, 2008; Krasner et al, 2006; Caughran et al, 1999; Krasner et al, 1989). However, N-DBPs are important because they may exert greater mutagenic or carcinogenic risk than currently regulated C-DBPs (Plewa et al, 2008; Richardson et al, 2008; Richardson et al, 2007; Plewa et al, 2004). Increased DON concentrations in surface water resulting from upstream wastewater discharges, agriculture runoff, and/or algal activity can lead to N-DBP formation upon application of disinfectants (Krasner et al, 2009; Dotson & Westerhoff, 2009; Nam et al, 2008; Lee et al, 2007; Reckhow et al, 1990). The degree of nitrogen enrichment, indicated by the DON/DOC ratio, corresponds to the propensity of precursors to form N-DBPs relative to regulated C-DBPs (Dotson et al, 2009; Wontae et al, 2007).

Although GAC is an efficient treatment process for the control of currently regulated C-DBPs, little information is available on the use of GAC to control unregulated N-DBPs. Furthermore, limited data exist on the change in N-DBP speciation (e.g., brominated versus chlorinated THMs) during organic matter breakthrough in GAC beds. This paper aims to document the removal of organic nitrogen during GAC treatment and illustrate how GAC treatment alters the speciation of N- and C-DBPs. This was achieved by using GAC in RCSSTs to evaluate the breakthrough behavior of DOC, DON, UV254-absorbing material, and bromide as well as subsequent DBP formation and speciation. Coagulated or otherwise pretreated waters were used in this study because these are the types of water that would be subsequently treated by GAC in an actual water treatment plant.

6.2 Materials and Methods

6.2.1 Water Sources

Water samples were collected using 55-gallon plastic (HDPE) drums from the sedimentation basins/impoundment of three water treatment plants (Plant A, Plant B, and Plant C) in the metropolitan Phoenix region, Arizona once per month (September 2007 to April 2008); 27 RSSCTs total. September is the period of the warmest annual water temperatures and high algae activity in the source waters (Baker et al, 2006). In these full-scale systems, meeting Stage 2 DBP regulations in the distribution system poses significant challenges. Therefore, GAC was evaluated as a means of improving DBP precursor removal to achieve compliance. Table 6.1 presents the characteristic parameters of representative feed water samples; all of the plants received water from the Colorado River, Salt River, or Verde River. Settled water was collected with a submersible sample pump and pre-filtered through a 10-μm glass fiber cartridge filter before RSSCTs to remove any remaining particulate matter and chemical floc. In all conventionally pretreated waters, DOC levels ranged from 2.3 to 3.7 mg L^{-1}, and specific UV254 absorption (SUVA) ranged from 1.1 to 2.4 L mg^{-1} m^{-1}. Three river waters, from the Salt River, Verde River, and Central Arizona Project canal, were also collected for this study once per month for five months (February to June 2008, 15 RSSCTs total). These river waters were pretreated with different processes for comparison with conventional treatments. River waters collected during February 2008 were pretreated in the laboratory with optimum enhanced coagulation (with ferric chloride dosage targeted to achieve 10% more of DOC removal than full-scale coagulation process; pH was targeted to be 6.8) as defined during bench-scale testing and filtration by a 10-µm cartridge filter. The enhanced coagulated water had DOC levels of 2 to 3 mg L^{-1} and SUVA averaging 1.6 L mg^{-1} m^{-1} (Table 6.1). The other four months of river waters were first mixed separately with 1) powdered activated carbon (PAC) (50 mg L^{-1}, 30 minutes), 2) chlorine dioxide (3 mg L^{-1}, 1 hour), 3) PAC (50 mg L^{-1}) and chlorine dioxide (3 mg L^{-1}, 1 hour), and 4) PAC (20 mg L^{-1}) and chlorine dioxide (3 mg L^{-1}, 1 hour), and then enhanced coagulation was conducted followed by RSSCT experiments. When both PAC and ClO_2 were used, the PAC was first added with vigorous mixing for 30 minutes and then ClO_2 was added with slow mixing for one hour. This was intended to simulate the pre-sedimentation process of full-scale plants and PAC was allowed to settle out as part of the process. The ClO_2 residuals at the end of pre-sedimentation were less than 0.3 mg/L and always non-detected at the end of enhanced coagulation. The DOC levels of the PAC/chlorine dioxide pre-treated surface waters ranged from 1.0 to 2.8 mg L^{-1}, and SUVA ranged from 0.6 to 1.7 L mg^{-1} m^{-1} (Table 6.1). In this study, conventional pre-treatment processes and enhanced coagulation reduced concentrations of DOC and UV254-absorbing material by 20 to 40 %; other advanced pre-treatment process reduced concentrations of DOC and UV254-absorbing materials by 35 to 70 %.

6.2.2 Rapid Small-Scale Column Tests (RSSCTs).

A commercial GAC[1] produced from bituminous coal was used. The BET surface area was 908.3 m^2 g^{-1}, and the total pore volume was 0.5 cm^3 g^{-1} for the GAC used. The GAC was pulverized and wet-sieved to obtain 140 × 170 mesh particle sizes, which resulted in an average particle diameter of 0.0049 cm. The proportional diffusivity RSSCT scaling relations developed by Crittenden et al (1986, 1987, and 1991) were used to determine the appropriate RSSCT parameters based on information on full-scale GAC contactors. According to Crittenden et al (1987), the minimum Reynolds numbers ($Re_{sc,min}$) for the RSSCTs should range from 0.02 to 0.13 to limit the effects of dispersion, and the $Re_{sc,min} \times Sc$ (Schmidt number) region should be between 200 and 200,000. The value of $Re_{sc,min} \times Sc$ used for RSSCTs in this study was 1000, which is consistent with other work (Summers et al, 1995). Table 6.2 summarizes the design and operating parameters and scaling equations for the RSSCTs used in this study. An empty bed contact time (EBCT) of 7.5 minutes at full scale was selected because it represents reconfiguration of filter beds to contain GAC over sand rather than anthracite over sand; deep-bed GAC filters were decided by the utilities to be too costly for adoption. The RSSCTs represent only organics removal by the GAC filter cap portion of a dual media filter.

The RSSCTs were constructed of glass, Teflon, and stainless steel to minimize the adsorption of organics. Glass columns[2] of 1.1 cm in diameter and 32 cm in length were used in the RSSCTs. Channeling effects and wall effects were avoided because the column diameter to particle diameter ratio was greater than 50. Piston pumps[3] (QG50) with stainless steel heads[3] (Q2CSC) were used to deliver feed water from a container to the GAC column. The temperature was constant (25 ± 2ºC), and the pH of feed waters ranged from 6.8 to 8 during RSSCT operation. Each RSSCT was operated until 80% breakthrough of the influent UV254 absorbance had been achieved. Effluent samples collected throughout the RSSCT were stored in clean ashed 40-ml amber glass vials.

6.2.3 Analytical Methods

DOC and total dissolved nitrogen (TDN) were measured using a TOC analyzer[4] (high-temperature combustion at 720°C and non-dispersive infrared detection with TNM-1 unit chemiluminescence detection). UV254 absorbance was measured using a UV/VIS spectrophotometer[5]. Nitrite and nitrate were measured using a chromatograph[6] with an IONPAC column (AS12-A) and a Dionex guard column (AG12-A). Ammonia was measured by a UV/VIS spectrophotometer[5] with a reagent kit[7]. DON (TDN minus dissolved inorganic nitrogen (DIN)) was calculated as described by Lee & Westerhoff (2005).

Simulated distribution system (SDS) tests were conducted with RSSCT effluent samples at 20%, 40%, 60% and 80% of UV254 absorbance breakthrough. Travel times in the actual distribution system in Phoenix vary from a few hours to up to 5 days (120 hours). Therefore, a chlorine residual test was performed to obtain a chlorine dosage that resulted in a 0.5 to 1 mg L^{-1} chlorine residual after 1-, 3-, 4- and 5-day incubation times. SDS samples were quenched by sodium sulfite and analyzed for THM and HAA5 according to EPA Method 551 by the laboratory of the 24th Street Water Treatment Plant, City of Phoenix, Arizona. Although HAN standards were not run initially with THM and HAA5 samples using EPA Method 551, semi-quantitative HAN values were determined afterward in conjunction with HAN/THM species concentration ratios obtained by running HAN and THM standards. Detection limits for THMs, HAAs, and dichloroacetonitrile (DCAN) and dibromoacetonitrile (DBAN) were 0.5 μg/L, 0.5 μg/L, and 0.2 μg/L, respectively.

6.3 Results and Discussion

6.3.1 Performance of RSSCTs for DOC and UV254 Absorbance Removal

In total, 42 RSSCTs were performed, and data representative of key findings are shown. Figure 6.1 presents RSSCT results from experiments conducted with water samples from the three different water treatment plants. DOC breakthrough occurred earlier than UV254 breakthrough over the RSSCT course for all water sources, which is in agreement with other work (Pontius, 1990). This illustrates that UV254-absorbing "fractions" of NOM are removed better than are other fractions; DOC is a surrogate for all of the NOM in water. The breakthrough curves vary for waters from different sources but tend to compress after normalization by feed water DOC (or UV254 absorbance) (shown in the inset in Figure 6.1). This was observed in all 42 RSSCTs regardless the pre-treatment process used. Thus, the normalized DOC or UV254 absorbance breakthrough curves for different sources were consistent, and the monthly differences were also negligible, which might be attributed to the small variation in influent DOC (3.0 ± 0.5 mg L^{-1}).

Figure 6.2 summarizes data from all 42 RSSCTs according to the number of bed volumes (BVs) treated to achieve specific breakthrough percentages of DOC, DON, or UV254 absorbance. The ratios of BV treated to achieve 20%, 40%, 60%, and 80% breakthrough between two components are summarized such that the relative preference to remove one component versus another can be assessed. For example, BV_{UVA} of 20% breakthrough represents the number of bed volumes treated before the RSSCT effluent contains a UV254 value (BV_{UVA}) that is 20% of that of the feed water UV254 value; likewise, BV_{DOC} of 20% breakthrough represents the number of bed volumes treated before the RSSCT effluent contains 20% of the feed water DOC concentration. A ratio of BV_{UVA}/BV_{DOC} greater than unity indicates that it took longer (more BVs treated) to achieve 20% breakthrough of UV254-absorbing components relative to the number of BVs necessary for the bulk DOC component. Similar and constant ratios (between 1 and 2) of BV_{UVA}/BV_{DOC} at 40%, 60%, and 80% were observed in all 42 RSSCTs regardless the pre-treatment process employed. Thus, UV254-absorbing components are preferentially removed over bulk DOC components. On the basis of the bar and whisker plots in Figure 6.2, breakthrough of UV254 absorbance can be used as a good tracer for DOC breakthrough throughout the RSSCT operation course because of the small variation in the ratios of BV_{UVA}/BV_{DOC}, even though DOC breakthrough occurred approximately 1.5 times faster than that of UV254-absorbing materials.

6.3.2 Performance of RSSCTs for Nitrogen Compound Removal

As a representative data set, Figure 6.3 presents data from Plant C including the normalized DOC, UV254 absorbance, TDN, DON, and DIN breakthrough curves. The breakthrough curves indicate that the removal of UV254-absorbing material and DOC exhibited a lag phase (0-1,000 BVs) in the beginning of breakthrough, but no lag stage was observed for DON, DIN, and TDN. The adsorption of DON by GAC was observed only over the first few hundred BVs (500 to 2,500 BVs), and DON broke through rapider than did DOC. After only 60 BV, 20% to 40% of the influent DON level was present in the RSSCT effluent. The breakthrough fraction of DON increased rapidly and was equal to influent levels after 10,000 BVs treated. NOM fractions enriched in DON have been characterized previously (Leenheer et al. 2007), and GAC removes them differently from NOM fractions enriched in UV254-absorbing materials.

The DIN concentration in the RSSCT effluent was constant (0.57 ± 0.03 mg-N L^{-1}) and equal to the DIN concentration in the feed water, indicating that the GAC column had no ability to remove nitrate, nitrite, or ammonia (i.e., DIN). Similar to DIN, in all tests GAC treatment did not remove other inorganic anions, including bromide ion (Br^-).

The inset in Figure 6.3 shows the SUVA value and DON/DOC ratio throughout the duration of RSSCT operation. The DON/DOC ratio was 0.7 mg-N/mg-C in the beginning and decreased to 0.1 mg-N/mg-C by 7,500 BV treated, after which the ratio remained the same as the feed water (DON/DOC = 0.11 mg-N/mg-C). The higher DON/DOC ratio in the RSSCT effluent than in the influent indicates that GAC preferentially removes DOC over DON before 7,500 BV treated. However (Figure 6.3 inset), the SUVA value exhibited an ascending trend through the RSSCT period and tended to approach the SUVA value of the feed water (1.7 L mg^{-1} m^{-1}). The lower SUVA in the RSSCT effluent than in the influent indicates that GAC selectively removed UV254-absorbing organic compounds over other organic materials, especially before 7,500 BV treated.

The ratios of BV treated values of DOC to DON and UV254 absorbance to DON are summarized in Figure 6.2. In general, DON breakthrough occurred 6 to 12 times faster than DOC or UV254 absorbance breakthrough in terms of BV treated before 60% breakthrough occurred. The GAC contactor showed limited adsorption capacity for all organics after 80% breakthrough occurred. The ratio of BV_{UVA}/BV_{DON} showed the highest variation over the course of the experiment. BV_{UVA}/BV_{DON} ratios higher than the 75th percentile were observed at all breakthrough stages for waters pretreated with chlorine dioxide and/or PAC combined with enhanced coagulation (river waters collected during March-June 2008). BV_{UVA}/BV_{DON} ratios less than the 25th percentile were observed for waters pretreated with conventional (water treatment plant settled waters) or enhanced coagulation only (river waters collected in February 2008). Based on the experimental findings, it appears that the pretreatment with chlorine dioxide and/or PAC combined with enhanced coagulation increased the number of BVs (by 2-3 times) which is required for UV254-absorbing materials to reach all breakthrough percentages (especially 20% breakthrough) but had a limited effect on DON breakthrough. A similar result was observed for BV_{DOC}/BV_{DON} ratios. In a previous study (Pontius, 1990), DOC breakthrough was suggested to be a function of influent DOC concentration. Advanced pretreatment processes, such as chlorine dioxide, PAC, or a combination, can prolong GAC operation time and delay exhaustion by reducing the influent DOC concentration and UV254 absorbance.

Detailed fractionation of organic matter indicates that hydrophobic fractions are deficient in organic nitrogen relative to more hydrophilic fractions and that higher UV254-absorbing organics are also nitrogen deficient (Leenheer et al, 2007). In this study and others, GAC preferentially removes hydrophobic organic matter that exhibits higher UV254 absorbance (Okada et al, 2003). Taken together, this is consistent with the observations in Figure 6.3 that GAC treatment removes UV254-absorbing components better than DON materials.

6.3.3 Performance of RSSCTs for THM and HAA Precursor Removal

When 20%, 40%, 60%, and 80% breakthrough of the initial UV254 absorbance occurred in the RSSCTs, effluent water samples were collected for SDS tests. DOC in each of these samples was measured, but because of the differential adsorption of DOC and UV254-adsorbing organics, the DOC values relate to different percentage breakthroughs than do UV254. Figure 6.4 shows TTHM and HAA5 data from a representative experiment. TTHM formation exceeded the TTHM goal (64 ppb) after 60% UV254 absorbance breakthrough with a 5-day SDS test; the 3-day SDS result exceeded the TTHM goal after approximately 70% UV254 absorbance breakthrough. All effluent water samples had HAA5 concentrations of less than 48 ppb (HAA5 goal), except HAA5 formation in feed water with a 5-day incubation time exceeded the goal. In this sample set, more THM than HAA5 was formed in GAC effluent, and THM exceeded the DBP goals before HAA5. Therefore, controlling TTHMs, rather than HAA5, is the key regulatory challenge for these utilities; this was true in all 42 RSSCTs.

Figure 6.5 shows the change in the bromide to DOC ratio (Br/DOC) in the RSSCT effluent versus the UV254 absorbance breakthrough percentage. At the early stage before 20% breakthrough, the Br/DOC ratio was high because GAC did not remove the bromide. A higher Br/DOC ratio should favor the formation of brominated DBPs over chlorinated analogs. As the Br/DOC ratio decreased, chloroform formation increased while bromoform formation decreased. The same phenomenon occurred in the formation of HAA species (results not shown).

Figure 6.5 also shows the bromine incorporation factor (BIF) values for THMs after 1-day and 5-day incubation. The equation for BIF calculation is:

$$BIF_{THM} = \frac{[CHCl_3]\times 0 + [CHCl_2Br]\times 1 + [CHClBr_2]\times 2 + [CHBr_3]\times 3}{[CHCl_3] + [CHCl_2Br] + [CHClBr_2] + [CHBr_3]} \qquad \text{EQN 1}$$

where all concentrations are in mole L^{-1}.

As the Br/DOC ratio decreased, so did the BIF value. The difference in BIF between 1-day and 5-day incubation samples is due to the chlorine dosage needed to achieve the target chlorine residual, which resulted in a larger chlorine-to-bromine driving force and greater chlorine demand by organics such that a higher relative formation of chlorinated THMs occurred. Based on the analysis by Shoaf and Singer (2007), the same trend should occur in brominated versus chlorinated HAAs, and this was indeed observed in this study. This study evaluated HAA5 data because it is a regulatory measurement. However, HAA5 is the sum of only five of the nine HAA species, and three of them are chlorine-containing-only species. In the early stage of GAC operation, HAA5 measurements underestimated the total HAA concentrations by 40 to 60 % in the effluent owing to the high bromine incorporation, as shown in the THM speciation. This outcome could attract concern because brominated DBP species have higher reported health risks than fully chlorinated species, an issue also mentioned by Shoaf and Singer (2007). Overall, the Br/DOC ratio shifts during GAC operations, which results in a shift from brominated to chlorinated THN and HAA species.

6.3.4 Performance of RSSCTs for N-DBP Precursor Removal

HANs (one group of N-DBPs) are of concern because of their potential toxicity (Muellner et al, 2007). Among the four main HAN compounds (DCAN, DBAN, bromochloroacetonitrile, and trichloroacetonitrile), DCAN and DBAN are typically the dominant species (Plewa et al, 2008). In this study, only DCAN and DBAN formation occurred at measurable concentrations. The total HAN concentrations were between 1 and 6 μg L^{-1}. The maximum DCAN concentration ($DCAN_{max}$) was in the feed water, whereas the maximum DBAN concentration ($DBAN_{max}$) occurred at 20% UV254 breakthrough, which had the highest Br/DOC ratio. The $DCAN_{max}$ range measured in this study was 0.7 to 2 μg L^{-1}, and the $DBAN_{max}$ range was 3.5 to 5 μg L^{-1}.

Figure 6.6 shows normalized HAN data after 1-day, 3-day, and 4-day incubation times. Instead of absolute concentrations, trends of normalized DCAN and DBAN as a function of BVs treated are shown. Normalized DCAN or DBAN concentrations relative to maximum observed concentrations ($DCAN_{max}$ or $DBAN_{max}$) are presented to highlight formation trends in the RSSCT effluent over its period of operation.

The $DCAN/DCAN_{max}$ ratio exhibited an increasing trend during RSSCT operation. However, the $DBAN/DBAN_{max}$ ratio tended to decrease over time. The observed trends indicate a HAN speciation shift over the RSSCT course. This shift of HAN species over operation time from brominated to chlorinated forms was similar to the trend in HAA and THM formation due to the decrease in the Br/DOC ratio. Moreover, total HAN (THAN) from a sample with 4 days incubation time was 0.5 to 2 μg L^{-1} less than that from a 1-day incubation time (data not shown), whereas THM and HAA concentrations increased with longer incubation time. The shift from brominated to chlorinated species and decrease in

HAN formation with longer incubation time indicate that HANs could be intermediates in the formation of other DBP groups, as suggested in a previous study (Reckhow et al, 2001). Furthermore, an increase in the DON/DOC ratio was suggested to increase N-DBP yields, including those for DCAN, trichloronitromethane (TCNM), and *N*-nitrosodimethylamine (NDMA) (Dotson et al, 2009; Wontae et al, 2007). The total HAN (DCAN and DBAN) yield in this study increased with increasing DON/DOC, but the low R-square value (R^2 = 0.45) might result from rapid DON breakthrough (60% DON breakthrough was reached before 5000 BVs treated).

Table 6.3 shows the linear regression results for DBP formation (TTHM, HAA5, and THAN) as a function of UV254 absorbance for all RSSCT experiments. TTHM and HAA5 concentrations positively correlated with UV254 absorbance according to the R-square of the regression, which was 0.67 to 0.85. However, the regression of THAN concentration to UV254 absorbance exhibited an inverse correlation (negative slope) and lower correlation coefficient (R^2). This result implied that THM and HAA precursors were more aromatic and hydrophobic, whereas HAN precursors were not necessarily aromatic. DON as N-DBP precursor broke through at an early stage of GAC service life (before 5000 BVs) owing to low adsorption ability. Thus, improved overall control of DON and improved control of N-DBPs in particular may necessitate reliance on processes other than GAC. Coagulation processes do not appear to be effective in removing large amounts of DON or specific nitrogenous organics such as amino acids (Dotson & Westerhoff, 2009; Lee et al, 2006). Ozonation can readily oxidize amine-containing organics, but this can also yield undesirable N-DBPs such as nitrosamines (Von Gunten et al, 2010; Dotson et al, 2009). A significant fraction of DON can be associated with colloidal fractions of organic matter (Song et al, 2010), so better removal of these colloids through the use of membrane processes (Hong et al, 2005) or electrocoagulation (Gamage & Chellam 2011) could complement GAC treatment for the control of currently regulated C-DBPs and emerging N-DBPs. Other than these approaches, little is known about how to specifically target removal of DON-enriched NOM during drinking water treatment.

6.3.5 Models for DOC and DON Breakthrough Curves Prediction

Models capable of simulating DOC breakthrough were developed to aid in understanding how GAC reactors would perform in removing DOC in a wide range of potential future scenarios. These include potential climatic variations in precipitation and runoff patterns that could lead to DOC levels up to 7 mg/L in raw water.

Figure 6.7 shows the simulated DOC breakthrough in each of these pretreated water sources. A logarithmic transformation of both the dependent and independent variables empirical model was used for modification in this study (Zachman et al., 2007). After back-transformation, the empirical model is expressed as a power-function equation as:

$$BV_X = A \times DOC_0^{B1} \times pH^{B2} \qquad \text{EQN 2}$$

Where A, B1 and B2 are the best-fit coefficients found by linear regression using STATA software, X represents the DOC breakthrough fraction (10, 20, 30,…80%), and BV_x represents the bed volumes reaching 10, 20, or 80% DOC breakthrough. The model intercept, A, varied with respect to GAC size, EBCT, and the DOC breakthrough fraction (Zachman et al., 2007). The power B1 over DOC_0 has a constant value of -1.0 in the normalized effluent concentration models and indicates the inverse relationship between running time and DOC_0 (Hooper et al., 1996). The power B2 over pH was selected as -1.5 in the normalized effluent concentration models and indicates stronger inverse relationship between running time and pH (Bond and DiGiano, 2004).

In this study, the GAC size is 140 x 170 mesh (0.0090 to 0.0106 cm), and the EBCT is 7.5 min. With these known, A can be expressed as:

$$A = 267.8 \times X^2 - 13974.3 \times X + 259794.7 \qquad \text{EQN 3}$$

The coefficients in equation A were found by best-fit linear regression of BV_x, DOC_0, pH, and X. The empirical model with new coefficients of A is called Model 1 throughout this study). 27 RSSCT breakthrough curves obtained with water treatment plant waters (data for training) were used to develop Model 1, which was then used to predict breakthrough curves for the remaining 15 observed RSSCTs (data for validation). As shown in Figure 6.7, the relatively high R-square values (0.85 to0.89) indicate a good fit between Model 1 and training data and relatively low R-square values (0.75 to 0.81) also indicate a good prediction for validation data (shown in Figure 6.8). The coefficients of intercept A is different from the coefficients found in Zachman et al., 2007 (e.g., $A=202\times X^2-5995\times X+261914$ was found with the model developed from the data using 8×30 mesh GAC size and 20 mins of EBCT). The difference was suggested to be the result of different GAC size, EBCT, GAC material, and water characteristics (Zachman et al., 2007).

However, this model cannot predict DOC at < 25% breakthrough well since the intercept A is a quadratic equation and only the data of >25% DOC breakthrough can fit the upper part of the parabolic curve. For better fitting and prediction of DOC breakthrough, Model 2 modified from the empirical model of Zachman was suggested in this study. Model 2 is expressed as:

$$BV_X = e^A \times DOC_0^{B1} \times pH^{B2} \qquad \text{EQN 4}$$

Parameters including BV_x, X, A, B1, and B2 are the same as described for Model 1. The data of $BV_x/(DOC_0^{B1}\times pH^{B2})$ was logarithmic transformed for best-fit linear regression with intercept A. The coefficients for A and R-square were summarized in Table 6.4 and the predicted data generated by both two models were shown in Figure 6.9 to compare with observed data. The power over DOC_0 and pH were -1 and -1.5 respectively found by best-fit linear regression (agreed with Bond and DiGiano, 2004). The R-square values (0.79, 0.77, 0.79) for training data, validation data, and overall data, respectively, from Model 2 is more consistent and higher than from Model 1 (R-square = 0.76, 0.64, 0.75). Moreover, Model 2 exhibited better prediction for the early stage (<25%) of DOC breakthrough times than Model 1 (shown in Figure 6.9). In addition, the modified

Model 2 could be applied for prediction of dissolved organic nitrogen breakthrough from GAC adsorber.

To provide a comprehensive DON breakthrough behavior from GAC adsorber to facilitate comparison between DON and DOC breakthrough curve simultaneously, a DON form of Model 2 was applied for best-fit linear regression and simulation of DON breakthrough curve. The expression of Model 2 for DON is the same as Model 2 for DOC but DOC_0 is substituted with DON in feed waters (DON_0).

$$BV_X = e^A \times DON_0^{B1} \times pH^{B2} \qquad \text{EQN 5}$$

Parameters including BV_x, X, A, B1, and B2 are the same as described for Model 2. Dependent variable (BV_x) and independent variables (DON_0 and pH) were used for linear regression to find the best-fit functional form of A. 9 sets of RSSCTs obtained with water treatment plant waters were used for model training and 12 sets of RSSCTs obtained with river water were used for validation (DON ranged from 0.1 to 0.7mg/L in this study). The coefficients in A and power B1 and B2 for best-fit of DON breakthrough curve are summarized in Table 6.4. The best-fit power B1 over variable DON_0 is -0.23 which is lower than B1 for DOC breakthrough. This low B1 coefficient for DON indicates a weak relationship between run time and DON_0 and implies lower affinity for GAC to adsorb organic nitrogenous compounds. According to R-square values, Model 2 fairly represented the DON breakthrough of RSSCT conducted with WTP waters (R-square = 0.63) but didn’t predict the breakthrough for validation data accurately

(R-square = 0.38) due to different pre-treatment conducted with WTP waters and river waters. In general, Model 2 for DON shows lower predictive ability than Model for DOC but a 0.5 R-square value for overall prediction can present the trend of DON breakthrough GAC adsorber. For the comparison between DOC and DON breakthrough curves based on modeling results, GAC selectively adsorbed DOC material over DON and, the BV treated for DOC doubled the BV treated for DON to reach the same breakthrough percentage (shown in Figure 6.10).

6.4 Conclusions

GAC preferentially removes UV254-absorbing material, and DOC is preferentially removed over DON. The low affinity for adsorption by GAC implies that DON compounds may be composed primarily of hydrophilic organic matter. UV254 absorbance is often a good indicator of DOC breakthrough from the GAC column because the trend of normalized UV254 absorbance breakthrough is analogous to that of normalized DOC breakthrough. The UV254 absorbance measurement is efficient and less costly compared with DOC measurement for facilities considering GAC breakthrough monitoring. Pretreatment of surface water with chlorine dioxide and/or PAC will reduce the amount of dissolved organics as well as UV254-absorbing material and extend the number of BVs treated, especially before 20% breakthrough occurs. Conventional treatment processes and enhanced coagulation show limited ability to reduce this dissolved organic matter, and waters pretreated with advanced processes, such as chlorine dioxide, PAC, or a combination, tend to prolong GAC bed life by reducing concentration of DOC and UV254-absorbing materials in adsorber influent. The breakthrough of DOC will affect the chlorine dosage and result in a shift in DBP speciation from brominated to chlorinated species. More highly brominated DBPs that form during early stages of GAC operation are a potential problem for water treatment plant operation because regulations are mass based. However, the overall reduction of DBP precursors by GAC compensates for this disadvantage before 10,000 BV treated. Furthermore, the presence of organic nitrogen can elevate the toxicity of DBPs, and this could be a major drawback for facilities considering installation of a GAC adsorber owing to the poor removal efficiency of DON by GAC. For DBAN, a key to controlling N-DBP formation is for treatment processes to include the removal of nitrogen-enriched dissolved organic matter fractions prior to the GAC adsorber. In this work, the poor removal of DON and rapid breakthrough of at least one N-DBP precursor class, that of HANs, provides initial evidence that GAC may not remove N-DBP precursors as well as THM or HAA precursors, but additional research on other N-DBP precursors using RSSCTs is necessary to fully understand the potential benefits of GAC treatment for controlling N-DBPs. Likewise, the observation that DON breakthrough occurs more rapidly than DOC breakthrough in GAC beds should be validated from full-scale GAC filter cap and contactor applications.

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Footnotes

[1] Norit GAC820; Norit Americas Inc., Marshall, TX.
[2] Ace Glass Inc., Vineland, NJ.
[3] Fluid Metering Inc., Syosset, NY.
[4] Shimadzu Corp., Tokyo, Japan.
[5] Shimadzu Corp., Tokyo, Japan.
[6] Dionex Corp., CA.
[7] HACH Company, Co.

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Table 6. 1 Characteristic parameters of representative feed water samples. Each water sample was conducted with one RSSCT. Only the results of the feed water conducted RSSCTs described in this study are summarized in this table.

		DOC ($mg\ L^{-1}$)	UV254 (cm^{-1})	pH	TDN ($mg\ L^{-1}$)	DIN[3] ($mg\ L^{-1}$)	Br^- ($\mu g\ L^{-1}$)
2007 October	Plant A	2.75	0.043	7.7	1.41	-[2]	102
	Plant B	2.30	0.031	7.7	0.58	-	85
	Plant C	2.71	0.043	8.0	1.34	-	90
2007 December	Plant A	3.04	0.063	7.1	0.30	-	62
	Plant B	2.50	0.035	8.0	0.55	-	94
	Plant C	3.69	0.076	8.0	0.31	-	40
2008 April	Plant A	2.87	0.046	7.0	0.97	0.69	88
	Plant B	3.09	0.036	8.4	0.73	0.40	65
	Plant C	3.39	0.058	8.1	0.94	0.57	-
Salt River water[1] (Feb, 2008)		2.71	0.046	6.9	0.73	0.60	100
Verde River water[1] (Feb, 2008)		2.81	0.062	6.8	1.40	1.00	85
CAP water[1] (Feb, 2008)		2.09	0.025	6.6	0.58	0.24	92
Salt River water[4] (June, 2008)		2.43	0.028	7.0	0.84	0.60	80
Verde River water[4] (June, 2008)		2.27	0.036	6.9	1.20	0.86	52
CAP Canal[4] (June, 2008)		1.00	0.010	6.8	0.63	0.42	62

[1] Plant A and C use Salt River and Verde River as raw water sources.

[2] Plant B used CAP canal as raw water source.

[3] river waters were pretreated with enhanced coagulation.

[4] river waters were pretreated with PAC(50mg/L)/ClO_2/enhanced coagulation.

[5] dissolved inorganic nitrogen (DIN) = nitrite + nitrate + ammonia.

[6] data which was not measured.

Br^-—Bromide, CAP—Central Arizona Project, DIN—dissolved inorganic nitrogen, DOC—dissolved organic carbon, RSSCT—rapid small-scale column test, TDN—total dissolved nitrogen, UV254—ultraviolet absorbance at 254 nm wavelength

Table 6. 2 Design and operation parameters and scaling equations of a pilot scale contactor and a RSSCT

Design Parameters	Simulated Pilot Scale Values	RSSCT Values	Scaling Equations[#]
Particle Radius (cm)	0.08025	0.0049	
EBCT (minutes)	7.5	0.46	$Eq.(1): \frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{d_{p,SC}}{d_{p,LC}}\right] = \frac{t_{SC}}{t_{LC}}$
Loading Rate (m hour^{-1})	14.67	9.18	
Length of Column (cm)	183.44	7.0	$Eq.(2): \frac{D_{SC}}{D_{LC}} = \left[\frac{d_{p,SC}}{d_{p,LC}}\right]$
Column Diameter (cm)	832	1.1	$Eq.(3): \frac{V_{SC}}{V_{LC}} = \left[\frac{d_{p,SC}}{d_{p,LC}}\right] \times \frac{\mathrm{Re}_{SC} \times Sc}{\mathrm{Re}_{LC} \times Sc}$
Media Volume (ml)	99678600	6.7	
Flow Rate (ml min^{-1})	1.33×10^7	14.54	$Eq.(4): \mathrm{Re} = \frac{V \times \rho_L \times d_p}{\mu}$
Bulk Density (g L^{-1})	0.49	0.49	$Eq.(5): Sc = \frac{\mu}{D_L \times \rho_L}$
Re×Sc	26170.27	1000	

[#] Note: EBCT = empty bed contact time; SC = small column (i.e. RSSCT column); LC = large column (i.e. pilot column); d_p = media diameter; t = run duration; D = effective surface diffusivity; V = loading range; Re = Reynolds number; Sc = Schmidt number; ρ_L = liquid density; μ = viscosity; and D_L = liquid diffusivity.

gpm—gallon per minute, RSSCT—rapid small-scale column test

Table 6. 3 The linear regression results of DBP formation as a function of UV254 absorbance (cm^{-1}).

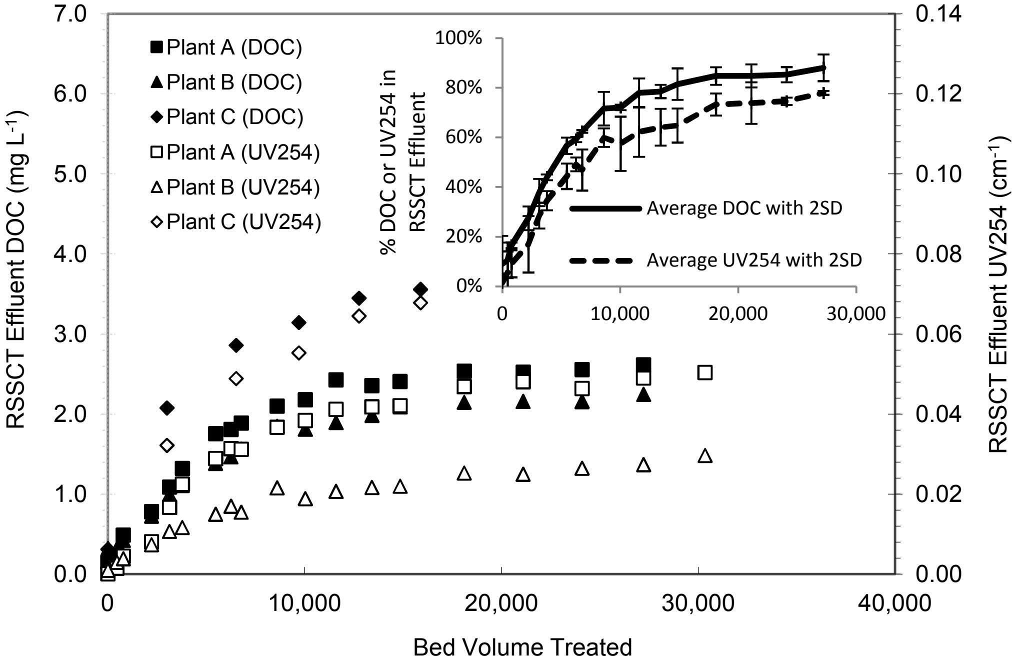
		As a function of	Sample Size	Slope	R-square
3-day incubation	TTHM (µg/L)	UV254 absorbance (cm^{-1})	189	1370	0.66
	HAA5 (µg/L)		45	10108	0.85
	THAN (µg/L)		35	-51.5	0.33
5-day incubation	TTHM (µg/L)		189	1620	0.67
	HAA5 (µg/L)		189	1070	0.72
	THAN (µg/L)		35	-61.2	0.44

DBP—disinfection by-product, HAA5—sum of five haloacetic acids, THAN—total haloacetonitriles, TTHM—total trihalomethanes, UV254—ultraviolet absorbance at 254 nm wavelength

Table 6. 4 Comparison of the best-fit coefficient and ability of prediction between Model 1, Model 2, and Model 2 for DON.

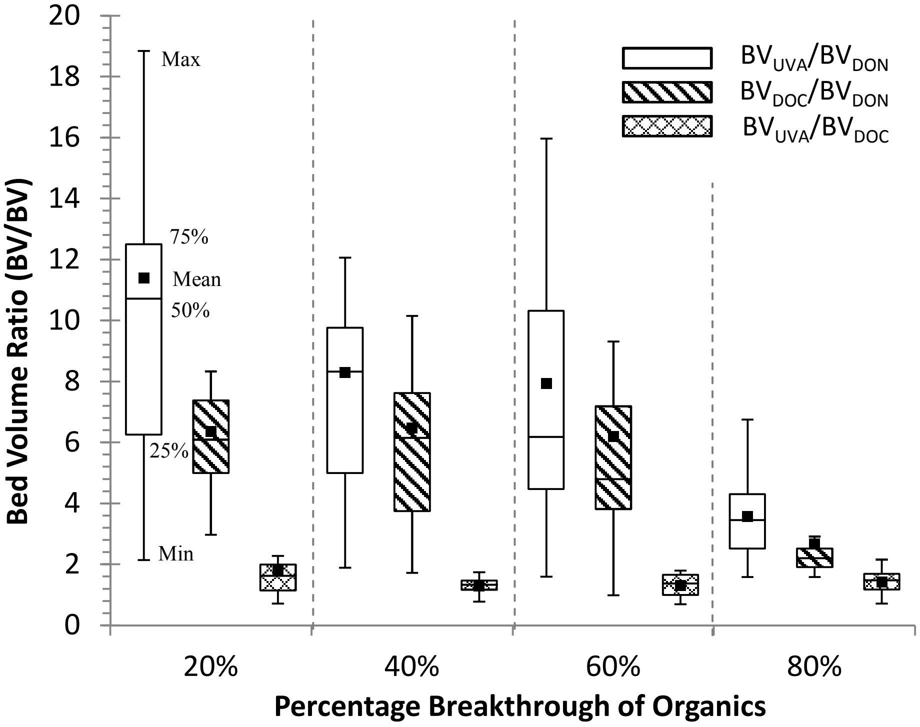
	Model 1	Model 2	Model 2 for DON
Coefficient of X2 in A	267.8	0.00021	0.00025
Coefficient of X in A	-13974.3	0.011	0.012
Constant in A	259794.7	11.3	10.0
B1	-1	-1	-0.23
B2	-1.5	-1.5	-1.96
R-square for training	0.761	0.787	0.628
R-square for validation	0.641	0.769	0.384
R-square for overall	0.746	0.786	0.482

DON – Dissolved Organic Nitrogen



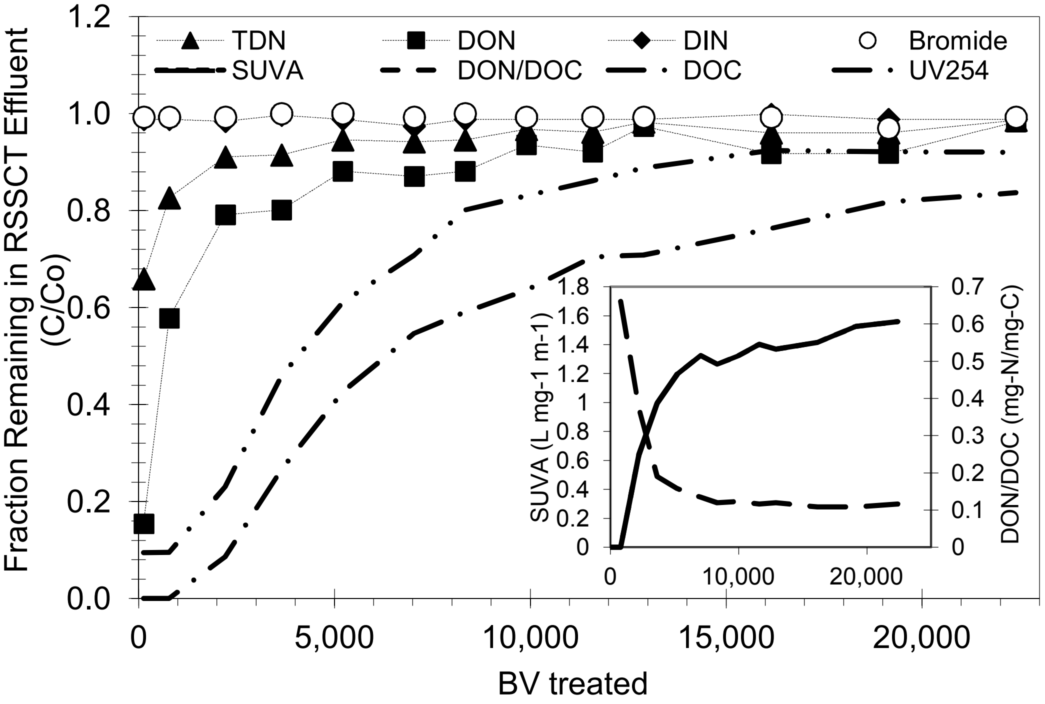
DOC—dissolved organic carbon, RSSCT—rapid small-scale column test, UV254—ultraviolet absorbance at 254 nm wavelength

Figure 6. 1 DOC and UV254 breakthrough curves of RSSCTs conducted with coagulated waters from three different water treatment plants (December 2007). (Influent DOC (UVA): Plant A = 3.04 mg L^{-1} (0.063 cm^{-1}); Plant B = 2.50 mg L^{-1} (0.035 cm^{-1}); Plant C = 3.69 mg L^{-1} (0.076 cm^{-1})). Inset illustrated the average of three normalized DOC and UV254 breakthrough curves with 2 standard deviations.



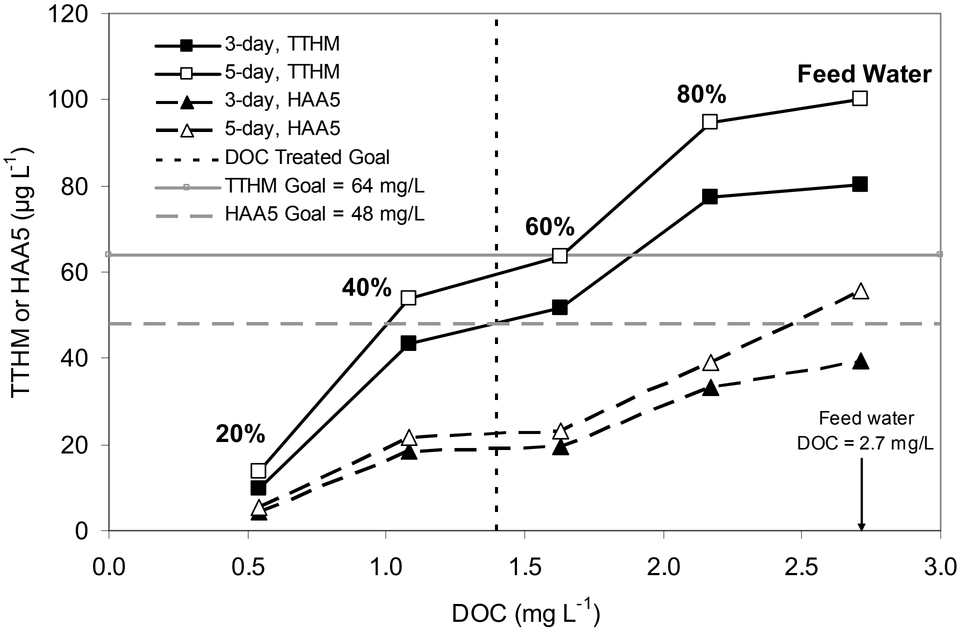
BV—bed volume, DOC—dissolved organic carbon, DON—dissolved organic nitrogen, UVA—ultraviolet absorbance at 254 nm wavelength

Figure 6. 2 The ratio of bed volume treated to achieve 20%, 40%, 60%, and 80% breakthrough between UVA, DON, and DOC.



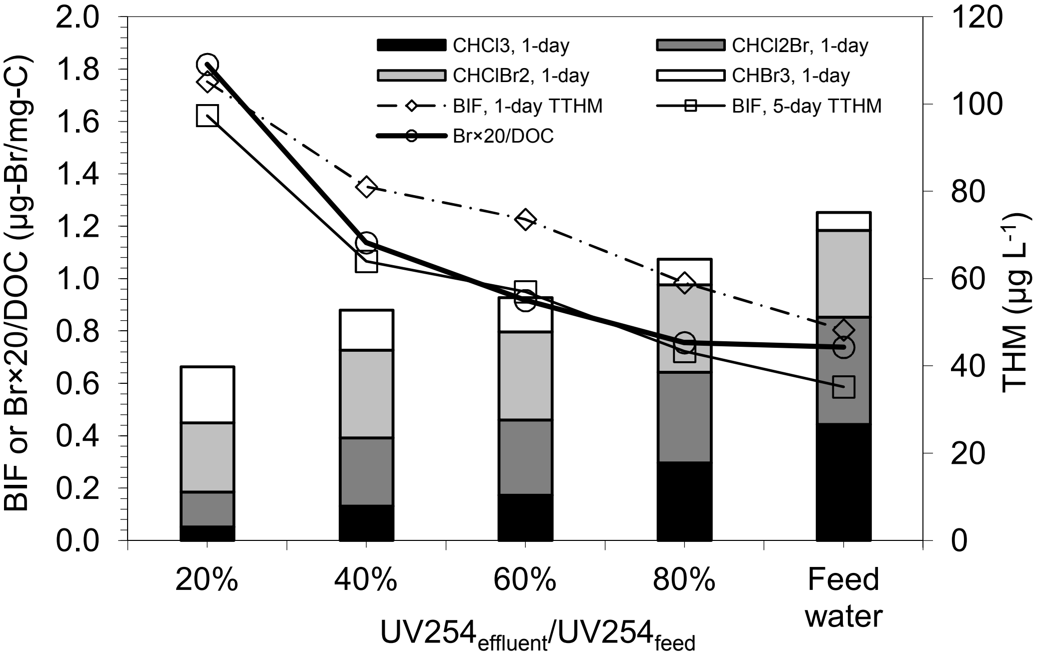
C—concentration, C_0—initial concentration, DIN—dissolved inorganic nitrogen, DOC—dissolved organic carbon, DON—dissolved organic nitrogen, RSSCT—rapid small-scale column test, SUVA—specific ultraviolet absorbance, TDN—total dissolved nitrogen, UV254—ultraviolet absorbance at 254 nm wavelength

Figure 6. 3 Normalized DOC, UV254, TDN, DIN, DON, and bromide breakthrough curves of RSSCT conducted with Plant C water (April, 2008, feed water parameters are summarized in Table 6.1). Inset illustrates the SUVA (L mg^{-1} m^{-1}) and DON/DOC (mg-N/mg-C) values.



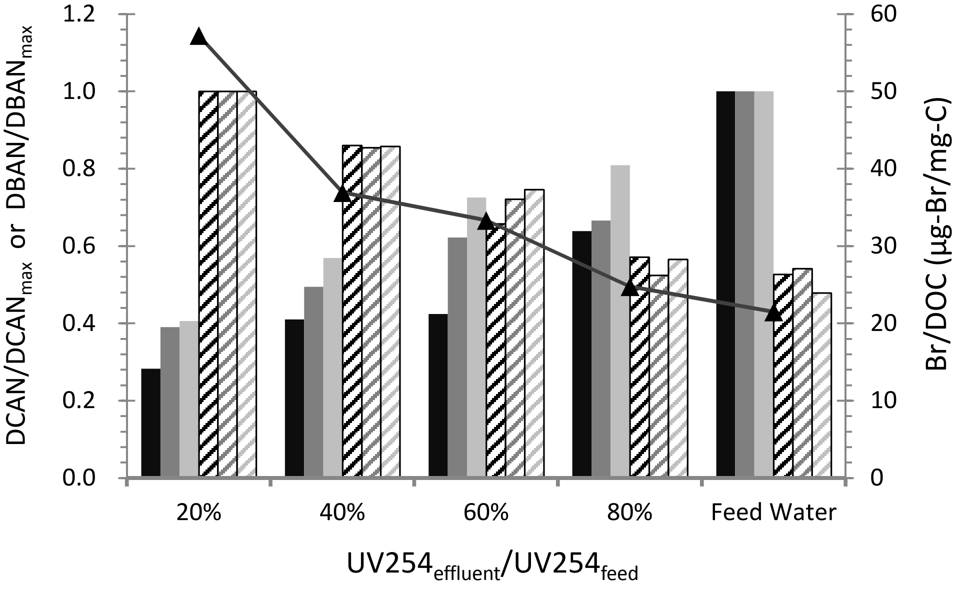
DBP—disinfection by-product, DOC—dissolved organic carbon, HAA5—sum of five haloacetic acids, TTHM—total trihalomethanes, UV254—ultraviolet absorbance at 254 nm wavelength,

Figure 6. 4 DBP formation and DOC concentration of RSSCTs conducted with Plant C water (October, 2007, feed-water parameters were summarized in Table 6.1) at 20%, 40%, 60%, 80% UV254 breakthrough, and in feed water. DOC treated goal was set as 1.4 mg L^{-1} and DBP goals were set as 80% of Stage 2 D/DBP Rule.



BIF—bromine incorporation factor, Br—bromide, DOC—dissolved organic carbon, RSSCT—rapid small-scale column test, THM—trihalomethanes, UV254—ultraviolet absorbance at 254 nm wavelength

Figure 6. 5 Formation of THM species of RSSCTs conducted with pretreated (enhanced coagulation) Salt River water (February, 2008, feed water parameters were summarized in Table 6.1), BIF and Br×20/DOC values at 20%, 40%, 60%, 80% UV254 breakthrough, and in feed water.



Br—bromide, C—concentration, C_{max}—maximum concentration, DBAN —dibromoacetonitrile, DCAN—dichloroacetonitrile, DOC—dissolved organic carbon, RSSCT—rapid small-scale column test, UV254—ultraviolet absorbance at 254 nm wavelength

Figure 6. 6 Ratios for DCAN (solid filled bars) and DBAN (stripe bars) formation with chlorine contact times of 1-day, 3-day, or 4-day (from left to right) for RSSCT influent (feed water) and effluent after reaching similar levels of UV254 breakthrough (20%, 40%, 60% and 80%). Bromide to DOC ratios are shown with a solid line. Sample (Verde River, Feb 2008) was pretreated with enhanced coagulation prior (feed-water quality shown in Table 6.1).

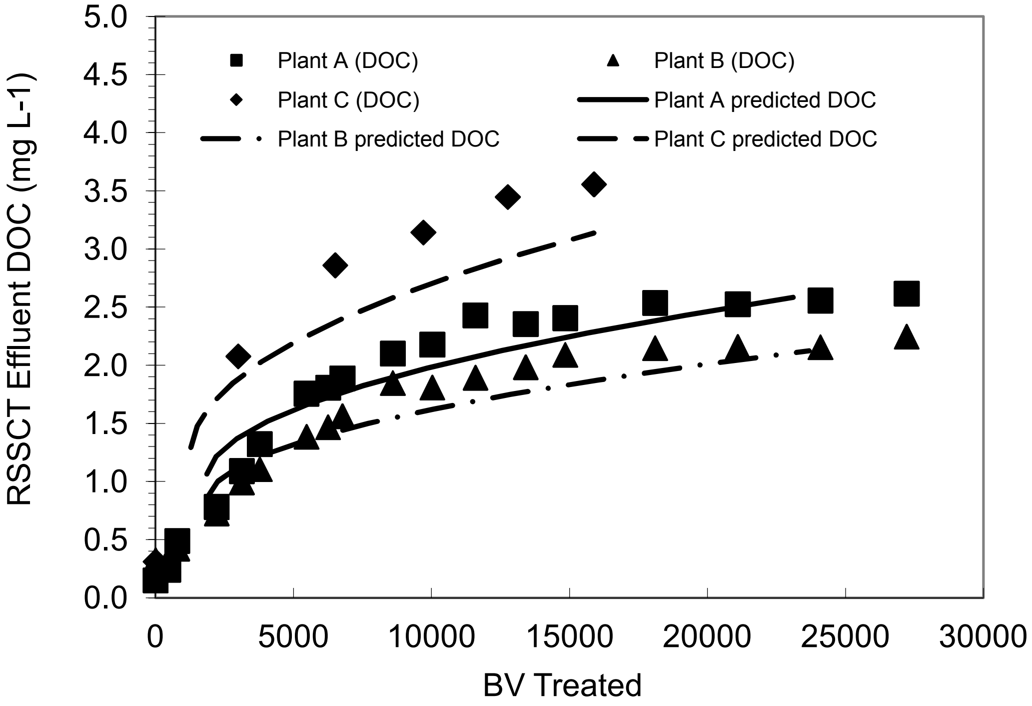


Figure 6. 7 DOC and UV254 breakthrough curves of RSSCTs conducted with coagulated waters from three different water treatment plants (December 2007) Simulated DOC breakthrough curves for each plant is shown using lines based upon Model 1. (Influent DOC: Plant A = 3.04mg/L; Plant B = 2.50mg/L; Plant C = 3.69mg/L.

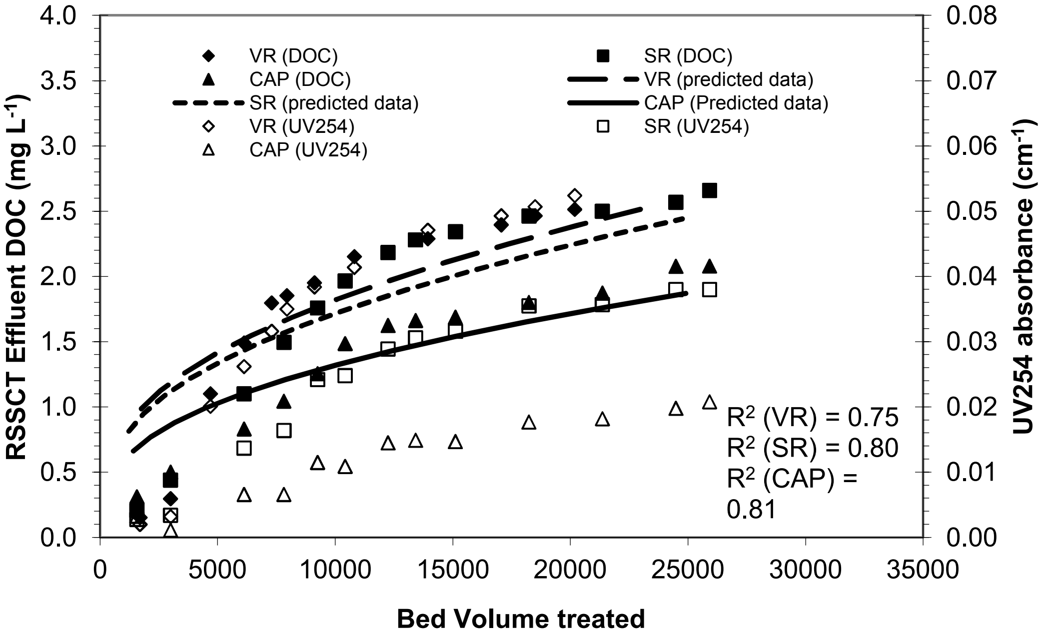


Figure 6. 8 DOC and UV254 breakthrough curves of RSSCTs conducted with three different feed water sources. Modeling results are showed as line. (Influent DOC: VR (Verde River) = 2.81mg/L; SR (Salt River) = 2.71mg/L; CAP = 2.10mg/L. Influent UV254: VR = 0.063/cm; SR = 0.046/cm; CAP = 0.025/cm).

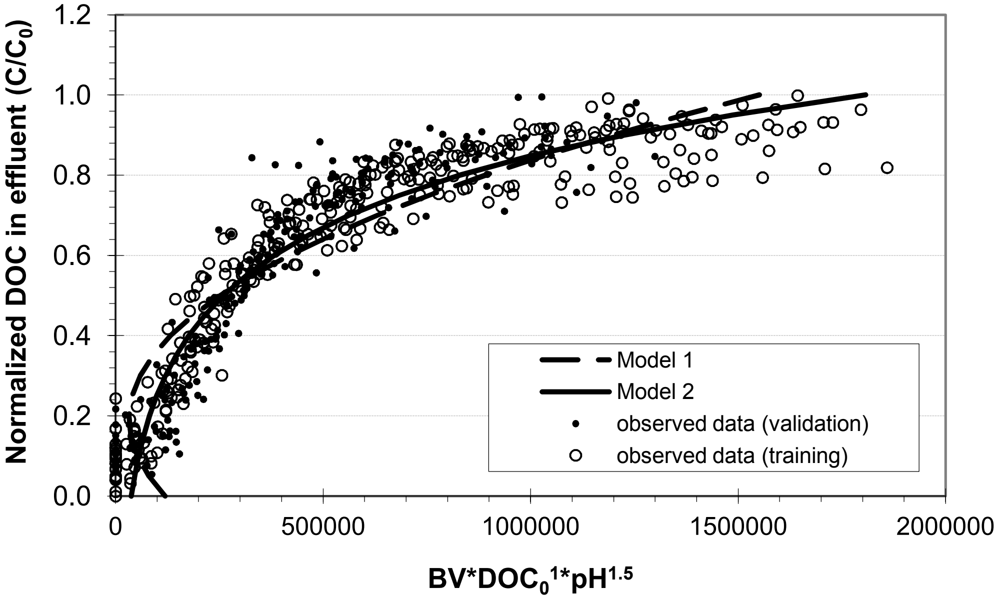


Figure 6. 9 Comparison between the DOC breakthrough curves predicted by Model 1 (EQN 1) and Model 2 (EQN 3) and the overall 42 RSSCTs results. The X-axis represents the independent value of $BV*DOC_0*pH^{1.5}$.

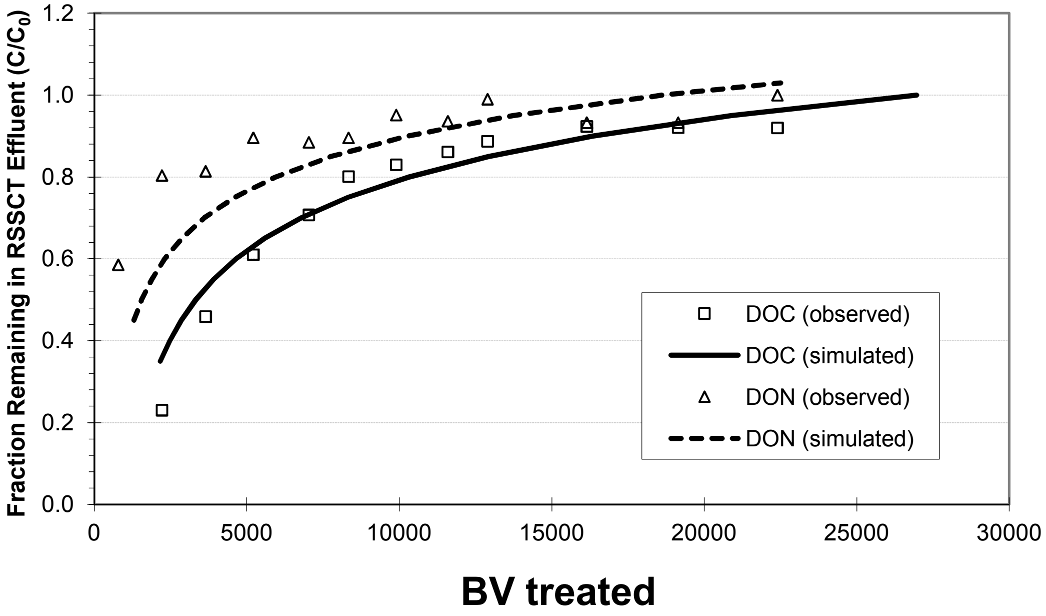


Figure 6. 10 Comparison of modeling results between DON and DOC breakthrough curves. RSSCT conducted with Plant C water (April, 2008) was used as representative result. DOC_0 = 3.39 mg/L and DON_0 = 0.36 mg/L.

CHAPTER 7

MODELING TEMPERATURE AND REACTION TIME IMPACTS ON HEMATITE NANOPARTICLE SIZE DURING FORCED HYDROLYSIS OF FERRIC CHLORIDE

Prepared for peer-reviewed submission to *Chemical Engineering Journal*

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Abstract

On the hypothesis that a mathematical relationship exists between synthesis conditions and hematite nanoparticle (NP) sizes, an empirical model was developed by synthesizing hematite NPs at different temperatures and hydrolysis times, and then correlating them with the obtained NP sizes. We found that the hematite NP sizes can be described by a simple relationship, $d_P = (0.49 \times T - 26.4) \times t^{0.33}$. The predictive capabilities of the model were validated by synthesizing NPs at randomly selected experimental conditions and comparing them to the model predictions. The experimental findings suggested that the model may be limited to predicting NP sizes smaller than 50 nm because of a possible shift from a slow, hydrolysis-driven growth mechanism to a mechanism characterized by rapid aggregation of the existing NPs.

Key words: hematite; nanoparticles; aggregation; reaction time; hydrolysis; empirical model

Abbreviations: NP, nanoparticle; HCl, hydrochloric acid; $FeCl_3$, ferric chloride; PALS, phase analysis light scattering; XRD, X-ray powder diffraction; HR-STEM, high-resolution scanning/transmission electron microscopy, JCPDS, Joint Committee on Powder Diffraction Standards; d_P, the diameter of NP (nm); α, empirical coefficient; K, temperature-dependent empirical growth rate constant (nm $hr^{-\alpha}$); a (nm $hr^{-\alpha}$ °C^{-1}) and b (nm $hr^{-\alpha}$), empirically fitted linear parameters; T, temperature (°C).

7.1 Introduction

Synthetic iron oxides have become a commonly engineered nanoparticles (NP) and widely used in commercial and industrial applications such as pigments, catalysts, adsorbents, and sensors [1-3]. The use of iron NPs as catalysts in advanced oxidation processes (AOPs) is a promising alternative to existing technologies for the decontamination of soil, groundwaters, sediments, and industrial effluents [4-6]. Once NPs enter the environment, they will inevitably come into contact with humans and other living organisms in the environment. The small size of NPs may induce various biological effects, including DNA damage [7-13].

It is well documented that the properties of nanomaterials, including their toxicity, strongly depend on particle size and its associated parameters [14-17]. The changes in the surface charge as particle size decreases will alter the adsorption affinity of NPs toward cells [14, 18]. For example, the adsorption of small iron NPs (< 50 nm) onto *E. coli* cells and human intestinal cells was faster than that of large NPs (> 75 nm) [14, 18]. The impact of iron NP size on aggregation behavior and stability under environmentally relevant pH and ionic strength conditions has been investigated [19-22]. Other studies also have shown that smaller particles are more readily adsorbed, which influences the transportation of NPs significantly. However, it can be difficult for researchers to prepare and use uniform dispersions of engineered NPs without modifying their surfaces with organic dispersants. These dispersants can alter the properties of the

NPs and seriously impact the outcome of experiments through which the engineering and environmental implications of NPs are investigated. For example, a study using zero-valent iron NPs for groundwater remediation suggested that polymer coatings decrease iron NP reactivity with trichloroethylene (TCE) significantly by blocking reactive surface sites [23]. Therefore, researchers engaged in researching the implications of these NPs must have the ability to consistently synthesize NPs with particular uniform sizes but without the addition of dispersing agents.

Iron oxide particles are among the most common natural mineral NPs and are frequently used for modeling the aggregation behavior of NPs [24-26]. Hematite (α-Fe_2O_3) is the most stable form of iron oxide, and as such hematite NPs are extensively used in biological applications such as cell conjugates [27, 28]. More importantly, hematite NPs are commonly used as a reference nanomaterial that mirrors the properties of many other metal oxides [13, 29, 30]. Iron oxide NP synthesis processes and their modifications have been well documented in the literature; some of the first studies were done by Matijević and his colleagues, who investigated formation mechanisms and morphological controls for the synthesis of colloidal hematite particles [31-37]. Although the published literature provides strong evidence that hematite NP formation strongly depends on the pH of the solution, temperature and time of the reaction, and type and concentration of the Fe^{3+} salt used as a hydrolysis precursor, no attempts have been made to describe mathematically how these factors impact the size of synthesized NPs [35, 38-51]. Furthermore, although intensive studies have been conducted on NP behavior and size dependence, no standardized synthesis procedure is available for preparation of a designated particle size systematically. Development of such a mathematical relationship that systematically describes how the synthesis conditions impact NP properties could be an invaluable tool for researchers engaged in research that necessitates uniform NPs with specific sizes.

On the hypothesis that a quantitative mathematical relationship could be developed to describe the impact of synthesis conditions on particle size, this study aimed to develop a mathematical model that describes hematite NP size as a function of hydrolysis temperature and time. To address this goal, (1) hematite NPs were synthesized by modifying the method reported by Matijević et al. [31], (2) NP sizes were characterized using phase analysis light scattering (PALS) and electron microscopy, and (3) a mathematical model that describes the relationship between the sizes of synthesized hematite NPs and the hydrolysis temperature and time was developed and validated.

7.2 Methodology

A modified method, originally published by Matijević et al., [31] was used to synthesize hematite NPs. Briefly, anhydrous ferric chloride ($FeCl_3$, Sigma-Aldrich reagent grade 97%) and hydrochloric acid (12.1 M HCl, EMD Chemicals Group ACS grade) were used to prepare 4 mM HCl solution and 0.25 M $FeCl_3$ stock solution. The $FeCl_3$ solution was then filtered through a 0.2-µm nylon membrane filter (Nalgene) using a vacuum pump filtration system to remove any impurities. The 4 mM HCl solution was transferred to an Erlenmeyer flask, placed on a hot plate, and brought to a boil. At this time, 40 ml of the 0.25 M $FeCl_3$ was pipetted into the boiling HCl solution to facilitate rapid nucleation; this hydrolysis approach was first reported by Wang et al. [35]. The solution was then placed in a constant-temperature oven (HP 5890 series II) at the desired temperature with a variability of ±1°C. Five temperatures were used in this study ranging from 60°C to 110°C. During the hydrolysis process, sample aliquots of 25 mL were taken from the solution at time points ranging from 0.5 hr to 144 hrs. The aliquots were placed into 40-mL centrifuge tubes, rapidly cooled in ice, and then stored in a refrigerator at 4°C. This temperature prevented further hydrolysis, which was confirmed with PALS (ZetaPALS, Brookhaven Institute Corporation). NPs synthesized by an independent technician at randomly selected temperatures and times were used to validate the model.

The phase analysis of hematite NPs was performed by X-ray powder diffraction (XRD) (Panalytical X'Pert Pro HR-XRD), and the phase identification was confirmed by comparing the measured diffraction pattern of as-prepared NPs with the pattern of the Joint Committee on Powder Diffraction Standards (JCPDS) database (Appendix 7.A). In addition to PALS analysis, two electron microscopic techniques were used for examination of the size and morphology of hematite NPs at different experimental conditions. Scanning electron microscopy (FEI Nova 200 FIB/SEM) was used to confirm the particle size data obtained with the PALS technique, and high-resolution scanning/transmission electron microscopy

(HR-STEM) was used (Phillips CM-200 UHR-STEM) to better understand the NP growth process.

An empirical model was developed by fitting the data using an exponential curve as described in Equation 1:

$$d_P = K \times t^{\alpha} \tag{1}$$

where d_P is the diameter of the synthesized hematite NP, nm; t is the hydrolysis time, hrs; α is a fitted empirical coefficient, unitless; and K is a temperature-dependent empirical growth rate constant, nm $hr^{-\alpha}$. The temperature dependence of the constant rate K can be described by Equation 2:

$$K = a \times T + b \tag{2}$$

where a (nm $hr^{-\alpha}$ $°C^{-1}$) and b (nm $hr^{-\alpha}$) are empirically fitted linear parameters and T is the hydrolysis temperature in °C. Confidence intervals at 95% were calculated to better understand the prediction capabilities of the model.

Upon development, the mathematical model was validated by a separate technician conducting a series of experiments and comparing the obtained data with the model predictions. The initial concentrations of $FeCl_3$ and HCl were the same as described above. The temperatures ranged from 80°C to 110°C, and the hydrolysis time ranged from 0.5 hr to 50 hrs.

7.3 Results

7.3.1 Hematite Nanoparticle Characterization

The SEM images in Figure 7.1 illustrate that relatively uniform spherical hematite NPs were formed during the forced hydrolysis of ferric chloride. The sizes of the particles corresponded well to the sizes obtained via the PALS technique, confirming its results. The XRD spectra obtained for the NPs (Appendix 7.A) confirmed that the NPs are composed of hematite.

7.3.2 Model Parameterization and Validation

Figure 7.2 illustrates the effect of hydrolysis time on NP size. As hypothesized, the diameters of hematite NPs increase as the hydrolysis time increases. Presented on a log-log scale, the experimental data and the fitted power curves have a similar slope described by an average value for $\alpha = 0.33$ ($\sigma^2 = 0.05$), except for experiments conducted at 60°C. The goodness of fit values (R^2) for the fitted curves were generally > 0.9 with the exception of the experimental values obtained at $T = 60°C$, which were characterized with a high value of $R^2 = 0.89$. The lower R^2 value for $T = 60°C$ suggested that the predictive capabilities of the model may be decreased at lower temperatures because temperature plays a key role in the forced hydrolysis of ferric chloride.

In contrast, however, the very high R^2 and very low variability of α suggested a good linear dependence of the empirical growth rate constant K on temperature. Figure 7.3 illustrates the linear correlation between K and hydrolysis temperature. From the experimental results, K increases with increasing temperature. The R^2 value for the fitted data is > 0.99, which implies almost ideal linear dependence of K as a function of T. The fitted intercept and slope of this linear function were determined to be $b = -26.4$ nm hr$^{-\alpha}$ and $a = 0.49$ nm hr$^{-\alpha}$ °C^{-1}, respectively.

By applying the values for the empirically obtained parameters described in Equations 1 and 2, a comprehensive model equation was derived as presented in Equation 3:

$$d_P = (0.49 \times T - 26.4) \times t^{0.33} \tag{3}$$

Figure 7.4 illustrates model predictions for the hydrolyzed hematite NPs. A comparison of the NPs synthesized by an independent technician and the model shows that the model was able to predict NP sizes for the given experimental conditions accurately. With the exception of one data point, which could be classified as an insignificant outlier, all sizes of the hydrolyzed NPs were within the 95% confidence intervals described by the model. The negligible divergences from the ideal model prediction are within a small experimental error, which is, unfortunately, unavoidable.

7.3.3 Impact of Increasing Hydrolysis Duration on Particle Aggregation

On the basis of the experimental findings, it appears that the model may be limited to predicting the experimental conditions for hydrolysis of particles that have sizes < 50 nm. This limitation appears to be directly related to the formation mechanism of large NPs and the limitations of the PALS technique. As illustrated in Figure 7.5, once NPs exceed approximately 50 nm, the average particle count rapidly decreases below the minimum particle count necessary for the instrument to provide reliable data. It was hypothesized that this rapid decrease in the number of NPs is a result of a shift from a slow, hydrolysis-driven growth mechanism to a mechanism driven by rapid aggregation of the existing NPs. HR-TEM provided evidence in support of the hypothesis that larger hematite NPs form from aggregation of smaller NPs. Figure 7.6 shows a large, irregularly shaped NP composed of several small NPs. From the experimental data, the aggregation growth mechanism becomes dominant when NPs approximately 50 nm. During this phase of the forced hydrolysis, the concentration of available ferric ions needed for NP growth may become so low that the aggregation mechanism becomes dominant. These hypotheses, however, was not within the scope of this study, and as such it was not pursued.

7.4 Conclusions

This study demonstrates the validity of the initial hypothesis that an empirical model can be developed to describe and predict hematite NP sizes as a function of time and hydrolysis temperature. The experiments conducted to test the capabilities of the model demonstrated that it was able to predict the hematite NP sizes with high accuracy and precision. The experimental findings, however, also suggested that this model may be limited to predicting the sizes of NPs that are smaller than 50 nm because of the probable shift from a slow, hydrolysis-driven growth mechanism to a mechanism driven by rapid NP aggregation. Although this model is limited to predicting hematite NP sizes obtained via forced hydrolysis of ferric chloride, it serves as a good foundation for a broad hypothesis that other NP synthesis processes could be described systematically in a similar manner. Further research, however, will need to be conducted to develop new models and validate this broad hypothesis.

Acknowledgements

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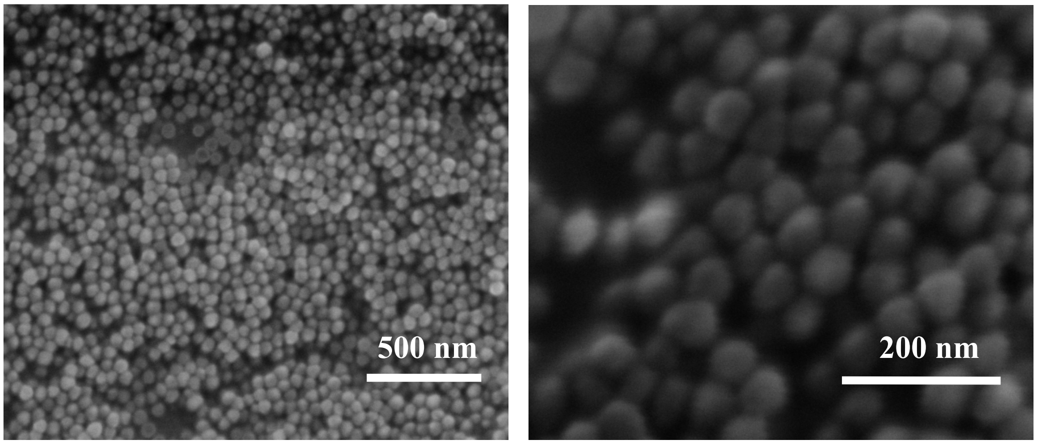

Figure 7. 1 Scanning electron microscopy confirmation of the synthesized hematite NPs hydrolyzed at 100 °C for a period of 10 hr.

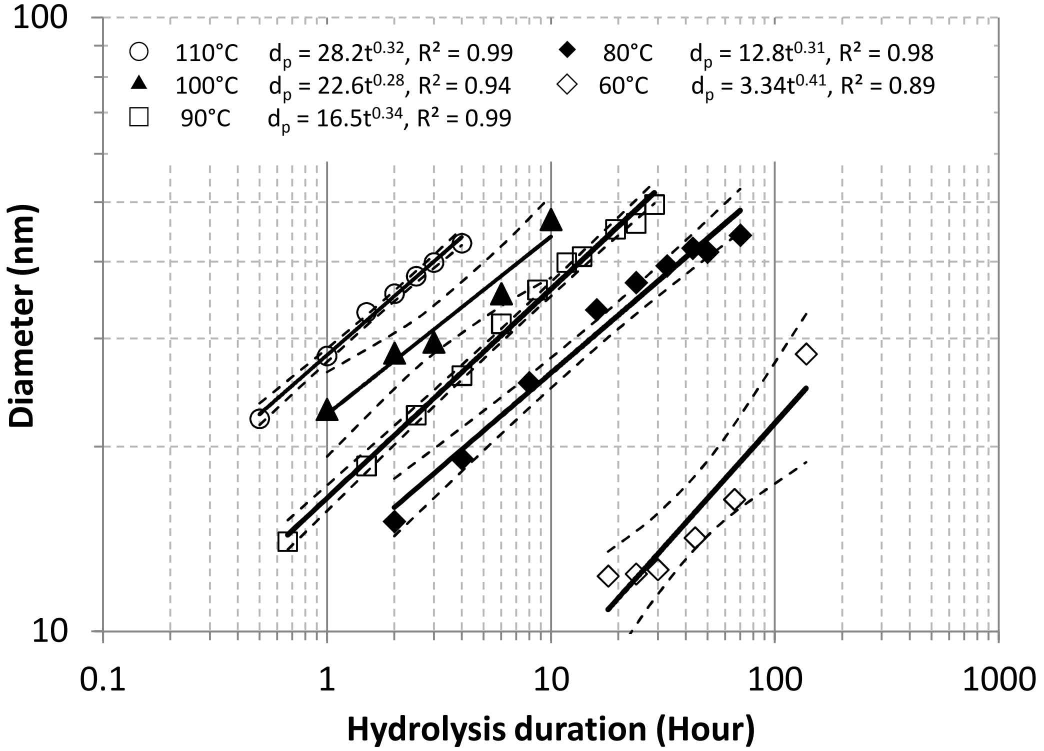

Figure 7. 2 Plot of hematite NP diameter against reaction time in hydrolysis under various incubating temperatures. Log-log regression and 95% confidence interval are also shown.

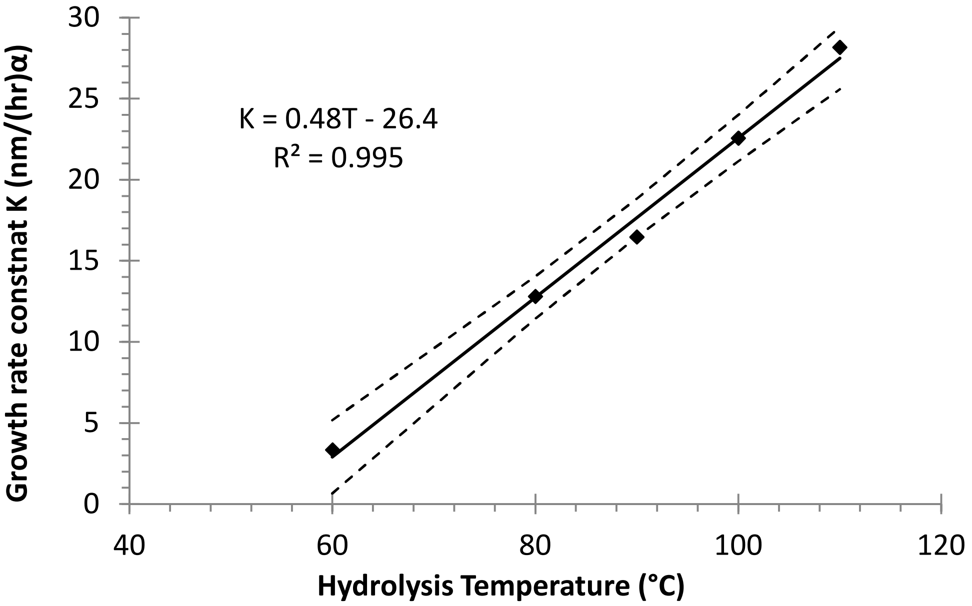

Figure 7. 3 Plot of empirical coefficient (intercept) K against incubating temperature during hydrolysis processes. The 95% confidence intervals are also shown.

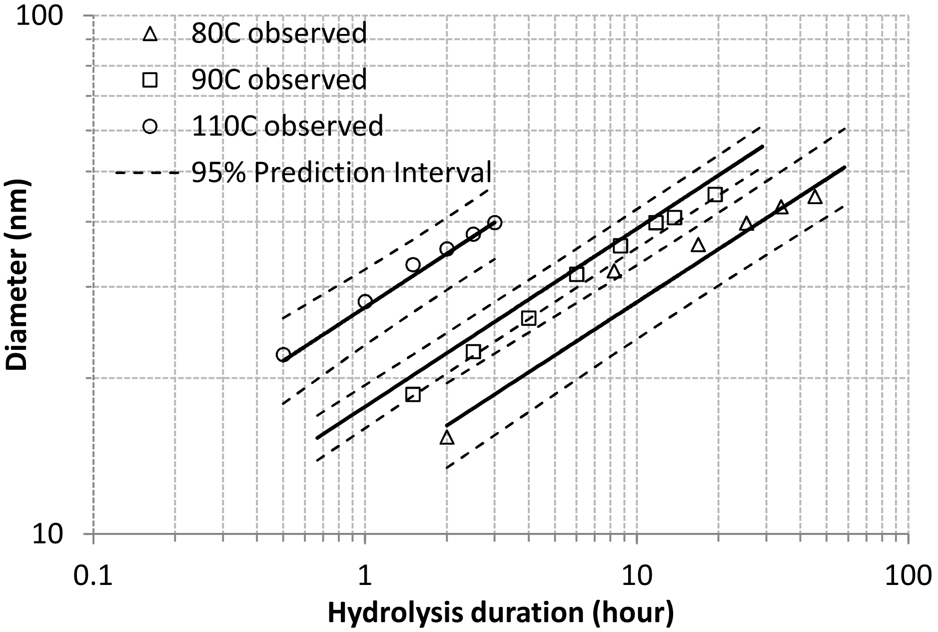

Figure 7. 4 Empirical model predictions and experimental data for the NP sizes obtained to validate the model. Full lines represent the model predictions at different temperatures. Dashed lines represent the 95% prediction boundaries.

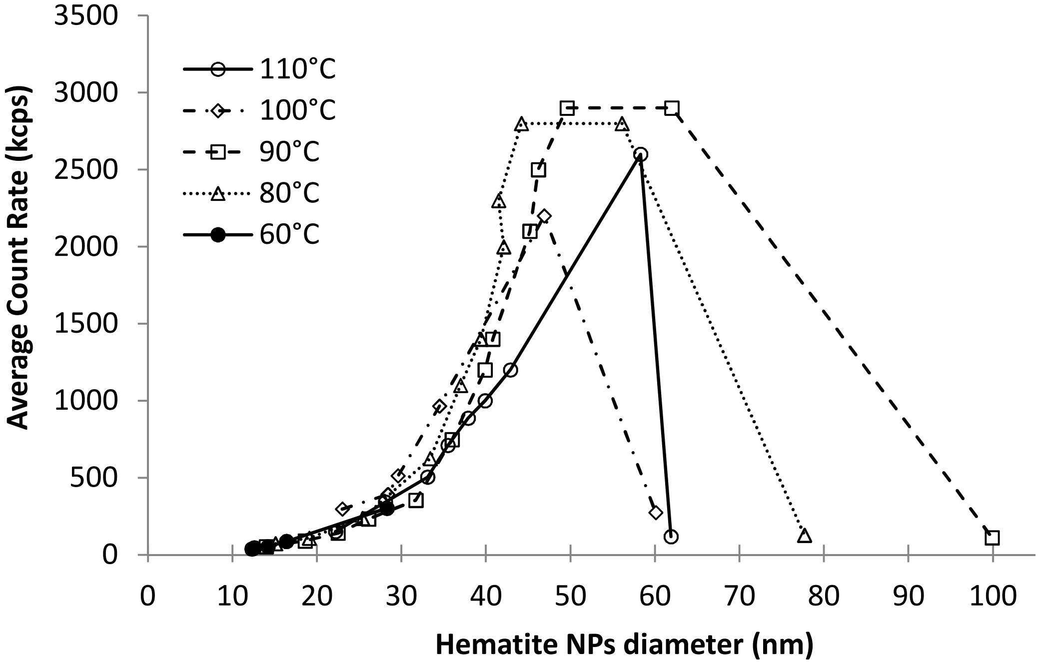

Figure 7. 5 Plot of particle count rate (kcps) against hematite NP size during hydrolysis processes.

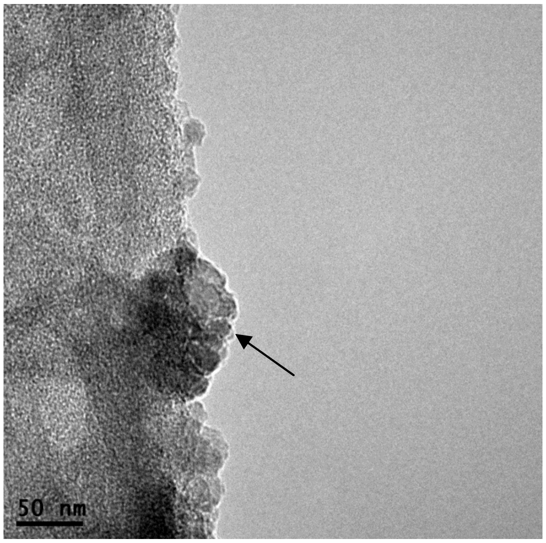

Figure 7. 6 High resolution transmission electron microscopy images of hematite NPs hydrolyzed for at 80 °C. Arrows emphasize the smaller NPs which comprise the larger NPs obtained by aggregation.

CHAPTER 8

COMPARISON OF TWO SYNTHESIZED IRON NANOPARTICLES FOR ORGANICS OXIDATION

Two laboratory synthesized iron nanoparticles (NPs) are used as catalyst for organic oxidation tests: hematite NPs and iron (hydr)oxide NPs. It is well known that this catalytic process (Fenton-like process) degrades a wide range of organic contaminants in soil and water by producing highly reactive and nonspecific free hydroxyl radical (·OH) (DeLaat and Gallard, 1999; Huling et al., 2000). It reacts with most organic compounds by adding to a double bound or by abstracting hydrogen atoms from organic molecules (Safarzadeh-Amiri et al., 1997; Buxton et al., 1988). The generated organic radicals then react with oxygen and lead to nearly complete mineralization to CO_2, H_2O, and mineral acids (Neyens and Baeyens, 2003). The key features of Fenton-like process, such as high reactivity and low energy requirement, provide a potential technique which can be applied to in-situ GAC regeneration.

8.1 Iron NPs Preparation

The method used in synthesis of the hematite NPs was originally published by Matijević et al (1978) with minor modifications. Anhydrous ferric chloride ($FeCl_3$, Sigma–Aldrich reagent grade 97%) and hydrochloric acid (12.1 M HCl, EMD Chemicals Group-ACS grade) were used for the preparation of the 4 mM HCl solution and 0.25 M $FeCl_3$ stock. The 4 mM HCl solution was transferred to an Erlenmeyer flask and placed on a hot plate and brought to boil. At this time 40 ml of the 0.25 M $FeCl_3$ was pipetted into the boiling HCl solution, which finally resulted in 500 mL of 20 mM $FeCl_3$. This final solution was placed in a laboratory constant temperature oven (HP 5890 series II) at 100 °C and incubated for 10 hours without further mixing. Hematite NPs sample was centrifuged, rinsed with nanopure water repeatedly in order to purify the produce. After five times of purification processes, hematite NPs were stored in 4 °C and diluted for desired concentration. The hematite NPs diameter was determined to be 46 ±3 nm by Phase Analysis Light Scattering (ZetaPALS, Brookhaven Institute Corporation).

Iron (hydr)oxide NPs were prepared by dissolving $FeCl_3{\bullet}6H_2O$ in nanopure water and mixed for four days prior to use. The stock solution of iron NPs contained 1.28 M as iron. The stock solution was diluted with nanopure water in order to get the desired concentration (Bach et al., 2008). Particle sizes of iron (hydr)oxide NPs were measured using ZetaPALS and the diameter was determined to be 50 ± 5 nm. . This result was in agreement with previous study of Zelmanov and Semiat (2008).

8.2 Experimental

These two types of iron NPs were mixed with model organic solution separately and then H_2O_2 was added to initiate the formation of $\cdot OH$ for organic oxidation. During the reaction, pH was slightly adjusted by 5 N NaOH to 2.5 to 3 which was suggested to be optimal pH value for Fenton-like process (Bach et al, 2010). After oxidation, pH of solution was adjusted by HCl to < 1 to stop the reaction (Bach et al., 2010). Two model organics were used for oxidation tests: methylene blue and phenol. These two organics are common model compounds selected as industrial contaminated water and they are readily oxidized (Gulshan et al., 2010; Fernandes et al., 2007; De Heredia et al., 2001; Cheng et al., 1995). Additionally, methylene blue is a good indicator for chemical oxidation experiment because the color is easy to be observed with unaided eye when reaction occurred rapidly. The concentration of phenol was determined as dissolved organic carbon (DOC) using a Shimadzu TOC-V_{CSH} analyzer (high temperature combustion at 720°**C** non-dispersive infrared detection) (Shimadzu Corp., Tokyo, Japan). The concentration of methylene blue was determined using spectrophotometer (HACH, DR5000, UV-Vis Spectrophotometer) at wavelength of 664 nm (Fernandes et al., 2007).

8.3 Results and Discussion

Table 8.1 summarized the results of using hematite NPs or iron (hydr)oxide NPs as catalyst for methylene blue oxidation tests. The completion of methylene blue oxidation can be observed easily by unaided eye especially when the reaction occurred quickly in several minutes. Absorbance at 664 nm was measured to confirm the completion of reaction.

First, hematite NPs was tested for the catalytic ability (Trial 1 in Table 8.1). The dosage of NPs and H_2O_2 were chose according to Zelmanov and Semiat's work on Fenton-like oxidation process (Zelmanov & Semiat, 2008), and the initial concentration of methylene blue was 80 mg/L. The degradation of methylene blue occurred slowly and reached 95% removal after 7 days. Trial 2 was exhibited using iron (hydr)oxide NPs as catalyst with the same dosage as Trial 1. Fast reaction rate was observed that almost 100% removal of mehtylene blue was achieved in 2 to 3 minutes, which was also confirmed by absorbance measurement. The fast reaction rate indicates that the application of iron (hydr)oxide NPs as catalyst for organic oxidation is more feasible than using hematite NPs, and the application for organic saturated-GAC regeneration can be practicable.

To optimize the ratio between iron (hydr)oxide NPs and H_2O_2 for organic oxidation, several tests were performed under the control of different H_2O_2 concentrations (Trial 3 to 8 in Table 8.1). When the concentration of H_2O_2 was 10 times lower (0.025 M, Trial 3), it took more than 15 minutes to achieve the same level of methylene blue removal as Trial 2; when the concentration of H_2O_2 was 10 times higher (2.5 M, Trial 4), it took about 5 minute to achieve similar removal of methylene blue. At the mean time, high dosage of H_2O_2 resulted in temperature increase (to 50 °C) which can cause H_2O_2 decomposition. Trial 5 to 7 showed that the reaction rates were similar when H_2O_2 dosage ranged from 0.25 to 0.75 M. However, when H_2O_2 dosage was reduced to 0.125 M (Trial 8), the reaction rate decreased. From the experimental findings, it appears that a molar ratio of 1:25 between iron (hydr)oxide NPs and H_2O_2 exhibits the optimized dosage. This value is comparable to the dosage suggested by USEPA report of in-situ GAC regeneration by Fenton reaction (USEPA 600/R-07/008, 2007), which was also tested as Trial 9 in Table 8.1.

Figure 8.1 shows the results of phenol oxidation using hematite NPs or iron (hydr)oxide NPs as catalysts. The experiment using iron (hydr)oxide NPs as catalyst removed 70% phenol after 30 minutes. The reaction rate of experiment with iron (hydr)oxide NPs tended to decrease over time which can be attributed to rapid consumption of H_2O_2; the depletion of H_2O_2 resulted in very slow reaction rate (flat slope) after 30 minutes of reaction. In comparison to iron (hydr)oxide NPs, hematite NPs as catalyst removed only 10% of phenol after 30 minutes and the reaction persisted for more than 40 hours which was attributed to slow consumption of H_2O_2.

Figure 8.1 (B) shows the results fitted by first-order reaction. The calculated reaction rate constants are 0.0024 and 0.0183 min^{-1} for experiments using hematite NPs and iron (hydr)oxide NPs, respectively. Higher rate constants of experiment using iron (hydr)oxide NPs in the first 30 minutes indicates that the oxidation of phenol is more efficient; this result is in agreement with experiments conducted with methylene blue.

8.4 Conclusion

Both hematite NPs and iron (hydr)oxide NPs shows ability to serve as catalysts in Fenton-like reaction. However, iron (hydr)oxide NPs is more effective than hematite NPs in terms of producing ·OH for organic oxidation. The optimal molar ratio between iron NPs and H_2O_2 for oxidation is 1:25. To achieve 100% of organic removal when concentration is high, addition of H_2O_2 after 30 minutes is preferred over increasing initial H_2O_2 concentration due to scavenging of ·OH by excessive H_2O_2 and temperature rise. The fast reaction rate in aqueous solution of this technique using iron (hydr)oxide NPs as catalyst is beneficial to the in-situ GAC regeneration.

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Table 8. 1 Oxidation trial of methylene blue (MB) using iron NPs/H_2O_2 processes

Trial	MB (mg/L)	Iron NPs (mM)	H_2O_2 (M)	Removal	Reaction duration	NPs type
1	80	9	0.25	95%	7days	hematite NPs
2	80	9	0.25	> 99%	2-3 minutes	iron (hydr)oxide NPs
3	80	9	0.025	95-98%	15 minutes	iron (hydr)oxide NPs
4†	80	9	2.5	> 99%	5-6 minutes	iron (hydr)oxide NPs
5	80	9	0.25	> 99%	2-3 minutes	iron (hydr)oxide NPs
6	80	9	0.5	> 99%	2-3 minutes	iron (hydr)oxide NPs
7	80	9	0.75	> 99%	2-3 minutes	iron (hydr)oxide NPs
8	80	9	0.125	> 99%	5 minutes	iron (hydr)oxide NPs
9‡	80	9	0.38	> 99%	2-3 minutes	iron (hydr)oxide NPs

†Temperature increased to 50°C after 15 minutes.

‡Dosages of iron NPs and H_2O_2 were selected according to USEPA 600/R-07/008 final project report.

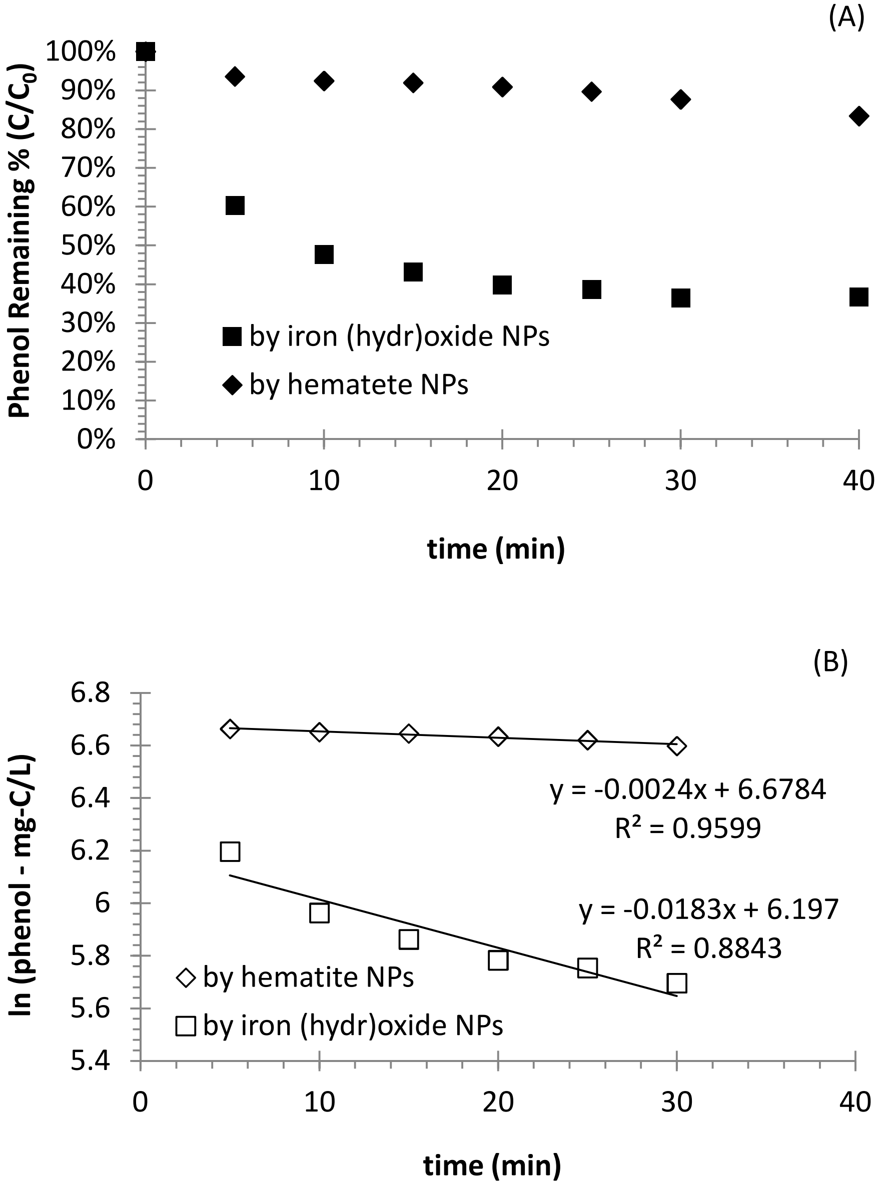

Figure 8. 1 (A) Phenol removal by iron (hydr)oxide NPs and hematite NPs as catalysts; (B) oxidation of phenol fitted by first-order reaction model. The initial phenol concentration was 1000 mg/L as phenol; the dosages of iron NPs were both 200 ppm as iron and the initial H_2O_2 concentration was 0.75 %. The molar ratio between iron and H_2O_2 is 1:60.

CHAPTER 9

IN-SITU REGENERATION OF PHENOL-ADSORBED GRANULAR ACTIVATED CARBON BY IRON OXIDE NANOCATALYST

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Abstract

Granular activated carbon (GAC) is widely used to remove trace organic pollutants and natural organic matter (NOM) from industrial and municipal waters. The aim of this paper is to evaluate an iron nanocatalyst approach, based upon Fenton-like oxidation reactions, to regenerate spent-GAC within a packed bed configuration after saturation by organic compounds. Specifically we focus on regenerating GAC packed beds equilibrated with varying influent concentrations of phenol, as a model compound. Iron nanocatalysts were synthesized using ferric chloride, a chemical already used as a coagulant at municipal WTPs, and reacted with hydrogen peroxide (H_2O_2) for the purpose of in-situ regeneration. Up to 95 % of phenol adsorption capacity was regenerated for GAC equilibrated with 1000 mg/L of phenol. At least 5 adsorption-regeneration cycles can be performed repetitively for the same batch of GAC using this technique with fresh iron nanocatalysts while achieving a 90 ± 5 % of regeneration efficiency between each loading. Moreover, iron nanocatalyst can be recovered and reused multiple times. Lower initial adsorbate concentrations (10 to 500 mg/L) resulted in lower saturated adsorbent-phase concentration of phenol and lower regeneration efficiencies (72 ± 5 %). Overall, in-situ regeneration of saturated-GAC could be practicable in larger scale of water cleaning process when combined with advanced oxidization technique using iron nanocatalyst/H_2O_2 reagent for readily adsorbable and easily oxidizable organics.

Key words: Fenton-Like, iron nanocatalysts, in-situ regeneration

9.1 Introduction

Granular activated carbon (GAC) adsorbers are frequently used to remove natural organic matter (NOM) or trace organic pollutants from drinking water, industrial wastewater, and groundwaters. However, operation of GAC adsorbers has a significant economic burden because exhausted or spent GAC must be periodically removed, regenerated thermally, and replaced back into the contactor (Alvarez et al., 2004; Moreno-Castilla et al., 1995). It is common for utilities to regenerate saturated GAC in order to save cost of purchasing fresh GAC. Biological and chemical regeneration are usually not efficient and require further treatment for biological sludge and extracted contaminants (Toledo et al., 2003; Scholz and Martin, 1998; Alvare et al., 2004).Traditionally thermal regeneration of spent GAC is accompanied by lengthy cut-of-service periods and significant energy demand due to high required temperature and considerable loss of GAC (5-15%) (Sabio et al., 2004; Alvarez et al., 2004; San Miguel et al., 2000). Smaller water treatment sites usually need to truck used GAC to incineration facilities for regeneration, which increases the already significant carbon footprint of thermal regeneration process due to CO_2 emitted during transportation (Sabio et al., 2004).

In-situ regeneration is an alternative and could offer new modes of GAC operation. GAC is usually run to complete exhaustion and then regenerated ex-situ, requiring removal, transportation and off-site processing. In-situ regeneration could do the same, with reduced downtime and material losses. Additionally, in-situ regeneration could allow fundamentally different operations. Instead of running to complete exhaustion of GAC sorption capacity, in-situ GAC regeneration could be conducted frequently. This would maintain high driving forces to remove organics from water. This paper advances curability to understand operational conditions of in-situ regeneration.

A Fenton-driven mechanism for regeneration spent GAC was recently proposed and tested (Huling et al., 2007; Kommineni et al., 2003). Fenton (ferrous iron and hydrogen peroxide) and Fenton-like (ferric iron and hydrogen peroxide) processes can oxidize a wide range of organic contaminants in soil and water via production of highly reactive and nonspecific free hydroxyl radical (·OH) (Delaat et al., 2004; Huling et al., 2000a; Huling et al., 2000b ; DeLaat and Gallard, 1999). ·OH reacts with most organic compounds by adding to a double bound or by abstracting hydrogen atoms from organic molecules (Safarzadeh-Amiri et al., 1997; Buxton et al., 1998) forming CO_2, H_2O, and organic acids (Neyens and Baeyens, 2003).

Fenton-like processes can be initiated by dissolution of colloidal iron (hydr)oxide nanoparticles (nanocatalysts) via protonation for advance organic aqueous phase oxidation (Bach et al., 2010a, 2010b; Zelmanov and Semiat, 2009, 2008a, 2008b). The high affinity of protons to iron (hydr)oxide surface helps release the ferric ion from the surface to the bulk solution, where it initiates a chain of reactions similar to Fenton processes. Iron (hydr)oxide nanocatalysts prepared by hydrolysis of ferric salt have been used for GAC regeneration batchwise but not in a packed bed (Bach et al., 2011, 2009; 2008). They observed during iron nanocatalysts synthesis that their diameter remained constant and mono-distributed after 6 hours of reaction. Bach et al. (2010a) claimed iron (hydr)oxide nanocatalysts can be stored and used for oxidization with the same efficiency as after being produce without aging problem. They also suggested that iron (hydr)oxide nanocatalysts can be recovered for reuse by pH adjustment after conducted with organic oxidization. These characteristics of iron (hydr)oxide nanocatalysts can be great benefits for application of in-situ regeneration which have not been demonstrated experimentally.

Previously, Fenton-like regeneration of GAC was usually conducted with relative high concentration of contaminants, e.g. 1000 ppm of phenol solution (Bach et al., 2008). Low adsorbate concentration might cause low regeneration efficiency because of lower concentration gradient between solid phase and aqueous phase. Huling et al. (2005) suggested that the effect of oxidation treatment on low-energy sites and low adsorbate concentrations may be different than on high-energy sites and high adsorbate concentrations. The effect of liquid-phase and solid-phase organic concentrations on regeneration efficiency of spent-GAC remains ill-defined.

To investigate the practicability of in-situ regeneration of spent-GAC by catalytic method using iron nanocatalysts, the objectives of this study are to 1) perform multiple adsorption-regeneration cycles of GAC while packed GAC is kept in-situ (within packed bed) throughout the experiment, 2) evaluate the performance of recycled iron nanocatalysts for in-situ regeneration of spent-GAC, and 3) determine the impact of adsorbate concentration on in-situ regeneration of spent-GAC based on iron nanocatalysts. By in-situ regeneration we mean an acidic solution containing iron nanocatalysts and H_2O_2 being passed through a GAC packed bed pre-loaded with phenol. Phenol was chosen as model organic contaminant because it is readily-adsorbed by GAC and easily oxidized to polar compounds and CO_2. Many phenol-based compounds are used as solvents or reagents in industrial processes and are therefore common contaminants in industrial wastewater and contaminated drinking water source; they are very harmful and highly toxic towards microorganisms (Cheng et al., 1995; De Heredia et al., 2001). In drinking water applications, removal of organics with phenol moieties is critical in minimizing formation of disinfection by-products such as trihalomethanes (THMs) (Zhang et al., 2007).

9.2 Experimental

9.2.1 Materials

Reagent grade chemicals were used: iron(III)-chloride hexa-hydrate, $FeCl_3 \cdot 6H_2O$ (reagent grade, Sigma Aldrich), 30% hydrogen peroxide, H_2O_2 (Ultrapure reagent, J.T.Baker), phenol (reagent grade, Acros Organics). Granular activated carbon (GAC) (URV, 8×30 mesh, Calgon Carbon Corp., Pittsburg, PA) derived from bituminous coal was crushed and sieved to 40×60 mesh (0.335 mm in average size to minimize wall effect in small column test). URV GAC was selected because it is activated in a manner designed to minimize H_2O_2 reactivity

(Hayden, 1998). Hydrogen chloride, HCl (12.1 N, ACS grade, EMD Chemicals Group), sodium hydroxide, NaOH (ACS grade, EMD Chemicals Group) were prepared for pH adjustment of solution. Iron (hydr)oxide nanocatalysts were prepared by dissolving $FeCl_3 \cdot 6H_2O$ in nanopure water and mixed for four days prior to use.

The stock solution of iron nanocatalysts contained 1.28 M as iron. The stock solution was diluted with nanopure water in order to get the desired concentration (Bach et al., 2008). Particle sizes of iron oxide-based nanoparticles were measured using Phase Analysis Light Scattering (ZetaPALS, Brookhaven Institute Corporation). All the measurements were performed at an angle of $\theta = 90^\circ$ with refractive index of 2.94 under wavelength of 659 nm. The particle sizes of synthesized iron (hydr)oxide nanocatalysts were measured for pH values used in regeneration processes (pH = 2-3) with an average size 55 nm and 0.23 of polydispersity after 1 day of reaction time. An example of measurement of iron (hydr)oxide nanocatalysts by Zeta PALS was shown in Appendix 9.A. This result was in agreement with previous study of Zelmanov and Semiat (2008). Iron samples were acid digested using the HNO_3/H_2O_2 digestion method for iron (US EPA SWA 846, Method 3050B) using an Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (iCAP 6000 Series, Thermo Scientific, Cambridge, UK).

Packed GAC beds were constructed of glass, Teflon, or stainless steel to minimize the adsorption of organics. Glass columns (Ace Glass Inc., Vineland, NJ, USA) of 1.1 cm in diameter and 32 cm in length were used for the packed GAC adsorption-regeneration studies. Channeling effects and wall effects are minimized because the column diameter to particle diameter ratio was greater than 25 (Sontheimer, 1979). Piston pumps (QG50) with stainless steel heads (Q2CSC) were used (Fluid Metering Inc., Syosset, NY, USA) to deliver the model phenol solution from the container to the columns with constant loading rate of 3.8 gpm/ft^2. GAC (1 g for each column) was packed (illustrated in Appendix 9.B) for the purpose of in-situ regeneration and the GAC stayed inside the columns during the adsorption-regeneration cycles. GAC columns were wrapped in tinfoil to minimize photolysis.

Phenol was measured as total organic carbon (TOC), to be sure any oxidation products were accounted for, and analyzed using a Shimadzu TOC-V$_{CSH}$ analyzer (high temperature combustion at 720°**C** non-dispersive infrared detection) (Shimadzu Corp., Tokyo, Japan).

9.2.2 In-Situ Adsorption and Regeneration Experiments

The initial phenol concentration was 1000 mg/L as phenol buffered by 1mM sodium bicarbonate. The high initial concentration of phenol in this experiment was chosen for rapid GAC adsorbate loading (Bach et al., 2008). Lower concentrations of phenol solution (from 10 to 500 mg/L as phenol) were also applied, separately, to evaluate effect of solid phase-phenol concentration on regeneration efficiency. During the adsorption step, 250 mL of 1000 mg/L phenol solution was pumped through GAC column as down-flow mode and the effluent was circulated back to phenol solution reservoir. Once the concentration of phenol in solution stayed constant, which means that phenol reached equilibrium between solid phase and aqueous phase, it was replaced by fresh phenol solution (250 mL) for further adsorption. This adsorption approach was repeated until the equilibrated phenol concentration ceased to increase further (i.e., GAC was saturated by phenol thoroughly). The pH values ranged from 6 to 7 during GAC adsorption.

After adsorption, in-situ regeneration of the GAC was achieved without removing from the column by an advanced oxidation process, Fenton-like system (nFe/H_2O_2) based on iron (hydr)oxide nanocatalysts. Nanopure water (10 times of column volume, about 300 mL) was pumped through the GAC bed as up-flow mode to washout the remaining phenol solution. A regeneration solution containing 500 ppm as iron was pumped in up-flow mode through the exhausted GAC bed. To initiate regeneration, 7 mL of 30% H_2O_2 was added to the solution reservoir to yield an initial H_2O_2 concentration of 0.24 M. The regeneration solution was recirculated at a flow rate that produced 75% GAC bed expansion for 30 minutes. The pH values during GAC regeneration ranged from 2 to 3. After in-situ regeneration, 300 mL of nanopure water was pumped through the column as up-flow mode to filter the remaining reagents to the waste. All in-situ regeneration experiments were carried out at room temperature. The regenerated GAC was loaded again with phenol solution by identical adsorption approach described above.

9.2.3 Recycle of Iron Nanocatalysts

According to the study of Bach et al. (2010), the iron (hydr)oxide nanocatalysts can be precipitated out due to aggregation by increasing pH to > 4. After precipitating and decanting undesired supernatant liquid, these iron-oxide nanoparticles can be recycled and purified by adjusting pH to < 3 with HCl (6N). After regeneration, the used regeneration solution was adjusted to pH = 5 with NaOH (5N) for aggregation of iron nanocatalysts. Iron-oxide precipitate was then separated by decanting supernatant and stored under room temperature for next regeneration cycle.

9.3 Results and Discussion

9.3.1 In-Situ Catalytic Regeneration of Phenol-Saturated GAC

Figure 9.1 shows profiles of phenol adsorbed by virgin and catalytic regenerated GAC by plotting the volume of phenol solution treated per unit mass of GAC versus the percentage of adsorbate residual at equilibrium before thoroughly saturation. As shown in Figure 9.1, 30% to 40% of phenol was adsorbed after first equilibrium in all adsorption experiments (i.e., 60% to 70% of phenol remained in aqueous phase). Four aliquots of 250 mL phenol solutions were used to saturate GAC while the percentages of adsorbed phenol ceased to increase. Saturated GAC was regenerated using iron nanocatalysts and hydrogen peroxide and re-equilibrate with phenol solutions until saturation. This cyclical adsorption-regeneration procedure was repeated four times after each saturation experiment. The phenol adsorption profiles of regenerated GAC are similar to those of virgin GAC. The results of a duplicated GAC bed conducted with one adsorption-regeneration cycle are also shown in Figure 9.1. The agreement between experiments shows that the technique can be performed with good reproducibility.

To quantitatively examine the change of adsorption capacity, the saturated adsorbent-phase concentration of phenol (q_e, mg of carbon/g of GAC) was calculated by the expressed equation:

$$q_e = \frac{\int_{i=1}^{n}\left[\left(C_0 - C_{eq,i}\right)\times V_i\right]}{m_{GAC}} \qquad \text{EQN 1.}$$

where C_0 is the initial concentration of the phenol solution in mg-C/L; C_{eq} is the equilibrium aqueous-phase concentration of phenol at the end of adsorption step i; V is the volume of the phenol solution in liter; n depends on how many portions of phenol solution that it takes to saturate GAC; m_{GAC} is the mass of adsorbent in gram. The numerator of this equation represents the total mass of adsorbent-phase phenol per unit mass of GAC at saturation. Table 9.1 shows the summary of q_e calculated for each adsorption-regeneration cycle (first row). Virgin GAC showed an adsorption capacity of 93 ± 3 mg-C/g-GAC when loaded with 1 liter of 1000 mg/L of phenol solution. The values of q_e for regenerated GAC (by fresh nanoparticles) after multiple cycles are similar and ranged between 79 to 88 mg-C/g-GAC. The regeneration efficiencies (E) were calculated as the ratios of q_e between virgin GAC and regenerated GAC (Table 9.1). The result shows that 85 to 95% of regeneration efficiency can be achieved in comparison to virgin GAC. Therefore, in-situ regeneration by iron nanocatalysts and hydrogen peroxide solutions can recover around 90% of phenol adsorption capacity within multiple (at least four) regeneration cycles in comparison to virgin GAC without significant reduction in adsorption capacity. Additionally, the q_e and regeneration efficiency of duplicate result (95 mg-C/g-GAC and 92 %, not shown in Table 9.1) virgin indicate a good reproducibility of this adsorption-regeneration process.

9.3.2 Regeneration Using Recycled Iron Nanocatalysts

Figure 9.2 shows the profiles of phenol adsorbed by virgin and regenerated GAC using recycled iron nanocatalysts. For virgin GAC, 60% of phenol remained in aqueous-phase after the first equilibrium was reached (i.e., equilibrated with 0.25 L of 1000 mg/L phenol solution). Recycled nanocatalysts-regenerated GAC, in comparison to virgin GAC, shows lower phenol adsorption capacity at this stage while more phenol remained (68% and 75%) in aqueous-phase (for first- and second-regenerated GAC, respectively). The efficiencies for GAC regenerated by first- and second-recycled nanocatalysts decreased gradually from 83% to 70%. The slight reduction of adsorption capacity indicates the loss of iron nanocatalyst mass or decline of regeneration ability.

During the regeneration process, 10% of iron nanocatalysts was filtered to the waste which suggested that the loss of regeneration efficiency might be resulted from the loss of iron nanocatalysts more so than decreased reactivity. To verify this assumption, 10% of fresh iron nanocatalysts was added to third-recycled nanocatalyst solution and the result was shown in Figure 9.2 as third-regenerated GAC. The result shows that the adsorption capacity of third-regenerated GAC was retrieved and the regeneration efficiency achieved the similar level (80%) as first-regenerated GAC (shown in Table 9.1). Consequently, recycled iron nanocatalysts showed lower regeneration efficiency of GAC adsorption capacity but can be compensated by adding 10% of fresh iron nanocatalysts. In addition, the iron concentrations in regeneration solution remained the same after regeneration (500 ± 10 ppm) and the iron contents in GAC only increased slightly from 1.5 ± 0.1 to 2.0 ± 0.2 mg-iron/g-GAC after regeneration. These evidences indicate that the loss of nanocatalysts attributed to retention in GAC is negligible.

9.3.3 Effect of Adsorbate Concentration on Efficiency of In-Situ Catalytic Regeneration

Figure 9.3 shows the profiles of phenol adsorbed by virgin and fresh nanocatalysts-regenerated GAC which were saturated with different adsorbate concentrations (10, 50, 100, 500, and 1000 mg/L as phenol). The saturation processes are the same as previous experiments and one cycle of adsorption-regeneration was performed for each GAC bed. Total phenol mass adsorbed by GAC at saturation varied according to the initial phenol concentration. For lower concentration of phenol solution, more volume of phenol solution was needed to achieve saturation of GAC. For virgin GAC, the maximum q_e (98 ± 5 mg-C/g-GAC) occurred when loaded with 1000 mg/L of phenol solution and the minimum q_e (46 ± 3 mg-C/g-GAC) occurred when loaded with 10 mg/L of phenol solution. The regeneration efficiency decreased from 91% to 76% as the adsorbate concentration decreased from 1000 to 500 mg/L (Table 9.2). However, the regeneration efficiencies of spent-GAC equilibrated with 100 mg/L, 50 mg/L, or 10 mg/L of phenol solution did not decrease further, ranging between 69% and 73% (Table 9.2 and Figure 9.4). A strong correlation (R^2 = 0.95) was found between regeneration efficiencies and logarithmic transformed adsorbate concentration (Figure 9.4).

The adsorption isotherm is examined to evaluate GAC before and after in-situ regeneration by iron nanocatalysts. The equilibrated adsorbent-phase (q_e) and aqueous-phase (C_e) phenol concentrations from GAC packed beds saturated by different adsorbate concentrations were used. Figure 9.5 gives the Freundlich adsorption isotherm for virgin and regenerated GAC with log-log scale plot for q_e and C_e; both virgin and regenerated GAC data fitted well by the Freundlich adsorption isotherm (R^2 = 0.86 and 0.93, respectively; Figure 9.5). The maximum phenol adsorption capacities (q_0) are 138 and 121 mg-phenol/g-GAC and the exponents (1/n) are 0.14 and 0.19 for virgin and regenerated GAC, respectively. The low exponent value (1/n) of virgin GAC in the linear range shows lower adsorption energy and stronger affinity between virgin GAC and phenol in comparison to regenerated GAC when initial phenol concentration ranged from 10 to 1000 mg/L. The changes in characteristics of GAC after regeneration contribute to the loss of phenol adsorption capacity when compared with virgin

GAC. However, the regeneration efficiencies tended to increase with increasing adsorbate concentration (> 500 mg/L as phenol) which might be resulted from the stronger driving force attributed to greater concentration gradient. From the observation of the result, 60% to 70% of GAC regeneration efficiencies are expected when adsorbate concentration is lower than 10 mg/L as phenol.

9.4 Conclusions

Fenton and iron nanocatalysts reagents have several advantages in common, e.g. high rates of pollutant oxidation and small dimension of equipment required, which are beneficial for on-site regeneration application. However, the main disadvantages of Fenton reagent are quick oxidization once prepared and production of iron slurry after reaction. This study presents investigation of the in-situ catalytic regeneration of GAC using iron nanocatalysts. GAC stayed in continuously flow bed during adsorption and regeneration cycles throughout this study. GAC saturated by high concentration of phenol solution was efficiently regenerated (> 90% recovery of adsorption capacity) by the technique of in-situ catalytic regeneration in the presence of iron catalyst and H_2O_2 without ultraviolet at room temperature. Experiment of multiple adsorption-regeneration cycles indicates that at least 5 cycles can be achieved without significant reduction of adsorption capacity of GAC. Higher adsorbate (phenol in this study) concentration shows significant effect on the regeneration efficiency of phenol-saturated GAC. Low adsorbate concentrations can result in low regeneration efficiency but the efficiency can stay constant (about 70%) when the concentration is lower than 100 mg/L. Despite the loss of iron nanocatalyst during regeneration, used iron nanocatalyst is possible to be retrieved efficiently for reuse in at least three more runs by pH adjustment and precipitating approach. The reported technique of in-situ regeneration of GAC loaded with organic matter provides insight to the practicability in larger scale water cleaning process.

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Table 9. 1 The saturated adsorbent-phase concentration of phenol (q_e, mg-C/g-GAC) and regeneration efficiency (E) for GAC regenerated by fresh and recycled nanocatalysts with multiple adsorption-regeneration cycles. The adsorbate concentrations are 1000 mg/L as phenol and q_e of virgin GAC = 93 mg-C/g-GAC.

Data represent: q_e, E	1st regenerated GAC	2nd regenerated GAC	3rd regenerated GAC	4th regenerated GAC
Regenerated by fresh nanocatalysts	85, 92%	86, 93%	79, 85%	88, 95%
Regenerated by recycled nanocatalysts	77, 83%	65, 70%	75, 80%	

Table 9. 2 The saturated adsorbent-phase concentration of phenol (q_e) and regeneration efficiencies (E) for GAC saturated by different phenol concentrations.

Adsorbate concentration	1000 mg/L	500 mg/L	100 m/L	50 mg/L	10 mg/L
q_e and E	98 (89) 91%	95 (70) 76%	72 (52) 73%	68 (48) 72%	46 (32) 69%

Note[1]: numbers in the parentheses represent the q_s of virgin GAC.

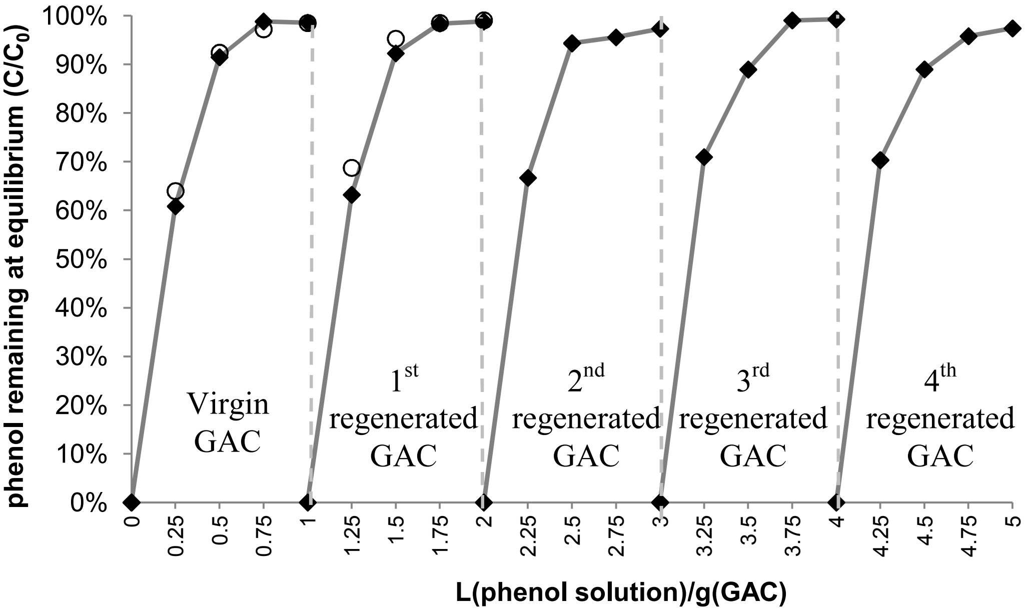

Figure 9. 1 Aqueous-phase phenol at equilibrium when adsorbed by virgin and fresh nanocatalysts (NCs)-regenerated GAC after multiple cycles. Phenol concentrations for GAC adsorption are 1000 mg/L as phenol and 1 liter of phenol solution was used to saturate GAC. Circle symbols represent duplicate results in a separated bed.

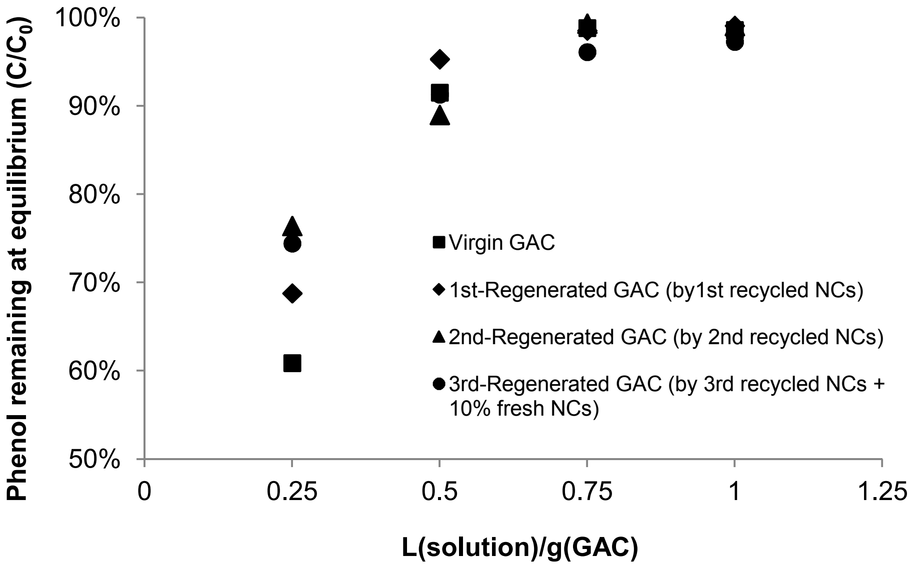

Figure 9. 2 Aqueous-phase phenol at equilibrium when adsorbed by virgin and recycled nanocatalysts (NCs)-regenerated GAC. Initial concentration of phenol: 1000 mg/L. Fresh nanocatalysts was used for first regeneration and recycled repeatedly for next cycle.

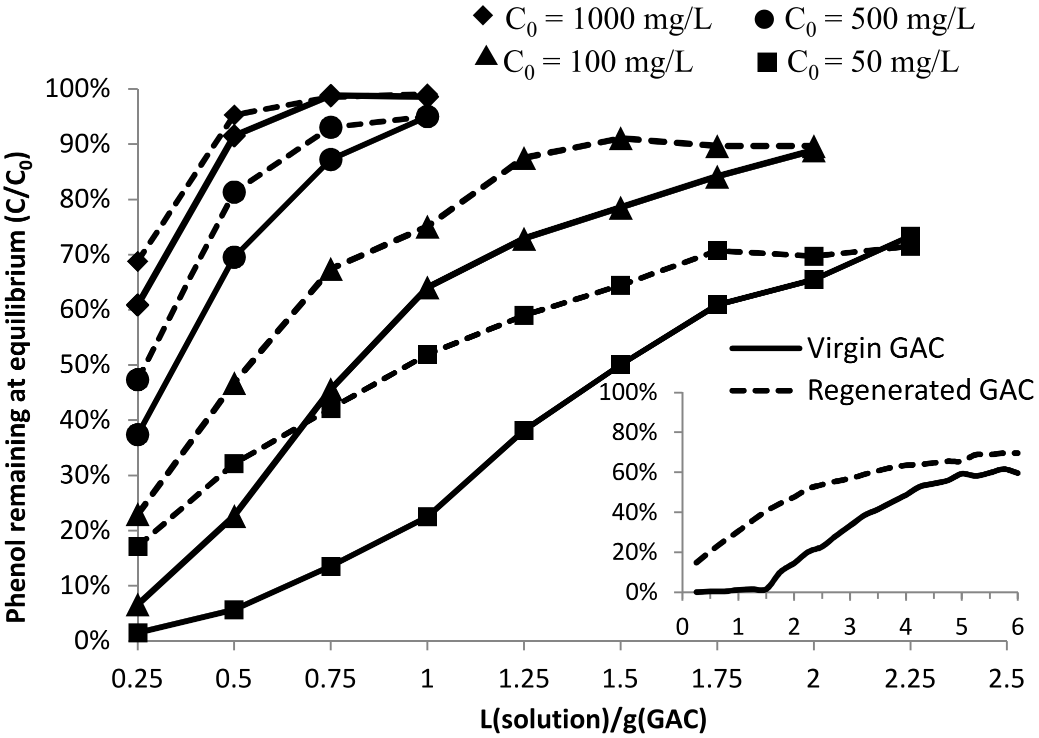

Figure 9. 3 Profiles of phenol adsorption on virgin GAC and regenerated GAC when loaded with different adsorbate concentrations. The inset shows the GAC saturated by 10 m/L of phenol solution and has the same units as primary graph.

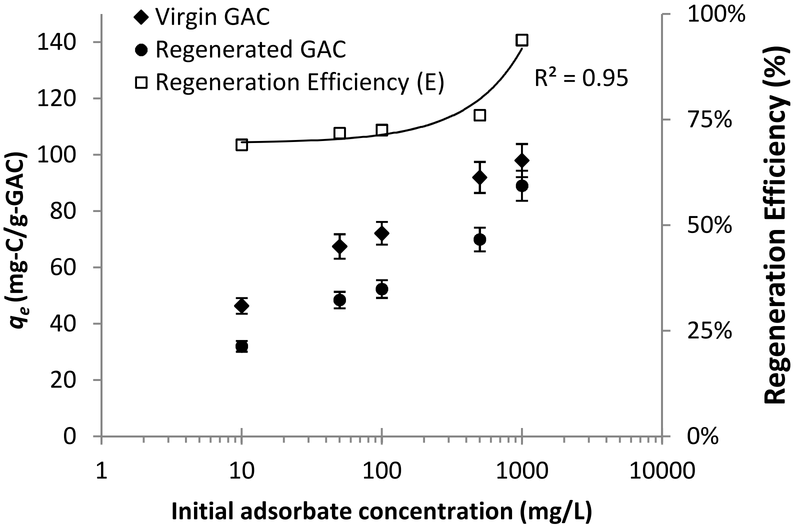

Figure 9. 4 The The relationship between regeneration efficiencies and adsorbate concentration and the differences of q_e between virgin and regeneration GAC.

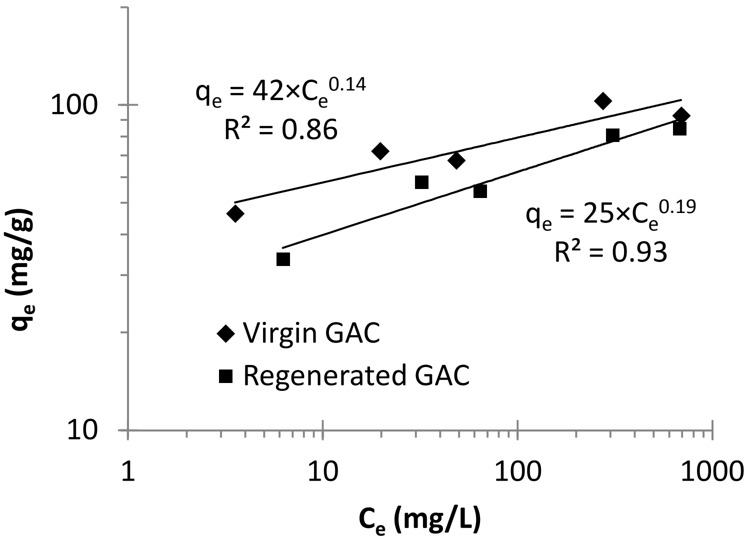

Figure 9. 5 The Freundlich adsorption isotherm ($q_e = k \times C_e^{1/n}$) for virgin and 1st-regenerated GAC fitting. k = (mg/g)/(mg/L)$^{1/n}$; 1/n is unitless.

CHAPTER 10

SYNTHESIS OF RESULTS

This chapter synthesizes findings of all the research chapters and supports the research goal of this dissertation. The goal of this dissertation was to investigate organic matter occurrences in Arizona waters and provide an integrated GAC (adsorption-regeneration) technology for water quality control. The motivation and impact of this dissertation is illustrated in Figure 10.1. This figure summarizes the influence of watershed DOC export and human activities with respect to DOC variation and increased CECs present in downstream water sources. The use of these types of impacted water challenges drinking water utilities because the water quality is more vulnerable which can form elevated concentrations of regulated and unregulated (nitrogenous) DBPs during peak flow period. To meet stringent regulation compliance, some utilities may convert from free chlorine to chloramines while others may implement more advanced unit process (Seidel, 2005). While GAC is suggested by USEPA for water utilities as the best available technology to control regulated C-DBPs, little is known about the control of emerging N-DBPs formed from DON or inorganic nitrogen by GAC. Additionally, the development of in-situ GAC regeneration can offer new GAC operation mode during peak flow seasons and reduce energy cost (from transportation and high required temperature) of off-site thermal regeneration.

Three main compartments of this dissertation are illustrated in Figure 10.1 and three hypotheses served as motivation for chapter 4 to 9. The objective of each chapter is restated here followed by three sections which synthesized the results presented in previous chapters (*Chapter 4* to *9*). Each section will address one of the hypotheses and support them with data from the previous chapters and additional data from the appendices. Along with each section, a brief discussion of its importance and interconnectivity to other sections is provided.

The six research objectives, as stated in the introduction (*Chapter 1*), are reintegrated below:

- *Chapter 3 & 4* describes the variation of dissolved organic carbon in three arid-region water supply reservoirs in Arizona. The effect of hydrologic variability on water quality response was investigated by comparison between different hydrologic years.
- *Chapter 5* investigates emerging contaminant occurrence in urban water system in Arizona and provides a case of anthropogenic activities impact on CECs occurrence in surface water.
- *Chapter 6* examines GAC breakthrough patterns of organic nitrogen and bulk organics, as precursors for C-DBP and N-DBP formation. Models are developed for both DOC and DON breakthrough prediction
- *Chapter 7* builds up an empirical model for synthesis of hematite iron-NPs using forced hydrolysis method. The effect of temperature and aging time on the particle size was examined. This chapter was designed to

synthesize hematite NPs which might be able to serve for in-situ GAC regeneration.

- *Chapter 8* compares hematite NPs to another synthesized iron (hydr)oxide NPs in the ability to serve as catalyst in catalytic oxidation process. The one which shows faster organic removal rate is selected for the test of in-situ GAC regeneration in *Chapter 9*.
- *Chapter 9* establishes in-situ GAC regeneration method and examines multiple adsorption-regeneration cycles and the effect of adsorbate concentration.

10.1 The Variability of Bulk and CECs Concentration in Reservoirs and/or Urban Water Systems Has Been Impacted by Meteorological Factors, Reservoir Operations, and/or Anthropogenic Activities.

The motivation for this aspect of the research was to answer a fundamental question when examining long-term (1999 to 2010) DOC variations of three reservoirs in Southwestern US area: why the trends of DOC variability in these three reservoirs differed from each other? Whereas autochthonous DOC and other algal extracellular by-products (methylisoborneol (MIB) and geosmin) originating in US Southwestern reservoirs has been discussed in literatures (Westerhoff et al., 2005; Mash et al., 2004), little is known about the impact of extreme meteorological events on the DOC responses in downstream reservoirs and utility water sources. With the projection of changes in extreme events globally (e.g., heavy precipitations, droughts, and heat waves) between now to 2100 (IPCC, 2007), arid region like Arizona with distinct dry and wet seasons serves as a great example for understanding the DOC response in drinking water sources upon impact of watershed runoff. Differing hydrology and water management practices of three surface water sources serving the metropolitan Phoenix in Arizona of 3.5 million peoples offer scenarios with respect to reservoir operation. Additionally, occurrence of CECs in raw water increases the variability of organic composition and many of them have been studied to exhibit adverse ecological impacts (Snyder et al., 2003; Ongerth & Khan, 2004; Warren et al., 2002; Foster & McIntyre, 2002; Ankley et al., 1998; Daston et al., 2003; Zhang & Emary, 1999). Collecting data over a watershed scale provides useful information to address public questions or concern, and the investigation aids in understanding the occurrence of CECs as well as their natural attenuation in the environment.

The following sections will address this issue based on analyzing the influences of watershed runoff on DOC occurrences and characteristics in three major reservoirs in Arizona, modeling approach for simulation of DOC transport in multi-lake system, and investigation of CECs occurrence.

10.1.1 Influences of Watershed Runoff on DOC Occurrences and Characteristics in Reservoirs in Arizona

Long term trends of DOC concentration in three major reservoirs showed different patterns during the last ten years (*Chapter 3*). In general, DOC concentrations tended to increase over the last ten years. Bartlett Lake exhibited largest water quality variability while Saguaro Lake and Lake Pleasant showed less variation (Figure 3.2). The characteristic and temporal pattern of DOC in reservoirs served for Metro-Phoenix area varied significantly within each year and among years (Figure 3.3). While DOC production during summer was found to be attributed to in-lake sources (e.g., algal activities) (Mash et al., 2004), spring runoff in western US brings in significant amount of terrestrial DOC which is more reactive to form DBPs, this is true for all three reservoirs.

Mass loading of DOC in the Bartlett Lake during early spring followed a predicted flow pattern (Figure 3.6). During the period of extreme events, like spring storms, DOC concentrations ranged from 3 to 7 mg/L and DOC mass exported from watershed was elevated to 50 times higher than in regular years. Depending on dry-rewet cycle, spring runoff contributed 50 to 90% of the total annual DOC input to Bartlett Lake which was operated with shorter upstream HRT. Longer dry seasons antecedent to first flush resulted in higher abundance of DOC in runoff water. The strong variation in DOC loading during early spring with allochthonous material can cause vulnerability to safe drinking water supply which will result in failure to operation of water treatment processes with respect to DBP control.

For Lake Pleasant, the yearly averaged DOC showed medium yearly variation compared with other reservoirs, and the stable DOC in Lake Pleasant might result from the relative long hydraulic residence time (400 days) and water management and operation as off-stream reservoir.

10.1.2 Modeling Approach for Simulation of DOC Transport in Multi-Lake System of Salt River

In *Chapter 3*, the yearly variation of DOC in Saguaro Lake was less than observed in other reservoirs. From the observation of long-term inflow, it appears that the water released from upstream reservoirs was regulated and the impact of watershed runoff can be barely correlated with the DOC loading into Saguaro Lake (Figure 4.7a). Although long overall HRT of multi-lake system in Salt River can contribute to the attenuation of DOC pulses observed in downstream, the DOC transport in each lake and the contribution of pump-back operation still remain unknown.

To evaluate the phenomena of DOC attenuation of abrupt DOC pulses, a dynamic model based on mass balance equation for Salt River four lakes system was established in *Chapter 4*. Based on measured DOC in inflow to Roosevelt Lake during 2002 to 2004, the impact of post-fire (Rodeo-Chediski Fire, 2002) storm events, which caused extreme DOC concentrations (30 mg/L) exported from watershed, was dampened to 5 mg/L in lower end Saguaro Lake. The impact of DOC pulses was delayed for about 1 year to elevate DOC concentrations in Saguaro Lake.

By using this dynamic model for multi-lake system, the long term DOC transport between each lake and the contribution of pump-back operation can be identified. Figure 4.4 shows the simulated DOC transport and the observed DOC concentrations in each lake on Salt River system. The dynamic modeling approach is capable to simulate the DOC occurrence and transportation between each lake in Salt River system. Most of the DOC degradation (> 40%) occurred in Roosevelt Lake with longest residence time and the operation of water pump-back also contributed to DOC attenuation significantly. Local utilities wanted to know for how long the DOC pulses observed in Salt River upstream would impact the raw water quality of water treatment plant downstream, and based upon the continuous time dynamic model a delay of DOC responses of 300 to 400 days was estimated.

10.1.3 Investigation of CECs Occurrence in Drinking Water System

Many municipalities are concerned about the potential for EDCs/PPCPs to occur in their water supplies because the presence of these compounds may affect future treatment decisions. To provide a metro-Phoenix-wide view of CECs present in Arizona waters, *Chapter 5* summarized 26 PPCP/EDCs concentrations collected from varied waters including three main water sources and from a selected drinking water treatment plant, wastewater treatment plants, and groundwater. Table 5.2 shows the distribution of 26 most investigated CECs detected in different water columns across the state of Arizona. Among different CECs sources, wastewater treatment plant effluent is known as the major source of such contaminants. Removal efficiencies from 60 to 70 % were observed in wastewater treatment plants adopting activated sludge and nitrification processes. These high concentrations of emerging contaminants might accumulate in sludge or be transformed by microorganisms. The disposal of the wastewater sludge as well as the discharge of treated wastewater into natural water systems must be carefully managed.

Groundwater and surface waters were detected with lowest CECs-containing levels (< 10 ng/L for each compound). However, some specific contaminants were detected with levels of 100 ng/L, for example, sulfamethoxazole and sucralose in groundwater, and oxybenzone, caffeine and sucralose in surface waters. The source of these CECs in groundwater might be from the wastewater discharge or intrusion of landfill sewage. For water treatment plants, the majority of CECs detected in surface water were also identified in WTP raw waters and sedimentation effluent. Oxybenzone was measured with highest level during summer while sucralose was the major contaminant measured in other seasons. Fortunately, the majority of CECs will be oxidized by chlorination; about 30 ng/L of total CECs residual is resistant to natural and WTP removal processes and presents in drinking water.

Arizona is known for its limited water sources, and the water is used for many purposes such as irrigating, water recreation, and drinking. Three case studies were conducted at upstream Verde River and Salt River to reveal the impact of recreational activities on occurrence of CECs in surface water. The results of these three cases shows that human activity exerted significant effect on CECs present in surface water even though wastewater was not discharged into river upstream directly. Additionally, observation of increasing oxybenzone, caffeine, and sucralose during the recreational activities of summer explains the occurrence of these compounds in raw water of water facilities downstream.

Tracking the occurrence and fate of these CECs in drinking water systems and establishing a database is important for water management of metropolitan Phoenix to control these unregulated organic compounds in case of emergent issue. The monitoring should at least focus on the 10 compounds detected most frequently and with highest concentration, including oxybenzone, caffeine, sucralose, DEET, sulfamethoxazole, acetaminophen, and dilantin.

10.2 GAC Removes Carbonaceous-DBP Precursors Better Than N-DBP Precursors

GAC is considered as barrier to handle broad range of bulk organics and CECs with variable concentration. While granular activated carbon is the best available technique (BAT) for controlling currently regulated carbonaceous DBPs, little information is available on the use of GAC to control unregulated nitrogenous DBPs, and none for DON specifically. The motivation of this study is to evaluate the performance of GAC with respect of DON and N-DBPs control. The following sections will address this issue based on evaluation of removal of C- and N- DBPs precursors using RSSCTs method, and development of modified models for both DOC and DON breakthrough prediction.

10.2.1 Evaluation of RSSCTs for Removal of C-DBPs and N-DBPs Precursors

The trend of increasing variabilities of DOC and CECs in drinking water sources (*Chapter 3, 4 & 5*) challenges utilities because of greater propensity to form elevated concentrations of regulated and unregulated DBPs (Mitch et al, 2008). This dissertation documents the removal of organic nitrogen during GAC treatment and illustrates how GAC treatment alters the speciation of N- and C-DBPs. Based on the RSSCTs result (*Chapter 6*), GAC preferentially removes UV254-absorbing material, and DOC is preferentially removed over DON. The low affinity for absorption by GAC implies that DON compounds may be composed primarily of hydrophilic organic matter. Figure 6.2 and Figure 6.3 summarized the relationship in terms of breakthrough stage between different organic compositions which can serve as fundamental knowledge for utilities to estimate relative breakthrough stages between organic carbon and nitrogen.

A unique aspect of this work is use of coagulated surface waters, rather than source waters, because coagulation tends to remove similar NOM fractions as GAC. Based on the experimental findings (*Chapter 6*), it appears that pretreatment of surface water with chlorine dioxide and/or powder activated carbon will reduce the amount of dissolved organics as well as UV254-absorbing material and extend the number of BVs treated, especially before 20% breakthrough occurs. Conventional treatment processes and enhanced coagulation show limited ability to reduce this dissolved organic matter, and waters pretreated with these processes tend to exhaust GAC faster.

In this work, the poor removal of DON and rapid breakthrough of at least one N-DBP precursor class, that of HANs, provides initial evidence that GAC may not remove N-DBP precursors as well as THM or HAA precursors, but additional research on other N-DBP precursors using RSSCTs is necessary to fully understand the potential benefits of GAC treatment for controlling N-DBPs.

This part of study has been submitted for publication in *Journal of American Water Works Association.* To my best knowledge, this is the first work showing data on DON removal by GAC compared against DOC removal as a means of removing N-DBP precursors.

10.2.2 Development of Modified Models for DOC and DON Breakthrough Prediction

For better understanding how GAC reacts under a range of influent NOM and operating conditions (EBCT), models capable of simulating DOC breakthrough are developed to aid in understanding. These influences include climatic variations that could lead to DOC levels from 2 to 7 mg/L. A modeling approach developed previously (Zachman et al., 2007) is modified for coagulated waters and expanded to include DON removal.

27 RSSCT breakthrough curves obtained with water treatment plant waters (data for training) were used to estimate best-fitted parameters, which was then used to predict breakthrough curves for the remaining 15 observed RSSCTs (data for validation). As a result, the model suggested by Zachman et al. didn’t show good prediction at < 25% of DOC breakthrough (Figure 6.7 and 6.8). Thus,

a modified model expressed as $BV_X = e^A \times DOC_0^{B1} \times pH^{B2}$ was suggested in this dissertation (*Chapter 6*, EQN4). The R-square values (0.79, 0.77, 0.79) for training data, validation data, and overall data, respectively, from proposed model is more consistent and higher than from model suggested in literature (R-square = 0.76, 0.64, 0.75). Moreover, this model exhibited good prediction for the early stage (< 25%) of DOC breakthrough (shown in Figure 6.9).

In addition to DOC breakthrough modeling, this model was modified for prediction of dissolved organic nitrogen breakthrough from GAC adsorber. The expression of DON breakthrough model is the same as DOC breakthrough model but DOC_0 is substituted with DON in feed waters (DON_0) (*Chapter 6*, EQN5). The best-fit power B1 over variable DON_0 is -0.23 which is lower than B1 for DOC breakthrough. This low B1 coefficient for DON indicates a weak relationship between run time and DON_0 and implies lower affinity for GAC to adsorb organic nitrogenous compounds. According to R-square values (Table 6.4), DON breakthrough model shows lower predictive ability than Model for DOC, which might be attributed to faster breakthrough and higher variation of DON_0 observed in feed waters after conducted with different pretreatment processes. For the comparison between DOC and DON breakthrough curves based on modeling results, GAC selectively adsorbed DOC material over DON and, the BV treated for DOC doubled the BV treated for DON to reach the same breakthrough percentage (Figure 6.10).

Overall, modeling approach effectively predicts DOC breakthrough in a GAC adsorber and modified model performs better by increase R-square value and predicting < 25% breakthrough stage. Model for DON also exists and is capable of providing correlation between DON and DOC in effluent of GAC adsorber. Further acclimation within the environmental engineering variable is required to provide more robust predictions

10.3 Synthesized Iron NPs Plus H_2O_2 Can Regenerate GAC In-Situ for Control of Dissolved Organics

As the BAT suggested by USEPA for compliance of more stringent regulations on DBPs and presence of CECs, taste and odor compounds, etc. in drinking waters, GAC installation can become more widespread in small scale drinking water utilities. However, operational costs for GAC can be extremely high in cases when NOM breakthrough occurs rapidly with limited number of bed volumes treated as a result of extreme weather antecedent to peak flow period (*Chapter 3 & 4*). The motivation of this study is to evaluate the feasibility of applying iron nanoparticles (NPs) as catalyst for in-situ GAC regeneration. The following section will address this issue based on synthesis and comparison of two different types of iron NPs with respect to catalytically oxidize organics, and evaluation of selected NPs for catalytic in-situ regeneration of organic-adsorbed GAC.

10.3.1 Synthesis and Comparison of Iron NPs for Catalytic Organic Oxidation

Synthetic iron oxides NPs have been widely used as catalysts and adsorbents in industrial applications. As the most widely applied and intensively investigated form of iron oxide, a simple (without high hydrolysis temperature and addition of dispersants) and systematic approach for hematite NPs synthesis still remains unavailable. This dissertation developed an empirical model capable to predict hematite NPs size under the control of hydrolysis duration and temperature (60 to 100 °C) without organic or inorganic additives (*Chapter 7*). Hematite NPs were then prepared in comparable size to another synthesized iron (hydr)oxide NPs; both these two iron NPs with similar particle size were tested for catalytic ability during Fenton-like reaction.

Based on the experimental findings (*Chapter 8*), both hematite NPs and iron (hydr)oxide NPs shows ability to serve as catalysts in Fenton-like reaction. However, iron (hydr)oxide NPs is more effective than hematite NPs in terms of producing ·OH for organic oxidation, for example, the first-order reaction rate are 0.0024 and 0.0183 min^{-1} for experiments conducted with hematite NPs and iron (hydr)oxide NPs, respectively. The optimal molar ratio between iron NPs and H_2O_2 for oxidation is 1:25. To achieve 100% of organic removal when concentration is high, addition of H_2O_2 after 30 minutes is preferred over increasing initial H_2O_2 concentration due to scavenging of ·OH by excessive H_2O_2 and temperature rise. The fast reaction rate in aqueous solution of this technique using iron (hydr)oxide NPs as catalyst is beneficial to the in-situ GAC regeneration.

Although hematite NPs were not selected as catalyst for following in-situ GAC regeneration in this dissertation, the NP size prediction model developed in *Chapter 7* could be an invaluable tool for researchers engaged in research that necessitates uniform NPs with specific sizes. Additionally, the use of iron (hydr)oxide NPs as reagent may result in occurrence of trace iron NPs in drinking water system, and it was suggested that the transformation of iron (hydr)oxide (basically Fe(O)OH reported by Bach et al., 2010) to hematite (α-Fe_2O_3) occurred naturally (Liang et al., 2006; Fan et al., 2005; Bustamante et al., 2005; Goss et al., 1987). This model can serve for fate and transport study of iron NPs in drinking water system in the future with respect to particle size.

10.3.2 Evaluation of Iron Nanocatalysts for In-Situ Regeneration Of Organic-Adsorbed GAC

Based on the experimental results in *Chapter 8*, iron (hydr)oxide NPs was selected to serve as catalyst (so called nanocatalysts) for in-situ GAC regeneration tests (*Chapter 9*). The in-situ regeneration is highlighted in this dissertation which was carried out by keeping GAC in continuously flow bed during adsorption and regeneration cycles throughout this study. To my best knowledge, this is the first study showing in-situ GAC regeneration using iron nanocatalyst technique.

GAC saturated by high concentration of phenol solution was efficiently regenerated (> 90% recovery of adsorption capacity) by the technique of in-situ catalytic regeneration in the presence of iron catalyst and H_2O_2 without ultraviolet at room temperature (Figure 9.1 and Table 9.1). At least 5 adsorption-regeneration cycles can be achieved without significant reduction of adsorption capacity of GAC. Higher adsorbate (phenol in *Chapter 9*) concentration shows significant effect on the regeneration efficiency of phenol-saturated GAC. Low adsorbate concentrations can result in low regeneration efficiency but the efficiency tends to be constant (about 70%) when the concentration is lower than 100 mg/L (Figure 9.4). This dissertation is also the first study showing GAC regeneration under circumstance of low adsorbate concentration (< 100 mg/L as phenol). Additionally, used iron nanocatalyst is possible to be retrieved efficiently for reuse in at least three more runs by pH adjustment and precipitating approach, which is beneficial to save more operation costs. The result also shows that GAC iron contents increased slightly from 1.5 ± 0.1 to 2.0 ± 0.2 mg-iron/g- GAC after regeneration, which indicates that the retention and elution of iron NPs is worth investigating (by model presented in *Chapter 7*).

By using this technique of catalytic in-situ GAC regeneration, utilities may be able to implement exhausted-GAC regeneration on-site during peak flow seasons (*Chapter 3 & 4*). This implementation can be tested by performing RSSCTs and the result is illustrated as in Figure 10.2. Instead of model compound, humic acid (HA, Fluka standard) was prepared as feed water for RSSCT test. The RSSCT column was packed according to the method/scaling equations described in *Chapter 6* to simulate the organic breakthrough occurred in drinking water utilities. The catalytic in-situ regenerations were conducted as described in *Chapter 9*. The breakthrough of DOC and TDN concentrations, and UV254 absorbance were monitored for comparison between virgin GAC and repeatedly regenerated GAC. As a result, regenerated GAC exerted similar removal ability for these three important indexes in terms of DBPs formation (*Chapter 6*). With respect to regeneration efficiency, 70 to 80 % of adsorption capacities for these three materials were recovered even after second adsorption-regeneration cycle. This significant result indicates that, even applied for GAC which is operated normally, this regeneration system is feasible for on-situ application, especially during peak flow seasons when organic level is high in raw water.

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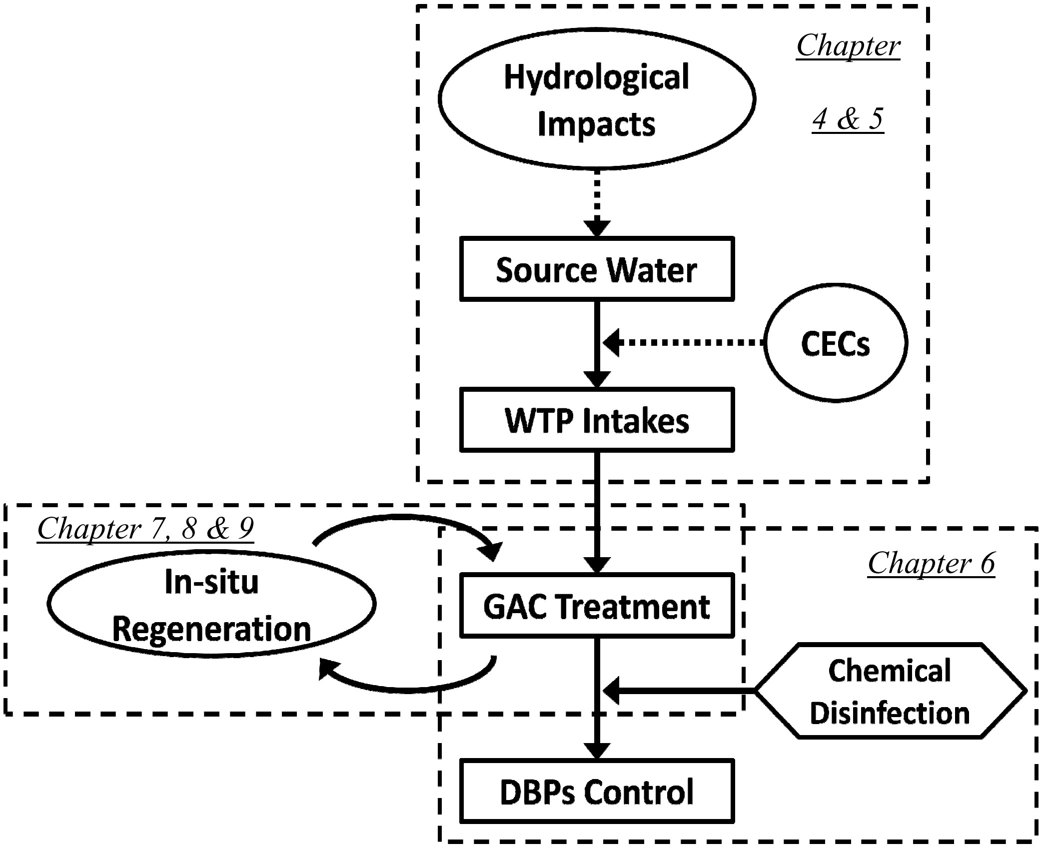


Figure 10. 1 Diagram of water source influence and water treatment processes.

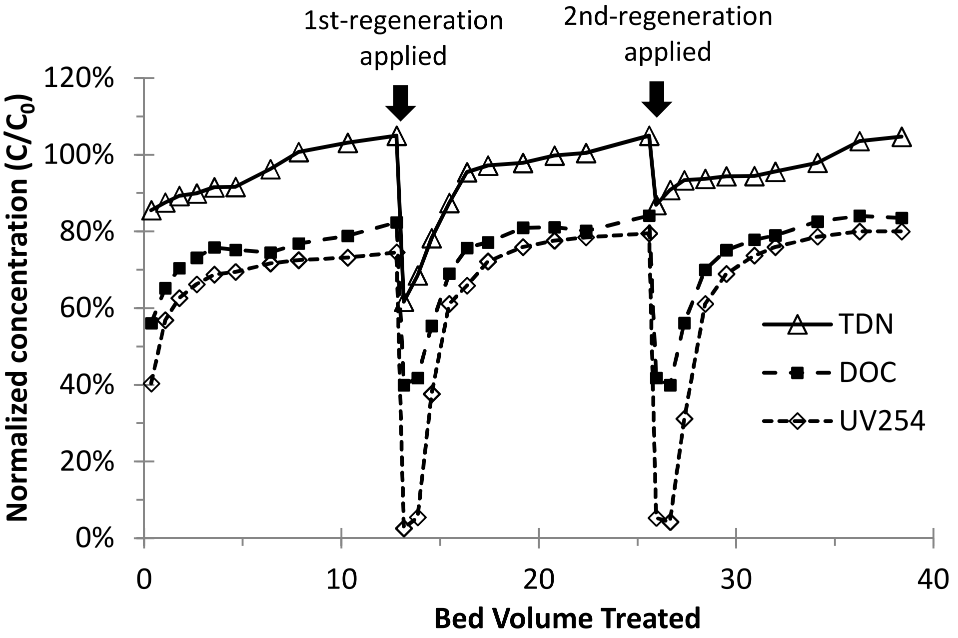


Figure 10. 2 UV254 and DOC breakthrough curves for virgin and repeatedly regenerated GAC conducted with RSSCTs. DOC concentration in feed water was 12 mg/L.

CHAPTER 11

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

The primary goal of this dissertation was to investigate the organic matter occurrence in Arizona waters and evaluate an innovative treatment method by GAC. The following summarizes the findings and conclusions in this dissertation.

1. DOC concentrations have tended to increase in three major water supply reservoirs for Metro-Phoenix area over the last ten years beyond the distinct monthly variation pattern in each lake. Monthly variations of DOC concentration in reservoirs were dependent upon climatic factors, organic characteristics, and reservoir operations.

2. Spring runoff brought more reactive organic matters with higher DBP formation potential. The relationship between volume of spring runoff and mass of DOC loading was found. Longer dry seasons antecedent to first flush resulted in higher abundance of DOC in runoff water

3. Multi-reservoir impoundment arranged in series could be beneficial to managing the quality of water supply downstream by (1) attenuating the impact of DOC loads from upstream watersheds, and (2) creating a lag time for DOC export due to increased hydraulic residence time. Roosevelt Lake serves as the major DOC sink in the Salt River system, thus understanding DOC cycling in Roosevelt Lake is important for water source management.

4. Dynamic modeling with consideration of pump-back operation simulates DOC transport between each lake and might be capable of predicting future water quality based on watershed hydrology.

5. Occurrence of CECs in Arizona waters merits monitored since the water source is limited and the water is used for multiple purposes. Anthropogenic sources like recreational activities can cause notable impact on raw water quality as can seasonal effects.

6. While suggested by USEPA as the BAT for compliance with the Stage 2 D/DBP Rule, GAC shows limited ability for unregulated N-DBP control in terms of DON removal. The operation cost for GAC can be extremely high when targeting removal of DON and high DOC level in raw water during peak flow seasons causes organic matter to breakthrough rapidly.

7. Iron (hydr)oxide can serve as a nanocatalyst for in-situ GAC regeneration. This technique shows better regeneration efficiency when the organic concentration in aqueous phase is high.

8. In comparison to other regeneration methods, this in-situ catalytic regeneration technique shows at least 4 advantages: (1) once prepared, this nanocatalyst is stable in aqueous phase; (2)there is no need for iron-slurry post-treatment after reaction; (3) these used-nanocatalysts can be recovered and serve for the next regeneration cycle; (4) this technique has low energy and transportation cost (save at least 120,000$/year for a 150 MGD capacity facility) and is therefore suitable for small scale utilities.

9. By using this technique, in-situ GAC regeneration could be conducted frequently with reduced downtime. This would maintain high driving forces to remove organics from water which is beneficial to DON control and DOC removal during peak flow seasons.

10. The hematite NPs size prediction model can serve for fate and transport study of iron NPs in drinking water systems since the iron (hydr)oxide nanocatalyst is likely to occur and tends to transform to hematite naturally.

Recommendations for Future Research

This research has focused on understanding the organic matter occurrence in Arizona drinking water sources and evaluating a better solution for water quality control by catalytic in-situ GAC regeneration. During this research, a number of questions were raised which require the attention of the research community. A list of areas in which further study would be beneficial is provided below:

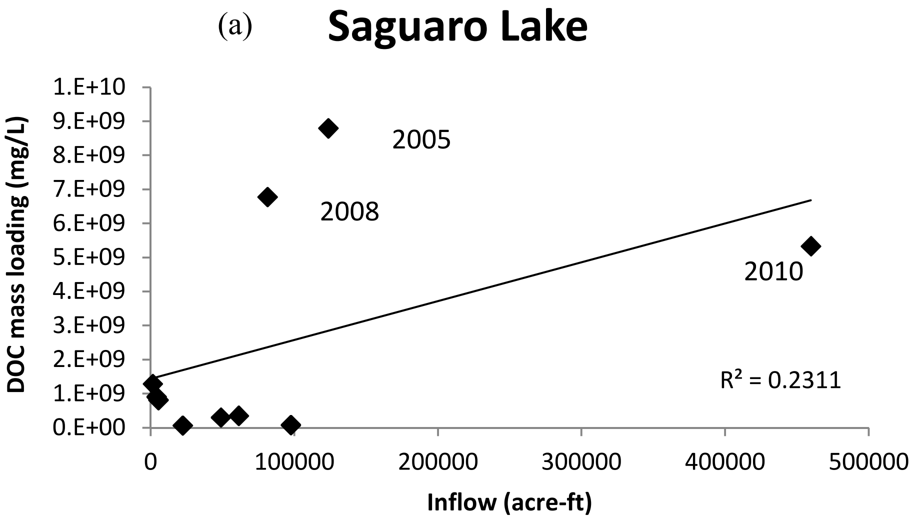
- According to modeling results, Roosevelt Lake is the important sink for DOC attenuation and provides a lag time for DOC export as a result of long HRT. Roosevelt Lake can exert ability to digest extreme DOC loading but can also cause water quality deterioration once the system collapses, such as algae bloom. Further research should focus on the DOC cycling and the potential nutrient import to Roosevelt Lake including in such conditions as post-wildfire runoff.

- The direct correlation between DON and N-DBPs still remains uncertain in using GAC for DON control. Further study of the GAC control for N-DBP precursors (e.g., N-nitrosodimethylamine (NDMA) and halonitromethanes (HNMs)) is required to clarify the significance of DON removal as varied N-DBP precursors.
- The modeling approach for DON breakthrough prediction is not as good as for DOC breakthrough. The tendency of rapid breakthrough and varied DON concentration in feed water might contribute to the poor predictability. The model might be improved by tracking DON breakthrough data more frequently before 100 % breakthrough is occurred. Additionally, more independent variables may exist which need to be considered in model development.
- The model for synthesized hematite size prediction is preliminary and only includes two variables: reaction time and temperature. Further study that controls the initial pH and $FeCl_3$ concentration is required to develop a more comprehensive predictive model.
- The technique of catalytic in-situ GAC regeneration was tested for the first time as a bench-scale experiment. The organic concentration was high (12 mg/L as DOC) in feed water for repeated adsorption-regeneration testing. Further study is required to assess the feasibility of this regeneration system when conducted with lower background organic concentration or in larger scale (pilot-scale) tests.

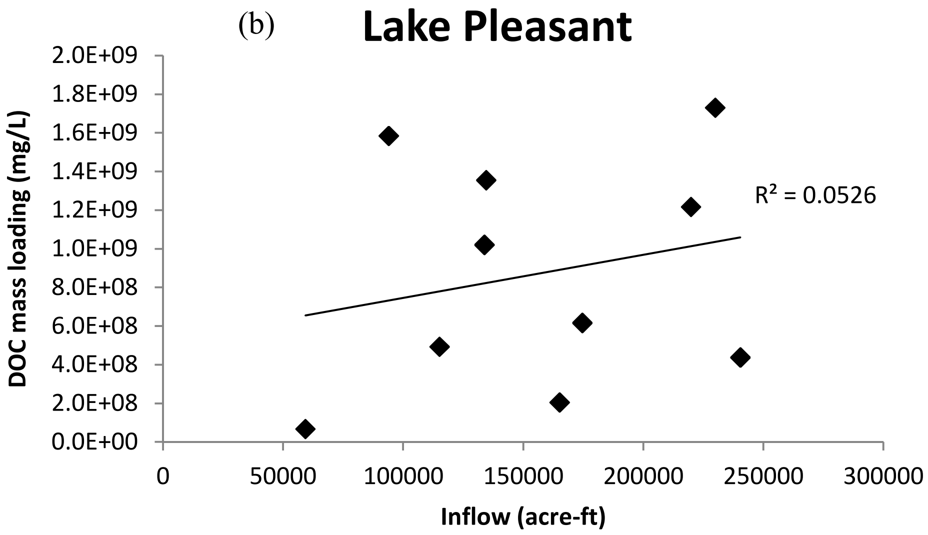
APPENDIX 3. A

LINEAR REGRESSION RESULTS FOR DOC MASS LOADING AS A FUNCTION OF INFLOW DURING EARLY SPRING OF SAGUARO LAKE (A) AND LAKE PLEASANT (B).

(a)

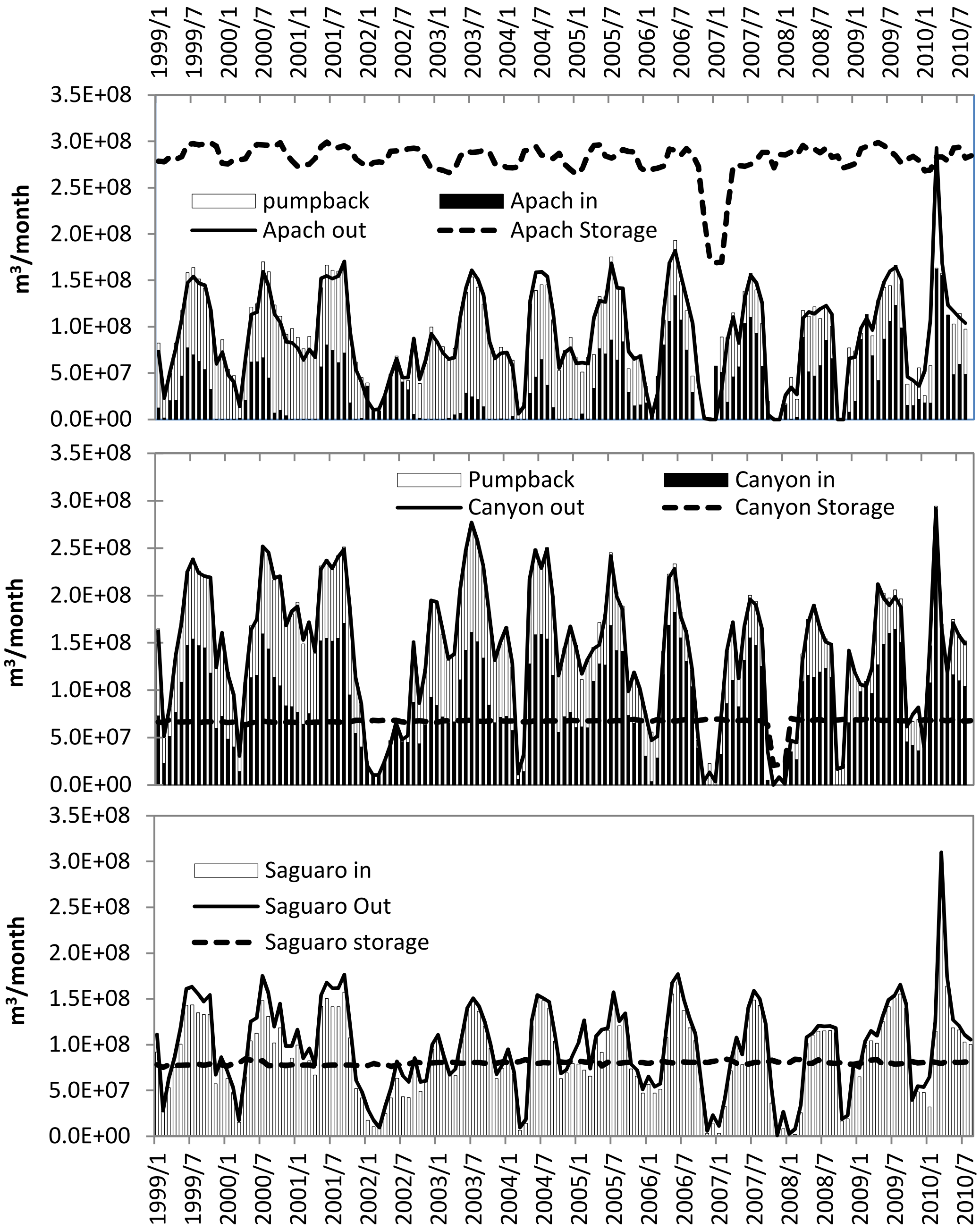


(b)



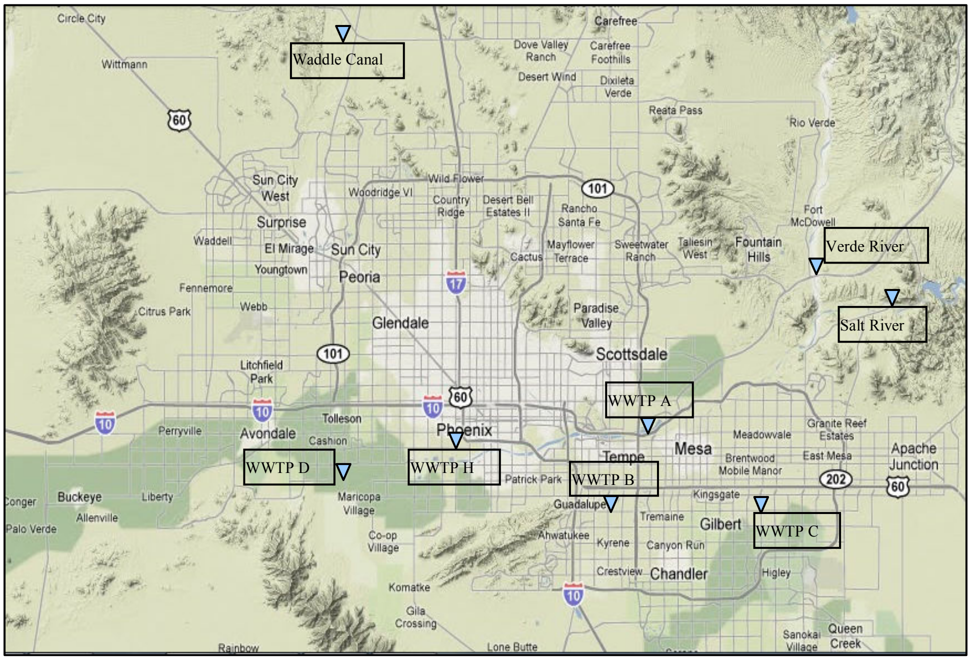
APPENDIX 4.A

OPERATION OF WATER RELEASE AND PUMP-BACK IN EACH LAKE ON SALT RIVER.



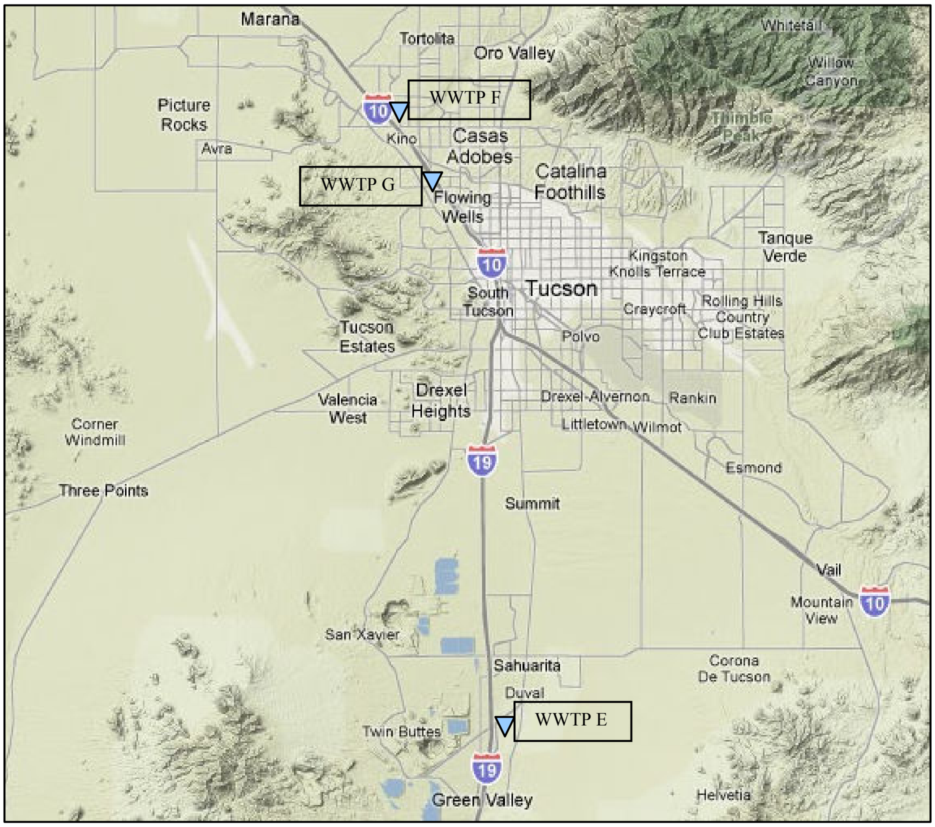
APPENDIX 5. A

SAMPLING SITES FOR SURFACE WATERS AND WWTPS IN METROPOLITAN PHOENIX



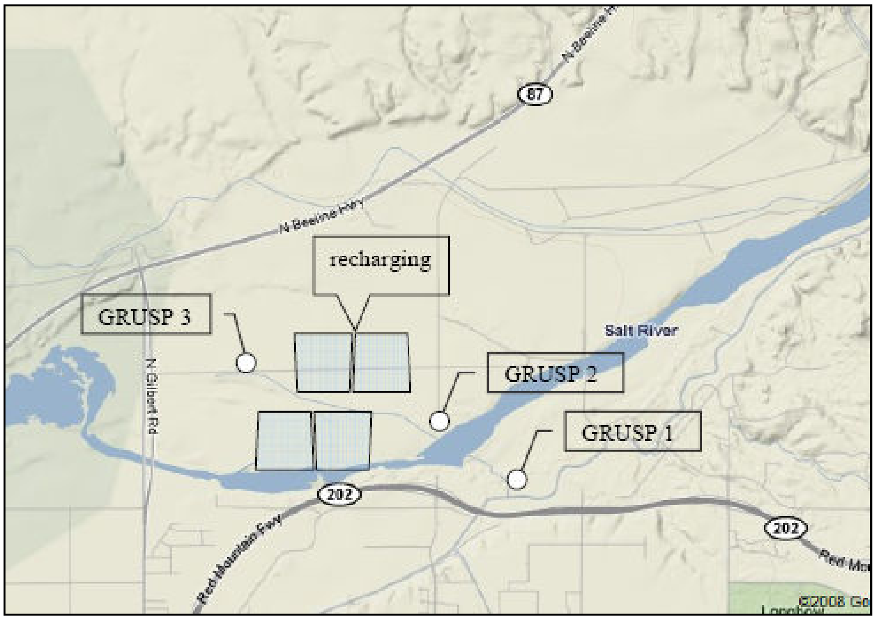
APPENDIX 5. B

MORE SAMPLING SITES FOR WWTPS IN TUCSON, ARIZONA



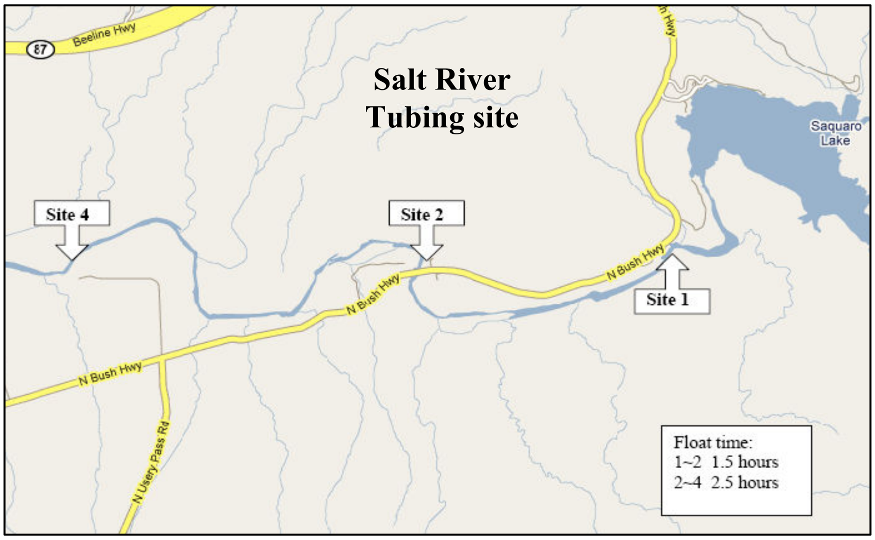
APPENDIX 5. C

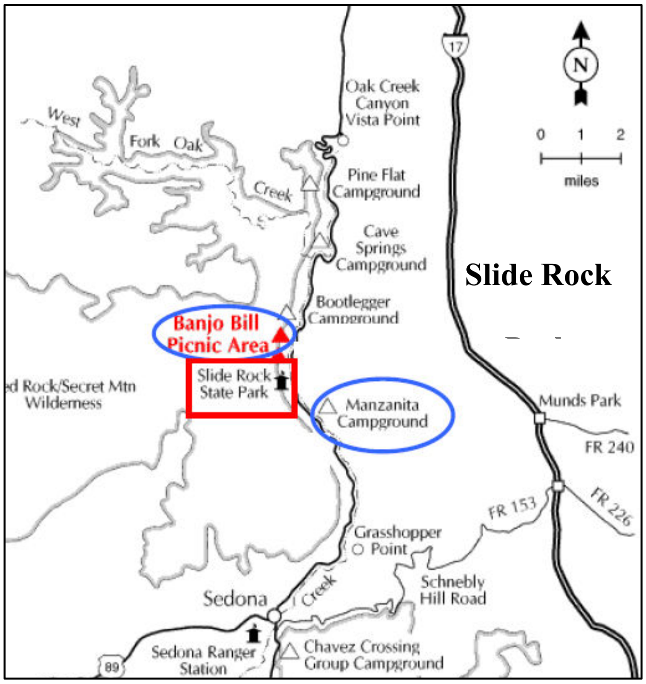
SAMPLING SITES FOR GROUNDWATER RECHARGING PROJECT NEAR PHOENIX, ARIZONA



APPENDIX 5. D

TWO WATER RECREATIONAL SITES NEAR METROPOLITAN PHOENIX





APPENDIX 5. E

SUMMARY OF DETECTION METHODS FOR EACH COMPOUND

Ionization Source	**Compound**	**Class/Use**	**Quantifier Ion**	**Qualifier Ion(s)**
			Q1/Q3	**Q1/Q3**
APCI Positive	Estradiol	Steroid/Estrogen	255.3/159.2	255.30/133.1
	Ethynyl Estradiol	Steroid/Synthetic Estrogen	279.2/133.0	279.2/159.1
	Progesterone	Steroid/Estrogen	315.3/97.3	315.3/109.0, 315.3/109.2
	Testosterone	Steroid/Androgen	289.3/97.3	289.3/109.2, 289.3/123.3
ESI Negative	Cotinine	Personal Care Product/Nicotine metabolite	177.2/80.2	177.2/98.3
	Diclofenac	Pharmaceutical/Anti-arthritic	294.3/250.0	294.3/214.0
	Dilantin (Phenytoin sodium)	Pharmaceutical/Anti-convulsant	251.4/102.0	251.4/180.0
	Ibuprofen	Pharmaceutical/Analgesic	205.1/159.0	205.1/161.0
	Naproxen	Pharmaceutical/Analgesic	229.0/169.0	229.0/185.1, 229.0/140.9
	Sucralose	Personal Care Product/Sweetener	395.3/359.0	397.2/361.1
	Tetrabromobisphenol A	Personal Care Product/Flame retardant	442.9/239.0	442.9/102.9
	Triclosan (Ingasan)	Personal Care Product/Antibiotic	287.2/34.9	287.2/241.1
	Warfarin	Pharmaceutical/Anti-coagulant	307.3/161.0	307.3/250.0, 307.3/117.0
ESI Positive	Acetaminophen	Pharmaceutical/Analgesic	152.1/110.2	152.1/65.3
	Atrazine	Pesticide	216.1/174.2	216.1/104.2
	Caffeine	Personal Care Product/Stimulant	195.2/138.3	195.2/110.0
	Carbamazepine	Pharmaceutical/Anti-seizure	237.3/194.0	237.3/179.3
	DEET	Personal Care Product/Insect Repellant	192.1/119.3	192.1/91.3
	Diazepam	Pharmaceutical/Muscle relaxant	285.2/193.3	285.2/154.0, 285.2/222.0
	Diuron	Pesticide	233.3/72.3	233.3/159.9
	Erythromycin-H2O	Pharmaceutical/Antibiotic	716.5/158.3	716.5/558.6
	Fluoxetine	Pharmaceutical/Anti-depressant	310.3/44.2	310.3/148.3
	Hydrocodone	Pharmaceutical/Analgesic	300.3/199.2	300.3/171.3, 300.3/128.3
	Imazamox	Pesticide	306.4/261.2	306.4/245.2
	Imazthapyr	Pesticide	290.3/245.2	290.3/177.2
	Meprobamate	Pharmaceutical/Anti-anxiety	219.2/158.3	219.2/97.3
	Oxybenzone	Personal Care Product/Sunscreen	229.3/151.2	229.3/105.1
	Pentoxifylline	Pharmaceutical/Blood thinner	279.4/138.2	279.4/99.2
	Primidone	Pharmaceutical/Anti-convulsant	219.2/162.1	219.2/91.3
	Prometryne	Pesticide	242.2/157.9	242.2/200.3
	Sulfamethoxazole	Pharmaceutical/Antibiotic	254.3/156.2	254.3/108.1
	Trimethoprim	Pharmaceutical/Antibiotic	291.3/123.3	291.3/230.4, 291.3/261.2
INST/Surrogate	Acetaminophen-D4		156.2/114.1	156.2/69.1
	Cotinine-D3		180.3/80.10	180.3/101.2
	Diazepam-D5		290.3/198.4	290.3/154.0, 290.3/227.4
	Estradiol-D5		260.3/161.10	260.3/135.10
	Fluoxetine-D6		316.2/44.2	316.2/154.2
	Hydrocodone-D6		306.3/202.3	306.3/174.3, 306.3/128.3

Note: both quantifier ion and qualifier ion are shown with the unit of m/z (mass-to-charge ratio)

APPENDIX 5. F

CONCENTRATION DETECTED IN BLANK SAMPLE

	Blank samples		
	Average (ave)	**Standard Deviation (SD)**	**ave+2SD**
Acetaminophen	0.2	0.3	0.9
Caffeine	1.0	1.0	3.0
Carbamazepine	0.1	0.3	0.7
Cotinine	0.1	0.1	0.3
DEET	1.1	1.0	3.0
Diazepam	0.1	0.2	0.5
Diclofenac	0.4	0.5	1.3
Dilantin	0.7	1.1	2.8
Erythromycin	0.1	0.3	0.7
Fluoxetine	0.3	0.4	1.1
Hydrocodone	0.5	0.8	2.0
Ibuprofen	0.6	1.0	2.6
Meprobamate	0.2	0.3	0.8
Naproxen	0.2	0.5	1.3
Oxybenzone	2.0	1.3	4.6
Pentoxifylline	0.2	0.5	1.1
Primidone	0.1	0.2	0.6
Sucralose	0.4	0.7	1.7
Sulfamethoxazole	0.3	0.7	1.7
TBBA	0.5	0.9	2.4
Triclosan	1.0	1.0	3.0
Trimethoprim	0.1	0.4	0.8

Note: this table shows the averaged concentration and standard deviation from all blank samples. The value of “average+2SD” is the criteria to obtain statistical significant concentration from field samples.

APPENDIX 5. G

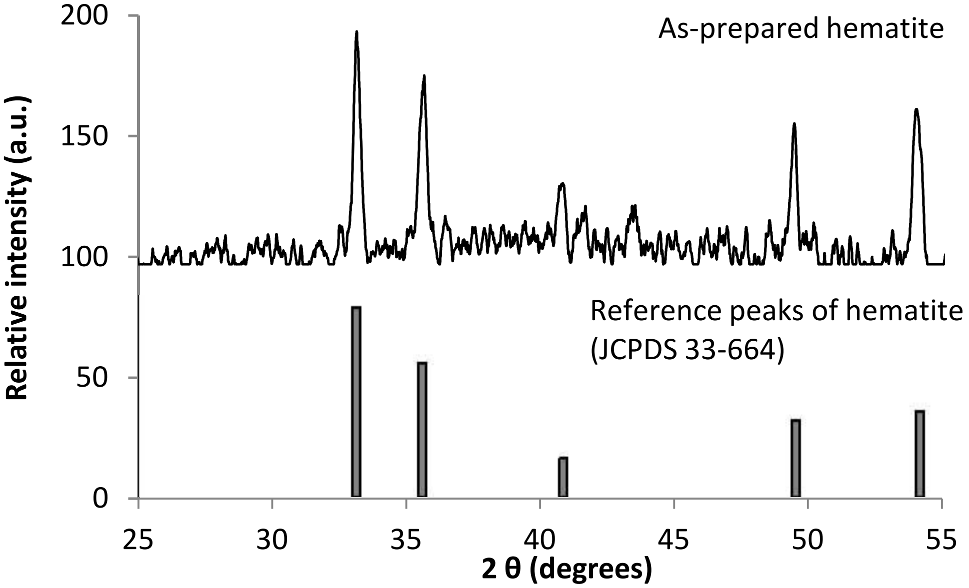
RECOVERY CORRECTION OF COMPOUNDS IN DIFFERENT WATER MATRICES AFTER SOLID PHASE EXTRACTION

	Surface water	WTP sedimentation effluent	WTP disinfection effluent	Raw wastewater	WWTP tertiary effluent
Acetaminophen	32%	31%	27%	14%	16%
Caffeine	61%	62%	61%	59%	33%
Carbamazepine	65%	79%	75%	54%	49%
Cotinine	65%	79%	75%	54%	49%
DEET	65%	79%	75%	54%	49%
Diazepam	65%	79%	75%	54%	49%
Diclofenac	65%	79%	75%	54%	49%
Dilantin	28%	27%	29%	23%	14%
Erythromycin	61%	62%	61%	59%	33%
Fluoxetine	32%	31%	27%	14%	16%
Hydrocodone	65%	79%	75%	54%	49%
Ibuprofen	65%	79%	75%	54%	49%
Meprobamate	65%	79%	75%	54%	49%
Naproxen	28%	27%	29%	23%	14%
Oxybenzone	32%	31%	27%	14%	16%
Pentoxifylline	61%	62%	61%	59%	33%
Primidone	65%	79%	75%	54%	49%

Note: the recovery correcting factor were obtain from the isotopes spiking in different water matrices. The loss of mass due to matrix effect during solid phase extraction were corrected by this recovery factor.

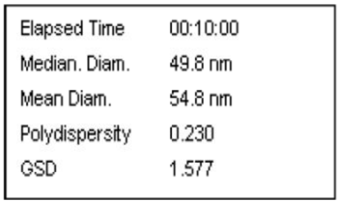
APPENDIX 7. A

X-RAY DIFFRACTOGRAMS OF THE AS PREPARED HEMATITE NPS.

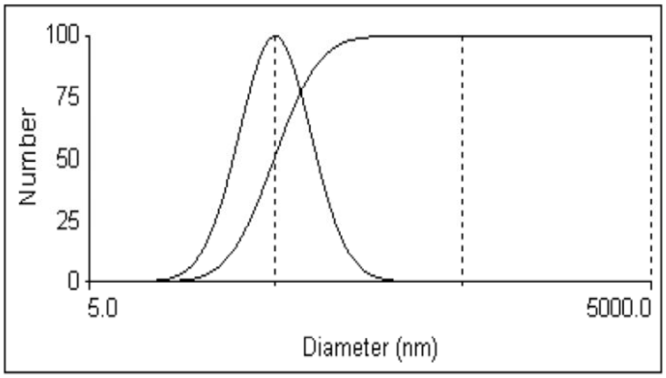


APPENDIX 9. A

SIZE DISTRIBUTION OF IRON OXIDE-BASED NANOPARTICLES MEASURED BY ZETAPALS.



Elapsed Time	00:10:00
Median. Diam.	49.8 nm
Mean Diam.	54.8 nm
Polydispersity	0.230
GSD	1.577



Lognormal Size Distribution

APPENDIX 9. B

SMALL SCALE GAC COLUMN SETTING FOR PHENOL ADSORPTION AND IN-SITU REGENERATION.