DISSERTATION

ENHANCING NATURAL TREATMENT SYSTEMS BY UTILIZING WATER TREATMENT RESIDUALS

Submitted by

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In partial fulfillment of the requirements

For the Degree of Doctor of Philosophy

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ABSTRACT OF DISSERTATION

ENHANCING NATURAL TREATMENT SYSTEMS BY UTILIZING WATER TREATMENT RESIDUALS

The current project envisions the application of riverbank filtration (RBF) and aquifer recharge and recovery (ARR) in series as preliminary treatment steps of a multi-barrier treatment approach for the City of Aurora's Prairie Waters Project. The primary focus of the project is the removal of phosphorus, nitrogen, and carbon from the source water resulting in biologically stable water that can be stored in the terminal reservoir. In addition to nutrients, perchlorate and three commonly used pesticides, atrazine, alachlor, and metolachlor have been studied in terms of removal with the RBF and ARR systems. Aluminum based water treatment residual (WTR) was considered along with other sorbents for enhanced phosphorus removal. The experimental studies include the monitoring of an RBF field site and pilot columns that simulate RBF and ARR systems. Possible benefits of WTR as an amendment were tested by amending a column with 30% WTR under RBF and ARR conditions. Also an application scenario of RBF followed by a WTR amended ARR infiltration basin and ARR was simulated by a column study.

Results of the studies indicated that the ability of the RBF and ARR systems to remove phosphorus is not sustainable and limited by the sorption capacity of the alluvial sand and minor biological activity. Use of the WTR amendment reduced phosphorus levels to less than the method detection limit of 0.03 mg/L with a high adsorption capacity. Another important finding of the study is that the RBF system can achieve

greater than 50% DOC removal, independent of influent concentrations and seasonality. The ARR system in sequential RBF-ARR application suffers from the lack of labile organic carbon and therefore microbially mediated treatment processes are limited. Amending the infiltration of the ARR system with organic carbon rich WTR can promote biological activity, thus allowing further biodegradation of contaminants. The type, source, and amount of WTR are important criteria to optimize an efficient and successful WTR amendment implementation to ARR systems. A strong linear correlation (R^2 = 0.96) between the amount of WTR and organic carbon leach was observed. For WTRs from different sources, there was no observable correlation between the organic carbon leach and the amount of WTR (5, 10, 20%), except the application ratio of 30% which showed a strong correlation (R^2 = 0.998), indicating that below a particular application ratio, the source of WTR is not important and the amount of organic carbon leach is mainly controlled by the application ratio.

Results of the study also indicated that the RBF system is a sustainable barrier for nitrate removal while labile carbon limited ARR cannot achieve significant nitrate removal. To use the ARR system as a secondary barrier for nitrate, a labile carbon source should be introduced to the system. WTR was used as a supply of organic carbon to the ARR system and the experimental studies indicated that, once optimized, WTR can promote biological denitrification through the ARR system. The field and column studies also showed that both RBF and ARR can achieve perchlorate removal as long as sufficient electron donating compounds (e.g. organic carbon) are present in the environment. WTR amendment has been shown to act as an organic carbon source and electron donor thus it promotes biological activity under anaerobic conditions to promote

perchlorate removal. Results of the study also indicated that the ability of the RBF and ARR systems to remove alachlor and metolachlor is limited by the biodegradation through the alluvial sand while they achieve sustainable atrazine removal. WTR was tested as an amendment alternative the ARR infiltration basin. Concentrations of selected pesticides were reduced to the method detection limit of 0.3 μg/L during 1-foot 30% WTR amended column treatment with the residence time of 1.25 days under both abiotic and biotic conditions. The removal mechanism was suggested as sorption on the aluminum (hydr)oxide particles in the WTR media. The study indicates that once optimized, WTR can be used as an amendment for the sequential RBF –ARR system to successfully remove pesticide contamination in the source water.

The overall study suggested that once the source and type of the WTR was selected, the optimum amount of WTR can be obtained by adjusting the application ratio and the media depth for the efficient removal of all contaminants of concern.

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CHAPTER I: INTRODUCTION

Quality and quantity of potable water resources are rapidly decreasing all around the globe due to the increasing population, industrial uses, and agricultural activities. As technology and industry evolve, more water contaminants which adversely influence human health are identified and drinking water quality standards are getting stricter. To satisfy these standards, more advanced and costly water treatment techniques are required. Recently, increased interest has been focused on cost effective and efficient innovative solutions. Beside improved water resource management practices, cost effective, passive, in-situ treatment technologies allow solutions for providing high quality drinking water.

One of the serious threats to water resources is excess nutrients loads including nitrogen, phosphorus and carbon. In various chemical forms, these three elements are the essential nutrients for life and are the building blocks for living organisms in aquatic life. They can also promote fertility of surface waters (eutrophication) and cause serious water quality impairment in fresh water bodies if they exist in excessive amounts.

Phosphorus is an important element for all life forms. It is a key part of the structural framework of nucleic acids, adenosine tri-phosphate (ATP), adenosine di-phosphate (ADP), and phospholipids in microorganisms. Within the major nutritional and structural components, phosphorus is the least abundant and limits the microbial growth in fresh water bodies (U.S. EPA, 1986; Wetzel, 2001).

Major phosphorus contributions to fresh water bodies come from anthropogenic sources including wastewater treatment plant discharges, phosphate mining fields, agricultural runoff, and urban runoff.

Except for the fact that phosphorus is a growth limiting nutrient in fresh water bodies, it does not have any known adverse health effects to humans, thus, there is no drinking water standard for phosphorus. However, The U.S. Environmental Protection Agency (U.S. EPA) published suggested levels of phosphorus in fresh water bodies to protect the water quality in lakes and rivers (U.S. EPA, 1986). The report emphasizes that the total phosphate as phosphorus should not exceed 25μg/L to prevent biological nuisances in lakes and reservoirs. Also 50 μg/L total phosphate as phosphorus is the critical limit for any stream at the point they enter any lake or reservoirs. The desired goal for discharges to lakes, reservoirs, or streams is that the discharge phosphorus content should not exceed 100 μg/L total phosphate as phosphorus (U.S. EPA, 1986). Recently, individual states have started developing nutrient criteria for lakes and reservoirs. The aim of these studies is to regulate nutrient loads to surface waters to improve water quality for multiple purpose of use (CWQCD, 2006).

Nitrogen is a lso a crucial element since it is an essential nutrient for living organisms and a constituent of vital organic compounds such as amino groups and amides that are the building blocks of proteins, DNA, and RNA (Williams, 2001). Even though the existence of nitrogen in fresh water is important for biological growth, it is the second limiting nutrient since it is the most abundant gas in the atmosphere (78.1%) and numerous microbiological species have the ability to fix atmospheric nitrogen (Williams, 2001; Wetzel, 2001).

Contamination of fresh water bodies with nitrogen is mostly due to the runoff from agricultural fields, urban storm water runoff and wastewater treatment plant effluents. The common inorganic chemical form of nitrogen, nitrate (NO_3^-), is a negatively charged molecule and very soluble. It easily becomes mobile and leaches to surface waters and groundwater aquifers (Williams, 2001).

The presence of nitrate is essential for aquatic plants, algae, and microorganisms as a nitrogen source, however, excessive concentrations in conjunction with other crucial nutrients can promote unwanted microbial growth and cause eutrophication in fresh water bodies. In addition to eutrophication, nitrate is potentially toxic to humans and animals. Excessive nitrate concentrations in drinking water can cause methemoglobinemia or blue baby syndrome (Winton et al., 2002). Nitrate is also a precursor of nitrosamines, which are reported to be carcinogenic. It was reported that long term exposure to nitrosamines may cause digestive system cancers (Fraser et al., 1980; Mitch et al., 2003a, b). Another possible adverse health effect of nitrate is on developing fetuses (Manassaram, 2006). Due to its toxic and possible carcinogenic effects on human health, nitrate is regulated by the U.S. EPA with the maximum contaminant level of 10 mg/L as nitrogen or 45 mg/L as nitrate (U.S. EPA, 1986). Since a conventional water treatment approach is not efficient in terms of nitrate removal, advance technologies are needed to treat high nitrate containing fresh water sources.

Carbon is a nutrient that can be fixed by photosynthetic organisms and can be utilized during the decay of dead organisms. Unlike phosphorus and nitrogen, it does not limit biological growth in surface waters. Inorganic carbon, carbon dioxide, exists in air and in inorganic minerals of calcium and magnesium. In water, organic carbon enters the

system by CO_2 fixation of algae and biodegradation of dead organic material. External sources of organic carbon are runoff from agricultural fields, forests, swamps and grassland. Residual carbon from wastewater treatment facilities is also an important source of organic carbon load to surface waters. The organic carbon content of surface waters includes a diverse set of compounds varying in structure, chemical reactivity and biodegradability. These properties determine the fate of carbon in water.

The primary concern of excessive organic carbon concentrations in water in terms of adverse health effects is the formation of disinfection by products (DBPs). Reaction of organic carbon with halogens, such as chlorine and bromide during disinfection process can form trihalomethanes (THMs) and haloacetic acids (HAAs). These compounds are known carcinogens and regulated by U.S. EPA at low levels.

Rapidly advancing technologies in analyses of a wide variety of chemicals has increased the interest in the occurrence and fate of a wide range of compounds, some that are currently regulated and many that are not. Perchlorate and pesticides are such chemical compounds that have recently studied for health effects by various researchers. Perchlorate (ClO_4^-) is both naturally occurring and a man-made anion with high solubility. High perchlorate containing Chilean caliche is the main source of naturally occurring perchlorate. Perchlorate has a wide range of uses, even though the 65% of perchlorate contamination in surface and ground waters in the U.S. comes from military and aerospace applications in which perchlorate is used as propellant in rockets and missiles (Dasgupta et al., 2006).

Perchlorate is an endocrine disruptor that interferes with the function of the thyroid gland. T_3 and T_4 hormones that are produced by the thyroid gland regulate growth

and development. Perchlorate competes with iodide, which is a crucial component of T_3 and T_4, and inhibits iodide transport. The phenomenon is called hypothyroidism that is a condition in which body suffers from insufficient thyroid hormone (NCR, 2005). Especially for pregnant women and fetuses perchlorate uptake may cause skeletal and nervous system development problems. Perchlorate has not been regulated by the U.S. EPA, however, it is in the Candidate Contaminant List (CCL). States have started issuing advisory standards individually for perchlorate levels in ground and surface waters ranging from 1 to 51μg/L (U.S. EPA, 2005a).

Pesticides are defined as "any substance or mixture of substances intended for preventing, destroying, repelling, or lessening the damage of any pest" (U.S. EPA, 2007). Their intensive application and frequent detection especially after the 1980s, has made them a center of attention for numerous scientific studies. Pesticide detections in surface and ground waters are mostly observed just after the runoff season following their applications to agricultural fields. Atrazine, alachlor, and methalochlor are among the most commonly applied pesticides in the U.S.

Their high solubility, low biological degradability, and possible carcinogenic effects forced U.S. EPA to regulate these compounds. Atrazine and alachlor are regulated with maximum contaminant levels (MCL) of 3 μg/L and 2 μg/L, respectively. Research on metholachlor is still in progress and this chemical is on the U.S. EPA's CCL with an advisory level of 8 μg/L.

Conventional water treatment techniques have limited removal efficiency for nutrients and micropollutants, therefore, to produce safe potable water, advanced treatment applications are required to treat highly contaminated fresh water sources. The

cost associated with advanced treatment techniques have encouraged authorities to search for innovative solutions. Riverbank filtration (RBF) and aquifer recharge and recovery (ARR) are two such treatment approaches since they are natural and semi-passive techniques to produce high quality potable water.

The riverbank filtration and aquifer recharge and recovery processes are similar natural, semi-passive treatment approaches. Both techniques have been used for centuries in primitive ways (Baker, 1948; Pyne, 1995). Modern RBF techniques have been successfully used for the production of drinking water for more than a hundred years in Europe and in the last 50 years in the US. (Kuenhn and Mueller, 2000; Ray et al., 2002a). Physical, chemical and biological processes play an important role to improve the water quality through RBF and ARR applications.

Besides being cost effective, other major advantages of RBF and ARR are that seasonal changes in influent water quality due to concentration and temperature do not alter the RBF and ARR efficiencies. RBF and ARR systems achieve pathogen removal, particle removal, dissolved organic matter reduction, thus, reduction in disinfection by-product formation, and production of biologically stable water. Finally, recent studies have shown that the application of RBF and ARR are efficient in biodegradation of trace organic materials, such as, pesticides and antibiotics (Grunheid et al., 2005; Heberer et al., 2001; Heberer et al., 2004).

Water treatment residuals (WTR) are drinking water treatment process byproducts that are predominantly settled sediment (clays, humic substances, and other suspended or dissolved materials in lakes and streams), aluminum (Al) or iron (Fe) hydroxide, activated carbon and polymer. WTR are organic carbon rich and contain Al (or Fe) in

amorphous hydrous oxide forms that have a great reactivity and high internal surface area. (U.S. EPA, 1996) Due to the cost associated with the disposal of WTR to landfills, possible beneficial uses of WTR are preferred by municipalities.

Numerous studies have reported the beneficial use of WTR for the removal of phosphorus from soil and water (Dayton et al., 2003; Ippolito et al., 2003; Makris et al., 2004). Recently, research has begun to focus on the possible benefits of WTR for the removal of an inorganic trace pollutant (perchlorate) and arsenic (Makris et al., 2006a and b; Sarkar et al., 2007).

I.1. Project Description:

This project was conducted as part of the City of Aurora's Prairie Water Project. Limited water supplies have driven the city to use South Platte River downstream of Denver as a drinking water source. The overall treatment approach was developed to include the application of riverbank filtration (RBF) and aquifer recharge and recovery (ARR) in series as a multi-barrier, semi-passive preliminary treatment technique. Following the indirect draw of South Platte River water through RBF with the residence time of approximately 20 days, RBF treated water will be pumped to ARR infiltration basin to percolate back into a controlled groundwater system. After a residence time of 25-30 days, water will be recovered by a series of production wells located at the periphery of the ARR basin. Pretreated water from the ARR site will be pumped to a terminal reservoir and then be treated further in a drinking water treatment plant in Aurora, Colorado (Figure I.1).

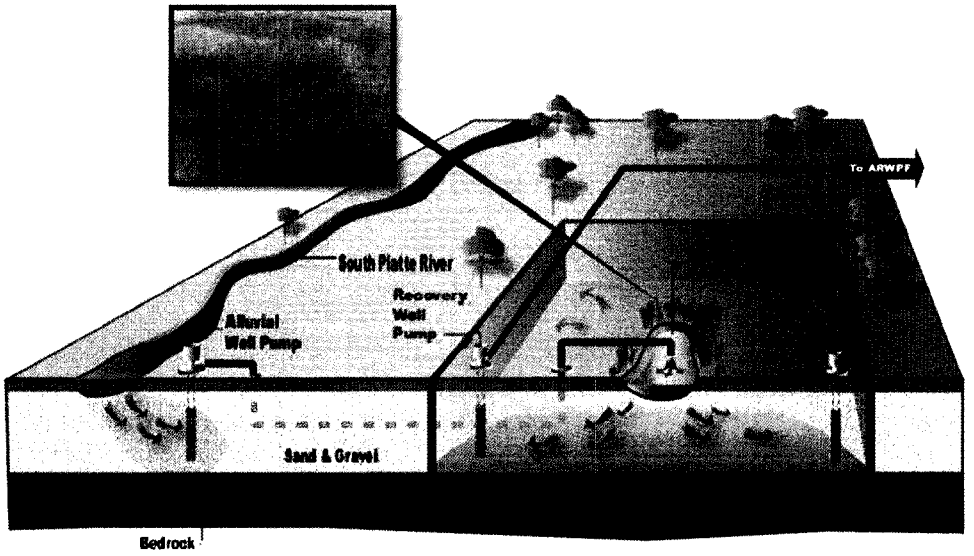


Figure I.1: Riverbank Filtration and Aquifer Recharge and Recovery (Courtesy of CH2MHill, Denver, CO)

Multiple studies were conducted to evaluate either RBF or ARR as independent treatment approaches. Apart from those associated with this project, applications of RBF-ARR systems in series have not been studied. The overall project focuses on the advantages and disadvantages of implementing a water treatment strategy of RBF followed by ARR as a two-barrier preliminary treatment step for the production of high quality drinking water.

Preliminary results of the project showed that phosphorus was not removed efficiently through the multi-barrier RBF-ARR approach. To overcome this problem, water treatment residual (WTR) was included as an alternate amendment among other options. This alternative approach includes the amendment of the infiltration basin of

ARR with WTR. This study focuses on the removal efficiency of contaminants, phosphorus, nitrate, organic carbon, perchlorate, and three types of pesticides (atrazine, alachlor, metholachlor), through a RBF-ARR multi-barrier treatment approach. As a secondary objective, possible benefits of amending the ARR with WTR will be studied and comparisons will be made between the amended and unamended RBF-ARR systems in terms of the removal efficiencies of the contaminants listed above.

I.2. Expected Outcomes and Experimental Tasks:

Expected Outcome 1: Phosphorus removal through sequential RBF-ARR treatment will be limited by the sorption capacity of alluvial material and the biological uptake capacity of microbial community. Amending the ARR infiltration basin with WTR will provide efficient phosphorus removal to levels that possible biological growth in the terminal reservoir will be prevented.

Experimental Tasks:

1. Determine phosphorus removal capability of field RBF
2. Determine phosphorus removal capability in laboratory columns simulating RBF and ARR
3. Determine benefits of amending ARR with WTR on phosphorus removal in laboratory columns simulating ARR
4. Determine phosphorus removal capability of sequential RBF - WTR amended ARR in laboratory columns
5. Determine the sorption capacity of WTR

Expected Outcome 2: Sequential RBF-ARR treatment will accomplish significant heterotrophic denitrification with most nitrate removal occurring during the relatively electron-donor-rich RBF step. Decreased denitrification kinetics will be observed during ARR due to low levels of labile carbon. Amending carbon limited ARR with WTR will contribute labile carbon to promote heterotrophic denitrification and will create a second barrier for nitrate treatment.

Experimental Tasks:

1. Determine nitrate removal capability during field RBF
2. Investigate factors affecting apparent denitrification at the field site
3. Determine nitrate removal capability in laboratory columns simulating RBF and ARR
4. Determine impact of labile carbon on denitrification removal
5. Determine benefits of WTR amendment on nitrate removal through carbon limited ARR in laboratory columns
6. Determine nitrate removal capability of sequential RBF – WTR amended ARR in laboratory columns

Expected Outcome 3: RBF treatment will accomplish organic carbon removal. Remaining organic carbon will not be sufficient to promote biological activity through ARR. WTR amendment can contribute required labile carbon to carbon limited ARR. Amount of labile carbon leaching from WTR depends on the type, source, and the amount of WTR that will be used for amendment.

Experimental Tasks:

1. Determine organic carbon removal capability during field RBF.
2. Determine organic carbon removal capability in laboratory columns simulating RBF and ARR.
3. Determine amount of carbon leach from WTR.
4. Determine organic carbon removal capability of sequential RBF- WTR amended ARR in laboratory columns.
5. Determine the effect of the type, source, and the amount of WTR amendment on the labile carbon contribution to the system

Expected Outcome 4: Sequential RBF-ARR treatment will accomplish limited perchlorate removal. WTR amendment can contribute required available carbon to carbon limited ARR to promote additional perchlorate removal.

Experimental Tasks:

1. Determine perchlorate removal capability during field RBF.
2. Determine perchlorate removal capability in laboratory columns simulating RBF and ARR.
3. Determine impact of labile carbon on perchlorate removal.
4. Determine benefits of WTR amendment on perchlorate removal through carbon limited ARR in laboratory columns.
5. Determine perchlorate removal capability of sequential RBF – WTR amended ARR in laboratory columns.

Expected Outcome 5: Sequential RBF-ARR treatment will accomplish limited pesticide removal. WTR amendment can contribute additional sorption surface and available carbon to carbon limited ARR to promote additional pesticide removal.

Experimental Tasks:

1. Determine pesticide removal capability during field RBF.
2. Determine pesticide removal capability in laboratory columns simulating RBF and ARR.
3. Determine benefits of WTR amendment on pesticide removal through ARR in laboratory columns.
4. Determine pesticide removal capability of sequential RBF - WTR amended ARR in laboratory columns.

I.3. Dissertation Summary:

The dissertation is based on the findings of the on-going Prairie Waters Project sponsored by City of Aurora. The project envisions downstream South Platte River as supplemental source water for the city. The fundamental preliminary treatment approach was decided as the application of riverbank filtration and aquifer recharge and recovery in series as a multi-barrier, semi-passive preliminary treatment techniques.

Experimental studies were started with the monitoring of a RBF field site for phosphorus, nitrate, total organic carbon, perchlorate, and three selected pesticides, atrazine, alachlor, and metolachlor. RBF conditions were also simulated in the laboratory with columns studies.

In addition to the RBF studies ARR conditions were also simulated with column studies. Possible benefits of water treatment residual were monitored for the removal of contaminants of concern. Finally, sequential RBF - WTR amended ARR system was tested as a final design alternative. Findings of this study will be used to develop design criteria for the construction of the system.

This dissertation has been structured around the papers that will be submitted to journals. The dissertation has been formatted as follows;

Chapter II "Literature Review" gives an extensive review and background information about the contaminants of concern, RBF, ARR, and WTR use and applications.

The Chapter III "Phosphorus Removal during Riverbank Filtration (RBF) and Aquifer Recharge and Recovery (ARR): Benefits of Water Treatment Residual (WTR)", Chapter IV "Sequential Natural Treatment: Impacts on Carbon Availability and Microbial Processes", Chapter V "Removal of Perchlorate through Riverbank Filtration and Aquifer Recharge and Recovery: Benefits of Water Treatment Residual", Chapter VI "Removal of Nitrogen during Riverbank Filtration (RBF) and Aquifer Recharge and Recovery (ARR): Benefits of Water Treatment Residual (WTR)", and Chapter VII "Removal of Pesticides through Riverbank Filtration and Aquifer Recharge and Recovery: Benefits of Water Treatment Residual" present the papers that will be submitted to journals. These chapters include a brief abstract, an introduction (briefly summarizes the previous studies and states the objectives of the study), materials and methods (summarizes the experimental methods and procedures followed in the study),

results and discussion (presents the findings of the study and evaluation of the results), and conclusion (brief explanation of ultimate findings) sections. Titles, tables, and figures were reformatted and the references section was removed to satisfy the dissertation format.

Chapter VIII "Conclusions and Future Research" reports the overall study findings and the future research needs that are required to improve the understanding and field applications of the treatment techniques covered in this study.

Chapter IX "References" includes the previous studies cited during the preparations of this document.

The Appendix section reports the raw data that was collected during the experimental efforts.

CHAPTER II: LITERATURE REVIEW

This chapter provides the review of literature for the contaminants of concern, the envisioned treatment techniques RBF and ARR, as well as the considered amendment material WTR. The contaminants (nutrients P, N, and C, and perchlorate and pesticides) are reviewed in the literature for their chemical characteristics, use in the industry, environmental cycling mechanisms, occurrence, environmental and health impacts, regulations, and applicable engineered and natural treatment approaches. The amendment media WTR was reviewed in literature for its chemical characteristic and previous application methods for the removal of related contaminants. The treatment approaches RBF and ARR were reviewed for their general characteristics and applications in environmental systems.

II.1. PHOSPHORUS:

Phosphorus is a multivalent nonmetal chemical element with the atomic number of 15 and the symbol of (P). Elemental phosphorus exhibits allotrophy, which implies the existence of the element in several physically different but chemically identical forms. All allotropes of phosphorus are synthetically prepared. The most common allotropes are white, red, and black phosphorus. Phosphorus is covalent in all its chemistry like nitrogen, however, it only forms natural compounds in stable (+5) oxidation state (Williams, 2001).

White phosphorus (P_4) is a white/yellow waxy transparent solid composed of 4 phosphorus atoms in a tetrahedral arrangement with six single bonds. P-P bonds in the tetrahedral structure are under a certain amount of strain, thus, making the molecule

highly unstable. The white allotrope is toxic and causes severe liver damage in ingestion. It is highly flammable and pyrophoric (self igniting) upon contact with oxygen. Exposure to oxygen (air) causes a greenish glow with a characteristic garlic smell. As a result of the oxidation white allotrope gets coated with white "(di)phosphorus pentoxide" (P_4O_{10}). White allotrope can be artificially synthesized by heating calcium phosphate, a derivative of a phosphate rock, in the presence of carbon and silica. Elemental phosphorus is then obtained as a vapor and collected under water. The phosphorus vapor and carbon monoxide produced by the reaction can be oxidized in the presence of moisture to produce phosphoric acid (Williams, 2001).

Red phosphorus is produced by heating the white allotrope to 250 °C or exposing it to sunlight. Red phosphorus is a three dimensional, amorphous macromolecule in structure and more stable then the white allotrope (Williams, 2001).

The third allotrope, black phosphorus, has an orthorhombic structure and the least reactive allotrope. It consists of six membered rings which are interlinked. Each atom is bonded three other atoms. Black allotrope is an iron gray crystalline solid that resembles graphite in appearance, properties and structure (Williams, 2001).

Elemental phosphorus does not exist in the nature. It widely exists in combination with the mineral and organic compounds (Pierzynski et al., 2005). Phosphate is the most common inorganic phosphorus form that exists in the environment. The most common phosphorus source and phosphorus containing mineral is the apatite family, $Ca_9(PO_4)_6$, and inorganic phosphates of aluminum and iron (Williams, 2001). Russia, Morocco, and U.S. States (Florida, Idaho, Montana, North Carolina, South Carolina, Tennessee, Utah,

Virginia, and Wyoming) have the largest apatite deposits in the world (Threlfall, 1951; U.S. EPA, 1986).

Phosphorus is a vital element for the ecosystem and all forms of life. The inorganic form of phosphorus, commonly referred to as orthophosphate (PO_4^{3-}), is an important constituent of nucleic acid molecules DNA and RNA where phosphorus forms part of the structural framework of these molecules. Also orthophosphate is used to transfer cellular energy in a controlled manner by the hydrolysis of adenosine triphosphate (ATP). It is believed that ATP is a universal energy supplier in all cellular processes. Beside the energy transfer, ATP also carries out an important process, phosphorylation, a key regulatory process in cells. Phosphate has a crucial role in the formation of phospholipids which are the main structural components of all cellular membranes. Phosphorus is also an essential component of bones, teeth, nerve, and brain tissue. Inorganic calcium phosphate salts are the primary constituents of bones and teeth with a major role to stiffen the bone and teeth structure (Williams, 2001).

Although the percentage of phosphorus in plant material is relatively low, it is a crucial macronutrient for agricultural crops and to grow plants for aesthetic and recreational purposes. It must be present in a simple inorganic form before it can be utilized by plants. Utilizable species of phosphorus are forms of the orthophosphate ion. In the pH range that is present in most soils, $H_2PO_4^-$ and HPO_4^{2-} are the predominant orthophosphate species (Pierzynski et al., 2005; Manahan, 2001).

Due to its importance for living organisms and its chemical properties, phosphorus has a wide range of uses. Phosphorus in the form of concentrated phosphoric acid is used to produce fertilizers for agricultural and farm production applications.

Beside the fertilizers, phosphorus has various industrial uses. Phosphates are used in the production of special glasses such as the one used in sodium lamps. Production of fine china requires the use of calcium phosphate (bone ash) salt. Sodium tripolyphosphate made from phosphoric a cid is used in laundry detergents and in the food industry, phosphoric acid made from elemental phosphorus is used in soda beverages. The acid is also a starting point to make food grade phosphates, such as mono-calcium phosphate which is employed in baking powder and sodium tripolyphosphate and other sodium phosphates. Among other uses mono-calcium phosphate and sodium tripolyphosphate are used to improve the characteristics of processed meat and cheese. Food grade phosphates are also used in toothpaste. Trisodium phosphate is used as a water softener in cleaning agents to prevent pipe/boiler tube corrosion. Formation of organophosphorus compounds is another common use of phosphorus. Organophosphorus compounds are synthesized from phosphorus through the intermediates phosphorus chlorides and the two phosphorus sulfides: phosphorus pentasulfide, and phosphorus sesquisulfide. Organophosphorus compounds have many applications, including in plasticizers, flame retardants, pesticides, extraction agents, and water treatment. Steel production is another industrial field in which phosphorus is used in the making of phosphor bronze, and in many other related products. Phosphorus has also been used for military purposes starting in the 1940s. White phosphorus has been used in military applications as incendiary bombs, for smoke-screening as smoke pots and smoke bombs, and in tracer ammunition. Red phosphorus is essential component for manufacturing matchbook strikers, flares, safety matches, pharmaceutical grade and street methamphetamine, and is used in cap gun caps. Phosphorus sesquisulfide is a component of strike-anywhere matches. In trace amounts,

in N-type semiconductors phosphorus is used as a dopant. Phosphorus isotopes, ^{32}P and ^{33}P are used as radioactive tracers in biochemical laboratories (Threlfall, 1951; Williams, 2001).

II.1.1. Phosphorus Cycle:

The biogeochemical cycle that explains the movement of phosphorus and phosphorus species through the atmosphere, lithosphere, hydrosphere, and biosphere is called the phosphorus cycle (Figure II.1). Except the transport with dust, there is relatively little exchange between the atmosphere and other environmental components in terms of phosphorus cycling due to the fact that the naturally occurring phosphorus species have low mobility, solubility and volatility. The most abundant form of phosphorus in natural systems is the phosphate ion and it exists as phosphate salts in the ocean sediments and in the rocks. The transfer of suspended solids from rocks and sediments to living organisms and back again is the main mechanism of geochemical cycle of phosphorus between oceans and the land.

Inorganic phosphorus is introduced to the environment by the minerals with high phosphorus content such as apatites, calcium, iron, and aluminum phosphates (Pierzynski et al., 2005). When the phosphorus containing geological formations are disturbed, phosphorus becomes mobile by desorption and dissolution mechanisms. Following desorption and dissolution of phosphorus from soil minerals and colloids, it enters the soil solution as a primary form of phosphate (PO_4^{3-}) and as a secondary form of orthophosphates (HPO_4^{2-}, $H_2PO_4^-$), varying in relative concentrations depending on the soil pH (Pierzynski et al., 2005). Mobile phosphate ion has a strong tendency to be associated with organic matter and soil particles rather than dissolved in solution (State of

Michigan DEQ, 2007). Immobilization of phosphorus from inorganic available forms to organic forms is carried out by organisms and plants (Prescott et al., 2005). Organic phosphorus can be mobilized by excretion in inorganic and organic forms from living microbiota or as the organisms die or lyse.

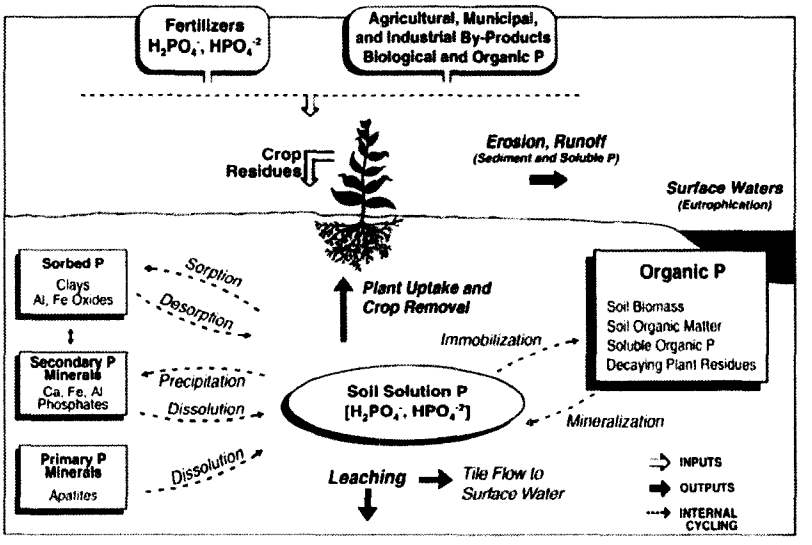


Figure II.1: Phosphorus Cycle (Pierzynski et al., 2005)

In addition to the natural mechanisms described above, major loads of phosphorus are introduced to surface waters by anthropogenic sources. Phosphorus can be released from mining activities, agricultural activity, and urban runoff. Excessive fertilizer applications in agricultural fields and urban lawns dissolve with irrigation and precipitation and move toward surface waters. Wastewater treatment plant discharges are also an important source of phosphorus contribution to the environment.

II.1.2. Phosphorus Cycle in Fresh Water Bodies:

The major forms of phosphorus in lakes and streams are inorganic and organic forms. The most significant inorganic and directly utilizable form of phosphorus in fresh

water bodies is phosphate (PO_4^{3-}), while the largest proportion (>90%) is organic phosphates, such as cellular constituents and organic phosphorus that is adsorbed to inorganic and dead particulate organic materials (Wetzel, 2001).

The total phosphorus content of unfiltered water includes particulate and dissolved forms of phosphorus. Particulate phosphorus consists of phosphorus in living organisms (DNA, RNA, and phosphoproteins, esters of enzymes, vitamins, nucleotide phosphate such as ATP and ADP), mineral phases of phosphorus in rocks and soil (hydroxyapatite, in which phosphorus is adsorbed onto clays, carbonates, and ferric hydroxides), and phosphorus adsorbed onto particulate organic matter. Dissolved phosphorus is composed of orthophosphate (PO_4^{3-}), polyphosphates, organic colloids of phosphorus combined with adsorptive colloids, and low molecular weight phosphate esters.

Chemical phosphorus analyses are based on the reactivity of phosphorus with molybdate and changing of the reaction kinetics during enzymatic and acidic hydrolysis of complex forms of phosphorus to orthophosphate. According to the ease of hydrolysis and particle size, the phosphorus content of the water is categorized into four major operational groups namely, soluble reactive P, soluble unreactive P, particulate reactive P, and particulate unreactive P.

Most of the phosphorus analyses of fresh water bodies refer to total phosphorus and soluble inorganic phosphorus (phosphate). Non-polluted fresh water bodies show total phosphorus concentrations between <1 μg/L and 200 mg/L depending on the phosphatic rock formations close by. Except for surface waters affected by phosphatic rock formations, total phosphorus levels are generally between 10 and 50 μg/L for

uncontaminated surface waters. In terms of the separation of total phosphorus to organic and inorganic components, 90% of the phosphorus that is present in surface water bodies is organic phosphorus and 70% of this is present as particulate organic material. Only 5% of total phosphorus is present as soluble inorganic phosphorus (phosphate) (Wetzel 2001). Soluble inorganic phosphorus, or soluble reactive phosphorus (SRP) averages about 10μg/L worldwide among unpolluted rivers and total dissolved phosphorus in these waters averages about 25μg/L (Wetzel, 2001).

Phosphorus levels of fresh water bodies are regulated by physical, chemical and biological processes. Adsorption, desorption, dissolution, complexation, chelation, biological uptake, and biological degradation processes are the most important mechanisms that govern the abundance of phosphorus in waters.

Kinetics of abiotic phosphorus adsorption and desorption on organic and inorganic particles comply with Langmuir isotherms. Fine particles (<0.1mm) are responsible for nearly all phosphorus adsorption with the sorption capacity of 0.1-1.0 μg P/g sediment per μg P/L water (Wetzel, 2001). Sorption of phosphates and polyphosphates to positively charged edges of the clays and substitution of phosphates for silicate in the clay structure are common reactions that occur in surface waters. High phosphate adsorption by clays is favored by low pH levels of 5-6. When the particles reach their sorption capacity, quasi-steady state, where the adsorption rate is equal to desorption, becomes established (Wetzel, 2001).

Dissolution reactions of calcium and ferric iron in the water body influences phosphorus content drastically by the formation of insoluble calcium phosphate and ferric phosphate salts. In turbid waters with low hardness, phosphates react with ferric ions and

form suspended particles of ferric hydroxide-phosphate. In hard waters, inorganic phosphorus levels decrease with the pH of 8.5 and above by the formation of highly stable calcium phosphate as hydroxyapatite. Calcium carbonate formation can also promote phosphorus precipitation in its crystals and adsorbed by carbonate surfaces under these conditions (Wetzel, 2001).

Phosphate, pyrophosphate, triphosphate, and higher phosphate anions can form complexes, chelates, and insoluble salts with metal ions (Wetzel, 2001). Relative concentrations of the phosphate anions, metal ions, the pH, and presence of other ligands (sulfate, carbonate, floride, and organic species) are the main factors that influence the complexing and chelation reactions. Complex formations with major abundant cations, such as calcium and magnesium, have a little influence in the distribution of these metal ions but may seriously affect phosphate concentrations in surface waters, since the phosphate concentrations are comparably low. Calcium concentration influences the formation of hydroxylapatite [$Ca_5(OH)(PO_4)_3$] at near neutral pH and higher pH levels promotes apatite formation (Wetzel, 2001). Moreover, increasing pH leads to formation of calcium carbonate that coprecipitates phosphate. Metal ions such as ferric iron, manganous manganese, zinc, and copper are present with concentrations equal or lower than phosphates. Complex formation with these cations can significantly affect the distribution of metal ions, phosphates, or both (Wetzel, 2001).

In fresh waters, algae, cyano-bacteria, bacteria, larger aquatic plants are the main species that utilize phosphorus. The major portion of the biological uptake is associated by microbiota attached to particles, while less than 5% of phosphorus utilization is achieved by macroinvertebrates and higher organisms. Biological phosphorus uptake by

algae and bacteria take place at much higher rates than is required for growth. Commonly, within 15-20 days phosphorus uptake rates reach a maximum then decline slowly and reach equilibrium with the growth rate. Phosphorus can be mobilized by excretion in inorganic and organic forms from living microbiota or as the organisms die or lyse (Wetzel, 2001).

Exchange of phosphorus between water and sediment is controlled by physical, chemical and biological factors such as mineral water equilibria, sorption processes, ion exchange, oxygen and other electron acceptor dependent redox interactions, and activity of microbial community associated with the sediment. In oligothrophic surface waters, there is movement of phosphorus from water into the sediment and in most cases phosphorus levels of the sediment are several orders of magnitude greater than the water (Wetzel, 2001).

Orthophosphate is bounded to sediment particles with different strengths (complex, covalent and ionic bonds) and mobilizes with desorption and dissolution mechanisms, particularly in conjunction with microbially mediated acidity, and ligand exchange mechanisms between phosphate and hydroxide ions or organic chelating agents (Stumm and Morgan; 1996). Biochemical mobilization process include mineralization by hydrolysis of phosphate-ester bonds, release of phosphorus from living cells as a result of changing environmental conditions, particularly redox, and autolysis of cells.

Except the upper few millimeters of the sediment, phosphorus exchange between overlying water and the sediment is regulated by slow diffusion. At upper levels of the sediment, turbulent mixing is the main mechanism of phosphorus exchange (Wetzel, 2001).

In oligotrophic waters, the upper few millimeters (0-5mm) of the sediment is oxygenated (>1mg/L) and below this zone sediments are extremely reducing. The oxygen level in this zone, microzone, is governed by the metabolism of bacteria, algae, fungi, planktonic invertebrates. Degradation of dead particulate matter in and near the sediments is the primary oxygen depleting process in lakes. The rate of oxygen depletion is governed by the rates of organic loading to the hypolimnion and by lake or reservoir morphology (Wetzel, 2001).

The oxidized microzone at the upper part of the sediments is a barrier for phosphorus mobilization. It prevents mobilized phosphorus in the anoxic zone from diffusing into the overlying water. Sorption on the aluminum and ferrous hydroxides and microbial uptake are the main mechanisms in this oxidized microzone (Wetzel, 2001).

The oxidized microzone barrier weakens with decreasing oxygen levels of the water near the sediment. As the redox potential decreases, reduction of iron, and manganese accelerates. Reduction of ferric hydroxides and other complexes, ferrous iron and adsorbed phosphate mobilize and diffuse in to the water (Wetzel, 2001). Also anoxic conditions promote the formation of hydrogen sulfide. Ferrous sulfide (FeS) is insoluble and precipitates, thus causes removal of important amount of iron from water and permitting soluble phosphate to accumulate in the hypolimnion (Wetzel, 2001).

II.1.3. Problems with Phosphorus in the Environment:

Phosphorus is an extremely important element for all life forms. It is a key part of the structural framework of nucleic acids, adenosine tri-phosphate (ATP), adenosine di-phosphate (ADP), and phospholipids in microorganisms. Within the major nutritional

and structural components, phosphorus is the least abundant and limits the microbial growth in fresh water bodies (USEPA, 1986).

Major phosphorus contributions to fresh water bodies come from anthropogenic sources. Wastewater treatment plant discharges are the major anthropogenic point source of phosphorus contribution to water bodies. Phosphate mining fields, urban runoff, and runoff from agricultural areas with excess fertilizer applications are the anthropogenic non-point sources of phosphorus (Pierzynski, 2005; Sharpley, 2000).

Except for the fact that phosphorus is a growth limiting nutrient in fresh water bodies, it does not have any known adverse health effects to humans at the concentrations that are found in surface waters. Since, it is the limiting nutrient, excessive amount of phosphorus inputs to fresh water bodies promotes excessive biological growth, i.e. eutrophication. Eutrophication is defined as "an increase in the fertility status of natural waters that causes accelerated growth of algae or water plants" (Pierzynski et al., 2005). Large amounts of plant, algae, and bacterial growth decrease the dissolved oxygen content and light penetration of fresh water bodies. Excessive biomass causes taste and odor problems as well as an increase in the organic carbon content. Decreased oxygen levels can be lethal to many beneficial animal species in the aquatic ecosystem.

There is no drinking water standard for phosphorus. The U.S. Environmental Protection Agency (U.S. EPA) published suggested levels of phosphorus in fresh water bodies to protect the water quality (U.S. EPA, 1986). The report suggests that the total phosphate as phosphorus should not exceed 25μg/L to prevent biological nuisances in lakes and reservoirs. Also 50μg/L total phosphate as phosphorus is the critical limit for any streams at the point they enter any lake or reservoirs (U.S. EPA, 1986). Release of

non-toxic byproducts from algal blooms that cause taste and odor problems in treated drinking water (USEPA, 1986, MWH, 2005). These compounds are costly to remove and require additional treatment (MWH, 2005). Also, excessive organic carbon content may interfere with disinfection processes and can cause excess disinfection by product formation. The best way to manage these problems is to control the productivity in the source water.

Even though there is no regulatory control mechanism over non-point source pollution, U.S. EPA has established a desired goal for point discharges to lakes, reservoirs, or streams. Suggested discharge phosphorus content should not exceed 100μg/L total phosphate as phosphorus (U.S. EPA, 1986). However, National Pollutant Discharge Elimination System (NPDES) permits are issued according to the receiving water quality, meaning as long as the discharge phosphorus concentrations do not exceed receiving water body phosphorus content, permit can be issued.

Recently, individual states have started developing nutrient criteria for lakes and reservoirs. The Colorado Water Quality Control Division (CWQCD), has recently started a study to regulate nutrient loads to surface waters. As the most crucial nutrient, phosphorus has shown a direct link with algal productivity in lakes and reservoirs changing with altitude and temperature. The aim of these studies is to regulate nutrient loads to surface waters to improve water quality for multiple purpose of use (CWQCD, 2006).

II.1.4. Engineered Phosphorus Removal Strategies:

Since phosphorus does not transform to easily removable chemical forms like nitrogen, phosphorus removal from water requires fixing phosphorus by chemical and

biological means and then removing the phosphorus rich precipitates or biomass from solution. Most of the treatment technologies are applicable for wastewater and industrial wastewater since phosphorus is not a regulated chemical for drinking water treatment. Chemical and biological phosphorus treatment technologies applied by industry are chemical precipitation, biological removal, crystallization, advanced chemical precipitation, ion exchange, and magnetic removal.

Chemical precipitation is based on the addition of divalent or trivalent metal salts to raw water and formation of P metal salt bond following by precipitation and sludge removal (Morse et al., 1998). Common chemicals that are used in chemical phosphorus precipitation are alum $Al_2(SO_4)_3 \cdot 18\ H_2O$], ferric chloride ($FeCl_3$), ferric sulfate [$Fe_2(SO_4)_3$], and hydrated lime [$Ca(OH)_2$]. Optimum pH ranges between 6.0 and 8.5 except for lime (Westerman and Bicudo, 2000). Chemical precipitation with lime requires an optimum pH of >10 and raw water alkalinity is the key variable for lime treatment (ASCE, 1992). Chemical precipitation can be applied at any stage of water treatment (Morse et al., 1998).

Biological phosphorus removal is based on the fact that under certain conditions microbial cells can take-up more phosphorus than it requires for normal biomass growth (Greenburg et al, 1955; Morse et al., 1998). The phenomenon known as "luxury uptake" is achieved in a multiple step treatment by introducing the raw water to an anaerobic and/or anoxic zone before an aerobic stage (Morse et al., 1998). When an electron donor and carbon source, such as acetic acid and sodium acetate, is introduced to the environment, certain bacteria (acinetobacter) release phosphorus to solution. In aerobic stage luxury uptake occurs with the increased phosphorus uptakes of 80-90%. Biological

phosphorus removal requires complex plant configurations and operating conditions. To ensure consistent removal efficiencies, the system may require complementary chemical precipitation step (Morse et al., 1998).

The crystallization process (DHV Crystalactor®) is based on the crystallization of calcium phosphate on a seeding grain, typically sand, within a fluidized reactor (Morse et al., 1998). Process conditions are adjusted by the addition of either caustic soda or lime. The process requires short retention times, thus, small basin volume. The process may require pre-degasification with the addition of sulfuric acid to prevent calcium carbonate formation and post-filtration using dual media (anthracite/sand) to ensure low phosphate effluent (Morse et al., 1998).

An advanced chemical precipitation process (HYPRO) focuses on nutrient removal (phosphorus, nitrate, and carbon). This technique combines pre-precipitation, sludge hydrolysis and biological denitrification. Ferric and aluminium chloride assisted by coagulants PAC remove up to 75% of the organic matter and most of the influent phosphorus from the raw water. The sludge produced in the process is then hydrolysed, converting the organic carbon containing compounds to soluble, easily biodegradable substances to be used in nitrification/denitrification stage. If the phosphorus removal is insufficient to meet effluent quality standards, further chemical or biological phosphorus removal stages can be added to the system (Morse et al., 1998).

In the ion-exchange-precipitation (RIM-NUT) process, phosphate ions are removed from tertiary wastewater to produce struvite. The process uses a basic resin to remove phosphate by adjusting the stoichiometry by the addition of phosphate and magnesium salts (Morse et al., 1998).

Magnetic water treatment system is essentially a tertiary treatment step, where lime is used to precipitate calcium phosphate. Precipitated calcium phosphate then bonds to magnetite and separated using an induced magnetic field. The magnetite is uncoupled from the phosphate unit by shear forces in a drum separator. Depending on the final product use, the suspension of calcium phosphate or carbonate in water can be further processed (Morse et al., 1998).

II.2. CARBON:

Carbon is a non-metal, tetra-valent chemical element with the atomic number of 6 and the symbol of (C). Having four electrons in it outer shell, carbon atoms can form multiple covalent bonds with each other and other atoms, thus, resulting in the formation of long chained and ring structures. Carbon exhibits allotropy, and has several allotropic forms (Williams, 2001).

The most common and naturally occurring allotropes are diamond and graphite. Recently, in 1985, new nano-structured allotrope forms were discovered. These allotropes consist of five and six-membered rings arranged in a sphere are called Buckministerfullerene, such as C60, nano-tubes, and nano-fibers. Other known carbon forms are coke, soot, and charcoal and are composed of minute crystals of graphite and considered as microcrystallines (Williams, 2001).

The property of carbon atoms to form multiple covalent bonds with each other and other atoms results in the formation of long chains and ring structures such as alkanes, alkenes, alkynes, and aromatic carbons. With this property, carbon is the basis of organic chemistry and an essential element for all organic life. When bonded with

hydrogen, carbon forms a wide variety of flammable organic compounds, hydrocarbons, which are the basis of fossil fuels. Beside the hydrocarbons, carbon and hydrogen containing compounds are important for plants and they form the plant components such as carotenoids and terpenes. Combinations of carbon (C) with oxygen (O) and hydrogen (H) is the origin of forming biologically crucial compounds such as simple and complex sugars, lignans, chitins, alcohols, fats, and aromatic esters. Combining with nitrogen, C-H-O containing compounds form alkaloids, and with the addition of sulfur antibiotics, amino acids and proteins can be formed. Addition of phosphorus to these elements creates organic structures DNA and RNA (Williams, 2001).

Carbon and carbon containing compounds have a wide assortment of industrial and scientific uses. One of the most important carbon containing compounds are hydrocarbons such as fossil fuel, methane gas, and crude oil that are used in the petrochemical industry. Crude oil is the raw material that is used to obtain gasoline, kerosene, and synthetic substance such as plastic after distillation and refining. Hydrocarbons are also used to produce cosmetics, detergents, dyes, fertilizers, food additives, pharmaceuticals, pesticides and polymers. One of the most important uses of elemental carbon is the isotope carbon-14 (^{14}C) which is used in the application of radiocarbon dating. One of the hardest materials known to humankind, diamond, is used in cutting, drilling, and polishing technologies, as well as decorative purposes. In the mining industry carbon (as coke) is used to reduce iron ore into iron. In the iron and steel industry, carbon is added to iron to produce steel. In nuclear applications, carbon is the neutron moderator in nuclear reactors. In metallurgical applications, carbon fiber is used to produce composite materials. Carbon black is used in the production of rubber and

plastic compounds to increase their strength. The powdered and caked form of graphite is used as charcoal for recreational purposes and in artwork. Activated charcoal is used in medicine to absorb toxins, poisons, or gases from the digestive system as well as in water treatment applications. Carbon dioxide is produced during the manufacturing of quicklime and fermentation and is used in fire extinguishers and as dry ice. Fullerenes materials in the form of nano-tubes are promising potential uses in composite material formations due to their high strength to weight ratio (Williams, 2001).

II.2.1. Carbon Cycle:

The biogeochemical cycle that explains the movement of carbon through the atmosphere, lithosphere, hydrosphere, and biosphere is called the carbon cycle (Figure II.2). Carbon exists in various forms through four major carbon reservoirs namely, atmosphere, biosphere (soil, fresh water bodies), the oceans, and the sediments (Williams, 2001).

Atmospheric gaseous inorganic carbon, carbon dioxide (CO_2), constitutes a relatively small but highly important part of the global carbon cycle. Some of the carbon dissolves in oceans and water bodies. Dissolved inorganic carbon, $CO_{2(aq)}$, dissociates as carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}) by a dynamic equilibrium depending on the pH of the water body (Manahan, 2001; Williams, 2001). Large amounts of inorganic carbon in the environment are associated with metal ions as minerals, particularly calcium ($CaCO_3$) and magnesium ($MgCO_3$) carbonates (Manahan, 2001).

Calcium and magnesium carbonate formation and dissolution reactions in water bodies depend on the relative concentrations of $CO_{2(aq)}$, $HCO_3^-{}_{(aq)}$, and $CO_3^{2-}{}_{(aq)}$. Many

aquatic animals use dissolved CO_2 to make shells which are basically composed of $CaCO_3$. When the aquatic organisms die, shells of these organisms can accumulate on the ocean floor and form limestone (Williams, 2001).

The global carbon cycle is largely based on the conversion of CO_2 to organic compounds in living organisms by photosynthesis and the release of CO_2 during aerobic respiration and decomposition of organic compounds (Williams, 2001). Photosynthesis is a process, which is performed by autotrophs (producers), fixes inorganic carbon as biological carbon, $\{CH_2O\}$, with solar energy (Manahan, 2001). Synthesized simple organic substances are then converted to more complex molecules (carbohydrates) in cellular metabolism. All other heterotrophs (consumers) in the ecosystem obtain the carbon they require from producers in the food chain. Organic and biological carbon, $\{CH_2O\}$, has energy rich chemical bonds, can react biochemically and chemically with molecular oxygen during aerobic respiration and combustion (wood or fossil fuel combustion) and regenerates CO_2 (Williams, 2001; Manahan, 2001).

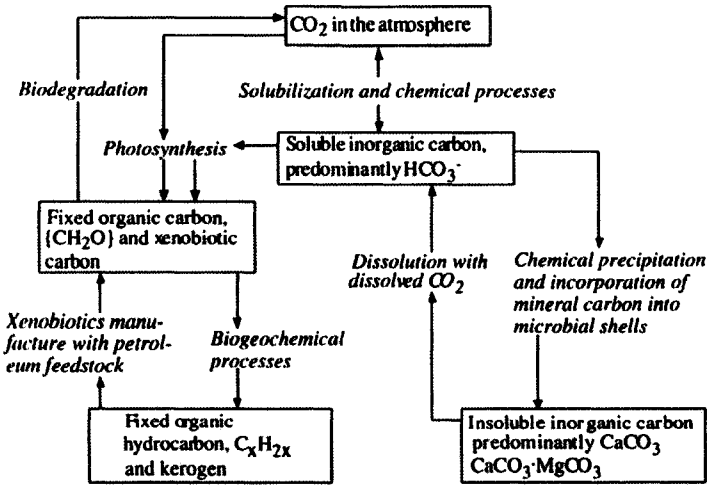


Figure II.2: The carbon cycle (Manahan, 2001)

When organisms die, organic carbon in the biomass is transformed to CO_2 during biodegradation, a form that may be released to the biosphere. The fraction of the organic material that is not oxidized is transported or re-deposited as sediment. This fixed fraction can form deposits of petroleum, natural gas, kerogen, coal, and lignite (Williams, 2001; Manahan, 2001). The biodegradation mechanism is also important for bioremediation. Microorganisms can degrade organic carbon from biomass, petroleum, and xenobiotic sources ultimately transforming it to CO_2 and releasing it to the biosphere (Manahan, 2001).

II.2.2. Carbon Cycle in Fresh Water Bodies:

Carbon in fresh water occurs as inorganic and organic species. A large fraction of carbon exists as inorganic carbon, mostly in the form of CO_2 and equilibrium products of carbonic acid (H_2CO_3). A minor amount of carbon exists in organic compounds such as dissolved and particulate detrital carbon, and a very small fraction exists as the carbon in living biota (Wetzel, 2001).

The atmosphere and carbonate minerals are the major sources of inorganic carbon in fresh waters. Atmospheric CO_2 content changes with location and industrialization. The global average of CO_2 as of 1991 is 0.036% by volume (Wetzel, 2001). CO_2 gas is a very soluble in water, approximately 200 fold more than molecular oxygen (O_2). CO_2 gas dissolves in fresh waters and hydrates by a slow reaction as follows;

$$CO_{2(g)} \Leftrightarrow CO_{2(aq)} + H_2O \Leftrightarrow H_2CO_{3(aq)} \qquad \text{(Eq. II.1)}$$

Carbonic acid, H_2CO_3, is a fairly weak acid and dissociates rapidly with pK_{a1} and pK_{a2} values of 6.43 and 10.43, respectively;

$$H_2CO_3 + H_2O \Leftrightarrow H^+ + HCO_3^- \qquad \text{(Eq. II.2)}$$

$$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-} \qquad \text{(Eq. II.3)}$$

Carbonate species, bicarbonate ion (HCO_3^-) and carbonate ion (CO_3^{2-}), establish further equilibrium in water, thus hydroxyl ions (OH^-) are formed by the dissociation of H_2CO_3;

$$HCO_3^- + H_2O \Leftrightarrow H_2CO_3 + OH^- \qquad \text{(Eq. II.4)}$$

$$CO_3^{2-} + H_2O \Leftrightarrow HCO_3^- + OH^- \qquad \text{(Eq. II.5)}$$

$$H_2CO_3 \Leftrightarrow H_2O + CO_2 \qquad \text{(Eq. II.6)}$$

As water percolates through the drainage basin, it receives CO_2 from plant and microbial respirations. The carbonic acid that forms during percolation solubilizes calcium rich rock formations and produces calcium bicarbonate [$Ca(HCO_3)_2$] and increases Ca^{2+} and HCO_3^- in water. Due to the addition of dilute HCO_3^- solution from drainage basin, OH^- ion concentration exceeds H^+ resulting from the dissociation of HCO_3^-, CO_3^{2-}, and H_2CO_3. Carbonate species, with the equilibrium reactions given above, create buffering action to resist pH changes in water (Wetzel, 2001).

Photosynthesis and respiration are two major mechanisms that affect CO_2 concentrations in surface waters. Changes in CO_2 concentrations due to photosynthetic utilization and/or biotic respiration tend to change the pH of the water body. The buffering action prevents pH changes by neutralizing H^+ ions with OH^- ions as long as the carbonate equilibria of carbonate species are operational (Wetzel, 2001).

If the solution CO_2 concentration decreases to a level that is not enough to maintain the equilibrium, with $HCO3^-$, CO_3^{2-} and $CaCO_3$, such as by photosynthetic uptake exceeding replacement of CO_2, insoluble $CaCO_3$ (marl) then precipitates until the

equilibrium is reestablished by the formation of sufficient CO_2. As $CaCO_3$ precipitates, inorganic (such as PO_4^{3-}) and organic compounds can be sorbed to or coprecipitate with the $CaCO_3$. Biological activity in the surface waters may be affected as a result of nutrient reductions (Wetzel, 2001).

Inorganic carbon is a major nutrient for photosynthetic metabolism. Carbon fixation occurs through algae, photosynthetic bacteria, including cyanobacteria, and aerobic chemolithoautotrophs (Prescott et al., 2005). However, phosphorus and nitrogen limit photosynthesis more frequently than does inorganic carbon, which occurs in much greater abundance.

The organic carbon content of surface waters consists of dissolved organic carbon (DOC) and particulate organic carbon (POC). DOC exists in larger amounts compared to POC with the ratio of 6:1 to 10:1 in lakes and streams (Wetzel, 2001). Living organisms constitutes a very small portion of POC and a significant amount of POC is composed of detritus organic matter (Wetzel, 2001).

Organic matter content of the surface waters are composed of an extremely diverse set of organic compounds originating from plants, microorganisms, and animals varying in structure, chemical reactivity and biodegradability. The organic matter content of fresh waters is classified into two major groups, labile organic compounds (non-humic substances) and recalcitrant compounds (humic substances) (Wetzel, 2001).

Non-humic substances are low-molecular-weight organic substances, such as carbohydrates, proteins, amino acids, fats, waxes, resins, and pigments. Humic substances are naturally occurring, high in molecular weight (most 700-5000 D) heterogeneous organic substances recalcitrant to rapid biological degradation. Humic

substances are formed by microbial degradation of cellulose and lignin of plant structural materials and constitute 70-80% of the organic matter of water and soils (Wetzel, 2001).

DOC is transported by water and it may adsorb to inorganic and organic particulate matter. By polymerization on the sorption surfaces, DOC may transform to particulate form, even though, only a small portion of DOC transforms to colloidal and particulate states. POC can be degraded by microorganisms with the release of DOC in soils and hydrosoils (Wetzel, 2001).

DOC can enter the water bodies from allochthonous origins which are considered as the primary source of external loading to surface waters. Dissolved organic matter (DOM) entering the surface waters from surface runoff and groundwater seepage has high C:N (50:1) ratios. It is due to the selective decomposition of more labile organic compounds of terrestrial and high aquatic plants by microflora during the transport to surface waters. DOM derived from the algal and cyanobacterial production (authochthonous) within water bodies has a lower C:N ratios (12:1), and is more easily biodegradable.

II.2.3. Problems with Carbon in the Environment:

Atmospheric carbon containing compounds, such as carbon dioxide (CO_2) and methane (CH_4) allow the absorption of long-wavelength (low energy) solar radiation reflecting form Earth surface to space. Absorption of reflecting radiation causes global temperature to settle within certain limits. Atmospheric CO_2 and CH_4 are known as the greenhouse gases and trapping of solar energy in the troposphere is known as the greenhouse effect (Williams, 2001).

Excessive fossil fuel combustion during industrialization increased the atmospheric CO_2 levels to 400ppm which is almost 2 fold larger than the levels in pre-industrialization of 280ppm (Spencer, 2007). Beside the CO_2, increase of synthetic green house gas emissions, such as chlorofluorocarbon (CFC), also promotes the absorption of solar energy, thus increasing the global mean surface temperature. Between years 1920 and 2000 global mean surface temperature has increased from -0.2°C to 0.5°C (Spencer, 2007). The phenomenon known as "global warming" is one of the crucial environmental problems of today's world.

Available carbon content in the fresh water bodies can contribute eutrophication in special cases where the carbon is the limiting nutrient when nitrate and phosphorus are at high levels. It is a very rare situation since there are many carbon sources in the environment such as atmospheric carbon, mineral carbon, and organic carbon sources available for the microbial growth in water bodies.

Organic carbon is present in fresh water bodies as an extremely diverse set of organic compounds originating from plants, microorganisms, and animals varying in structure, chemical reactivity and biodegradability (Sachse et al., 2005). One of the most important health concerns related with natural organic matter in fresh water bodies, known as natural organic matter (NOM), is the formation of disinfection byproducts (DBP), during water treatment processes.

Chlorine is the most widely used disinfectant in drinking water treatment to prevent waterborne diseases due to its properties of high oxidizing potential, formation of chlorine residual to prevent microbial recontamination in the distribution system (Sadiq et al., 2004). The major drawback of chlorine use as a disinfectant was first realized in

1974 with the formation of disinfection by products when it reacts with natural organic matter ubiquitously present in raw water (Rook, 1974).

Today, there are more than 700 DBPs that have been identified including chloroform (Serodes et al. 2003), haloacetic acids (HAAs) (Koch et al., 1991; Tan & Amy, 1991; Nissinen et al., 2002), haloacetonitriles (HANs) (Tan & Amy, 1991; Nissinen et al., 2002, Kim et al., 2002), haloketones (HKs) (Koch et al., 1991; Tan & Amy, 1991), short chain carboxylic acids, acetones, chlorinated phenols and phenolic acids (Kronberg, 1999), chlorinated quinines, benzoic acids and heterocyclic compounds (Blatchley et al., 2003).

Most DBP compounds are considered carcinogenic, mutagenic and/or tetratogenic (Black et al., 1996; Singer, 1999; Villanuevaa et al., 2003). Between DBPs, THM and HAA are dominant compared to other species. They constitute about 50-75% of the total halogenated DBP and only account for 25-50% of the total organic halides (TOX) (Krasner et al., 1989).

Among the DBPs bromate, chlorite, haloaceticacids (HAA5), and total trihalomethanes (TTHM) are regulated by the U.S. EPA with maximum contaminant levels of 0.01, 1.0, 0.06, and 0.08 mg/L, respectively (U.S. EPA, 2006a).

II.2.4. Engineered Carbon Removal Strategies:

The major health related problem with organic carbon presence in the surface waters is that NOM is a precursor for DBP formation. The best applicable method to avoid DBP formation during the disinfection process is to minimize the amount of organic carbon that reaches the disinfection process in water treatment (USEPA, 2006a; MWH, 2005).

In water treatment applications, the conventional method to remove NOM is coagulation, flocculation and settling processes before the disinfection step (MWH, 2005). The removal mechanism of NOM in conventional water treatment includes the addition of aluminum and iron salts (aluminum sulfate and ferric chloride) as coagulants to raw water. Negatively charged colloidal NOM particles are neutralized by the addition of coagulants. Neutralized NOM and soil particles in raw water tend to agglomerate and precipitate as humates and fulvates and also coprecipitation by adsorption on the metal hydroxides (Randtke, 1988). Efficiency of NOM removal during conventional water treatment depends on the nature of coagulant as well as the pH (Uyak & Toroz, 2007).

Due to the importance of removing NOM before it reaches the disinfection process, U.S. EPA has recognized enhanced coagulation (EC) and granular activated carbon (GAC) applications as the best available technology (BAT) for contorting DBP precursors (U.S. EPA, 1998).

The EC process is defined as the coagulation process to provide treatment conditions that still sustain effective turbidity removal while also increasing NOM removal (Uyak & Toroz, 2007). The main emphasis is the optimization of coagulant type and dosage, as well as pH, for enhanced NOM removal. The optimum coagulant type changes with changing raw water quality. In most cases ferric chloride is a more effective coagulant compared to aluminum sulfate (Kawamura, 2000). The coagulant dosage also depends on the raw water quality and is determined with jar tests. In most cases pH adjustments of $pH<6.0$ is optimum to accomplish enhanced NOM removal (Kawamura, 2000). The major drawback of enhanced coagulation is the cost associated with chemical

use and the corrosive effect of acidified water. pH adjustment is needed after enhanced coagulation to bring the water pH to natural levels (Kawamura, 2000).

GAC is a substitute for granular medium filters in a conventional treatment process mostly for the removal of organic compounds, pesticides, and other synthetic organic compounds (Kawamura, 2000). The removal mechanism of NOM through GAC beds includes physical adsorption and biological process. GAC beds are extremely efficient in terms of organic carbon removal, whereas, the cost associated with the media and the maintenance is high (Kawamura, 2000).

Advanced filtration technologies are also available for NOM removal such as, ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). However, the energy cost that is associated with the operation and the formation of a highly concentrated brine solution are the major drawbacks of these techniques (Kawamura, 2000).

II.3. NITROGEN:

Nitrogen is a non-metal chemical element with the symbol of (N) and atomic number of 7. Nitrogen readily reacts with itself to form colorless, odorless, and tasteless diatomic gas (dinitrogen gas, $N_2(g)$). Five electrons in its outer shell make nitrogen trivalent in most compounds. Due to the strong triple covalent bond between two nitrogen atoms, nitrogen gas is extremely resistant to chemical reactions and considered as inert or unreactive under typical atmospheric conditions (Williams, 2001).

Nitrogen is a major chemical element in nature. It exists as a dinitrogen gas form in the atmosphere with the abundance of 78% by volume and 76% by weight. Beside the dinitrogen gas it also exists as oxidized gas forms such as nitrous oxide (N_2O), nitric oxide (NO), and nitrogen dioxide (NO_2), reduced gases such as ammonia (NH_3), and in

aerosols such as nitrates, nitric acid, and ammonium sulfate with the abundance of only 0.001% earth's atmosphere by volume. In earth's crust, apart from nitrate deposits, it is rarely found combined in mineral ores (Williams, 2001).

Nitrogen is an essential nutrient for all life forms in the ecosystem. It is the major building blocks of DNA, RNA, and amino acids (proteins), thus it is incorporated into all plant and animal tissues. Organic and inorganic forms of nitrogen can be attained by living organisms according to their level on the food chain. The organisms high on the food chain obtain nitrogen in an organic form by consuming plants, other animals, and bacteria. The organisms at the bottom of the food chain attain nitrogen in inorganic forms. Even though nitrogen is abundant in the atmosphere as dinitrogen gas (78.1% of the atmosphere) the dinitrogen gas is not readily available for all living organisms. Since nitrogen gas is inert and very slightly soluble in water, more reactive forms of nitrogen are needed to be present for utilization by organisms. Different organisms use different forms of nitrogen as a nitrogen source, therefore, first, nitrogen gas should be converted to more chemically reactive form such as ammonium (NH_4^+) and nitrate (NO_3^-) (Williams, 2001).

Due to its importance for living organisms and its chemical properties, nitrogen has a wide range of uses. Nitrogen gas is formed by the fractional distillation of liquid air for industrial applications. Nitrogen gas is used in food industry to preserve freshness of packaged or bulk foods. Nitrogen gas is an inexpensive alternative of argon gas in ordinary light bulbs as well as it is used for the production of electronic parts such as transistors, diodes and integrated circuits. Also dried and pressurized nitrogen gas is used as a dielectric gas for high voltage equipment. Another use of nitrogen gas is for the

production of stainless steel. It is also used as a safety measure for liquid explosives and for military aircraft fuel systems to reduce explosion and fire hazard. The most important use of nitrogen gas is for the production of fertilizers in which nitrogen gas is converted to ammonia under high temperature and pressure by the process called Haber process.

II.3.1. Nitrogen Cycle:

The biogeochemical cycle that explains the transformation of nitrogen and nitrogen containing compounds in nature is called the nitrogen cycle. Figure II.3 illustrates the different phases and dynamic nature of the nitrogen containing compounds in the ecosystem. Since the nitrogen is an essential nutrient for all life forms, availability of nitrogen in various forms is essential. The basic processes that occur in the nitrogen cycle are nitrification, denitrification, and nitrogen fixation.

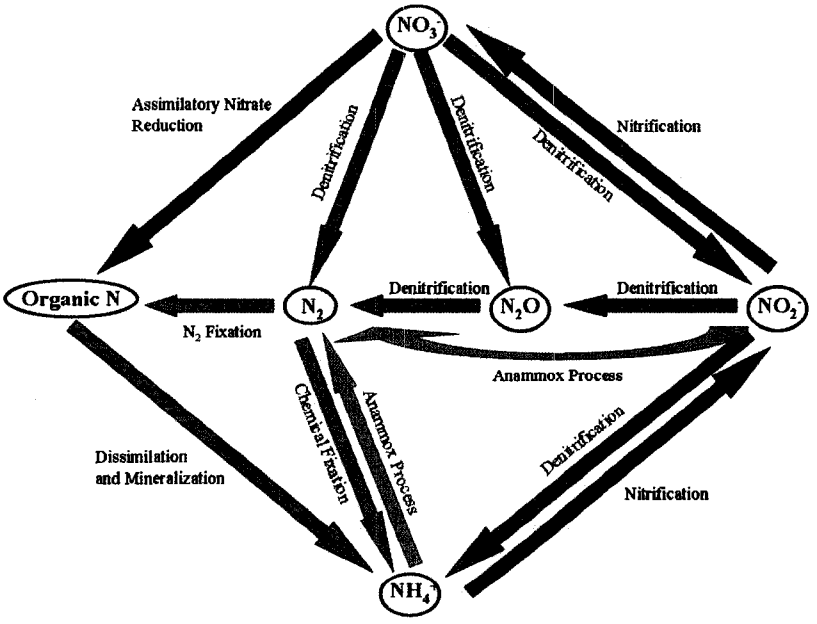


Figure II.3: The nitrogen cycle (Adapted from Prescott et al., 2005)

The process of assimilating nitrogen gas (N_2) into organic nitrogen compounds is called biological nitrogen fixation. Biological nitrogen fixation can be carried out by aerobic and anaerobic prokaryotes. A wide range of free living microbial genera (*Azotobacter, Azospirillum*) can fix nitrogen under aerobic conditions. Under anaerobic conditions the most important free-living nitrogen fixers are members of genus *Clostridium*. Nitrogen fixation by cyanobacteria such as *Anabaena* and *Oscillatoria* can lead to the enrichment of aquatic environments with nitrogen. In addition, nit rogen fixation can occur through the activities of bacteria that develop symbiotic associations with plants. These associations include *Rhizobium* and *Bradyrhizobium* with legumes, *Frankia* in association with many woody shrubs, and *Anabaena,* with *Azolla*, a water fern important in rice cultivation (Prescott et al., 2005).

Nitrogen gas can also be converted to biologically available form, ammonia (NH_3) by a chemical process that was discovered in early 1900s by Fritz Haber. The process that is also known as Haber Process includes the reaction of nitrogen and hydrogen gases under high pressure and temperature to produce ammonia (Galloway, 1998; Hardy and Havelka, 1975). The Haber Process has been widely in use for the production of nitrogen fertilizers (Galloway, 1998; Hardy and Havelka, 1975).

Nitrification is an aerobic process that includes the oxidation of ammonium ion (NH_4^+) to nitrite (NO_2^-) and subsequent oxidation of nitrite to nitrate (NO_3^-) by using oxygen as the terminal electron acceptor. The first step of the two-step reaction is carried out by bacterial genera *Nitrosomonas* and *Nitrosococcus* while the second step is carried out by *Nitrobacter* and similar chemolithoautotrophic bacteria. As an exception, the oxidation of ammonium ion to nitrite (NO_2^-) and nitric oxide (NO) under anaerobic

conditions has been discovered recently. The bacterial specie *Nitrosomonas eutropha* carries out this process by using nitrogen dioxide (NO_2) as an oxidant. Also in acidic environments, bacteria and fungi contribute significantly to heterotrophic nitrification (Prescott et al., 2005).

Denitrification is a dissimilatory process in which nitrate is used as an oxidant under anaerobic conditions. The major heterotrophic bacterial specie that contributes the denitrification mechanism is *Psedomonas denitrificans*. The products of denitrification process include nitrogen gas (N_2) and nitrous oxide (N_2O) and also in some circumstances nitrite (NO_2^-) can accumulate. Nitrate can also be reduced to ammonia in dissimilatory reduction by variety of bacteria, including *Geobacter metallireducens*, *Desulfovibrio* spp., and *Clostridium* (Prescott et al., 2005).

The chemolithotrophic members of planctomycetes can couple the anaerobic oxidation of ammonium ion (NH_4^+) with the reduction of nitrite (NO_2^-) to produce nitrogen gas. The recently discovered process is called anammox process (anoxic ammonia oxidation) and is used to reduce nitrogen content in sewage plant effluents as an alternative to conventional nitrification-denitrification process (Prescott et al., 2005).

II.3.1. Nitrogen Cycle in Fresh Water Bodies:

Nitrogen is one of the essential and major constituent of organisms as well as carbon, hydrogen and phosphorus. Its major role in the formation of DNA, RNA, and protein molecules makes nitrogen a major nutrient which affects and controls the productivity of fresh water bodies.

The cycling of nitrogen in fresh water bodies is a complex biochemical process in which various forms of nitrogen is altered by nitrogen fixation, assimilation, and

denitrification. Most of the processes occur during the cycling of nitrogen in fresh water bodies are microbial in nature. Oxidation and reduction of nitrogen compounds are coupled with photosynthetic assimilation and utilization by algae, photosynthetic bacteria, and larger aquatic plants (Wetzel, 2001).

The major forms of nitrogen containing compounds in fresh water bodies include dissolved molecular nitrogen (N_2), ammonia nitrogen (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-), and a number of organic compounds such as amino acids, amines, nucleotides, proteins, and humic compounds with low nitrogen content (Wetzel, 2001). The nitrogen speciation in fresh waters depends on the redox and pH conditions as it is illustrated in Figure II.4. In most aquatic systems, under equilibrium, the dominant inorganic forms of nitrogen are N_2, NO_3^-, and NH_4^+.

The quantity of nitrogen forms in freshwater bodies is regulated by the nitrogen inputs and losses from the aquatic ecosystem. The major sources of nitrogen inputs to freshwater bodies are nitrogen contained in particulate form (dry fallout) and precipitation, nitrogen fixation in the water and the sediment, and inputs of nitrogen from surface and groundwater drainage. Nitrogen leaves the aquatic system by the outflow from the water body, reduction of NO_3^- to N_2 by bacterial denitrification followed by a loss of N_2 to the atmosphere, and sedimentation of inorganic and organic nitrogen forms to the sediment.

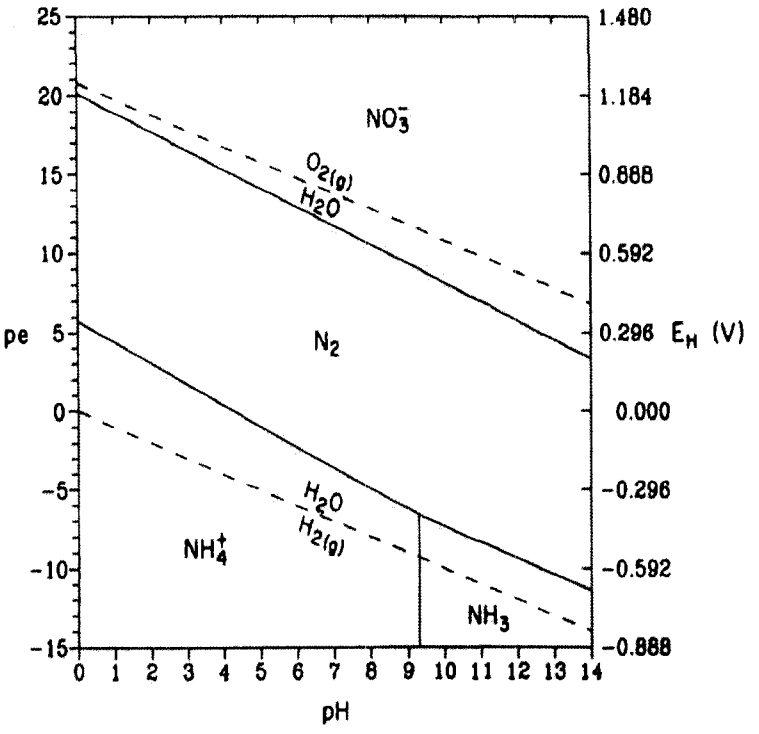


Figure II.4: Nitrogen forms with respect to pe and pH (Pankow, 1991)

The major source of nitrogen input to lakes and streams is the microbial fixation of atmospheric nitrogen gas by bacteria in soil. The wetlands surrounding lakes or adjacent to streams can add significant amounts of combined nitrogen to freshwater ecosystems by the bacterial N_2 fixation. The N_2 fixation by heterotrophic bacteria and certain cyanobacteria in the water bodies is quantitatively less significant unless under certain conditions where severe depletion of inorganic nitrogen compounds exist (Wetzel, 2001). During the periods of turbulent mixing, the N_2 content of water is usually in equilibrium with the N_2 in the atmosphere. In stratified eutrophic lakes N_2 content varies with the depth. While the N_2 content in the epilimnion declines with reduced solubility

due to the raise in temperature, the N_2 content of the hypolimnion increases due to the denitrification of nitrate (Wetzel, 2001).

Within the freshwater bodies, N_2 fixation that is accomplished by cyanobacteria is usually more excessive than by the heterotrophic bacteria. The N_2 fixation by cyanobacteria is light dependent and is affected by the spatial and temporal distribution of the bacteria. The extent of N_2 fixation also depends on the presence of NH_4^+-N and NO3-N since the energy requirements for the assimilation of these nitrogen forms are follows the order of N_2-N> NO_3-N> NH_4^+-N. Thus, N_2 fixation by cyanobacteria is increases when NO_3-N and NH_4^+-N concentrations decrease (Wetzel, 2001).

The primary nitrogenous end product of bacterial metabolism is ammonia. Heterotrophic bacteria produce ammonia as an end product of decomposition of proteins and other nitrogenous organic compounds. The end product, ammonia, is present as ammonium ion (NH_4^+) in natural waters and the concentrations of (NH_4^+) are usually low in aerobic water due to the utilization by plants and bacterial nitrification in which ammonium ion is oxidized to nitrite (NO_2^-) and nitrate (NO_3^-) through several intermediate steps (Wetzel, 2001). When the productivity of a lake increases, bacterial nitrification of ammonia ceases in the anaerobic hypolimnion as well as the NH_4-N adsorptive capacity of the microzone at the sediment-water interface, thus NH_4-N concentration increases (Wetzel, 2001).

Ammonium ion in the freshwater bodies is oxidized to nitrite (NO_2^-) and to nitrate (NO_3^-) with a subsequent reaction through the process of nitrification. The oxidation of NH_4^+ to NO_2^-, is largely accomplished by nitrosomonas but also by other bacteria, including methane oxidizers, and the oxidation of NO_2^- to NO_3^-, is achieved by

nitrobacter that is the dominant bacterial genus involved. Nitrite is readily oxidized and rarely accumulates except in the metalimnion, upper hypolimnion, or interstitial water of sediments of eutrophic lakes. Nitrate concentrations are usually low (<100 μg/L) unless organic pollution is high (Wetzel, 2001).

The inorganic nitrate is assimilated and aminated into organic nitrogenous compounds within the microorganisms. During the metabolism of the organisms, the organic nitrogen is bound and cycled within the organisms and when the organism dies the nitrogen is liberated as ammonia and enters the aquatic system (Wetzel, 2001). Nitrate nitrogen is the common form of inorganic nitrogen and enters the basin from surface waters, groundwater, and precipitation. The basaltic rock formations, nitrate loading from atmospheric sources, especially from antrophogenic combustion emission products can dominate nitrogen loadings to freshwater bodies (Wetzel, 2001).

The biochemical reduction of oxidized inorganic nitrogenous ions (NO_3^- and NO_2^-) to nitrous oxide (N_2O) and nitrogen gas occurs during the bacterial denitrification. Nitrous oxide is rapidly reduced to nitrogen gas and is not commonly found in freshwater bodies. Many genera of facultative anaerobic bacteria can accomplish denitrification by utilizing nitrate as an exogenous terminal hydrogen acceptor during the oxidation of organic substrate. Denitrification occurs in the hypolimnia of eutrophic lakes and in anoxic sediments, where oxidizble substrates are relatively abundant (Wetzel, 2001).

Over 50% of total soluble nitrogen in freshwaters are dissolved organic nitrogen (DON). Over 50% of the DON occurs as amino nitrogen compounds, mostly as polypeptides and complex nitrogen compounds. The ratio of DON to particulate organic

nitrogen (PON) of streams and lakes are usually from 5:1 to 10:1 and when the freshwater body becomes more eutrophic, DON:PON ratios decrease (Wetzel, 2001).

The ratio of organic carbon to nitrogen (C:N) in freshwaters is a good indicator of the complex mixtures of organic compounds to resist decomposition due to the fact that proteolytic metabolism by fungi and bacteria removes more nitrogen than carbon. Relatively high C:N ratios commonly occur in residual organic carbons, which are more resistant to decomposition. Organic materials that are originates from wetlands (allochtonous) commonly have C:N ratios ranging between 45:1 to 50:1 and contain humic compounds of low nitrogen content. On the otherhand, organic matter that is produced by the decomposition of plankton (autochthonous) tends to have higher protein content with C:N ratios of around 12:1 (Wetzel, 2001).

The total nitrogen content of the sediments occurs in the forms of relatively unavailable for microbiological utilization. The biologically available nitrogen is generally in soluble form in the water and in the interstitial water of the sediments. In eutrophic lakes, the turnover rate of NH_4^+ is rapid in water but slower in sediment, whereas NO_3^- turnover is slower in the water than in sediment due to the rapid denitrification to N_2 (Wetzel, 2001).

The major sources of inorganic nitrogen to rivers and lakes are excess fertilization of agricultural fields, sewage discharges, and anthropogenic atmospheric pollution. Even though phosphorus availability is the principle limiting factor for unproductive oligotrophic lakes, as phosphorus loadings to fresh waters increases and they become more productive, nitrogen becomes the growth limiting nutrient (Wetzel, 2001).

Nitrogen is used repeatedly as it travels in running waters. The physical and biological retentiveness by the microbiota attached to the streambed affects the utilization and release rates. The average distance in which a nutrient atom travels downstream during one cycle through the water, biotic, and substrata compartments is referred as spiraling length (Wetzel, 2001). Biological productivity in small rivers does not commonly suffers from nutrient limitations since the nutrients are efficiently retained and recycled whereas in larger rivers, nutrient retentions are less and nutrient limitations can become more prevalent (Wetzel, 2001).

The nitrogen cycling in streams and rivers are similar to lakes. The cycling of nitrogen in running waters is influenced to a larger extent by bacterial, fungal, and other microbial metabolisms. Attached bacteria, fungi, and algae are the primary organisms controlling the spatial and temporal variations within the water. Nitrification and denitrification processes occur simultaneously and reciprocally in running water sediments , where many microzones of steep redox gradients occur in the hyporheic zone of the streambed (Wetzel, 2001).

II.3.2. Problems with Nitrogen in the Environment:

The disruption of the nitrogen cycle by human activities causes serious environmental impacts on the atmosphere, fresh water bodies and groundwater. The environmental concerns related to nitrogen containing compounds are ranging from affecting the atmospheric ozone, global warming, and surface water eutrophication. Also the presence of certain nitrogen containing compounds in the atmosphere and in drinking water causes adverse health effects on humans.

The natural sources of nitrogen oxides include lightening, volcanic eruptions and bacterial processes in the soil. Naturally formed nitrogen oxides are not considered as pollutants and overweight the releases from anthropogenic sources such as fossil fuel combustion from the vehicles and power plants, and fertilizer applications. Nitrogen oxides that are released from anthropogenic sources are NO, NO_2, N_2O, HNO_2, and HNO_3 (Williams, 2001).

Nitrogen dioxide (NO_2) is considered as a pulmonary irritant, and long term exposures to this chemical causes breathing problems and leads to diseases such as oedema or emphysema. Various researches also indicated that NO_2 damages sensitive skins and increases susceptibility to hay-fever (Williams, 2001).

Nitrogen oxides play important roles in atmospheric chemistry and have a major role in acid deposition. Nitrous oxide is a greenhouse gas and can trap heat near earth surface like carbon dioxide and water vapor and causes increase in the atmospheric temperature. Furthermore, nitrous oxide in the stratosphere is broken down by ultraviolet light into NO_2 and NO, which can catalytically reduce ozone (Williams, 2001).

The inputs of nitrogenous materials to freshwaters, mainly from agricultural runoff (nitrogenous fertilizers and animal excreta), sewage effluent (urea, proteins, amino acids and ammonia) and industrial effluent (nitric acid and ammonia) can also disrupt the nitrogen cycle. A high nitrate concentration in freshwaters contributes to eutrophication. Moreover, high nitrate concentration in drinking water is another concern since they cause methaemoglobinaemia or blue-baby syndrome in infants (Winton, 2002). The disease is caused by the effect of nitrate on hemoglobin by decreasing its ability to carry oxygen. Furthermore, in the presence of high nitrate concentrations, the formation of

carcinogenic compounds, nitrosamines, can form during chlorination of both water and wastewater. The direct consumption of n-nitroso compounds are linked to digestive system cancers. It is thought that ingested nitrates can lead to the formation of n-nitroso within the digestive tract (Mitch et al., 2003a). Finally, there is also a concern that nitrates may create adverse effects on developing fetuses in pregnant women. There is epidemiologic evidence suggesting that animals exposed to elevated nitrate or nitrite levels experienced negative reproductive effects (Manassaram et al., 2006). However the relationship between nitrate consumption and reproductive health in humans is unclear due to uncertainties in the human epidemiologic studies (Manassaram et al., 2006).

II.3.3 Engineered Nitrogen Removal Strategies:

Nitrate content of the drinking water is one of the most important concerns due to its known adverse health effects on humans. Nitrate concentration in drinking water is regulated by the U.S. EPA as 10mg/L as N (45 mg/L as NO_3^-). Since nitrate is a small and negatively charged ion, the removal applications during water treatment are limited and costly. The three major removal technologies that are applied to remove nitrate from source water are; reverse osmosis (RO), ion exchange, and biological denitrification.

The reverse osmosis is based on forcing raw water through a semi-permeable membrane by applying high pressures. Depending on their size, contaminants are kept in one side of the membrane while treated water is collected on the other side. Reverse osmosis is an effective technique in terms of nitrate removal however high pumping costs to achieve operating pressures of 300-600 psi and the operational cost that is associated with the proper disposal of the brine solution that is created during the application with high nitrate concentrations are the major drawbacks of the system (Dahab, 1987).

The ion exchange technique is a physico-chemical process in which electrostatically held ions on the surface of ion exchange media are exchanged for ions of similar charge in a solution. The most commonly used ion exchange media are synthetic, inorganic or natural polymeric, strongly basic, mono-functional or bi-functional anion exchange resins. The resins are usually packed into a column, in which contaminated water is passed through, and contaminant ions are exchanged for other resin ions such as chlorides or hydroxides. During the nitrate removal, resin with chloride is mostly used and while nitrate ions bind the resin, chloride ions are released. The process requires the resins to be replaced periodically when the contaminant adsorption capacity is attained. Even though resins can be regenerated and reused, contaminant rich brine solution is created during the regeneration process. Moreover, the presence of similarly charged ions as nitrate, can decrease the efficiency of the system (Dahab, 1987).

Biological denitrification is another alternative for nitrate removal from source water. The technique depends on exploiting denitrifying bacteria by using their metabolic activity to reduce nitrate to non-reactive nitrogen gas. This technique is known as the most cost effective nitrate treatment application (Dahab, 1987; Galloway, 1998).

Biological denitrification process is a dissimilatory process implying the nitrogen that is used in the process does not incorporated into the cellular mater of the microorganism. The process includes several steps and each step is performed by using nitrogen compound with varying oxidation level as an electron acceptor and sequentially reducing the nitrogen compound until it reaches to most reduced form, moleculer nitrogen gas.

The complete denitrification pathway includes several steps. Each step is performed by using the nitrogen compound as an electron acceptor and sequentially reducing it until reaching the end product, molecular nitrogen gas (Rittmann, 2001). Equation II.7 shows the sequential reduction of nitrate to molecular nitrogen gas.

$$NO_{3(aq)}^{-} \rightarrow NO_{2(aq)}^{-} \rightarrow NO_{(g)} \rightarrow N_2O_{(g)} \rightarrow N_{2(g)} \quad \text{(Eq II.7)}$$

During denitrification, each sequential step uses different kind of enzyme. The overall reaction reduces nitrate nitrogen with the oxidation state of +5 to molecular nitrogen gas with the oxidation state of 0 (Rittmann, 2001). The reduction half reactions and the enzymes that are used during these reactions are given in Eq. II.8 – Eq. II.11.

$$NO_{3(aq)}^{-} + 2e^{-} + 2H^{+} \xrightarrow{Nitrate\ reductase} NO_{2(aq)}^{-} + H_2O \quad \text{(Eq. II.8)}$$

$$NO_{2(aq)}^{-} + e^{-} + 2H^{+} \xrightarrow{Nitrite\ reductase} NO_{(g)} + H_2O \quad \text{(Eq. II.9)}$$

$$2NO_{(g)} + 2e^{-} + 2H^{+} \xrightarrow{Nitric\ oxide\ reductase} N_2O_{(g)} + H_2O \quad \text{(Eq. II.10)}$$

$$N_2O_{(g)} + 2e^{-} + 2H^{+} \xrightarrow{Nitrous\ oxide\ reductase} N_{2(g)} + H_2O \quad \text{(Eq. II.11)}$$

Biological denitrification can be performed by two different types of bacteria. According to their use of electron donor and carbon source denitrifying bacteria are classified as heterotrophic and autotrophic bacteria. Heterotrophic bacteria use the organic carbon as their source for cellular carbon as well as the electron donor during the redox reactions while autotrophic bacteria use inorganic carbon such as carbon dioxide or bicarbonate as carbon source and inorganic compounds such as reduced iron, sulfur or hydrogen gas as their electron donors. Although autotrophic denitrification exists and has been used in engineered systems, heterotrophic denitrification is more common and

natural environmental conditions usually favor heterotrophic denitrification (Korom, 1992).

The energy that is needed by bacteria to complete the denitrification reactions are provided by coupling oxidation and reduction reactions. To maximize the energy yield, bacteria prefers the electron acceptor that provides the maximum energy. Figure II.5 illustrates several common electron acceptors and the order in which they are used by bacteria to maximize the energy yield.

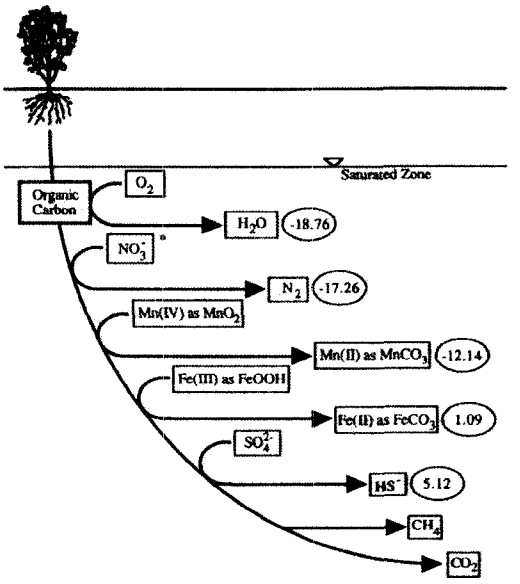


Figure II.5: Energy ladder of electron acceptors (Korom, 1992)

Biological denitrification is affected by several factors, such as; availability of nutrients, availability of electron donor / organic carbon source, presence of dissolved oxygen, temperature, and pH.

To sustain and carry out metabolic activity, denitrifying bacteria requires nutrients in available forms of carbon, phosphorus, nitrogen, oxygen, and hydrogen (Hiscock et. al., 1991; Korom, 1992). Along these, organic carbon is crucial since it is used as electron

donor as well as carbon source for heterotrophic bacteria. The most common carbon source for heterotrophic bacteria in natural waters is dissolved organic matter (DOM) that acts as both an electron donor and carbon source. The characteristic of the carbon source is very important since it affects the ability and rate of denitrification by denitrifying bacteria. The organic matter that is present in natural waters are mostly in dissolved form and the ratio of DOM to particulate organic matter (POM) ranges between 6:1 to 10:1 (Alken and Cotsaris, 1995; Wetzel, 2001).

DOM in natural waters is classified into two major groups; labile organic compounds (non-humic substances) and recalcitrant compounds (humic substances) (Wetzel, 2001). Non-humic substances are low-molecular-weight organic substances, such as carbohydrates, proteins, amino acids, fats, waxes, resins, and pigments. Humic substances are naturally occurring, high in molecular weight (most 700-5000 D) heterogeneous organic substances recalcitrant to rapid biological degradation. Humic substances contain many aromatic functional groups and are formed by microbial degradation of cellulose and lignin of plant structural materials and constitute 70-80% of the organic matter of water and soils (Wetzel, 2001).

Recent studies indicated that heterotrophic bacteria can also utilize humic organic carbon sources (Moran and Hodson, 1991). The study of Pfenning and McMahon (1996) examined the rate of denitrification in riverbed sediment in terms of the type of organic carbon present for utilization. The authors indicated that the rate of denitrification was faster when the bacteria are incubated with acetate as liable organic carbon source compared to fulvic acid. However, the study also showed that denitrification proceeded

with a slower rate when incubations were amended with surface water fulvic acid and groundwater fulvic acid (Pfenning and McMahon, 1996).

The presence of dissolved oxygen negatively affects the heterotrophic denitrification by bacteria. Dissolved oxygen is known as an inhibitor to denitrification procedure since many denitrifying bacteria are facultative anaerobes (Korom, 1992; Trudell et al., 1986). When the dissolved oxygen is present, bacteria prefers oxygen as an electron acceptor to yield the maximum energy. When the oxygen is depleted, facultative anaerobic bacteria has the ability to switch their metabolic function to use different electron acceptor such as nitrate.

Temperature is one of the factors that affect biological denitrification. Generally, the rate of denitrification increases with increasing temperature (Korom, 1992). This relation is based on the facts that the increase in temperature promotes the microbiological metabolism and decreases the solubility of oxygen. Stanford et al (1975) showed that the rate of denitrification in soil increases linearly between 15°C and 35°C. The study indicated that with the temperature of 11°C and below, rate of denitrification decreases drastically (Stanford et al., 1975). Pfenning and McMahon (1996) reported that denitrification in incubated sediment decreased 77% when the temperature of incubation was reduced from 22°C to 4°C (Pfenning and McMahon, 1996).

Another factor that affects the denitrification process is pH (Hiscock et al., 1991). Depending on the pH of the environmental matrix that denitrification takes place, conversion of $N_2O_{(g)}$ to $N_{2(g)}$ may not be accomplished by the bacteria. Simek et al (2002) reported that when denitrification occurs in soils with the pH of 7 and above, $N_{2(g)}$ is the dominant final product of denitrification. In acidic conditions with the pH<7, production

of $N_2O_{(g)}$ becomes dominant over $N_{2(g)}$. Since $N_2O_{(g)}$ is considered as a greenhouse gas, the optimum pH of the denitrification process should be above 7 to minimize the $N_2O_{(g)}$ production.

Engineered biological denitrification processes can use both autotrophic and heterotrophic bacteria. The autotrophic systems are less common due to the source of electron donor used and growth rate of the autotrophic denitrifiers. Hydrogen gas and reduced sulfur are the two common electron donors for autotrophic bacteria. Hydrogen gas has a low solubility in water thus it is hard to transfer it into the solution. Moreover, hydrogen gas is an explosive gas and storage and transportation of the gas creates great risk. Also using reduced sulfur as an electron donor creates problems with sulfate levels in the finished water since sulfur is oxidized to sulfate during the process. Finally, slow growth rates of autotrophic bacteria requires larger reactor volumes compared to the heterotrophic bacteria (Kapoor and Viraraghavan, 1997).

The most commonly used engineered denitrification systems are packed-bed and fluidized-bed bioreactors. Even though these systems are proven technologies to effectively remove nitrate, some cases with high breakthrough of biomass into the finished water were reported (Soares, 2000). Moreover, high cost is associated with these systems to build and operate. The requirement of collection and proper disposal of the excess biomass is another issue that has to be considered.

II.4. PERCHLORATE:

Perchlorate (ClO_4^-) (Figure II.6) is both naturally occurring and a man-made soluble anion, commonly associated with the solid salts of ammonium, sodium, potassium, calcium, magnesium and lithium. Even though, perchlorate naturally exists in

the environment, the major perchlorate loads to the environment are anthropogenic, commonly in the form of ammonium and sodium salts that are synthetically produced (Tikkanen, 2006). The most commercially available form of perchlorate is perchloric acid.

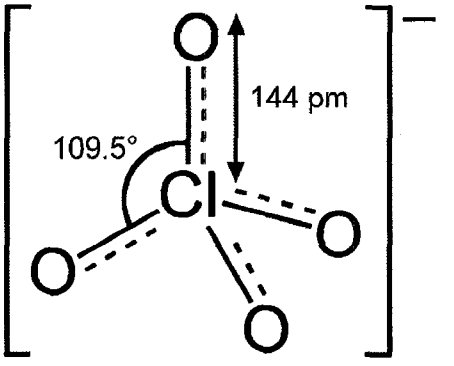


Figure II.6: Molecular structure of perchlorate

The chemical structure of perchlorate ion involves one Cl atom in the center of a tetrahedral formation with four oxygen atoms. Despite the thermodynamic properties, which require the perchlorate ion to be very reactive and unstable, high activation energy needed for the conversion of ClO_4^- to ClO_3^- and Cl^- makes perchlorate relatively stable. The tetrahedral formation and evenly dispersed charges make the compound hard to combine with positively charged metallic ions. Due to the extremely soluble and unreactive nature of perchlorate salts and perchlorate ion, reduction or precipitation reactions with common reducing agents and cations are limited (Urbansky, 1998).

II.4.1. Uses of Perchlorate:

Even though perchlorate is used in a variety of industrial applications, its ability to be used as an oxidizer in oxygen deficient environments makes perchlorate a crucial

chemical for the military and aerospace industry. The salts of perchlorate have been used as an oxidizer in solid propellant in rockets, missiles, as well as fireworks (Bull et al., 2004).

Other common uses of perchlorate are in air bag initiators of vehicles, bleaching agent, flash powder for photography, chemical laboratories for analytical testing, leather tanning, ejection seats in airplanes, oxygen generators, paints and enamels, electroplating operations, electropolishing, perchloric acid production, production of matches, etching of brass and copper, engine oil testing, road flares, and fertilizers. (Bull et al., 2004)

II.4.2. Sources of Perchlorate Contamination and Transport:

As a naturally occurring and man-made chemical, the sources of perchlorate contamination in the environment can be either natural or antrophogenic. One of the natural perchlorate sources is the formation of perchlorate in the atmosphere. Perchlorate can be formed from NaCl aerosol by lightning or by chemical reaction of chloride ion with ozone. Dasgupta et al. (2005) reported detections of perchlorate in precipitation with concentrations of up to 1.6 μg/L.

The major source of naturally occurring perchlorate is Chilean caliche which is widely used for the production of commercial nitrogen fertilizers due to its high nitrogen content. The fertilizers that are produced from the caliche also contain high levels of perchlorate and the application of these fertilizers can be an important contributor of perchlorate to the environment (Bull et al., 2004, Urbansky et al., 2001). It is reported that the Chilean caliche containing fertilizers comprises only 0.1% of the market in the U.S. (Sanchez et al., 2005). Despite the fact that the use of Chilean caliche containing

fertilizers is limited, they still can be a source of perchlorate contamination for the soil and surface waters at the point of application.

Perchlorate use in missiles and rockets goes back to the Second World War, thus making the military and aerospace industry waste disposals the major source of anthropogenic perchlorate contamination in ground of surface waters (Bull et al, 2004). In the USA, 65% of all groundwater and surface water perchlorate contamination is related to defense and aerospace activities such as rocket motor, bomb testing and ammunition waste disposal (demilitarization of explosives) in soils (U.S. GAO, 2005).

When released to the environment, perchlorate transport is very similar to other dissolved minerals. Even though many bacteria have evolved enzymatic reactions to reduce perchlorate, the extremely soluble character (2kg/L), relatively low sorption affinity on soil particles, and low concentrations (10^3 to 10^5 times less than other dissolved minerals) make this anion easily transported to ground and surface waters for long periods of time (Bull et al, 2004; Xu et al., 2003).

II.4.3. Occurrence of Perchlorate in the Environment:

Perchlorate was manufactured for the first time in 1908 in the U.S. The extensive manufacturing and use was started in 1940s, especially for defense industry. Even though perchlorate was extensively used starting with mid 20th century, the first detection in the environment was in the State of California in 1985 due to the lack of available technology to detect perchlorate at ppb levels (Tikkanen, 2006). Following its first detection, monitoring studies were focused on perchlorate in several states. The monitoring studies in California, Nevada, and Utah showed highly contaminated groundwater sources with the maximum detections ranging 51.4 to 630 μg/L. After the

development of perchlorate analysis methods with a method detection limit of 4 μg/L, many studies have been conducted in California, Massachusetts, Texas, and Arizona.

The California Department of Public Health Service (CDPHS) began extensive perchlorate monitoring studies from drinking water wells in 1997. The studies showed numerous detections with the most remarkable perchlorate level of 8000 μg/L in the drinking water wells of Sacramento County. The high contamination was associated with the wastewater injection to groundwater aquifer for the treatment of volatile organic chemicals by the rocket testing facility of Aerojet General Corporation (CDPHS, 2007). The CDPHS reported the results of monitoring efforts over 7,000 drinking water sources between 1997 and 2005. The following table (Table II.1) summarizes the findings of the study.

The Massachusetts Department of Environmental Protection (MDEP) first reported perchlorate detection in drinking water wells in 2000. Two years later, in 2002, perchlorate contamination in three drinking water wells were reported near Massachusetts Military Reservation (MMR) in Cape Cod. Based on these occurrences, MDEP initiated a statewide perchlorate monitoring program in 2004. MDEP was monitored 209 sites between 2004 and 2006 and reported perchlorate contamination in 14 sites with concentrations ranging between 1μg/L and 1,300 μg/L (MDEP, 2007).

A statewide monitoring program with the cooperation of Arizona Department of Environmental Quality and Arizona Department of Water Resources was conducted in the State of Arizona in 2004. The study examined both potable and non-potable water sources by sampling 85 sites. The study indicated the presence of perchlorate in 33 sites with the concentrations of 2 μg/L and above (Brandhuber and Clark, 2005).

Table II.1: CDPHS perchlorate monitoring results (1997-2005)
(Adapted from CDHS, 2007)

County	Number of yearly detections									TOTAL No. of detections	Peak level (µg/L)
	1997	1998	1999	2000	2001	2002	2003	2004	2005		
Los Angeles	54	31	21	13	8	24	7	12	7	177	159
San Bernardino	31	1	1	8	34	8	3	4	5	95	820
Riverside	14	5	5	11	16	19	10	3	1	84	73
Orange	-	20	-	-	1	9	7	-	-	37	11
Sacramento	10	2	-	1	-	1	-	1	9	24	400
Tulare	-	-	-	2	11	1	-	-	-	14	24
Santa Clara	-	-	1	2	1	2	3	-	1	10	8.5
San Diego	-	-	-	-	1	-	-	4	-	5	7
Ventura	-	1	1	-	-	-	-	2	-	4	20
Imperial	-	-	-	-	3	1	-	-	-	4	6
Sonoma	-	-	-	1	-	-	-	-	-	1	5
Stanislaus	-	-	-	-	-	-	1	-	-	1	3.3
TOTAL	**109**	**60**	**29**	**38**	**75**	**65**	**31**	**26**	**23**	**456**	-

The Texas Commission of Environmental Quality initiated a study to determine the extent of perchlorate contamination in the state of Texas in 2002. Under this study Texas Tech University monitored 254 public and private wells and they reported perchlorate detection in 88 wells with the levels of 4µg/L and above (Brandhuber and Clark, 2005).

The U.S. EPA documented the perchlorate occurrence data between 2001 and 2005 under the Unregulated Contaminants Monitoring Rule (UCMR). The data includes the evaluation of 34,193 samples in 3,858 public water systems (PWS) (serves to 225 million people). The U.S. EPA reported perchlorate contamination in 160 PWSs (4.1%) of the PWSs (serves to 16.8 million people) in 26 states and 2 territories with the method detection limit of 4µg/L. The average of positive detections was reported as 9.85 µg/L with a median of 6.40 µg/L (U.S. EPA, 2006b).

In 2005, the U.S. EPA's Federal Facilities Restoration and Reuse Office (FFRRO) compiled perchlorate occurrence data from U.S Department of Defense facilities, facilities of other federal agencies, private sites, locations of UCMR detections, and Texas Tech University's West Texas Study locations for drinking water sources, groundwater, surface water, and soil (Figure II.7). The maximum concentrations were reported as 811 μg/L in drinking water, 3,700,000 μg/L in groundwater, 120,000 μg/L in surface waters and 2,000 mg/kg in soil (U.S. EPA 2005a).

The National Research Council (NRC) also reported in 2005 that over 11 million people have perchlorate in their public drinking water supplies at concentrations of 4μg/L or higher (NRC, 2005).

II.4.4. Adverse Health Impacts of Perchlorate:

Endocrine disruptors are defined as the chemicals which impede or interfere with hormone levels in the body. Even though numerous studies have been conducted, the chemical reactions and the mechanisms of endocrine disruptors in human bodies are not totally discovered, therefore, acute and chronicle effects in humans are hard to assess (Briggs, 2006).

As an endocrine disruptor, perchlorate has also such complex and undetermined effects on humans. The major health effect that has been reported is that perchlorate interferes with the function of thyroid glands. Perchlorate has been used in the treatment of thyroid dysfunctions, such as thyrotoxicosis, since 1960s in the U.S. (Wolff, 1998).

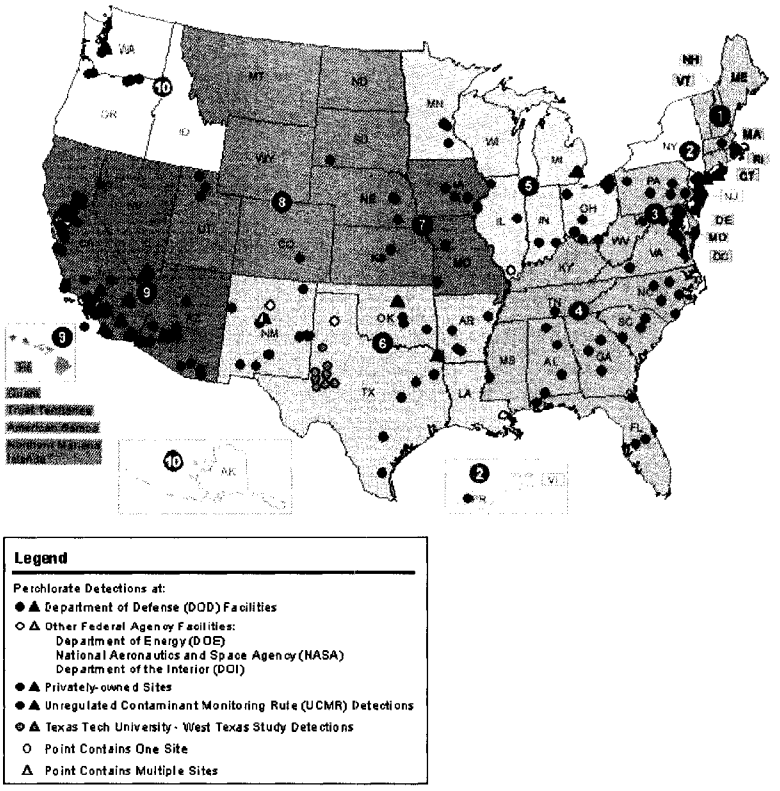


Figure II.7: National perchlorate detections by EPA Region, September 23, 2004 (U.S. EPA, 2005)

The thyroid gland produces T_4 hormone, which is a precursor hormone, is then converted to active thyroid hormone T_3. The active thyroid hormone T_3 controls the growth of neurons and supporting cells, and also regulates the connection between neurons, the formation of the myelin sheaths, and the development of neurotransmitters. The active thyroid hormone T_3 is an important hormone for central nervous system and skeletal development in infants and adults (Wollf, 1998; NRC, 2005).

The presence of perchlorate ion at high levels in the human body causes a condition, hypothyroidism, in which thyroid gland cannot produce sufficient thyroid hormone. Perchlorate ion competes with iodine, which is a key component of hormones

T_3 and T_4, and inhibits iodine transport and uptake in the thyroid gland, thus, interferes with thyroid hormone production (Wolff, 1998).

The negative health impacts of perchlorate as an endocrine disruptor is an issue of debate for the scientific community. Various studies reported contradictory results of the effect of perchlorate on iodine uptake of thyroid gland and thyroid hormone production.

Greer et al. (2002) studied the short term effects of perchlorate on thyroid iodine uptake. Thirty seven male and female volunteers were subjected to 0.007, 0.02, 0.1, or 0.5 mg/kg-day of perchlorate for 14 days. A significant thyroidal radioiodine inhibition was reported for the dose groups of 0.02, 0.1, and 0.5 mg/kg-day, even though no change in thyroid hormone levels was observed. The authors suggested that the observation of decrease in the iodine uptake with constant thyroid hormone levels is due to the ability of thyroid gland to store and to release hormones when the production is interrupted. The study concluded that perchlorate doses of 5.2 and 6.4 μg/kg-day (approximately 180 or 220 μg/L) do not have any adverse health effects in iodine sufficient populations (Greer et al., 2002).

Braverman et al. (2006) studied the effects of perchlorate exposure on 13 healthy volunteers for 6 months. A daily exposure dose of 0.5 and 3.0 mg potassium perchlorate were used to determine the effects on thyroid gland iodine uptake and function. The study indicated that there were no observable complications in iodine uptake rates and thyroid hormone levels (Braverman et al., 2006).

Blount et al. (2006) examined the relationship between urinary levels of perchlorate and serum levels of thyroid stimulating hormone (TSH) and total tyroxine (T_4) in 2299 men and women subjects with ≥ 12 of age between 2001 and 2002. It was

concluded that perchlorate was not a significant predictor of T_4 and TSH in men, however, in women, with urinary iodine levels of <100μg/L, perchlorate was a significant negative predictor of T4 and a positive predictor of TSH. Also for women with urinary iodine levels of ≥100 μg/L, perchlorate was a significant positive predictor of TSH but not T_4 (Blount et al., 2006).

These different studies with different results do not support each other. However, this is understandable considering the complex nature of endocrine disruptors, different sensitivities of species, genders, external affecting conditions such as temperature and the levels of perchlorate.

II.4.5. Perchlorate Regulations:

Especially after 1900s, the increasing concerns about possible adverse health effects forced U.S. EPA to closely examine the health effects and occurrence of perchlorate. For this purpose, perchlorate was included on the Contaminant Candidate List (CCL) in 1998. As a contaminant in CCL, perchlorate was extensively monitored under Unregulated Contaminants Monitoring Rule (UCMR) with prioritized researches and data collection about the occurrence and adverse health effects nationwide. Results of these studies will help U.S. EPA to decide the necessity of regulating the contaminant (U.S. EPA, 1998b).

Due to the uncertainties in toxicological effects, inconsistencies between health impact studies, the complex nature of endocrine disruptors, the debate between defense industry, federal government and rational scientific risk assessments, perchlorate has not yet been regulated with a maximum contaminant level (MCL) by U.S. EPA, even though numerous studies have been conducted under UCMR.

Even though U.S. EPA has not regulated perchlorate with an MCL, an official reference dose (RfD) was recently issued as 0.0007 mg/kg/day (U.S. EPA, 2007b). The determination of the RfD will be a base for quantitative risk analysis and future regulatory process of determining the MCL.

The American Water Works Association (AWWA) reported their comments about regulating the contaminants in the CCL. The report claims that U.S. EPA has collected sufficient data and information to regulate perchlorate with an MCL, based on the occurrence data of perchlorate in PWSs in several states, the issued Rfd, the presence of reliable detection methods, and National Research Council's (NRC) reports on the adverse health effects (AWWA, 2007)

Despite the fact that perchlorate has not been regulated with a MCL, several states have been already issued advisory levels for perchlorate concentrations in drinking water, ground water and surface water. Following table (Table II.2) summarizes the advisory levels applied by various states.

II.4.6. Determination of Perchlorate:

The perchlorate in surface and groundwater samples has been reported as highly stable in clear plastic bottles for storage duration of up to 300 days, and the storage temperatures of 22 ± 4 °C without the direct sunlight exposure (Stetson et al., 2006). Despite the reported long storage periods and temperatures, all methods that were approved by the U.S. EPA require storage periods of less than 28 days with refrigeration.

Table II.2: Advisory perchlorate levels (U.S. EPA, 2005)

State	Advisory Level	Comment
Arizona	14 µg/L	1998 health-based guidance level; based on child exposure; to be reviewed after EPA issues final Reference Dose (RfD)
California	6 µg/L public health goal (PHG) for perchlorate in drinking water	Emphasized human clinical study; includes 10X uncertainty factor; California EPA (CalEPA) is anticipating a proposed maximum contaminant level (MCL) in 2005
Massachusetts	2 µg/L	Precautionary recommendation to local water districts for children and at risk populations
Maryland	1 µg/L	None
New Mexico	1 µg/L only for monitoring	Drinking water screening level
New York	5 and 18 µg/L	5 µg/L for drinking water planning level; 18 µg/L for public notification level
Nevada public	18 µg/L Notice standard	For contaminated groundwater
Texas	17 and 51 µg/L	17 µg/L for residential protective cleanup level (PCL); 51µg/L for industrial/commercial PCL

U.S. EPA approved "Method 314.0: Determination of Perchlorate in Drinking Water Using Ion Chromatography" in 1999. The method suggests the use ion of chromatography for perchlorate detection in drinking water with the minimum reporting limit of 4µg/L (U.S. EPA, 1999). Even though the method is applicable for drinking water samples, the need for lower detection limits and the problems related with the analysis of more complex matrices such as surface and ground water samples required more sophisticated analytical methods. The major problem in complex matrices is the presence of similar anions, such as sulfate (SO_4^{2-}), which elute at similar retention times as perchlorate, thus interfering with the quantification.

To improve the method detection limit and to achieve the evaluation of complex matrices, the application of ion chromatography with electrospray ionization mass

spectrometry (IC-ESI-MS) with evaporative preconcentration technique was reported (Hendrix and Munch, 2004). The method successfully decreased the method detection limit to 0.2μg/L, however the method has also certain limitations such as the co-elution of contaminants with the same mass to charge ratios (m/z) as perchlorate (HSO_4^- with natural sulfur isotope of ^{34}S), high background noise causing low signal-to-noise ratio, suppression of gas phase ion formation at high contaminant concentrations, and loss of sensitivity over time.

The U.S. EPA has accepted the "Method 314.1: Determination of Perchlorate in Drinking Water Using Inline Column Concentration/Matrix Elimination Ion Chromatography with Suppressed Conductivity Detection" in 2005. The method detection limit was decreased to 0.130-0.140 μg/L (U.S. EPA, 2005b).

The U.S. EPA was also accepted the "Method 332.0 Determination of Perchlorate in Drinking Water by Ion Chromatography with Suppressed Conductivity and Electrospray Ionization Mass Spectrometry" in 2005. The method is applicable for identifying and quantifying perchlorate in raw and finished drinking water. (U.S. EPA, 2005c)

Winkler et al. (2004) and Backus et al. (2005) reported the application of high performance liquid chromatography coupled with tandem mass spectrometry (HPLC/MS/MS) for the detection and quantification of perchlorate. The methods overcome the interference problems by using a matrix elimination system including barium (Ba, eliminates sulfate), silver (Ag, eliminates chloride, bromide, and iodine), and hydrogen (H, eliminates alkaline earths and transition metals as well as neutralizes highly alkaline samples) guard cartridges before the HPLC analysis. Both methods suggest an

evaporative concentration technique and it was shown that the methods are reliable for the detection and quantification of perchlorate in complex matrices such as surface water and ground water. The method detection limits were reported as 0.05 and 0.2 μg/L, respectively (Winkler et al., 2004; Backus et al., 2005).

II.4.7. Engineered and Natural Perchlorate Treatment Technologies:

The engineered and natural treatment applications for removing perchlorate from drinking water, groundwater, and soil include ex-situ and in-situ techniques; ion exchange, liquid phase carbon adsorption, membrane technologies, bioreactor, in-situ bioremediation, permeable reactive barrier, phytotechnology, and composting.

Ion exchange is the most commonly applied ex-situ technique for perchlorate removal in drinking water, groundwater, surface water, and environmental media. The technique is a physico-chemical process in which electrostatically held ions on the surface of ion exchange media are exchanged for ions of similar charge in a solution. The most commonly used ion exchange media are synthetic, inorganic or natural polymeric, strongly basic, mono-functional or bi-functional anion exchange resins. The resins are usually packed into a column, in which contaminated water is passed through, and contaminant ions are exchanged for other resin ions such as chlorides or hydroxides (U.S. EPA, 2005a). It has been reported in 11 full scale and 3 pilot scale ion exchange applications and has achieved perchlorate removal from influent levels of 10-350,000 μg/L to effluent levels of non-detect (MDL of 0.35 μg/L) to 2,000 μg/L (U.S. EPA, 2005a).

The efficiency of the ion exchange technology is highly sensitive to the presence of a wide variety of untreated water contaminants and characteristics. The presence of

competing ions, such as nitrate, sulfate, and bicarbonate, can reduce the perchlorate removal efficiency of the system, thus resulting in more frequent bed regeneration requirement. The presence of organics, suspended solids, calcium, and/or iron can cause fouling and reduction in the treatment efficiency of perchlorate due to clogging of the resin bed. Also the presence of oxidants in the effluent water can impede performance of the ion exchange systems (U.S, EPA, 2005a).

The cost associated with the ion exchange applications are generally compare unfavorably with costs for aboveground water treatment technologies. The major factors affecting the system cost include the technique that is used for resin regeneration and the pretreatment requirements that are based on the influent water quality (presence of suspended solids, oxidants, and metal ions) (U.S. EPA, 2005a).

Liquid phase carbon adsorption technology, which is an ex-situ technology to remove perchlorate from groundwater and surface water, involves the use of adsorbent media such as granular activated carbon (GAC), activated alumina (AA), or other proprietary media packed into a column. GAC is the most commonly used adsorbent media that is widely used for the removal of metal ions and organic contaminants. The removal of contaminants occurs by the adsorption on GAC media while the contaminated water passing through the GAC bed. When the media is reached the adsorption capacity, it can be either regenerated by thermal decomposition or disposed of and replaced (U.S. EPA, 2005). Two full-scale and two pilot-scale applications were reported with the complete removal (<0.35μg/L of MDL) of influent perchlorate concentrations of 1.8-92 μg/L (U.S. EPA, 2005a).

Perchlorate removal efficiency of the GAC beds depends on the flow rate, polarity and water solubility of other contaminants, and fouling. Increasing flow rate through the GAC bed decreases the contact time of contaminants with the media thus decreases the removal efficiency. The presence of soluble contaminants with high polarity can reduce the ability of GAC to remove other contaminants such as perchlorate. Also, the presence of suspended solids, organics, silica, or mica can foul the GAC media by accumulating in the GAC bed, causing pressure drop (U.S. EPA, 2005a).

The cost of GAC bed applications are generally high and are associated with the GAC media and regeneration applications or disposal cost of the media (U.S. EPA, 2005a).

Membrane treatment, which is ex-situ treatment technologies, involves the application of semi-permeable or permeable membranes for perchlorate removal. The two most common membrane technologies for perchlorate removal from groundwater, surface water, and wastewater are electrodialysis and reverse osmosis (RO) (U.S. EPA, 2005a). Electrodialysis is a membrane technology which involves the application of an electric current to perchlorate contaminated water as it passes through channels of alternating permeable membranes selective of anions and cations. Negatively charged perchlorate ions (anion) then accumulate at the cationic-selective membrane and are collected as concentrate or salty water. Another membrane technique, reverse osmosis, works on the principle of the high pressure application at the inlet to force water molecules against the concentration gradient from the contaminated water in to fresh water section by passing through a semi-permeable membrane. A study reported the application of electrodialysis with the removal of varying influent perchlorate levels of

15-130μg/L to 11-17μg/L (U.S. EPA, 2005). Also, a bench scale study was reported on the application of RO. The study indicated that the influent perchlorate concentration ranged from125 μg/L to 2,000 μg/L while the effluent concentrations ranged from 5 μg/L to 80 μg/L (U.S. EPA, 2005a).

The potential limitations of electrodialysis are the reduced perchlorate removal efficiencies due to the fouling and low selectivity of the semi-permeable membrane. Moreover, the perchlorate rich concentrate that is formed during the electrodialysis applications requires further treatment prior to disposal. The RO systems are suitable for point-of-use or small system applications. Post-treatment is required to make water palatable and prevent fouling of the distribution system by the application of sodium chloride or sodium bicarbonate (U.S. EPA, 2005a).

The cost associated with the electrodialysis and RO methods generally compare unfavorably with the costs for aboveground treatment technologies. The cost of electrodialysis and RO applications are mostly associated with the energy requirements and further treatment of the concentrate solutions (U.S. EPA, 2005a).

Bioreactors are another ex-situ treatment technology in which perchlorate contaminated water is treated with direct contact of microorganisms. Denitrifying bacteria have been shown capable of reducing perchlorate into chloride and oxygen in a three-step reduction process catalyzed by two enzymes, perchlorate reductase (ClO_4^- to ClO_3^- and then to ClO_2^-) and chlorite dismutase (ClO_2^- to Cl^-). The process requires an anaerobic environment with the presence of electron donor. Under these conditions perchlorate serves as an electron acceptor (oxygen source). Acetic acid, ethanol, methanol, and hydrogen are commonly used as external electron donors. Addition of

nutrients such as ammonia and phosphorus may be required to enhance the biological activity (U.S.EPA, 2005a).

Fluidized bed and packed bed reactors are the two most common types of commercially available bioreactors. The packed bed or fixed bed reactors are made up of sand or plastic media to support the biofilm growth. Sand and activated carbon are used in fluidized bed reactors for providing a large surface area for microbial activity and biomass growth (U.S. EPA, 2005a). A total of four full scale (three environmental media and one drinking water) and five pilot scale (four environmental media and one drinking water) applications were reported with the influent perchlorate concentrations ranging from 55-200,000 μg/L and the effluent concentrations ranging from 2 to 18μg/L in groundwater. For drinking water projects, influent perchlorate levels of 75 to 2,500μg/L and effluent levels of <4μg/L (MDL) were reported (U.S. EPA, 2005a).

The potential limitations of bioreactors are the extremely low DO levels, presence of nitrate, and nutrient feed One study indicated that the optimum DO levels for perchlorate reduction is between 0.5 and 1.0mg/L since the levels below 0.5 mg/L develops anaerobic conditions that promotes hydrogen sulfide formation in the presence of sulfate anions. Another study indicated that the complete removal of nitrate ions is required prior to achieve successful perchlorate reductions. To achieve consistent perchlorate reductions adequate dosage of carbon (electron donor) and nutrients are required for the growth of the biomass in the reactor (U.S. EPA, 2005a).

The cost associated with bioreactor applications are about the same as costs for aboveground treatment technologies. Even though the treated effluent is suitable for

environmental discharge, for drinking water applications bioreactor effluent may require additional polishing steps to remove biosolids present in the effluent (U.S. EPA, 2005a).

In-situ bioremediation (ISB) is a controlled biological process that is used to biologically convert perchlorate to chloride and oxygen under anaerobic conditions. Degradation of perchlorate occurs by a three-step enzymatic biological reaction. The technique requires the amendment of the system with nutrients and an electron donor to promote the biological activity (U.S. EPA, 2005a).

ISB of perchlorate involves enhancement techniques, meaning select species of microorganisms, mostly bacteria (*Ideonella dechloratans, Proteobacteria, Vibrio dechloraticans, Cuzensove* B-1168, *Wolinella succinogenes* HAP-1, *Dechloromonas,* and *Dechlorosoma*), and sufficient amounts of nutrients (i.e. phosphorus) and electron donors. External electron donors include organic acids such as acetate, citrate, and lactate, sugars such as glucose, alcohols such as ethanol and methanol, and protein rich substances such as casamino acids and whey. Also vegetable oils and vegetable oil emulsions can serve as electron donors. ISB includes the injection of nutrients and electron donors into the contaminated zone (U.S. EPA, 2005a).

Ten pilot scale ISB studies (six for groundwater and four for soil remediation) were reported. It was reported that the effluent perchlorate concentrations ranged from 4μg/L to 22 μg/L for six pilot-scale groundwater projects. Pilot scale ISB soil applications showed the perchlorate degradation with the final perchlorate concentrations of 40 to 500 μg/L (U.S. EPA, 2005a).

Selection of appropriate amendments is crucial to provide adequate amounts of carbon, nitrogen, and phosphorus for the microbiota. pH levels are also important since

the solubilities and availabilities of many constituents as well as the biological activity depends on pH conditions especially in the soil. The limitation of ISB is that the ISB treated water may not be acceptable for drinking purposes since the presence of bacteria in finished water due to the biotreatment. Moreover, the strong reducing conditions in the aquifer may cause the mobilization of metals including iron and manganese, and formation of methane (U.S. EPA, 2005a).

The cost associated with the ISB applications is based on the external feed of nutrients, electron donors, and pumping cost. Compared to other groundwater treatment technologies, ISB is favorable in terms of operation and maintenance cost (U.S. EPA, 2005a).

A permeable reactive barrier (PRB) is an in-situ treatment approach in which a zone of reactive material is installed in a permanent, semi-permanent, or temporary manner to chemically or biologically degrade or immobilize the targeted contaminants while groundwater flows through the system. To treat groundwater contaminated with perchlorate, either the growth of indigenous microorganisms can be promoted or the system may be inoculated with anaerobic bacteria that are capable of degrading perchlorate (U.S. EPA, 2005a). To show the capability of the system to degrade perchlorate, two full-scale and one pilot scale studies were reported (U.S. EPA, 2005a). In one of the full scale studies, groundwater perchlorate level of 13,000μg/L was reduced below the MDL of 0.45μg/L. Another full-scale study suggested the degradation of perchlorate level from 120μg/L to 20μg/L. A pilot-scale study reported by U.S. EPA (2005) indicated that the removal of perchlorate with the initial concentration of 10,000μg/L and final concentration of less then MDL of 4 μg/L.

The selection of appropriate barrier media to support the biological activity by supplying adequate amounts of carbon, nitrogen, and phosphorus is crucial for a successful a RBF application. Also the hydrogeology of the site is very important for the design, installation, and operation of a PRB system. In case the PRB system loses its reactive capacity, it is necessary to support the system with external sources or to replace the PRB media. Additional maintenance may be required if the system is clogged or fouled biologically (U.S. EPA, 2005a).

The cost of PRB applications are generally considered lower than the average costs of other groundwater treatment technologies. Additional costs after installation may require maintaining the system (U.S. EPA, 2005a).

Phytotechnology is a process in which plants are used to remove contaminants from media including groundwater, surface water, and soil. Two mechanisms play an important role in the application of this technology. Contaminants can be either biodegraded by the microbiota present in the soil surrounding the roots of the plant (rhizodegradation) or the plant itself can uptake the contaminants and degrade them biologically. The removal of perchlorate with phytotechnology is not well established, however, bench scale studies provide promising results that suitability of certain plant species for perchlorate removal.

It is reported that the initial perchlorate concentration of 34 mg/L was reduced to 23 mg/L in groundwater within a one-year study. The study suggested that the mass of perchlorate taken up by the poplar trees and/or degraded within the rhizosphere was 0.144 kg/d by using 425 poplar trees on a 0.7 acre demonstration site (U.S. EPA, 2005a).

The efficiency of the phytotechnology process depends on the selection of plant species and the concentration of contamination. Perchlorate may exert toxic effects on certain species, therefore, the selection of suitable species is necessary for the application of this technology. Also excess amount of perchlorate may fatally affect the plants, thus, the tolerance levels of the plants should be studied extensively before the application. Climatic changes are also a concern due to their impact on plants. The phytotechnology is an advantageous technique over engineered above ground treatment applications (U.S. EPA, 2005a).

Composting is a controlled biological process in which microorganisms degrade perchlorate under anaerobic and thermophilic conditions (54 to 65 °C). The heat produced by the microorganisms increases the temperature of the compost pile. The system also requires organic amendments such as wood chips, hay, manure, and vegetative wastes.

One full-scale and three pilot scale studies were reported to show the efficiency of the system on perchlorate removal. The full-scale study indicated reduction of perchlorate concentrations in soil form 500 mg/kg to 270 mg/kg. The pilot scale studies showed reduction of perchlorate from the average of 4200 mg/kg to a range of 0.1 to 23 mg/kg in seven days (U.S. EPA, 2005a). Composting was shown a cost effective and efficient perchlorate removal technique in soil.

II.5 PESTICIDES:

The U.S. Environmental Protection Agency (U.S. EPA) defines the term pesticide as any substance or mixture of substances that are intended for preventing, destroying, repelling, or mitigating any pest (U.S. EPA, 2008). The term pesticide is generally used as a general term for insecticides, herbicides, fungicides, and various other substances that are used to control pest. The term pest is described as the living organisms that occur where they are not wanted or that cause damage to crops or humans or other animals. Insects, mice and other animals, unwanted plants (weeds), fungi, and microorganisms such as bacteria, viruses, and prions are considered as pests.

This report mainly focuses on the herbicides atrazine, alachlor and metolachlor because of their intensive use for agricultural purposes and frequent detection in ground and surface waters. The word pesticide is used interchangeably with herbicide and both refer to atrazine, alachlor and metolachlor herbicides.

Atrazine, 2-chloro-4-(ethylamine)-6-(isopropylamine)-s-triazine, [6-chloro-N-ethyl-N_-(1-methylethyl)-1,3,5 triazine-2,3-diamineis a triazine group herbicide, which is characterized by a triazine ring. Atrazine is mainly used for pre and post-emergence control of annual grass and broad-leaved weeds in maize, sorghum, corn, asparagus, vines, fruit orchards, citrus groves, sugar cane, grassland, and forestry. Atrazine herbicide controls weeds by inhibiting photosynthesis (U.S. EPA, 2006c).

Alachlor, 2-chloro-2',6'-diethyl-N-(methoxymethyl)acetanilide, is an acetanilide herbicide and it is mainly used for pre and post-emergence control of most annual grasses and many broad-leaved weeds in maize, sorghum, groundnuts, soybeans, lima beans, oilseed rape, brassicas, radish, oil radish, cotton, sunflowers, sugar cane, potatoes, peas,

tobacco, and some ornamentals. Alachlor controls weeds by elongase inhibition, and inhibition of geranylgeranyl pyrophosphate (GGPP) cyclisation enzymes, part of the gibberellin pathway (U.S. EPA, 2006d).

Methalochlor, 2-Chloro-*N*-(2-ethyl-6-methyl-phenyl)-*N*-(1-methoxypropan-2-yl) acetamide, is also an acetanilide herbicide and it is mainly used for pre and post-emergence control of most annual grasses and many broad-leaved weeds in maize, sorghum, groundnuts, soybeans, lima beans, oilseed rape, brassicas, radish, oil radish, cotton, sunflowers, sugar cane, potatoes, peas, tobacco, and some ornamentals. Its mode of action on weeds is the same with alachlor and it inhibits elongase, and geranylgeranyl pyrophosphate (GGPP) cyclisation enzymes that is a part of the gibberellin pathway (U.S. EPA, 1995).

Molecular structures of these herbicides are given in Figure II.8. Table II.3 summarizes the chemical properties and drinking water criteria for these herbicides.

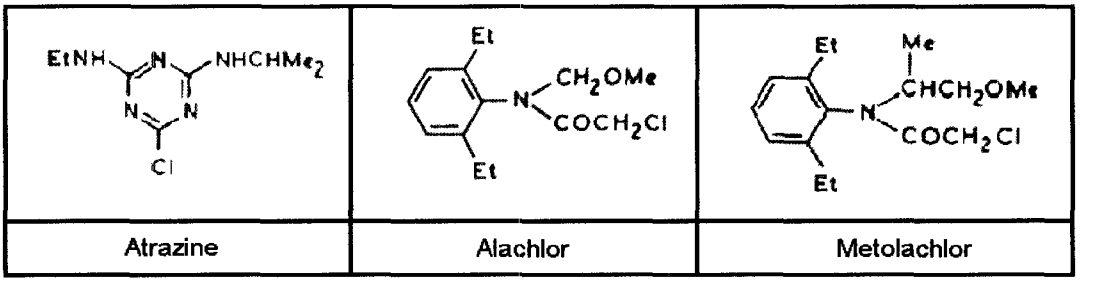


Figure II.8: Molecular structures of atrazine, alachlor, and metolachlor

Table II.3: Chemical properties and drinking water criteria for herbicides

	Atrazine	Alachlor	Metolachlor
Chemical Family	Triazine	Acetanilide	Acetanilide
Molecular Formula	$C_8H_{14}ClN_5$	$C_{14}H_{20}ClNO_2$	$C_{15}H_{22}ClNO_2$
Molecular Weight	215.69	269.77	283.8
Specific Gravity	1.187	**1.133	*1.12
Melting Point °C	176	40	
Boiling Point °C	-	100	100
Solubility in Water (mg/L)	*28	**242	*530
Vapor Pressure (mPa)	*0.04	**2.9	*1.7
Sorption Coefficient Koc (mg/L)	100	170	200
PK_a	1.7	-	-
Soil Half Life (days)	60	15	20
Maximum Contaminant Level (mg/L)	3	2	-
Health Advisory (mg/L)	3	-	70
Canadian Aquatic Life Guidelines (mg/L)	2	-	8
Cancer Group	C	B2	C

* at 20°C
** at 25°C
Information obtained from The Agrochemicals Handbook 3rd Edition. Cambridge, England : Royal Society of Chemistry, (1991), Goolsby and Pereira, (1995), and EPA

II.5.1. Occurrence of Pesticides:

By the early 1960s, pesticides started to be used widely for agricultural applications across the United States (Battaglin et al., 2003). Pesticide use increased by more than 800 percent between 1960 and 1980 (Lin et al., 1995; Aspelin and Grube, 1999; Battaglin et al. 2003). As a result of this increase, pesticides have become one of the most important contaminants in ground and surface waters. Their recurrent detection in groundwater (Barbash and Resek, 1996), surface water (Larson et al., 1997), aquatic biota and sediment (Nowell et al., 1999), the atmosphere (Majewski and Capel, 1995),

and their impacts on human health have forced state and federal agencies to develop monitoring and management programs (Barbash et al., 2001).

One of the most important nationwide studies was conducted by the U.S. Environmental Protection Agency. The U.S. EPA conducted a survey for determination of pesticide and nitrate in domestic and community drinking water wells (EPA National Survey of Pesticide in Drinking Water Wells, 1990). In this study, the EPA sampled approximately 1300 community water systems wells and rural domestic wells for the presence of 101 pesticides, 25 pesticide degrades, and nitrate (127 analytes) between 1988 and 1990. The survey results statistically represented approximately 94,600 drinking water wells at 38,300 community water systems and over 10.5 million rural domestic wells nation-wide. Results of this survey were summarized in the Phase I Report (U.S. EPA, 1990) indicating that 10.4% of community water systems and 4.2% of rural domestic wells contain at least one pesticide or pesticide degrades at detectable levels. The most commonly detected analytes were the degradate of DCPA (dimethyl tetrachloroterephthalate) (6.4% of community water systems and 2.5% of rural domestic wells above the survey minimum reporting limit 0.10μg/L) and atrazine (1.7% of community water wells and 0.7% rural domestic wells above the survey minimum reporting limit 0.12μg/L). In the report EPA estimated 0.8% of community water wells and 0.6% of rural domestic wells were possibly contaminated by pesticides nationally.

Following the National Pesticide Survey, the EPA implemented Pesticide Management Plans (PMPs) for the pesticides that were deemed as "high leaching potential" (USEPA, 1991; 1993a). Five pesticides, atrazine, simazine, alachlor, metolachlor, and cyanazine which were used for agricultural purposes, were focused on

for the first set of proposed PMPs. Cyanazine was removed from the list after its registration was cancelled for all uses in December 1999 (Jones, 2000).

The National Water-Quality Assessment (NAWQ) program of the US Geological Survey (USGS) was conducted between 1993 and 1995. A total of 2227 sites (springs and wells) were sampled in 20 major hydrologic basins throughout the U.S., representing approximately 60 to 70% of water use in the USA, for 83 pesticides and pesticide transformation products (Koplin et al., 1998a). Comparison of this study with the previous nationwide studies was reported by Barbash et al. (1999). Results of this study for five pesticides in the proposed PMPs (atrazine, simazine, alachlor, metolachlor, and cyanazine) and two additional pesticides (acetochlor and prometon) were discussed in detail by Barbash et al. (2001). It was reported that the most frequently detected pesticides were atrazine, simazine, prometone, and metolachlor with 30.1%, 14.3%, 11.8%, and 11.7% of the samples at detectable levels, respectively. 98% of detections of four pesticides were less than 1μg/L. Maximum contamination levels and health advisories for reported pesticides were exceeded in only 2 sampling sites.

Spahr et al. (2000) reported the occurrence of pesticides in surface waters of the Upper Colorado River Basin study unit (UCOL), CO, between 1996 and 1998. The authors indicated that the occurrence of the pesticides depend on the time, rate, and location of pesticide application as well as the crop type, precipitation/irrigation event following pesticide application, and the chemical characteristics of the pesticides. The UCOL study indicated that most commonly detected herbicides were atrazine, alachlor, and metolachlor with 69%, 57%, and 46% detections out of 100 samples. During the 2

year monitoring study, the maximum detected concentrations were 1.04, 0.751, and 0.442 μg/L for atrazine, alachlor, and metholachlor, respectively.

Dennehy et al. (1998) studied the water quality in the South Platte River between 1992 and 1995. The authors reported that more than 2 million pounds of active pesticide ingredients were applied to the South Platte River Basin. Atrazine was detected in 90% of the surface water samples and 6 percent of the groundwater samples with the maximum concentration of 100μg/L. Alachlor was detected in 21% of the surface water samples and 1% of the groundwater samples with the maximum concentration of 30μg/L. Metolachlor detections were observed in 50% of the surface water samples and 10% of the groundwater samples with the maximum concentration of 100μg/L. It was reported that the highest concentrations were observed in June during the three year monitoring effort.

II.5.2. Adverse Health Impacts of Pesticides and Regulations:

The U.S. EPA (2006) was reported that short-term atrazine exposure by dietary, drinking water, and occupational sources potentially cause congestion of heart, lungs, and kidneys low blood pressure, muscle spasms, weight loss and damage to adrenal glands when the level of exposure is above the maximum contaminant level (U.S. EPA, 2006c). Long-term atrazine exposures have the potential to cause weight loss, cardiovascular damage, retinal and some muscle degeneration, and cancer when the exposure levels above the maximum contaminant level (U.S. EPA, 2006c).

The pesticide, alachlor, was classified as category III or IV in terms of acute toxicity. The low acute toxicity of the pesticide has found potentially cause slight skin and eye irritation. Also in terms of chronic toxicity, alachlor has the potential to cause

liver, kidney, and spleen damage, lining of nose and eyelids. The U.S. EPA's Carcinogenic Risk Assesment studies indicated that alachlor was classified as Class B2 carcinogen meaning "likely" to be a human carcinogen at high doses but "not likely" at low doses (U.S. EPA, 1998c).

Metolachlor was considered as slightly toxic by the oral, dermal, and inhalation routes and has been placed in Toxicity Category III. The pesticide was reported as non-irritating to the eyes and skin but it causes skin sensitization. As a possible human carcinogen, metolachlor was classified as a Group C carcinogen with the evidence of increased liver tumors in animal tests. Animal studies also indicated that there is possible link between developmental problems and metolachlor exposure (U.S. EPA, 1995).

Atrazine and alachlor concentration in drinking water is regulated by the U.S. EPA under Primary National Drinking Water Regulations (PNDWR) due to the potential adverse health impacts on human. The U.S. EPA has regulated atrazine and alachlor with the maximum contaminant level (MCL) of 0.003 mg/L and 0.002 mg/L. The U.S. EPA has also suggested non-enforceable maximum contaminant level goals (MCLG) for atrazine and alachlor as 0.003 mg/L and 0.0 mg/L, respectively. Metolachlor has not been regulated by the U.S. EPA however it is on the Contaminant Candidate List (CCL) which identifies and lists unregulated contaminants that may require a national drinking water regulation in the future.

II.5.3 Engineered Treatment Applications for Pesticides:

A conventional surface water treatment generally includes pre-setling, coagulation/flocculation, granular filtration, corrosion control, and disinfection. The U.S.

EPA's Office of Pesticides Programs (2001) was reported removal efficiencies of several pesticides through conventional water treatment processes during experimental and field applications. The report defines a conventional surface water treatment application as the series of processes including pre-setling, coagulation/flocculation, granular filtration, corrosion control, and disinfection.

The removal efficiencies of atrazine, alachlor, and metolachlor were reported with jar tests for coagulation process. The maximum removal efficiencies were reported as 0%, 4%, and 11% for atrazine, alachlor and metolachlor with the initial pesticide concentrations ranging between 34.3 and 93.4 μg/L. The alum doses were reported between 15 to 30 mg/L (U.S. EPA, 2001). The field application results from a lime soda softening process indicated that no pesticide removal was achieved with the initial concentrations of 7.24, 3.62, and 4.64 μg/L for atrazine, alachlor, and metolachlor, respectively (U.S. EPA, 2001). Also sedimentation and filtration processes were reported as ineffective in terms of the removal of the three pesticides. Full scale chlorination applications were reported to show no removal for atrazine and slight removal efficiencies for alachlor and metolachlor by 7% to 9%. As a conclusion the report indicated that the conventional water treatment application is insufficient for pesticide removal.

The major water treatment applications that are reported to be effective on pesticide removal are chemical oxidation, powdered activated carbon (PAC), granular activated carbon (GAC), and membrane treatment technologies such as reverse osmosis (RO), and nanofiltration (NF) (U.S. EPA, 2001).

A lab scale chemical oxidation process with ozone was reported as a promising technique to remove alachlor with the removal rates ranging from 75-97% for alachlor with the initial concentration of 5 to 145 μg/L (U.S. EPA, 2001).

PAC technology is usually applied for taste and odor control in public water systems. A full-scale testing indicated that removal of pesticides atrazine and alachlor was achieved by the adsorption mechanism on to the PAC media. The type and dose of the commercially available PAC media were shown as important factors that affect the removal efficiencies. The removal efficiencies increased with the increased PAC dose. The optimum dose of 33 mg/L PAC was reported with the removal efficiencies of 87% and 94% for atrazine and metolachlor, respectively (U.S. EPA, 2001).

Like PAC, GAC is also used for taste and odor control in public water systems. The ability of GAC to adsorb wide variety of organic compounds as well as pesticides has been reported (U.S. EPA, 2001). Full scale testing with GAC media indicated that removal of triazine and acetanilide pesticides with the removal efficiencies of 47%, 72%, and 56% for atrazine, alachlor, and metolachlor, respectively.

Membrane technologies, RO and NF are demonstrated to remove organic pollutants and pesticides form contaminated waters. RO systems are designed to use a semi-permeable membrane as a diffusion barrier for dissolved constituents in water. Hydrostatic operational pressures of 300-1000 psi are applied to drive feedwater through a semi-permeable membrane that are typically composed of cellulose acetate, polyamide membranes, and thin film composites. Field scale and laboratory studies indicated that thin film composite membranes have superior performances in removing pesticides compared to those of cellulose acetate and polyamide membranes. Removal efficiencies

for triazine pesticides were reported as 23%-59%, 68%-85%, and 80%-100% for cellulose acetate membrane, polyamide membrane, and thin film composite, respectively. Acetanilide pesticide removal rates were reported as 70%-80%, 57%-100%, 98.5%-100% for cellulose acetate membrane, polyamide membrane, and thin film composite, respectively (U.S. EPA, 2001).

Nanofiltration process that is a similar process with RO requires lower operational pressures and does not cause significant changes in water salinity. A field scale pilot plant study indicated that 80%-90% atrazine removal can be achieved with NF application (U.S. EPA, 2001).

II.6. DRINKING WATER TREATMENT RESIDUAL (WTR)

Conventional water purification includes the coagulation process with the addition of metal salts as coagulants to neutralize negative charges on colloidal particles. Neutralized particles then are allowed to agglomerate into larger particles during mixing in flocculation basins. The larger and heavier particles, flocs, are removed by settling in the sedimentation basins and during filtration in sand or multimedia filters (U.S. EPA, 1996). Collected sludge (water treatment by-product) formed by the addition of aluminum, iron, and calcium salts to remove colloids, color, sediments and contaminants, is classified as drinking water treatment residuals (WTR) (Elliott and Dempsey, 1990). As a non-hazardous water treatment by-product, WTR, can be stored and disposed by landfilling, discharge to a wastewater treatment plant, or underground injection. Use of WTR in beneficial applications (agriculture, silviculture, land remediation, and

composting) has become a research interest by many scientists and agencies (Dayton et al., 2003).

General composition, physical and chemical properties of WTR change with the quality of intake water (suspended and dissolved materials, clays, and humic substances), the dosage and the type of chemicals that are used as coagulant (U.S. EPA, 1996). Generally, WTRs consist of sediment, aluminum or ferric (hydr)oxide, activated carbon and polymers (Elliott and Dempsey, 1990b). When dried, WTRs are generally in the form of fine soils such as clay-like or sand-like in texture (U.S. EPA, 1996).

The most common metal salts that are added in drinking water treatment include ferric chloride (FeCl3), aluminum sulfate (Al2(SO4)3.14H2O) and organic polymers. The coagulant dosage determines the aluminum (Al) and iron (Fe) content in the WTR with typical Al and Fe concentrations of 5 to 15% of dry solids in WTR (U.S. EPA 1996).

Total Al and Fe content of WTR are typically within the measured levels in soil (U.S. EPA, 1996). While Al forms in soils are aluminosilicates, WTR contain Al (or Fe) in amorphous hydrous oxide forms with greater reactivity than crystalline soil forms (U.S. EPA, 1996). The amorphous Al in WTR has a greater surface area than aluminosilicates, thus, has greater surface availability for adsorption reactions.

Carbon is a major component of WTR. The carbon content of WTR is generally higher than typical soils (<30g/kg soil) ranging between 23-225 g total C kg^{-1} WTR with a greater fraction of organic carbon (Dayton et al., 2003; Dayton and Basta, 2005; Makris et al., 2004). The high carbon content of WTR is attributed to sediment organic mater, dissolved organic matter, coagulated algal cells, carbonate addition for pH adjustment,

and small amount of activated charcoal or organic polymers added during water treatment processes (Dayton et al., 2003, Dayton and Basta, 2005).

II.6.1. Beneficial Uses of WTR:

Beneficial uses of WTR are of increasing interest for municipalities and scientists due to the high cost and excessive land requirements associated with WTR management. With high Al and Fe content and large specific surface area, WTR has become an important material for controlling excessive phosphorus in soil and in runoff.

Phosphorus Immobilization with WTR:

Adsorption of phosphorus in soils was shown strongly related to the soil's amorphous metal oxide (Al and Fe) content (Sparks, 1995; McBride, 1994; Sposito, 1989). Based on this fact, numerous studies were focused on the relation and adsorption mechanism of phosphorus with metal oxide content of WTR.

The ability of two alum based WTR, cement kiln dust, and treated bauxite red mud to control excessive amount of bioavailable phosphorus in soil was studied by Basta and Peters (1996). The study showed that all waste materials significantly decreased phosphorus concentrations after 9 weeks of incubation. Alum based WTRs with higher amorphous aluminum oxide content achieved greater phosphorus reduction. It was also reported that one alum based WTR with higher Ca achieved better phosphorus reduction with a suggested additional removal mechanism of calcium phosphate precipitate formation. The study concluded that the addition of alum based WTR to high P soils would prevent non-point source runoff of bioavailable P to surface waters (Basta and Peters, 1996)

Moore et al (1999) studied controlling phosphorus content in soil and animal manure (Moore et al., 1999). They reported that the soluble phosphorus, which is adsorbed on amorphous aluminum hydroxides, transforms into stable and non-soluble crystalline minerals such as variscite ($AlPO_4 \cdot 2H_2O$) and wavellite ($Al_3(PO_4)_2(OH)_3 \cdot 5H_2O$). These aluminum phosphate species are shown to be very stable under a wide range of physical and chemical conditions, thus, making alum based WTR, with high aluminum and aluminum hydroxide content, suitable for controlling phosphorus in soil and animal manure (Moore et al., 1999).

The surface application of WTR to pasture land treated with poultry litter and the reductions of N and P in surface runoff was studied by Gallimore et al. (1999). Two types of WTR were tested on three different types of soil treatments consisting of high broadcast (44.8 Mg ha^{-1}), low broadcast (11.2 Mg ha^{-1}), and a buffer strip (Mg ha^{-1}). Results of the surface application study indicated that the mean dissolved phosphorus content in the high broadcast and in the buffer strip was reduced by 43% and 46%, respectively. The reduction mechanism was attributed to the amorphous aluminum oxide content of the WTR and the WTR with higher aluminum oxide content achieved higher P fixation. The comparison between the broadcast and buffer strip showed that more efficient P removal was achieved in the buffer strip due to the fact that the surface runoff water had greater contact with WTR. The researchers indicated that the homogeneity of the WTR-soil media and the slopes are important to avoid short circuits, thus, less efficient P fixation (Gallimore et al., 1999).

Elliot et al (2002) investigated the benefits of amending low P-sorbing sandy soil material with WTR to prevent downward P movement form biosolids. The research

involved the application of three different types of WTR formed by different coagulant processes. WTRs from alum based (Al-WTR), ferric based (Fe-WTR), and lime soda softenting (Ca-WTR) coagulation processes were tested for the phosphorus reduction efficiencies in laboratory equilibrium studies. The authors showed that the ability of different WTRs to reduce soluble P followed the trend Al-WTR>Fe-WTR>Ca-WTR (Elliot et al. 2002). The study suggested that the abilities of WTRs to fix soluble P were a function of the reactivity of the oxide components in each material. The P sorption on WTR surfaces was related to the oxalate-extractable Al and Fe (Al_{ox} + Fe_{ox}) fractions of WTR material. Study also suggested that the crystallinity of Al and Fe species are not as efficient as oxalate-extractable species in terms of P sorption. Al_{ox} + Fe_{ox} content for WTRs were reported as 2.7 mol kg^{-1}, 1.1 mol kg^{-1}, and 0.18 mol kg^{-1} for Al-WTR, Fe-WTR, and Ca-WTR, respectively with the general soil application rate of 2.5% by weight (Elliot et al., 2002).

An extensive study was conducted by Dayton et al. (2003) to determine performance of WTR as P sorbent to reduce P in runoff water from manure applied land. Researchers examined twenty one Al based WTRs from Oklahoma utilities for the chemical components responsible for P removal. Chemical characterizations of Al-WTRs were performed to determine general properties and Al_{ox} and Fe_{ox} contents. The Al_{ox} and Fe_{ox} content of Al-WTRs ranged between 1.33-48.7 g/kg WTR and 0.23-7.44 g/kg WTR with medians of 23.5 g/kg WTR and 2.94g/kg WTR, respectively. Batch equilibrium studies were conducted on Al-WTRs with the particle size of <2mm to determine the P sorption maxima (P_{max}) based on Langmuir and Fruendlich isotherms. Fifteen-hour batch tests showed significant ($p<0.001$) quadratic relationship between P_{max} and Al_{ox} content

of WTR. The calculated P_{max} values ranged between 0.30 g/kg WTR and 5.14 g/kg WTR with the median of 1.33 g/kg WTR. Laboratory scale runoff water studies indicated that 14.0-84.9% P removal with a median reduction of 53.8% form an average 55 mg/L P for different types of Al-WTRs. A significant linear relationship ($p<0.05$) was observed between P_{max} and Al_{ox} content of WTR in runoff studies. Authors concluded that the ability of surface applied WTRs to reduce P varies with the chemical composition of the WTR. It was suggested that the empirical relationship between P_{max} and Al_{ox} content of WTR may be used to predict the ability of Al-WTR to sorb P, thus, to calibrate the WTR for surface applications (Dayton et al., 2003).

Dayton and Basta (2005) studied a method to determine the phosphorus sorption capacity of Al based WTR. The study's objective was to develop better correlation between the Al_{ox} and Fe_{ox} content of WTR and P_{max}. For the bench scale batch tests, 18 air dried Al-WTR samples were sieved with 2mm and 250μm sieves. The authors indicated that the relationship between P_{max} and Al_{ox} becomes highly nonlinear at >75 g/kg Al_{ox} as in the previous study (Dayton et al., 2003). They suggested that at high WTR Al concentrations the oxalate in the extraction solution may be limiting and not capable of extracting all of the amorphous Al in the WTR. To overcome this problem, the standard acid ammonium oxalate extraction method (McKeague and Day, 1993) to determine noncrystalline reactive Al (Al_{ox}) and Fe (Fe_{ox}) was modified by changing the oxalate solution to soil ratio from 40:1 to 100:1. With smaller size fraction (<250μm), greater oxalate solution ratio (100:1), and longer testing time (6 days), improved correlation between P_{max} and Al_{ox} (g/kg) and Al_{ox} + Fe_{ox} (mol/kg) was observed with

correlation coefficients of (r^2 = 0.916) and (r^2 = 0.916), respectively (Dayton and Basta, 2005).

Ippolito et al (2003) studied the effectiveness and the mechanism of P removal from solution by WTR. Al-based WTR was obtained from the Englewood Water Treatment Plant, CO. Bench scale P sorption tests were conducted by using 0.1-0.3 mm size fraction of air-dried WTR over 200 days. The authors' previous study (Ippolito et al., 2001) suggested a P sorption capacity of 2.178 mg P/kg WTR, whereas, in this study, P sorption maxima was 12.500 mg P/kg WTR, even though the same WTR was used (Ippolito et al., 2003). The difference between the sorption capacities was explained by the use of non-fractioned WTR in the previous study. The higher sorption capacity of fractioned WTR was explained by the greater available surface area for P sorption. The suggested mechanism of P sorption was ligand exchange where P replaced singly coordinated OH^- groups and then reorganized into a very stable binuclear bridge between cations. The P loaded WTR in bench tests showed two-stage progression for further P adsorption. The initial fast stage with linear decrease in solution P concentrations was attributed to sorption on variable charged surfaces followed by a second slower linear decrease corresponding to the precipitation of calcium phosphates. The long term phase changes of P were associated with WTR Ca as calcium P that precipitates due to the slight alkaline nature of the WTR. During the study, X-Ray diffraction (XRD) and electron microprobe-wavelength dispersive spectroscopy (EMPA-WDS) were used to identify the elemental associations with P. The XRD studies could not verify the presence of calcium or aluminum phosphate mineral precipitates, although they may exist in amounts less than the method detection limit. The EMPA-WDS study showed that the

sorbed P is associated with the Al fraction of WTR. It is concluded that P is either sorbed to or precipitated with amorphous aluminum (Ippolito et al., 2003).

Makris et al. (2004) studied the three-dimensional P removal mechanism, distribution of P in WTR particles for long duration of P loading, and stability of sorbed P. Two types of (Al-based and Fe-based) WTRs were examined with batch tests of up to 80 days. WTRs were air-dried and sieved (<2mm). Specific surface areas (SSA) of WTRs were determined for micropores with CO_2 and N_2 gas sorption and for macropores with mercury intrusion porosimetry (pores sizes 1.8-184.000 nm in diameter). Electron microscopy, energy-dispersive X-ray spectrometer (SEM-EDS), and electron microprobe coupled with a wavelength-dispersive spectrometer (EPMA-WDS) were used to determine P distribution in P treated WTRs. The batch tests were started with the P load of 10,000 mg P/kg WTR. Al-WTR sorbed all P within 10 days while Fe-WTR sorbed 9,100 mg P/kg WTR after 80 days. WTR surface analyses with SEM-EDS showed that there are no discrete surface metal-P phases. EPMA-WDS analysis of cross-sectional P distribution in WTR particles indicated that P moves in a three-dimensional fashion toward the interior of the WTR particles with a uniform amorphous Al-P and Fe-P association throughout the particles rather than accumulating in the particle surface as by precipitation. Mercury intrusion analysis suggested that there are negligible macropores with the pore diameter of >50 nm. The CO_2 gas sorption for both WTRs was greater than N_2 sorption suggesting that N_2 diffusion was restricted by narrow micropore openings. The SSAs that are calculated by CO_2 sorption method decreased with phosphorus treatment implying that P diffusion and sorption to micropores sizes ranging between 0.5

to 2 nm. The authors concluded that the overall P sorption to WTRs is based on the intraparticle P diffusion in micropores (Makris et al., 2004).

Alternative Beneficial Uses of WTR:

An increasing number of scientific studies have been focusing on the beneficial uses of WTRs for a variety of chemical contaminants. Recent studies examined the removal efficiency and kinetics of perchlorate and arsenic from water and soil (Makris et al., 2006a; Makris et al., 2006b; Sarkar et al., 2007).

Makris et al. (2006a) studied the removal mechanism, kinetic, and efficiency of perchlorate in the presence of Al-WTR. Batch tests were set up with perchlorate solutions of 10, 50, 100, and 200 mg/L including air dried and <1mm sieved Al-WTR. The samples were analyzed for perchlorate and chloride at 1, 2, 24, and 96 hours. The greatest perchlorate removal of (65%) was observed with the lowest perchlorate load of (10mg/L) after 2 hours of contact time. The removal efficiency was increased to 76% after 96 hours. 96 hour perchlorate removal efficiencies were decreased from 76% to 31% with increasing initial solution perchlorate concentrations (from 10 to 200 mg/L). The authors speculate the removal mechanism as intraparticle diffusion-limited P sorption. However, the formation of Cl^- and significant correlation ($p<0.001$) between removed perchlorate and Cl^- between 2 hours and 96 hours ($r^2 = 0.95$) supports the possible removal mechanism of hydrodechlorination in the presence of aluminum oxide as a proton donor. Alternatively, they suggest the organic matter in Al-WTR may function as the electron source for chemical reduction of perchlorate to chloride (Makris et al., 2006a).

The ability of WTR to remove arsenic (As(V) and As(III)) was evaluated by Makris et al. (2006b). Two WTRs, namely Al-WTR and Fe-WTR, were used in batch

experiments to optimize the maximum As(V) and As(III) sorption capacities. The study indicated that both WTRs exhibited high affinities for soluble As(V) and As(III). Both WTRs showed Freundlich type of adsorption with no obvious plateau after a reaction time of two days with 15.000 mg/kg WTR. Al-WTR achieved highly effective As(V) and As(III) removal, although As(III) removal was exhibited comparably slower removal rate. The Fe-WTR showed greater affinity for As(III) and reached As(III) sorption capacity levels similar to those obtained with the As(V) –Al-WTR system (15.000mg/kg WTR). The authors speculated the removal mechanism as diffusive sorption and abiotic reductive dissolution for As(III) removal with Fe-WTR.

Sarkar et al. (2007) evaluated As immobilization in soil with two types of WTR (Al-WTR and Fe-WTR) amendment. The bench scale experiments indicated that Al-WTR achieved complete As removal regardless of the initial load (225 to 7500mg As/kg WTR) within 0.5 hours. The Fe-WTR showed a significant ($p<0.001$) interaction between As load and reaction time. The sorption of As showed a linear pattern at small reaction times (up to 2 hours) for all initial Al loads and proceeded slower thereafter, finally reaching 100% sorption by the contact time of 48 hours. In soil amendment studies, As sorption capacities showed significant increase with increasing WTR rate (2.5 % to 10%). Researchers suggested that the main removal mechanism was the sorption on Al and Fe hydroxides (Sarkar et al., 2007).

II.6.2. Long Term Fate of Immobilized Contaminants on WTR and Environmental Impacts of WTR:

Long term fate of contaminants that are immobilized by adsorption on WTR particles is a crucial subject. During the land applications and after WTR particles reach

their sorption capacities, it is important that the adsorbed contaminants should not be mobilized with varying soil conditions. The leaching potentials of metals (Al, Fe) during long term applications are also important. If excessive heavy metal leaching occurs, then WTR will be considered as toxic waste and the land applications will not be permitted.

In terms of P adsorption, it was shown that in long term applications, adsorbed phosphorus on amorphous aluminum hydroxide transforms to stable (not redox active) crystalline aluminum phosphate compounds such as variscite and wavellite. These compounds were shown to be highly stable under a wide range of physical and chemical soil conditions (Moore et al., 1999).

Makris et al. (2005) studied long term sorption characteristics of phosphorus on Al and Fe-WTRs. Their study showed that P is diffused and sorbed by amorphous Al and Fe hydroxide micropores and resists desorption even in 5mM oxalate solution (Makris et al., 2005). Also, Ippolito et al. (2003) suggested that WTR is an effective sorbent for P and immobilized P is stable in the long-term as sorbed to Al hydroxides and precipitated as Al and Ca salts.

Agyin-Birikorang et al. (2007) researched the long-term P immobilization in heavily manure applied field. The study indicated that 60% soluble P was reduced and WTR-immobilized P remained non-labile during 7.5-year of study. They also speculated that even WTR-P erodes to surface waters, bioavailability of the immobilized P would be minimal.

Sarkar et al. (2007) and Makris et al. (2006b) evaluated the As removal with WTR, Both studies indicated that As desorption from WTR is negligible. Makris et al. (2006a) studied perchlorate removal with WTR. Authors suggested that hysteritic

adsorption of perchlorate on WTR, thus, stable immobilization of perchlorate over the course of the study.

The potential metal mobility from WTR was assessed under field conditions by Elliot et al. (1990). The study suggested that most heavy metals are bound in forms not readily released into solution due to their strong sorption and coprecipitation by Al and Fe hydroxides. Gallimore et al. (1999) reported that the land application of Al based WTR did not increase sediment or soluble Al in surface runoff. Basta and Peters (1996) determined that adverse potential environmental impacts from salinity, pH, Al, and total and extractable metals were insignificant from application of Al-WTR. Sarkar et al. (2007) examined the two types of (Al and Fe based) WTRs with Toxicity Characteristic Leaching Procedure (TLCP) (EPA Method 131) before and after the As treatment. Toxicity characteristics for As and other metalloids and metals for the WTRs were lower than those to classify them as hazardous wastes.

II.7. RIVERBANK FILTRATION (RBF) AND AQUIFER RECHARGE AND RECOVERY (ARR):

II.7.1. Riverbank Filtration (RBF):

The riverbank filtration process can be defined as the infiltration of river water and the water from the surrounding aquifer through the porous alluvial media into the collection well by the mechanical hydraulic gradient created (Figure II.9). Physical, chemical, and biological processes play an important role as the surface water is subjected to subsurface flow prior to extraction from vertical or horizontal wells (Ray et al., 2002b; Eckert and Irmscher, 2006).

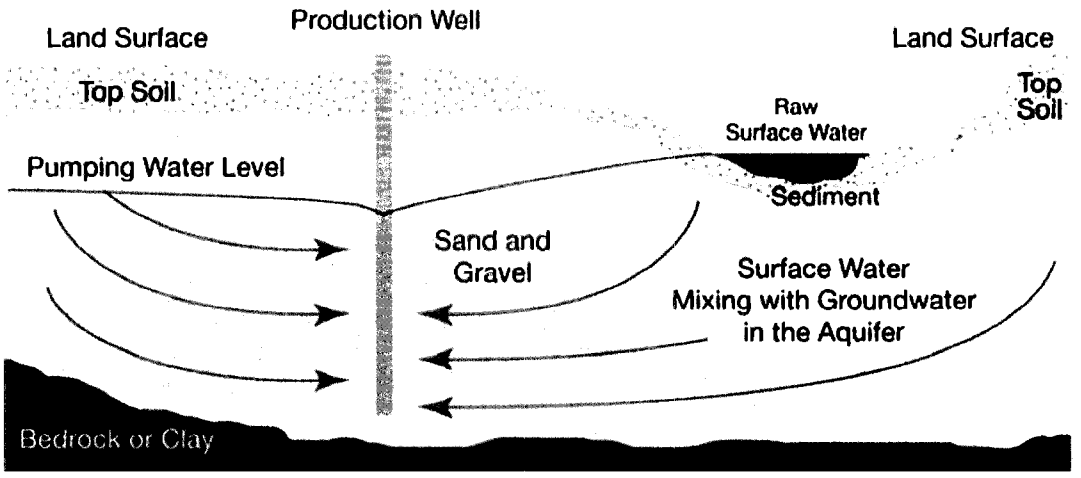


Figure II.9: Conceptual riverbank filtration (RBF) system (Ray et al., 2002a).

The filtration of large particles in river water while they pass through alluvial material is the primary physical process that occurs in RBF systems. The physical filtration is also coupled with electrostatic attachment of particles by alluvial material (Ray et al., 2002a). The particles such as suspended soil and floating conglomerations of algae and other detritus commonly found in river water are the main constituents removed through the RBF.

The chemical processes that are involved in RBF systems are adsorption, ion exchange, and chemical reactions (Kuenhn and Mueller, 2000; Ray et al., 20002a). Adsorption mainly occurs onto alluvial soil containing sand, gravel, clay, and other organic particles. Following the immobilization of contaminants, they become susceptible to biological degradation. Physical and chemical characteristics of alluvial soil strongly influence the ion exchange capacities (Kuenhn and Mueller, 2000).

Oxidation and acid/base dissociation reactions also occur with varying pH and oxygen concentration observed in RBF systems (Ray et al., 2002b; Kuenhn and Mueller, 2000).

The microbiological activity is most intense within the first meter of riverbed and aquifer interface (Eckert and Irmscher, 2006). Formation of a biofilm type growth at the interface similar to a "schmutzdecke" in slow sand filtration provides organic carbon dissolved oxygen, nutrient, and pathogen removals. Characteristics of the biofilm and the biological activity after the biofilm depend on the organic carbon and dissolved oxygen levels in the river water. With low levels of organic carbon and high initial dissolved oxygen levels, the RBF system remains oxidizing, otherwise, anaerobic conditions may be established. If the oxygen level is low enough, RBF becomes reducing and achieves nitrate and micropollutant removals (Kuenhn and Mueller, 2000; Eckert and Irmscher, 2006).

The major advantages of RBF systems are; (i) seasonal changes influent water quality due to concentration and temperature do not alter the RBF efficiency (Kuhen and Mueller, 2000), (ii) RBF and ARR systems achieve pathogen removal, particle removal, dissolved organic matter reduction, thus, reduction in disinfection by-product formation, and production of biologically stable water. Finally, recent studies report that the application of RBF is efficient in biodegradation of trace organic materials, such as, pesticides and antibiotics (Ray et al., 2002a).

During the operation of RBF systems possible drawbacks may occurs; (i) flooding events interfere with the travel times thus decrease the efficiency of the system, (ii) flooding and drought seasons influence the infiltration rates and the alluvial soil's saturation thus the system efficiency, (iii) drastically changing river water quality

influences the system performance. Due to these drawbacks RBF applications are followed by additional engineered treatment systems such as multi-barrier treatment approaches (Eckert and Irmscher, 2006).

Even though there are some disadvantages, RBF applications, as a part of multi-barrier approach, minimize the need for chemicals (disinfectants and coagulants) in water purification, and thus decrease the costs to the community without increased risk to human health (Ray et al., 2002a).

Riverbank Filtration Applications:

The primitive applications of RBF date back to the Romans who dug channels adjacent to lakes and rivers to utilize the advantage of natural filtration through alluvial material (Baker, 1948). The first modern RBF system was put in operation adjacent to the river Rhine in 1870 after the cholera outbreak in Dusseldorf, Germany (Eckert and Irmscher, 2006). For the first 80 years RBF systems without additional treatment (except disinfection) supplied drinking water to the City of Dusseldorf. The quality of Rhine water started to deteriorate after the 1950s due to the increasing population, industrial activities, and direct discharge of wastewater to the river. In 1967, engineered treatment steps of ozonation, biological filtration, and granular activated carbon were added downstream of the RBF system to achieve drinking water limits at all times.

The RBF systems have been frequently and successfully used in Europe for more than 100 years for the production of high quality drinking water for the first step of a multi-barrier approach in which RBF is assisted with complementary engineered treatment processes (Kuenhn and Mueller, 2000). RBF has started attracting attention

within last 50 years in the U.S. and several applications were reported as the first step of multi-barrier approach (Ray et al., 2002a).

The main operational difference between European and the U.S. RBF facilities is the retention times. European facilities are mostly designed for the retention times of several weeks to several months, whereas the U.S. facilities are designed for the retention times ranging from several hours to days or several weeks (Grunheid et al, 2005). This difference also supports the fact that RBF applications in North America are designed with the primary objective of pathogen removal and reduction of the cost of conventional water treatment. The longer retention times that are applied in European facilities also aims at the removal of DOC and trace organic pollutants (Grunheid et al, 2005).

The literature is reviewed for the benefits of RBF applications in terms of water treatment perspective. Removal efficiencies of turbidity, temperature, organic carbon, bacteria and viruses, trace organics, perchlorate, and phosphorus in RBF systems are the focus of the literature cited.

Successful and consistent turbidity removals by RBF systems were reported at Flehe site that is located on the bank of Rhine river in Dusseldorf (Ray et al., 2000a) Eckert and Irmscher, 2006). It was reported that clay and soil particles are in the infiltrating water are filtered and deposited in the upper layer of the water aquifer interface. Turbidity readings in the RBF treated water were observed as less then 0.1 FNU. The particles that were deposited in the upper layer of the aquifer caused clogging in the river bed. The authors suggested that the permeability of the alluvial material is drastically changed due to clogging and the infiltration sites are moving from the bank toward the middle of the river. In the areas where the river flow rate is high enough,

sufficient shear force is able to remove the deposited particles. During the flood events the reverse flow from the riverbank to the river is also an important mechanism to remove particles that cause clogging. Despite the clogging, and changing infiltration rates, the Flehe RBF site has been operational for more then 100 years with consistent low turbidity levels.

The removal efficiency and redox effects of organic carbon in different RBF sites were studied extensively (Grunheid et al., 2005; Eckart and Irmscher 2006). Eckart and Irmscher (2006) reported the DOC monitoring of Flehe RBF site between 1975 and 2004. They reported between 1975 and 1980 high DOC levels of 7.5 mg/L and up were observed in the river while riverbank filtrate never exceeded the DOC level of 3 mg/L. Especially after 1985 the river water quality was improved and DOC levels were decreased to less then 4 mg/L. Following 1985, constant bank filtrate DOC levels were observed and the DOC level in the bank filtrate never exceeded 2 mg/L. The DOC content of the riverbank filtrate was considered as non-biodegradable carbon content of the river water. It was suggested organic carbon was degraded within the first meter of the water aquifer interface showing a similar mechanism as slow sand filtration. Even though the dissolved oxygen levels were generally sufficient to satisfy oxic conditions, anoxic/anaerobic conditions were observed in the RBF system. These conditions caused mobilization of iron and manganese. Grunheid et al. (2005) reported the monitoring of DOC in Berlin RBF site between 2002 and 2004. The RBF site is located on the bank of Lake Tegel. The lake water had an average of 7.4 mg/L DOC throughout the study. The bank filtrate showed average DOC level of 4.7 mg/L with the retention time of 4.5 months. The authors reported that the observation of fast DOC oxidation near the bank in

the short aerobic zone. In the subsequent anoxic/anaerobic transition significantly slower DOC degradation was observed. It was suggested that the 4.7 mg/L of bank filtrate DOC is the non-degradable portion of the organic carbon.

The RBF systems have shown very effective in reducing or eliminating bacteria, viruses and parasites (Gollnitz et al., 2003). The removal mechanisms of pathogens through RBF were explained by filtration, sorption, and biological degradation, which are the similar processes observed in slow sand filtration. These mechanisms in RBF were confirmed with field studies (Gollnitz et al., 2003). The study performed by the Dusseldorf waterworks showed an approximately 3-log bacteria removal with complete parasite removal and complete inactivation of viruses (Ray et al., 2002a).

Eckert and Irmscher (2006) studied the removal efficiencies of pathogenic bacteria in Flehe RBF site by monitoring indicator organism E.coli. The plate counts of E.coli in Rhine River were ranged from 100 to 10,000. Complete E.coli removals were reported during the study except for the flooding events. The plate counts of up to 10 were observed during the flood events. The authors stated that additional disinfection step is necessary during the flood events and Dusseldorf waterworks performs ozonation to ensure high drinking water quality.

Weiss et al. (2003) studied the pathogen removal efficiencies of three mid-western RBF sites in Jeffersonville IN, Terre Haute IN, and Parkville MO. They monitored *Clostridium* and two bacteriophages E.coli C and E.coli F-amp. In three sites river water *Clostridium* counts were between 122 and 183. After RBF treatments *Clostridium* counts were observed as <0.07 (MDL) with the log removals of >3.4.

Bacteriophage counts were reported between 6 and 147 and all sites showed treated water counts of <0.07 with log removals of 1.9 to >3.3 due to the varying influent counts.

Removal of the emerging contaminant perchlorate with RBF has not been reported in the literature. Bioremediation of perchlorate with engineered and natural systems was reported (U.S. EPA, 2005) under anaerobic condition in the presence of electron donating compounds. Anoxic/anaerobic transition following an aerobic zone during RBF treatment was reported by various studies (Grunheid et al. 2005; Eckart and Irmscher, 2006), therefore it is most likely to observe biological degradation of perchlorate in RBF treatment.

The literature reviewed for RBF applications has not reported any study on phosphorus removal. Phosphorus removal through RBF treatments is based on the sorption to alluvial material and biological uptake by microorganisms present in the aquifer water interface. Mostly the types of soils in riverbanks are sandy. Poor and limited sorption capacities of sandy soils were documented by numerous studies (He, 1999; Del Bubba, 2003). Research on another natural treatment application, constructed wetlands, showed that P sorption capacities of natural soils are limited and biological uptake is the main removal mechanism (Del Bubba, 2003). However, limited organic carbon levels as an electron donor and carbon source also suppress the biological activity through RBF, thus may cause limited biological phosphorus uptake rates as well.

II.7.2. Aquifer Recharge and Recovery (ARR):

The ARR system envisioned in this study includes the continuous feeding of an infiltration basin in the center of the ARR site with raw water followed by the percolation to a controlled aquifer surrounded by a slurry wall. After retention time of approximately

30 days in the aquifer water will be recovered from collection wells located at the periphery of the basin.

The ARR technique is based on a similar natural system aquifer storage and recovery (ASR). The ASR approach can be defined as the storage of high quality water to a confined aquifer by injection and recovery of water from the same injection point when it is needed (Pyne, 1995). The application of ASR has been practiced in a primitive way for several centuries in Kara Kum Plain, Turkmenistan, and the Kutch District of Gujarat State in western India. The modern applications of ASR have been used in the U.S., Canada, England, The Netherlands, Australia, and Israel (Pyne, 1995). In modern applications, treated water with drinking water quality is injected into a deep aquifers, stored, recovered when additional water demand occurs, and supplied to the distribution system either without further treatment application or only additional disinfection (Pyne, 1995). The ASR systems were mainly used to store treated water of excess volumes for long terms with avoiding water treatment facility expansion, thus reducing the capital cost (Pyne, 1995). Beside the long term storage, additional benefits of ASR such as DOC reduction (Vanderzalm et al., 2006), DBP precursors and DBP reduction (Thomas et al., 2000; McQuarrie and Carlson, 2003) from the feed waters by biological activity in ASR were reported.

The natural systems that are similar to ARR system in this study were reported as artificial groundwater recharge and recovery (AGRR) in the literature. Natural waters were used as feed water in AGRR systems and physical, chemical, and biological removal mechanisms are reported as similar to RBF applications.

ARR Applications:

Grunheid et al. (2005) reported the application of artificial recharge at Lake Tegel, Berlin, Germany. The system includes the pumping of lake water to infiltration basin and recovery of aquifer water from a production well with the retention time of 50 days. When compared to the RBF application at the same site, artificial recharge site showed an aerobic characteristic during the retention time of 50 days while RBF showed mostly anoxic and anaerobic characteristics just after a short aerobic zone. DOC reduction form the influent concentration of 7.4 mg/L to recovered water concentration of 4.7 mg/L was reported with the similar removal rate as in RBF. Most of the DOC was oxidized within <3 days of retention time (~5.3 mg/L) indicates the fast aerobic DOC degradation.

Kolehmainen et al., (2007) studied the NOM removal efficiency of three AGRR sites in Finland. All sites showed reduction of average influent TOC from 12-14mg/L to less than 2 mg/L. The study also showed that large molecular fractions of NOM are removed more efficiently than smaller fractions. The study also examined the total bacteria counts in the AGRR system. The influent water total bacteria counts were ranged between $14.3x10^5$ to $24.0x10^5$ cells/mL. The effluent total bacteria counts from three different sites close to each other and ranged between $0.6x10^5$ and $1.0x10^5$ cells/mL. The cell counts of the chemically treated water were reported as $0.1\ x10^5$ cells/mL before the disinfection process. A positive correlation between the DOC reduction and total bacteria cell counts were reported suggesting the biological activity as the main removal mechanism for bacterial removal.

As in RBF, removal of perchlorate with ARR has not been reported in the literature. The aerobic nature of the ARR sites may not support biological perchlorate degradation. In case of anoxic/anaerobic transition in ARR with available electron donating compounds may promote the biological activity that may achieve perchlorate biodegradation.

Also as in RBF, phosphorus removal has not been studied in the literature reviewed. The low phosphorus sorption capacity of alluvial sand and insufficient biological phosphorus uptake may cause limited phosphorus removals in ARR systems as well.

II.8. SUMMARY OF LITERATURE REVIEW:

Phosphorus is a limiting nutrient in fresh water bodies. Excessive amounts of phosphorus loads to surface waters, especially from wastewater treatment plants, agricultural and urban runoffs, promote excessive biological growth and cause eutrophication. Even though phosphorus does not have direct health effects to humans, excessive algal and bacterial growth in the freshwater bodies deteriorates water quality by depleting dissolved oxygen, increasing organic carbon content, and causing taste and odor problems. The phosphorus level in drinking water has not been regulated by U.S. EPA, however individual states have started regulatory studies to improve water quality of surface waters for multiple purposes of use. Engineered phosphorus treatment techniques are mostly related to wastewater applications. Generally, the high cost associated with these techniques is the major drawback.

Carbon is an essential nutrient for all biological life forms in fresh water bodies. The cycle of carbon between organic and inorganic forms via photosynthesis and aerobic

respiration is an important mechanism for all organisms. Beside the inorganic carbon fixation from atmosphere, organic carbon loads from wastewater treatment facilities, agricultural fields, forests, swamps, and grassland can alter the carbon dynamics in surface waters. The organic carbon content of surface waters includes a diverse set of compounds varying in structure, chemical reactivity and biodegradability. These properties determine the fate of carbon in water. Biodegradable carbon is used as a carbon source and electron donor for wide variety of organisms.

The primary concern of excessive organic carbon concentrations in water in terms of adverse health effects is the formation of disinfection by products (DBPs). These compounds are known carcinogens and regulated by U.S. EPA at low levels. The best approach to eliminate DBP formation is to decrease the organic carbon content of water before it reaches to disinfection process. Various engineered carbon removal strategies have been developed with high initial, operational, and maintenance costs associated with them.

Nitrogen is an essential nutrient for all life forms in the ecosystem. It is the major building blocks of DNA, RNA, and amino acids (proteins), thus it is incorporated into all plant and animal tissues. Since the nitrogen is an essential nutrient for all life forms, availability of nitrogen in various forms is essential. In the environment, the various forms of nitrogen can be converted to one another by nitrogen cycle. The basic processes that occur in the nitrogen cycle are nitrification, denitrification, and nitrogen fixation and all are biologically mediated in nature. The major forms of nitrogen containing compounds in fresh water bodies include dissolved molecular nitrogen (N_2), ammonia nitrogen (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-), and number of organic compounds such as

amino acids, amines, nucleotides, proteins, and humic compounds with low nitrogen content. Among these nitrate is the significant nitrogen specie that causes inverse health impacts on humans. Due to the known adverse health impacts, nitrate is regulated by the U.S. EPA with the MCL of 10 mg/L as N. Various engineered treatment alternatives are available to eliminate nitrate contamination in drinking water with major drawbacks generally related to the cost. Biological denitrification has been applied as one of the most effective treatment alternatives in terms of cost and removal efficiency.

Perchlorate is both naturally occurring and a man-made anion with high solubility. Even though natural sources of perchlorate have been identified, the major sources of perchlorate contaminations are anthropogenic. Perchlorate is an endocrine disruptor and affects the function of thyroid gland. Perchlorate has not been regulated by the U.S. EPA but it is in CCL. Individual states have already issued advisory limits for perchlorate levels in surface waters. Engineered treatment approaches have been developed for perchlorate removal with major drawbacks mostly related with the cost.

By the early 1960s, pesticides started to be used widely for agricultural applications across the U.S. The drastic increase in the pesticide use up to 1980s made these chemicals one of the most important contaminants in surface water by mostly runoff from the agricultural fields. Numerous studies have been conducted by governmental agencies reporting pesticide occurrences with high concentrations in surface and ground waters. Atrazine, alachlor, and metolachlor have been reported as most widely used in agriculture and most commonly detected pesticides in surface and ground waters. Due to the reported possible adverse health impacts on humans, atrazine and alachlor are regulated by the U.S. EPA with the MCLs of 3.0 μg/L and 2.0 μg/L,

respectively. Even though metolachlor has not been regulated yet, studies about this herbicide continue and the U.S. EPA has taken the first step to regulate metolachlor levels in drinking water by placing it on the CCL. Conventional water treatment practices have been shown as ineffective on pesticide removals. There are advance water treatment alternatives for eliminating pesticide contamination in drinking water, however, the high cost associated with these techniques requires more cost effective treatment alternatives to be applied.

WTRs are drinking water treatment process byproducts. The high Al and Fe content of WTRs lead to their use as a novel sorbent for phosphorus in soil, biosolids, and surface runoffs. Other possible beneficial uses of WTRs have been recently documented for perchlorate and arsenic removal. It is a known fact that WTRs have high organic carbon content but the possible techniques to utilize the organic carbon associated with WTRs have not been studied yet.

RBF and ARR have been documented as semi-passive, natural, cost effective treatment alternatives for various contaminants. Aerobic and anoxic/anaerobic characteristics of these natural systems promote microbial activities to biodegrade and use lots of contaminants from surface waters. The characteristic and levels of carbon is crucial for effective remediation of contaminants throughout RBF and ARR applications. Except our study, application of RBF and ARR systems in series has not been reported. We believe the removal of easily biodegradable carbon through the RBF system will limit the bioremediation efficiency of ARR system. The removal capability of RBF and ARR on phosphorus has not been documented presumably due to the low sorption capacities related to alluvial sand and insufficient microbial activity to achieve

satisfactory biological uptake of phosphorus. Beside the enhancing phosphorus adsorption capability, amending the ARR system with WTR will provide easily biodegradable organic carbon to promote biological activity, thus enhanced bioremediation efficiencies for the contaminants of concern.

CHAPTER III: PHOSPHORUS REMOVAL DURING RIVERBANK FILTRATION AND AQUIFER RECHARGE AND RECOVERY: BENEFITS OF WATER TREATMENT RESIDUAL

(PAPER WILL BE SUBMITTED TO A JOURNAL)

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Abstract

Riverbank filtration (RBF) and aquifer recharge and recovery (ARR) are well known natural, semi-passive, treatment techniques. An on-going municipal project envisions the implementation of these systems in series to obtain high quality water for long-term storage in a reservoir. Phosphorus loads to surface waters can result in severe degradation of water quality in downstream impoundments. This study focuses on the removal efficiency of phosphorus through a multi-barrier, sequential RBF and ARR system. The study includes the monitoring of a pilot scale field RBF system and column simulation studies. Results of the study indicated that the ability of the system to remove phosphorus is not sustainable and limited by the sorption capacity of the alluvial sand and minor biological activity. As a novel sorbent for phosphorus, the possible benefits of water treatment residual (WTR) were tested by amending the ARR infiltration system. Phosphorus levels were reduced less than the method detection limit of 0.03 mg/L with WTR amendment column simulation studies. Once the amendment design is optimized, WTR can be used to enhance the system's ability to remove phosphorus for long term, effective removal of this important nutrient.

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III.1. INTRODUCTION:

Finding new water sources to support the population growth is one of the major dilemmas of modern cities. Generally, the most feasible approach is to exploit the closest available sources. However, the impaired quality of the source may require advanced treatment applications and a high cost is often associated with them.

The City of Aurora (CO) is facing a similar problem. After gaining water rights on South Platte River, the city is considering an innovative approach to cut the high cost associated with the source water treatment. As part of the Prairie Waters Project, they envisioned the application of sequential riverbank filtration (RBF) and aquifer recharge and recovery (ARR) as a semi-passive, multi-barrier preliminary treatment technique before collecting the treated water in a terminal reservoir (Figure III.1). The City's major concern is the efficiency of a sequential RBF – ARR application in terms of the removal of nutrients, such as phosphorus, nitrogen, and carbon before storing the water. Among these contaminants, phosphorus is the primary focus of this paper.

Phosphorus is an important element for all life forms. It is a key part of the structural framework of nucleic acids, adenosine tri-phosphate (ATP), adenosine di-phosphate (ADP), and phospholipids in microorganisms. Within the major nutritional and structural components, phosphorus is the least abundant and limits the microbial growth in fresh water bodies (Williams, 2001).

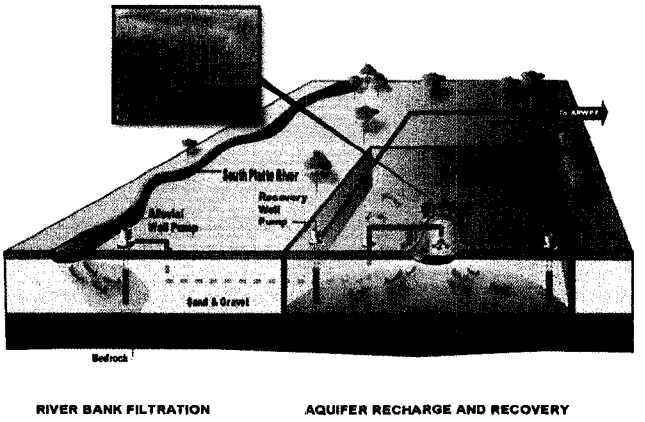


Figure III.1: Sequential riverbank filtration (RBF) and aquifer recharge and recovery (ARR) (Courtesy of CH2MHill, Denver, CO).

The majority of phosphorus loads to surface waters come from anthropogenic origins of point sources such as wastewater treatment plant discharges and confined livestock operations, and non-point sources such as soil erosion, runoff from agricultural fields, lawns and gardens, small livestock operations, and fertilizer applications (Pierzynski et al., 2005).

Even though phosphorus does not have a known adverse health effects on humans, the phenomenon that is known as eutrophication, "an increase in the fertility status of natural waters that causes accelerated growth of algae or water plants", (Pierzynski et al., 2005) promotes the growth of large amounts of plant, algae, and bacterial biomass that interfere with dissolved oxygen content in fresh water bodies and causes taste and odor problems in water. Eutrophication does not accelerate under natural conditions, since the biological productivity is limited by the availability of phosphorus.

The U.S. EPA suggested that the total phosphate levels should not exceed 25 μg P/L to prevent biological nuisances in lakes and reservoirs. Also 50 μg P/L of total

phosphate is the critical limit for any streams at the point they enter any lake or reservoirs (U.S. EPA, 1986). Even though phosphorus discharge limits have not yet been regulated, a desired goal for point discharges to lakes, reservoirs, and streams is suggested as total phosphate levels of <100μg P/L (U.S. EPA, 1986). Also, individual states have recently started studies to regulate nutrient loads to surface waters to improve freshwater qualities for multi-purpose uses (CWQCD, 2006).

Riverbank filtration (RBF) and aquifer recharge and recovery (ARR) processes are similar natural, semi-passive treatment approaches. Both techniques have been used for centuries in primitive ways (Baker, 1948; Pyne, 1995). Modern RBF technique has been successfully used for the production of drinking water for more than a hundred years in Europe and in the last 50 years in the US. (Kuenhn and Mueller, 2000; Ray et al., 2002a). ARR applications are in use in the United States, Canada, Israel, England, The Netherlands, and Australia (Pyne, 1995).

Physical, chemical and biological processes play an important role to improve the water quality through RBF. Physical removal occurs at the soil pores as well as electrostatic attachment to soil particles (Ray et al., 2002b). The major chemical processes include adsorption, ion exchange, and chemical reactions (Kuenhn and Mueller, 2000; Ray et al., 2002b; Kelly and Rydlund, 2006). Physical and chemical characteristics of the soil influence ion exchange capacities causing some soil types to have a very high capacity for ion exchange and adsorption, while others are very limited (Kuenhn and Mueller, 2000). Varying pH and oxygen concentrations affect acid/base dissociation reactions as well as the oxidation state of many compounds (Kuenhn and Mueller, 2000; Ray et al., 2002a). Microbiological activities involve the degradation of

hydrophobic compounds that are adsorbed to soil surfaces and the consumption of organic carbon through various heterotrophic metabolic activities. Most of the microbial activity takes place at the interface between the riverbed and the aquifer (Kuenhn and Mueller, 2000; Ray et al., 2002a). The nutrients in the river water encourage the growth of a biofilm. Flow rates can be similar to those of slow sand filters which means that riverbank filtration may be comparable to or more effective than a slow sand filter. The biofilm is responsible for the initial degradation and removal of organic carbon, nutrients, and pathogens as well as micronutrients (Kuenhn and Mueller, 2000; Ray et al., 2002b; Kelly and Rydlund, 2006).

As in RBF, physical, chemical, and biological processes are the key elements of ARR applications. Microorganisms are present in aquifers to depths of at least 1500 feet (Pyne, 1995), therefore, ARR can result in biological degradation, as well as physical and chemical removal mechanisms, providing there are sufficient electron donors.

The major advantages of RBF and ARR applications are; seasonal changes of influent water quality due to concentration and temperature do not alter the RBF efficiency (Pyne, 1995). RBF and ARR systems achieve pathogen removal, particle removal, dissolved organic matter reduction, and nitrogen reduction, thus, reduction in disinfection by-product formation, and production of biologically stable water.

Poor phosphorus sorption capacity of sandy soils is well documented (He et al., 1999; Del Bubba et al., 2003). Removal of phosphorus through RBF and ARR has not been studied in literature, however, the major phosphorus removal mechanisms are assumed to be the sorption on alluvial material and biological uptake. As a similar natural technique to RBF and ARR, research on constructed wetlands showed that P sorption

capacities of natural soils are limited and biological uptake is the main removal mechanism (Del Buba et al., 2003).

Drinking water treatment process byproducts, either dried solids or sludge, are broadly classified as water treatment residuals (WTR) and primarily consist of sediment, aluminum and/or iron (hydr)oxides, activated carbon and polymer (Elliott and Dempsey, 1991). Instead of being disposed of in landfills, using WTR as a P sorbent provides economical and environmental benefits to communities and municipalities (Dayton and Basta, 2003). Recent research has focused on the use of WTR as a cost effective amendment to reduce soluble P in soils and runoff (Haustein 2000, Ippolito 2003, Gallimore 1999).

Sorption mechanisms and kinetics of phosphorus on WTR were studied for short (Dayton et al., 2003, Dayton and Basta, 2005) and long term (Makris et al., 2004; Markis et al., 2005). Short term studies indicated that there is a strong correlation between the oxalate extractable (amorphous) Al and Fe content and maximum P sorption capacity. Intraparticle diffusion of P into amorphous Al and Fe hydroxide particles has shown to be the main mechanism with negligible amounts of desorption from the WTR.

Multiple studies were conducted to evaluate either RBF or ARR as independent treatment approaches. Apart from those associated with this project, application of RBF-ARR system in series has not been studied. The overall project focuses on the advantages and disadvantages of implementing a water treatment strategy of RBF followed by ARR as a two-barrier preliminary treatment step for the production of high quality drinking water.

Due to the possible limitations of a sequential RBF-ARR approach in phosphorus removal water treatment residual (WTR) was explored as an amendment. This alternative approach includes the amendment of the infiltration gallery of ARR with WTR. The objectives of this study are (i) document the removal efficiency of phosphorus through RBF-ARR multi-barrier treatment approach, (ii) assess possible benefits of amending the ARR infiltration process with WTR for phosphorus removal. (iii) evaluate the phosphorus levels in WTR amended system and confirm the levels are suitable for suggested surface storage total phosphate level of <0.025 mg P/L.

III.2. MATERIALS AND METHODS:

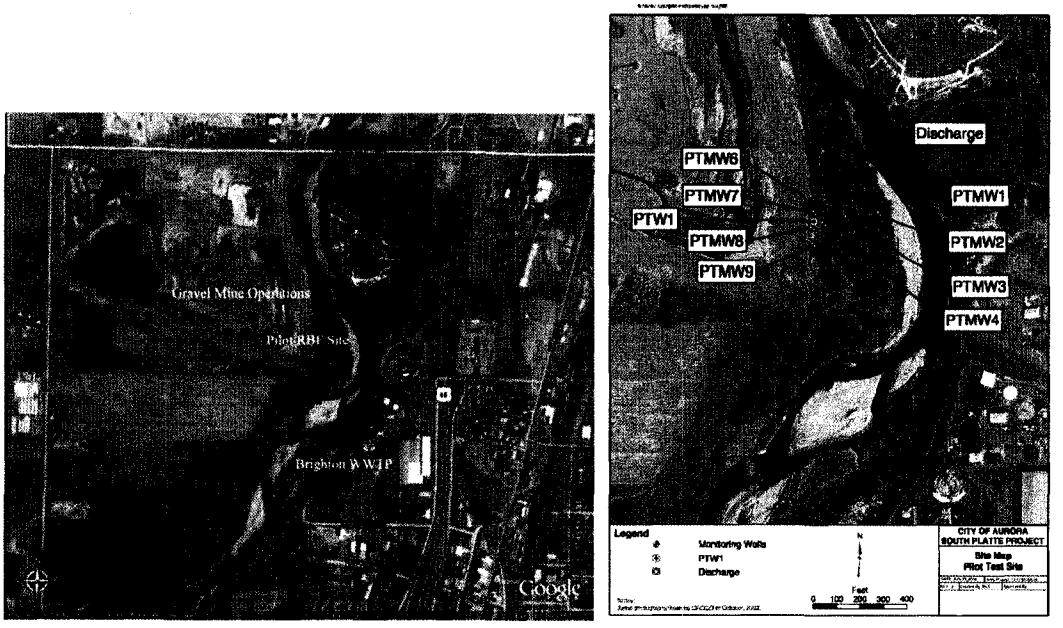
Riverbank Filtration Field Study

The RBF field study site is located north of City of Brighton, CO, between the South Platte River and a non-operational gravel mine. The gravel mine is surrounded by a slurry wall to keep groundwater and river water out of the site, isolating the west shore from surrounding groundwater, thus, creating a convenient study site. The production well (PTW-1) and the monitoring wells (PTMW-2, PTMW-3, PTMW-4) are located on the west shore between the slurry wall and the river. PTMW-1 is an imaginary well where the river samples were collected. Production and monitoring wells were installed in November 2004 and the RBF system has been in continuous operation since December 2004 except for short periods of time during the power outages. Figure III.2 shows the riverbank filtration site, the gravel mine, and production and monitoring wells.

The production well, PTW1, is 18 inches in diameter and is constructed with a stainless steel casing, and pumps water with the flow rate of 450gpm. All monitoring

wells are 2.0-inch, PVC wells. Construction details for production and monitoring wells are given in Table III.1 below.

South Platte River, monitoring wells, and the production well were monitored twice a month between February 2005 and September 2006 for phosphorus. River samples were collected via grab samples. Monitoring wells were sampled by using an EPA approved low-flow method with dedicated Teflon tubing, and a peristaltic pump. The production well was sampled from a port that is installed in the discharge piping near the well. Samples were collected in HDPE bottles and kept in a cooler during the transport. Samples were filtered with 0.45μm glass fiber filters and kept at 4°C before analysis.



(a) (b)

Figure III.2: (a) Aerial photo of RBF field study site generated using Google Earth (Newton,2007) (b) RBF field study site with production and monitoring wells, photo by Tetra Tech RMC (Longmont, CO).

Table III.1: RBF field study well construction details.

Well ID	Well Diameter (in)	Total Well Depth (ft)	Depth of Water (ft)	Distance form River (ft)	Residence Time (days)
PTMW-2	2	32	17	137	10
PTMW-3	2	30	14	258	15
PTMW-4	2	30	14	374	22
PTW-1	18	45	33	418	25

Pilot Scale Column Studies:

For all column studies, 4-foot acrylic columns with an internal diameter of 6 inches were used. Each column has 3 sampling ports, which are 1 foot apart, on the side of the column. Sampling ports are made from stainless steel tubing and they reach to the center of the column cross section for representative sample collection. Each sampling port is screened at the end to prevent column media loss from the ports. To distribute the inflow equally to the column, column caps are built with multiple injection points (Figure III.3). During the course of the study, all columns were kept at 60° F and wrapped with aluminum foil to prevent photosynthetic microbial activity.

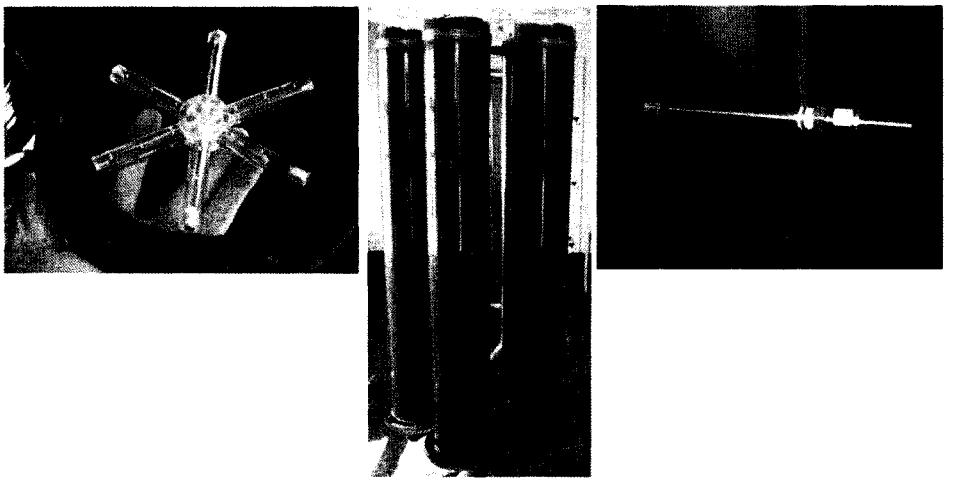


Figure III.3: Column setup for column simulation studies.

Alluvial sand that was used in the column media was obtained from the west river bank at the RBF field study site approximately 2 feet under the surface. Alluvial sand then was sieved with no.10 (<2mm) sieve to obtain uniform particle size. Water treatment residual (WTR) that was used in the column simulation studies was obtained from the City of Wellington Water Treatment Plant, CO (Table III.2). Aluminum based WTR was first dried in the oven at 180°C overnight then ground and sieved with no.10 (<2mm) to be consistent with the alluvial sand size distribution.

All columns were acclimated by feeding the columns with a flowrate of 1 mL/min from bottom to top for 15 days, followed by 3 mL/min of top to bottom flow for 30 days. Feed water was different for each specific study. Preconditioning steps were repeated before each column simulation studies. To feed the columns, peristaltic pumps were used with Teflon tubing throughout the study.

Table III.2: General chemical properties of WTR.

WTR Source	pH	EC	Total						Oxalate Extractable		
			P	Al	Fe	Ca	Mg	K	P	Fe	Al
		mmhos/cm	%	%	%	%	%	%	%	%	%
	7.4	1.2	0.113	15.08	0.586	0.861	0.043	0.161	0.0123	0.0887	14.47
Wellington Water Treatment Plant Wellington, CO					Total						
	Sand	Silt	Clay	Texture	C	TOC	$CaCO_3$	CO_3-C			
	%	%	%		%	%	%	%			
	96	2	2	Sand	16.33	16.07	2.21	0.26			

Samples were collected in HDPE bottles and kept in a cooler during the column simulation studies. Samples were filtered with 0.45μm glass fiber filters and kept at 4°C before analysis.

RBF Column Simulation Study:

Three RBF columns (C-RBF, C-RBF-Control, C-RBF-WTR) were built for the RBF column simulation study. Columns were monitored twice a month for phosphorus from all sampling ports and the effluent between June 2005 and Decmber 2006. Table III.3 summarizes the content of the column media and the operating conditions. Figure III.4 gives a sketch of the experimental column setup. Following the initial preconditioning step described above, C-RBF was fed with 1mL/min (5 days of hydraulic residence time) of river water to simulate RBF conditions. C-RBF-Control, an abiotic control column, was fed with 1 mL/min of 2mM sodium azide spiked river water to prevent microbial activity in the column. To observe the possible benefits of water treatment residual on phosphorus removal, C-RBF-WTR was fed with 1 mL/min of river.

Table III.3: RBF column simulation study: Column media content and operating conditions.

	RBF Column (C-RBF)	**Abiotic Control Column (C-RBF-Control)**	**RBF Column amended w/ WTR (C-RBF-WTR)**
Media	Natural alluvial sand (sieved with no.10 sieve)	Natural alluvial sand (sieved with no.10 sieve)	70% v/v natural alluvial sand and 30% v/v WTR (sieved with no.10 sieve)
Condition	Wet/saturated	wet/saturated	wet/saturated
Media Mass in Column	Sand = 32.5kg	Sand = 32.5kg	Sand = 21.6kg WTR = 10.6kg Total = 32.2kg
Feed water	South Platte River	South Platte River Spiked with 2mM Sodium Azide	South Platte River
Flow Rate	1mL/min	1mL/min	1mL/min
HRT	5 days	5 days	5 days

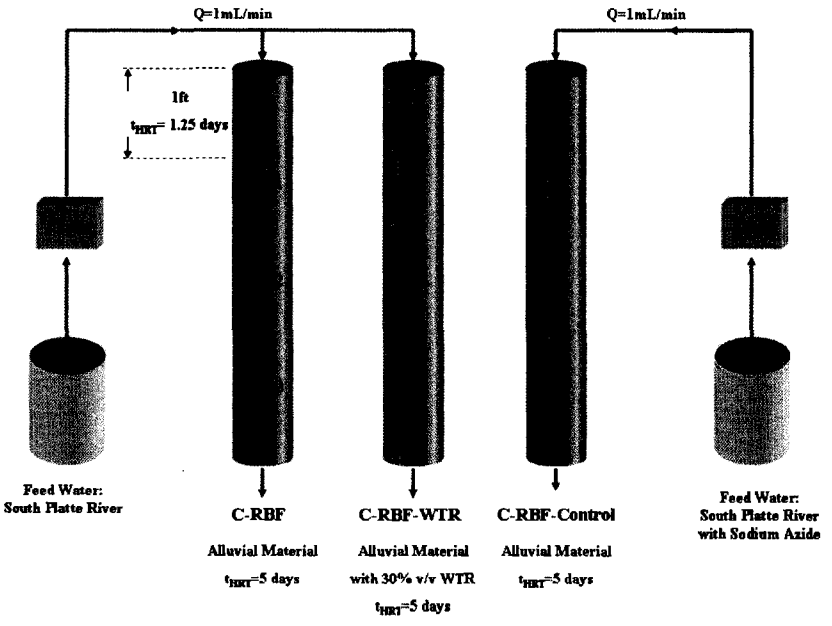


Figure III.4: RBF column simulation study experimental setup.

ARR Column Simulation Study:

An ARR column simulation study was conducted by using RBF treated production well (PTW-1) water as the feed water. Columns that were used for RBF column simulation studies were acclimated with production well water according to the procedure described above and were used in this study. Columns (C-ARR, C-ARR-Control, C-ARR-WTR) were sampled monthly between February 2006 and October 2006. The content of the column media and the operating conditions are summarized in Table III.4 below. Figure III.5 shows a sketch of the experimental column setup. The C-ARR column was used to simulate ARR conditions and the column was fed with 0.2mL/min of production well water. With this flow rate, the hydraulic retention time was 25 days. To observe the removal efficiency of phosphorus under abiotic conditions, the

C-ARR-Control column was fed with 0.2mL/min of 2mM sodium azide spiked production well water. Under these feed conditions, the hydraulic retention time was 25 days. To understand the benefits of alum based water treatment residual on phosphorus removal, column C-ARR-WTR was fed with 1mL/min of production well water. C-ARR-WTR was sampled from all sampling ports and the effluent, whereas, C-ARR and C-ARR-Control were sampled from the effluent port only.

Table III.4: ARR column simulation study: column media content and operating conditions.

	ARR Column (C-ARR)	**Abiotic Control Column (C-ARR-Control)**	**ARR Column amended w/ WTR (C-ARR-WTR)**
Media	Natural alluvial sand (sieved with no.10 sieve)	Natural alluvial sand (sieved with no.10 sieve)	70% v/v natural alluvial sand and 30% v/v WTR (sieved with no.10 sieve)
Condition	wet/saturated	wet/saturated	wet/saturated
Media Mass in Column	Sand = 32.5kg	Sand = 32.5kg	Sand = 21.6kg WTR = 10.6kg Total = 32.2kg
Feed water	Production Well Water (PTW-1)	Production Well Water (PTW-1) Spiked with 2mM Sodium Azide	Production Well Water (PTW-1)
Flow Rate	0.2mL/min	0.2 mL/min	1mL/min
HRT	25 days	25 days	5 days

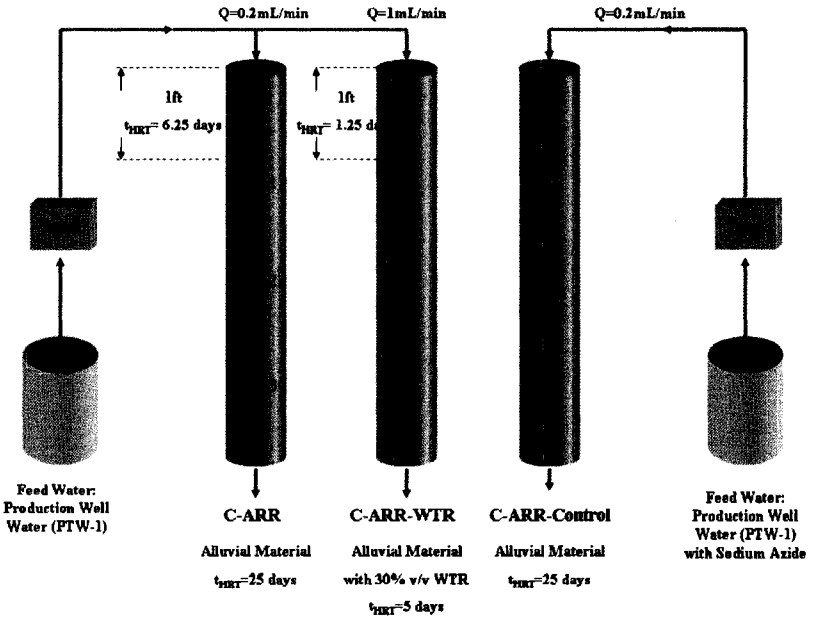


Figure III.5: ARR column simulation study experimental setup

Sequential RBF – WTR Amended ARR Column Simulation Study:

A sequential RBF – WTR amended ARR column simulation study was conducted to understand the efficiency of the system in terms of phosphorus removal. During this study, RBF treated production well (PTW-1) water was used as the feed. Columns that were used for ARR column simulation studies were acclimated with production well water as the procedure described above and were used in this study. An additional amended abiotic control column (C-ARR-WTR-Control) was built and was acclimated as others. Operation of columns (C-ARR-WTR, C-ARR, C-ARR-WTR-Control, C-ARR-Control) began in March 2007 and columns were sampled monthly between May 2007 and July 2007. The composition of the column media and the operating conditions are summarized in Table III.5 below. Figure III.6 shows a sketch of the experimental column

setup. The top 1 foot media of C-ARR-WTR column was used to simulate the amended ARR infiltration basin and the C-ARR column was used to simulate the alluvial sand ARR part. C-ARR-WTR was fed with 1mL/min of production well water. After a foot media depth (port 1, C-ARR-WTR-1) water was withdrawn with a flowrate of 0.2mL/min and fed to the C-ARR column. Hydraulic retention times were 1.25 days and 25 days for C-ARR-WTR-1 and C-ARR, respectively. To observe the removal efficiency of phosphorus under abiotic conditions, an identical column set was used and fed with sodium azide spiked production well water. Samples were collected from C-ARR-WTR-1, C-ARR-WTR-4, C-ARR, C-ARR-WTR-1C, C-ARR-WTR-4C, and C-ARR-Control for both biotic and abiotic column setups.

Table III.5: Sequential RBF – WTR amended ARR column simulation study: Column media content and operating conditions.

	ARR Column amended w/ WTR (C-WTR-1) 1 ft media depth	**ARR Column amended w/ WTR (C-WTR-4) 4 ft media depth**	**ARR Column (C-ARR)**	**ARR Column amended w/ WTR Control (C-WTR-1C) 1 ft media depth**	**ARR Column amended w/ WTR Control (C-WTR-4C) 4 ft media depth**	**ARR Column Control (C-ARR-C)**
Media	70% v/v natural alluvial sand and 30% v/v WTR (sieved with no.10 sieve)	70% v/v natural alluvial sand and 30% v/v WTR (sieved with no.10 sieve)	Natural alluvial sand (sieved with no.10 sieve)	70% v/v natural alluvial sand and 30% v/v WTR (sieved with no.10 sieve)	70% v/v natural alluvial sand and 30% v/v WTR (sieved with no.10 sieve)	Natural alluvial sand (sieved with no.10 sieve)
Condition	wet/saturated	wet/saturated	wet/saturated	wet/saturated	wet/saturated	wet/saturated
Mass in Column	Sand = 5.4kg WTR = 2.65kg Total = 8.05kg	Sand = 21.6kg WTR = 10.6kg Total = 32.2kg	Sand = 32.5kg	Sand = 5.4kg WTR = 2.65kg Total = 8.05kg	Sand = 21.6kg WTR = 10.6kg Total = 32.2kg	Sand = 32.5kg
Feed water	Production Well (PTW-1)	Production Well (PTW-1)	C-WTR-1 Water	Production Well (PTW-1) (spiked with 2mM sodium azide)	Production Well (PTW-1) (spiked with 2mM sodium azide)	C-WTR-1C Water
Flow Rate	1mL/min	1mL/min	0.2 mL/min	1mL/min	1mL/min	0.2 mL/min
HRT	1.25 days	5 days	25 days	1.25 days	5 days	25 days

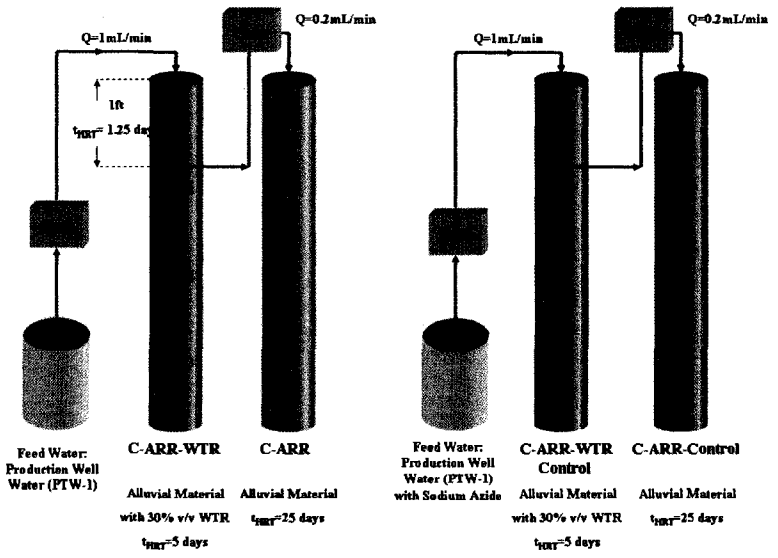


Figure III.6: Sequential RBF- WTR amended ARR column simulation study experimental setup.

Phosphorus Analyses:

Total reactive phosphorus ($PO_4^{3-}P$) analyses were conducted by Standard Method 4500-P-E the ascorbic acid method with the method detection limit of 0.03 mg/L. Colorimetric evaluation of phosphorus was made by using HACH DR/3000 Spectrophotometer (HACH Company, Loveland, CO). For every set of samples, 6 point calibration points were determined. With each set, adsorption readings of samples were taken as background response. Additionally, HPLC grade water samples were analyzed to assure the accuracy of the calibration standards.

The chemical characterization of WTR was conducted by Soil-Plant-Water Testing Laboratory of Colorado State University. The chemical characterization of WTR was conducted by EPA Method 3050 "Acid Digestion of Sediments, Sludges, and Soils" and EPA Method 6010 "Iductively Coupled Plasma Atomic Emission Spectroscopy".

III.3. RESULTS AND DISCUSSION:

III.3.1. Riverbank Filtration Field Study:

The riverbank filtration field study involved monitoring of the South Platte River, three monitoring wells and the production well for approximately 19 months for phosphorus. The following figure summarizes the 19 month study phosphorus levels from the RBF field study.

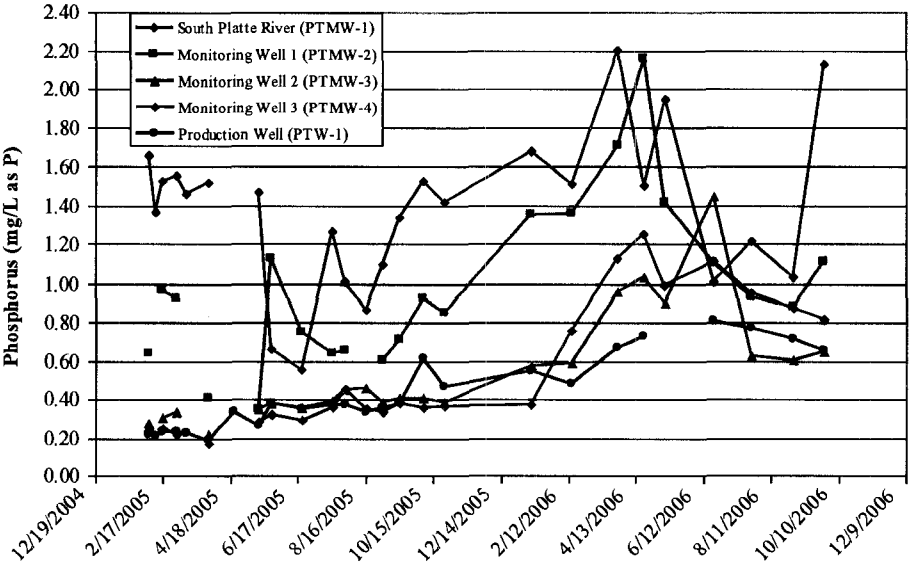


Figure III.7: RBF field monitoring study for phosphorus.

The phosphorus level in the South Platte River fluctuates throughout the year. The flow rate of the river is one of the major factors that affect the phosphorus level. The snow runoff season and the discharge from the Brighton WWTP directly affect the phosphorus levels in the river. During the monitoring study, the highest and lowest

phosphorus concentrations in the river were recorded as 2.21 mg/L as P in April, 2006 and 0.55 mg/L as P in June 2005, respectively.

Highly fluctuating phosphorus concentration in the river influences the phosphorus levels in the monitoring wells causing fluctuations there as well. Fluctuation in the phosphorus levels decreases with increasing retention times as it is seen in Figure III.7 toward PTMW-2 to the production well, PTW-1. The production well shows the most stable phosphorus levels compared to the river and the monitoring wells. At certain sampling events, as in April and June 2006, it was observed that the monitoring well phosphorus levels are greater then the river. This situation is likely due to the fact that the instant concentration decreases in the river show their effects after approximately 10, 15, 22, and 25 days in the monitoring wells PTMW-1, PTMW-2, PTMW-3, and the production well (PTW-1), respectively.

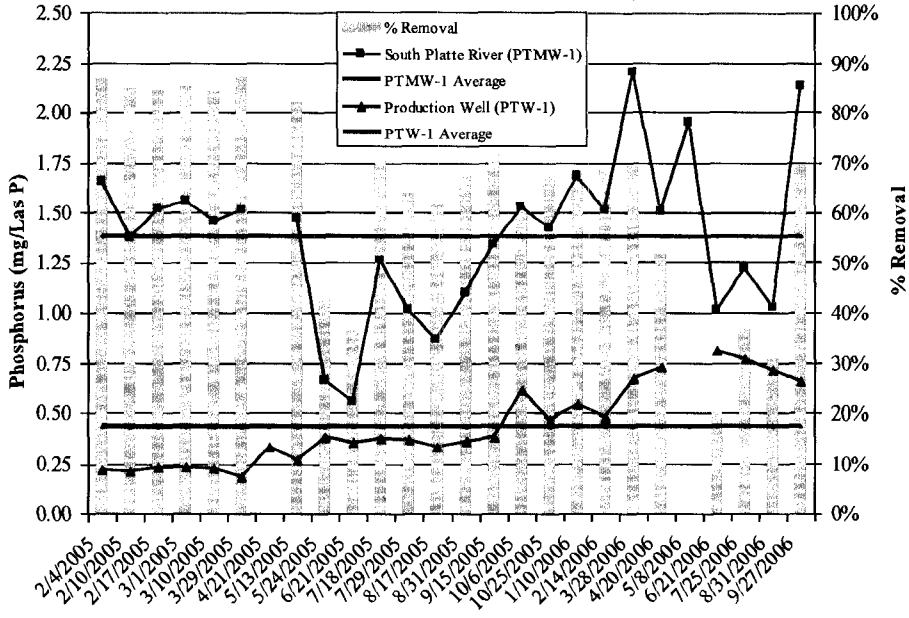


Figure III.8: Phosphorus levels in South Platte River and production well.

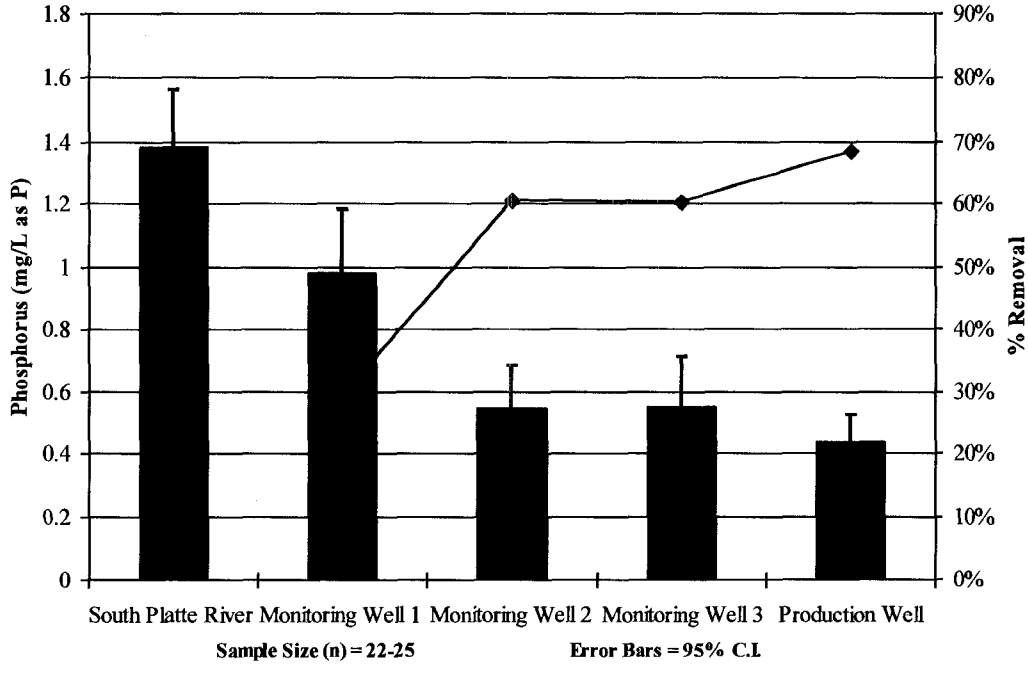


Figure III.9: RBF field study: Average phosphorus levels.

Figure III.8 and Figure III.9 show instantaneous and average phosphorus monitoring results and removal efficiencies, respectively. Phosphorus removal is observed to a certain extent during river bank filtration. When the overall system efficiency (Figure III.8) is considered, within 19 months, the average of 1.38 mg/L as P of phosphorus in the source water was reduced to 0.44 mg/L as P in RBF finished water with 69% removal. At the beginning of the study finished water phosphorus levels as low as 0.19 mg/L were achieved, however, with the observation of a constant increase, these levels were reached up to 0.81 mg/L close to end of the study. These results might be linked to the phosphorus increase in the source water; however, decrease in the removal efficiencies proves that the ability of the system to remove phosphorus is diminishing. Decreasing phosphorus removal efficiencies would be related with the limited phosphorus sorption capacity of alluvial sand (He et al., 1999; Del Buba et al., 2003). When alluvial sand reaches its maximum phosphorus sorption capacity, the only available phosphorus removal mechanism is the biological uptake, therefore the extent of the biological uptake determines the phosphorus removal efficiency in the system.

Even though considerable amount of phosphorus has is removed from the source water during the application of riverbank filtration, the levels that were observed are not suitable for surface storage (i.e. a reservoir). U.S. EPA suggests that the phosphorus level in a lake or a reservoir should not exceed 0.025 mg/L as P to prevent excessive biological activity (U.S. EPA, 1986). During RBF field study, the lowest finished water concentrations are ten fold greater than this level, and the average finished water phosphorus concentration is twenty fold larger than the suggested value. Furthermore, increasing phosphorus levels in the RBF treated water imply that the phosphorus sorption

capacity of the alluvial sand is reaching its maximum sorption capacity. The extent of biological phosphorus uptake was studied in column simulation studies to understand if the RBF system can achieve consistent and sustainable phosphorus removal by depending on the biological uptake mechanism.

III.3.2. Riverbank Filtration Column Simulation Study:

During the course of the study (5256 hours), columns were systematically sampled from the influent, the sampling ports, and the effluent. The column C-RBF was monitored for 5256 hours (315L, 14.18 bed volumes). There is a variation in the influent phosphorus concentration since the feed water is raw South Platte River water (Figure III.10). The C-RBF column achieves 28% phosphorus removal with the average influent concentration of 1.24 mg/L as P and the average effluent concentration of 0.9 mg/L as P (Figure III.11). Compared to the highly fluctuating phosphorus concentrations in the feed water, effluent of the column C-RBF shows a much more stable pattern with an observable increasing trend. Effluent phosphorus concentrations were doubled with the increase from 0.64 mg/L as P to 1.16 mg/L as P after 4872 hours of operation.

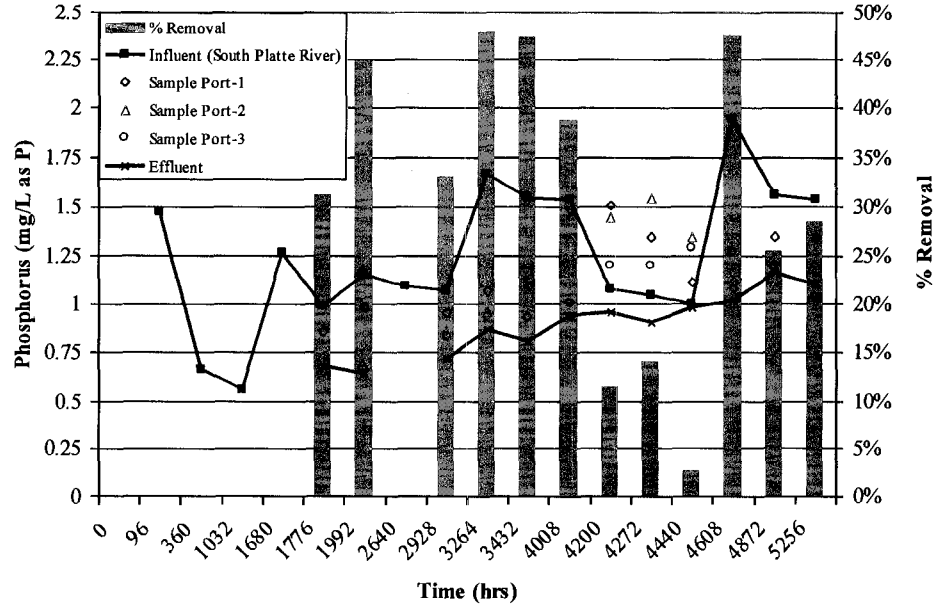


Figure III.10: RBF column simulation study: C-RBF.

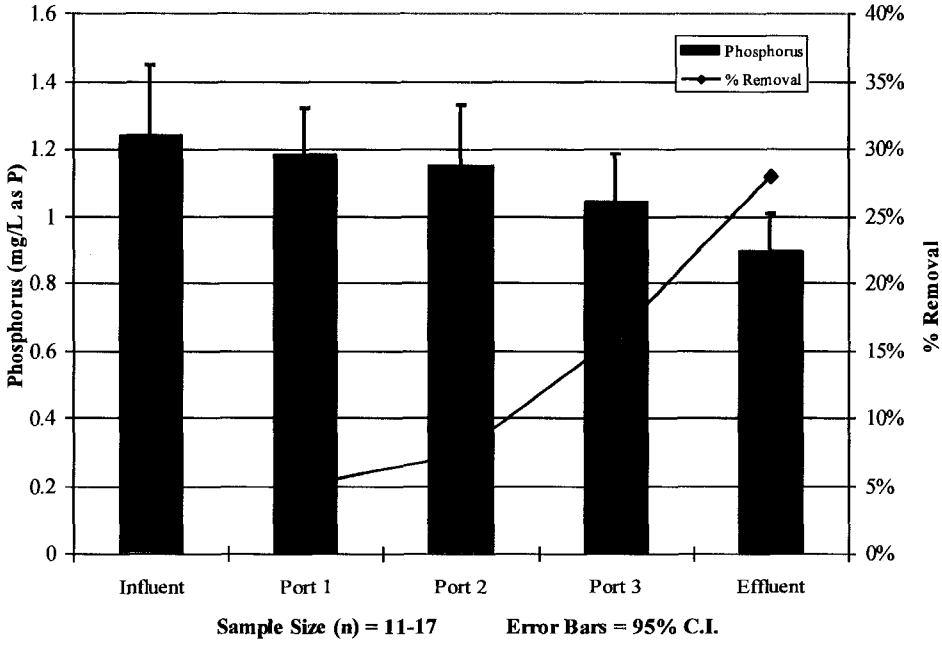


Figure III.11: RBF column simulation study: C-RBF average phosphorus levels.

Phosphorus removal that is achieved with C-RBF (28%) with the hydraulic residence time of 5 days, is very close to the removal efficiency that is observed in the first monitoring well (PTMW-2) of the RBF field study (29%) in terms of average phosphorus concentrations. C-RBF also shows an increasing trend in the effluent phosphorus levels. Increase in the effluent concentration is a clear indication of the sorption capacity of the alluvial sand is limited and is reaching its maximum capacity. Maximum sorption capacity is accepted as the point where the influent concentration is equal to the effluent concentration. Developing a breakthrough curve (C_{inf}/C_{eff} vs. run time) is one method to observe if the system is close to reaching its maximum sorption capacity. Due to the highly fluctuating influent concentration, application of some sort of normalization is needed. For this study, the breakthrough curve is established by drawing C/C_{ave} vs. run time, where C is the instantaneous effluent concentration from sampling ports and the effluent, and C_{ave} is the overall average influent concentration. The breakthrough curve for C-RBF is given in Figure III.12. After 4872 hours of run (292L, 13.14 bed volume), C-RBF effluent concentration that is normalized to overall influent concentration shows effluent as 93%, which is essentially the maximum sorption capacity.

To understand the effect of microbial uptake on phosphorus removal through RBF, abiotic control column, C-RBF-Control, was monitored for 5256 hours (315L, 14.18 bed volumes). The overall average phosphorus levels observed from the ports are less than the effluent levels due to the collection of less samples (3-4 samples). Overall removal efficiency in the C-RBF-Control (12%) column is less than C-RBF (28%) due to the lack of biological uptake. As it is seen in Figure III.13, and III.14, C-RBF-Control

column achieves 12.1% phosphorus removal with the average influent concentration of 1.31mg/L as P and the average effluent concentration of 1.15mg/L as P. Similar to C-RBF, the effluent P levels of C-RBF-Control has an increasing trend (Figure III.12) and the phosphorus concentration was increased from 0.79mg/L as P up to 1.51mg/L as P during the study. Due to the increasing effluent phosphorus concentrations, the breakthrough curve (Figure III.14) was drawn to test if the media has reached its maximum sorption capacity.

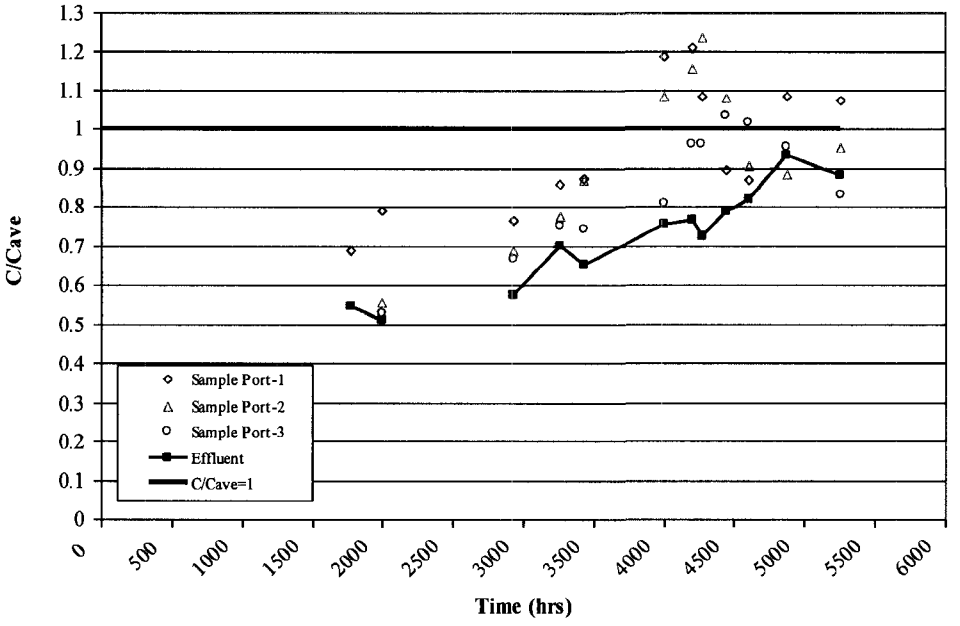


Figure III.12: RBF column simulation study: C-RBF breakthrough curve.

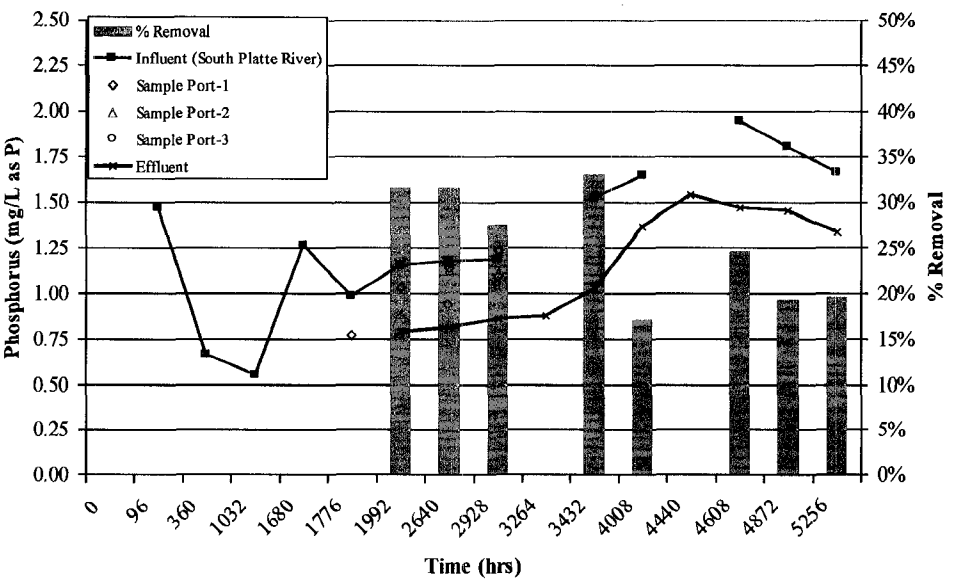


Figure III.13: RBF column simulation study: C-RBF-Control.

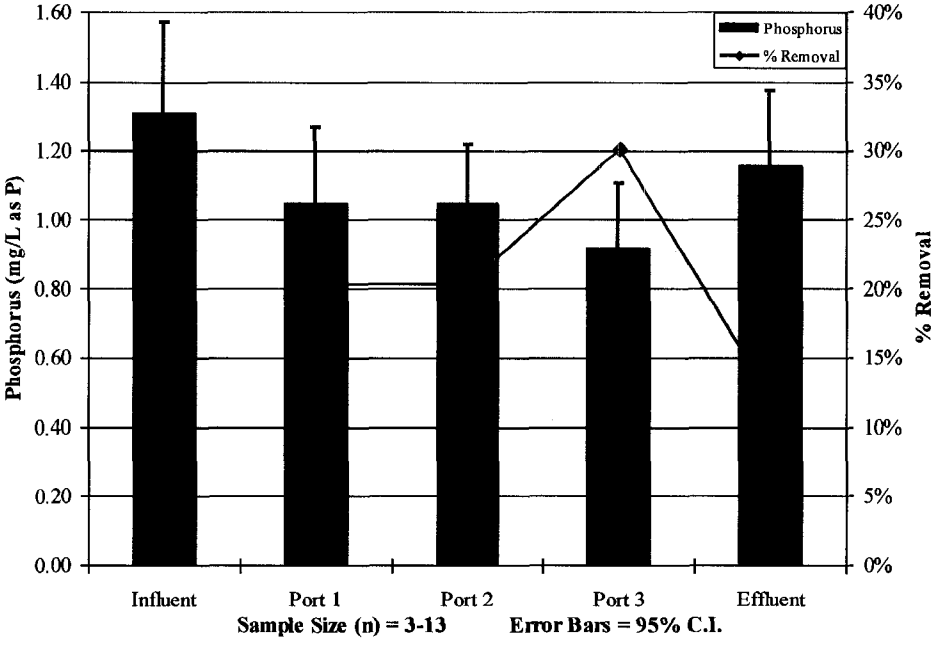


Figure III.14: RBF column simulation study: C-RBF-Control average phosphorus levels.

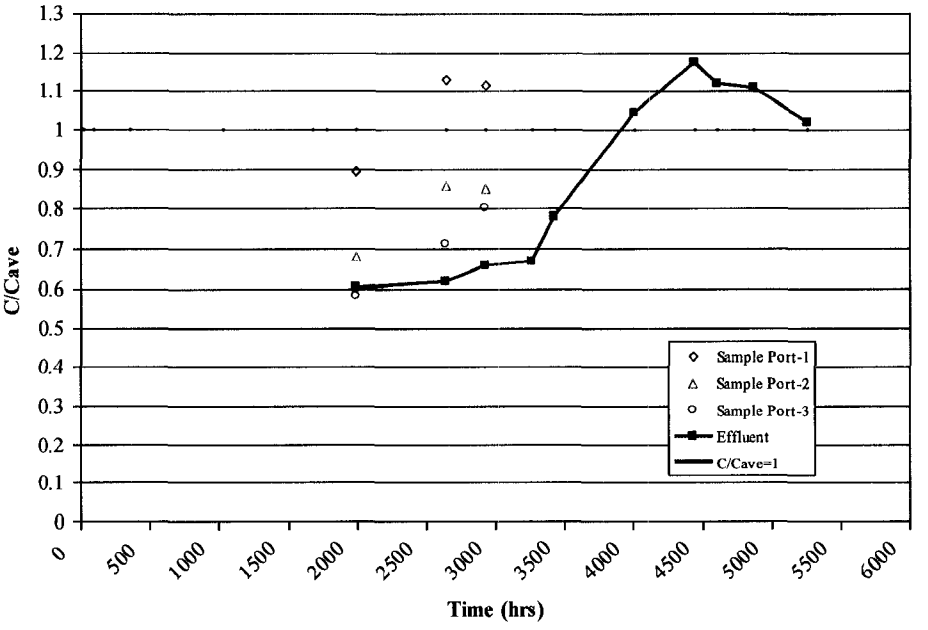


Figure III.15: RBF column simulation study: C-RBF-Control breakthrough curve

After 4008 hours of operation (240.5 L, 10.81 bed volume), the C-RBF-Control effluent concentration that is normalized to the overall influent concentration shows effluent as 104%, which is the maximum sorption capacity.

C-RBF-WTR was built to observe the benefits of WTR on phosphorus removal and monitored for 5832 hours (349L, 15.73 bed volume). Even though the influent phosphorus concentration is highly fluctuating, after a foot media depth (HRT = 1.25 days, port 1), stable phosphorus concentrations were observed close to the method detection limit of 0.03mg/L (Figure III.16). The average phosphorus concentrations throughout the study also show essentially 100% removal at and after 1 foot media depth (Figure III.17).

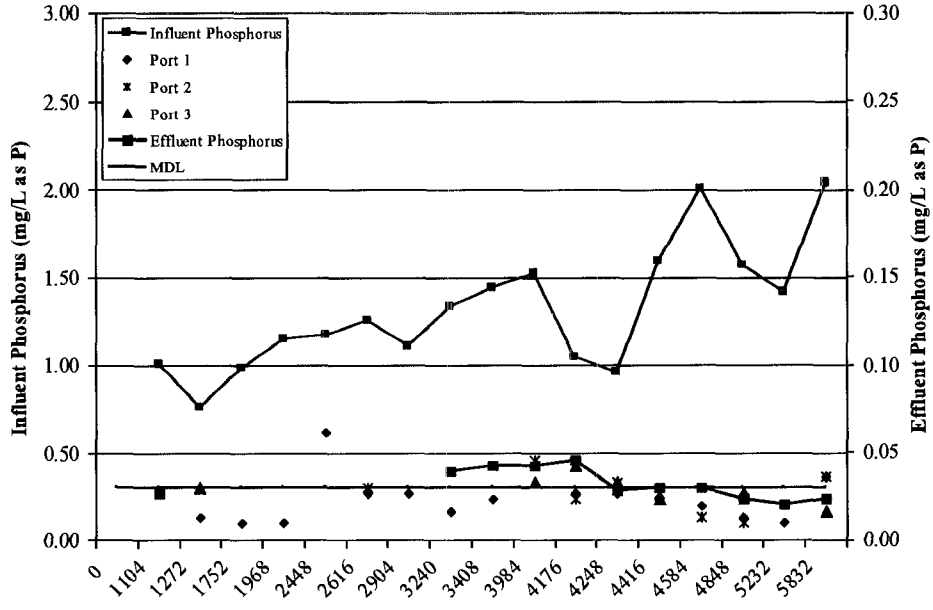


Figure III.16: RBF column simulation study: C-RBF-WTR

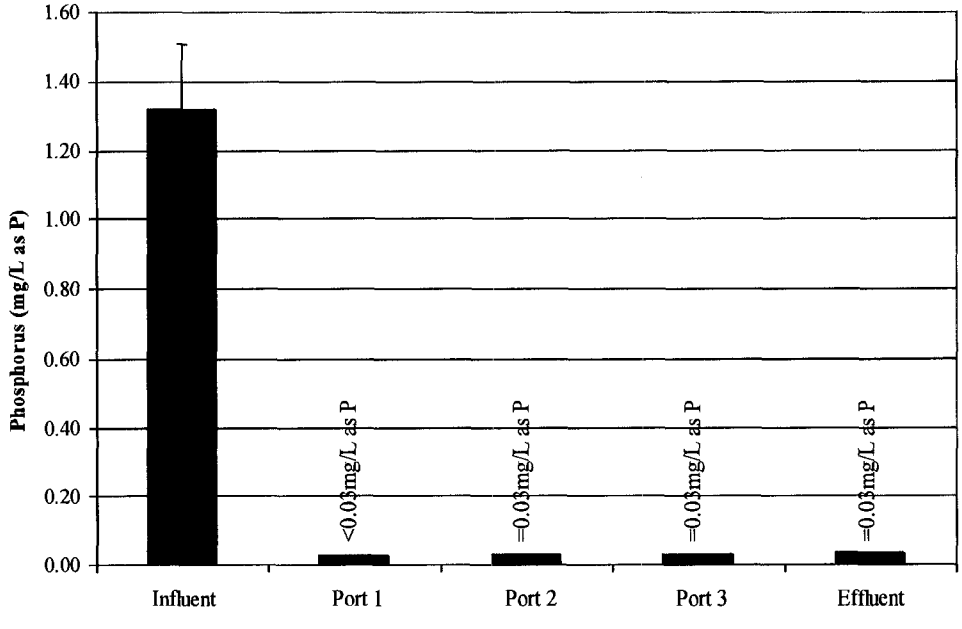


Figure III.17: RBF column simulation study: C-RBF-WTR average phosphorus levels.

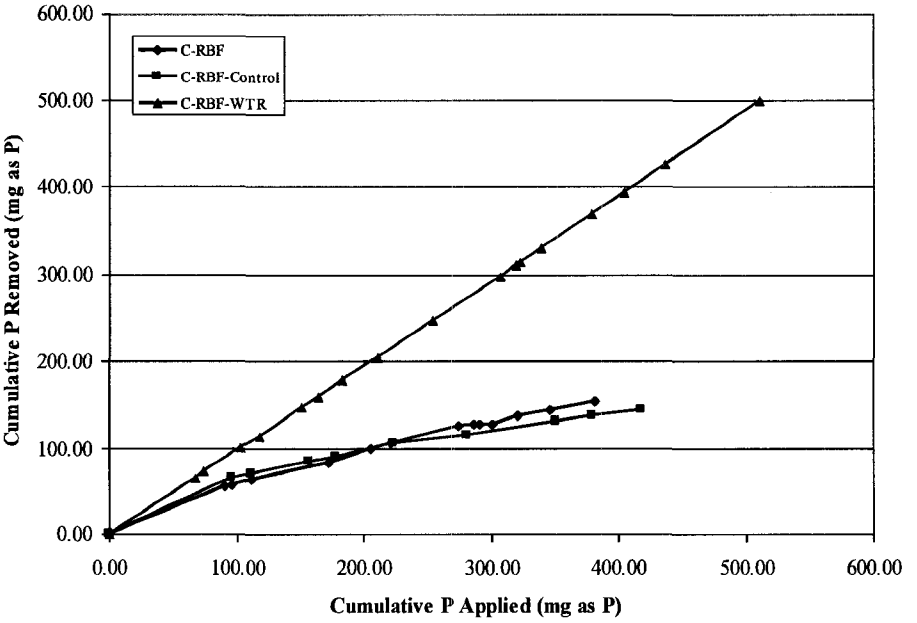


Figure III.18: RBF column simulation study: Cumulative phosphorus removed vs. cumulative phosphorus applied.

Table III.6: RBF column simulation study: Phosphorus sorption through columns

Column	C-RBF	C-RBF-Control	C-RBF-WTR (1ft media)
Column Media	Alluvial Sand	Alluvial Sand	Alluvial Sand (70%) WTR (30%)
Mass of Alluvial Sand (kg)	32.50	32.50	5.40
Mass of WTR (kg)	n/a	n/a	2.65
Media Mass (kg)	32.50	32.50	8.05
Run Time (hrs)	5256	5256	5832
Bed Volume (L)	14.80	14.80	15.73
Cumulative P Removed (mg)	154.85	145.20	498.71
Sorption Capacity of Sand (mg P/kg Sand)	4.46	4.47	4.46
Biological Uptake	0.30	n/a	0.30
Sorption by WTR (mg P/kg Sand)	n/a	n/a	177.59
Total Sorption Capacity (mg P/kg Media)	4.76	4.47	61.95

Phosphorus sorption limits for C-RBF, C-RBF-Control, and C-RBF-WTR columns are also shown in Figure III.18. As the column media reaches its sorption capacity, the graph begins to plateau. Columns C-RBF and C-RBF-Control demonstrate a plateau. C-RBF-Control reaches a plateau comparably faster than C-RBF due to the lack of biological phosphorus uptake. There is no sign of plateau for the column C-RBF-WTR so far and the column continues efficiently removing phosphorus.

Phosphorus sorption efficiencies of columns are given in Table III.6. The C-RBF column media is expected to reach its maximum sorption capacity that is 4.76 mg P/kg of alluvial sand. Sorption capacity of C-RBF-Control shows a slight difference of 4.47 mgP/kg alluvial sand. The difference, 0.3 mg P/kg alluvial sand is due to biological activity in the columns. This is a clear indication that the biological phosphorus uptake through RBF is negligible compared to the sorption on the alluvial sand surface. After a total run time of 5256 hours (14.80 bed volume) both RBF columns have reached their sorption limits, proving that RBF itself cannot be a sustainable barrier for phosphorus removal.

Column C-RBF-WTR provides complete phosphorus removal within the life span of this study. The column media (30% WTR, 70% alluvial sand) has sorbed 61.95mg P/kg media for 1 foot of media depth with the hydraulic retention time of 1.25 days. There is no indication that the column is breaking through and it is far away from reaching its maximum sorption capacity. This column was used for the following studies to test the ultimate phosphorus sorption capacity of WTR amendment.

III.3.3. Aquifer Recharge and Recovery (ARR) Column Simulation Study:

There columns, C-ARR, C-ARR-Control, and C-ARR-WTR were monitored to understand phosphorus removal under ARR conditions. Columns were sample at the effluents with retention times of 25 days except for column C-ARR-WTR, which was monitored from all sampling ports and the effluent with retention times of 1.25, 2.5, 3.75, and 5 days. Figure III.19 shows the average phosphorus concentration results for this study.

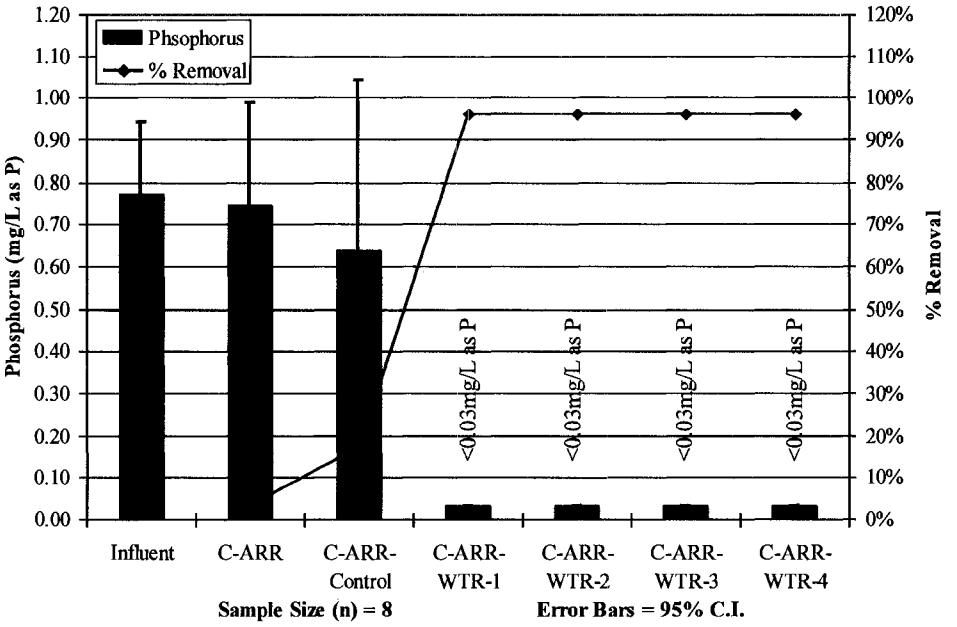


Figure III.19: ARR column simulation study: Average phosphorus levels.

Column C-ARR shows a slight phosphorus removal of 3.4% and the control column shows a higher removal efficiency of 17.5% with 95% confidence intervals. Due to the high uncertainty observed in the C-ARR and C-ARR-Control effluents a clear comparison cannot be made in terms of removal efficiencies. The C-ARR-WTR column

shows complete phosphorus removal even at the 1 foot media depth and all monitored concentrations for this column were less than the method detection limit of 0.03 mg/L.

III.3.4. Sequential RBF and WTR Amended ARR Column Simulation Study:

Figure III.20 and Figure III.21 show the average results for the actual and the abiotic control column setups, respectively. The average phosphorus level of 0.06 mg/L was measured in the WTR amended C-ARR-WTR-1 (C-ARR-WTR 1st port, 1ft media) column at the 1-foot depth port. Following the 1 ft media of C-ARR-WTR the flow was directed to C-ARR, thus receiving 0.06 mg/L of phosphorus load. The influent phosphorus level of 0.06 mg/L was increased to 0.17 mg/L after 25 days of residence time in the column C-ARR. The increase in phosphorus level within the C-ARR column is due to the possible desorption and dissolution of phosphorus from alluvial sand since the same column is used in RBF column simulation studies and reached its maximum sorption capacity. The high organic carbon load leaching from the WTR media (Chapter IV) may have been caused an anoxic/anaerobic condition thus affecting the sorption/desorption and dissolution mechanisms of phosphorus that was adsorbed on the alluvial sand media in C-ARR. At the end of 4 ft WTR amended media, phosphorus levels were reduced to less than the method detection limit of 0.03mg/L.

Similar results were observed from the control column setup. After the 1ft WTR amended media with a residence time of 1.25 days, phosphorus levels were reduced to less then 0.03mg/L. Following the feed of amended media treated water to C-ARR-Control column, the phosphorus level increased to 0.16mg/L. Again, chemical desorption-dissolution mechanism likely plays an important role on the increase of phosphorus levels during C-ARR-Control step.

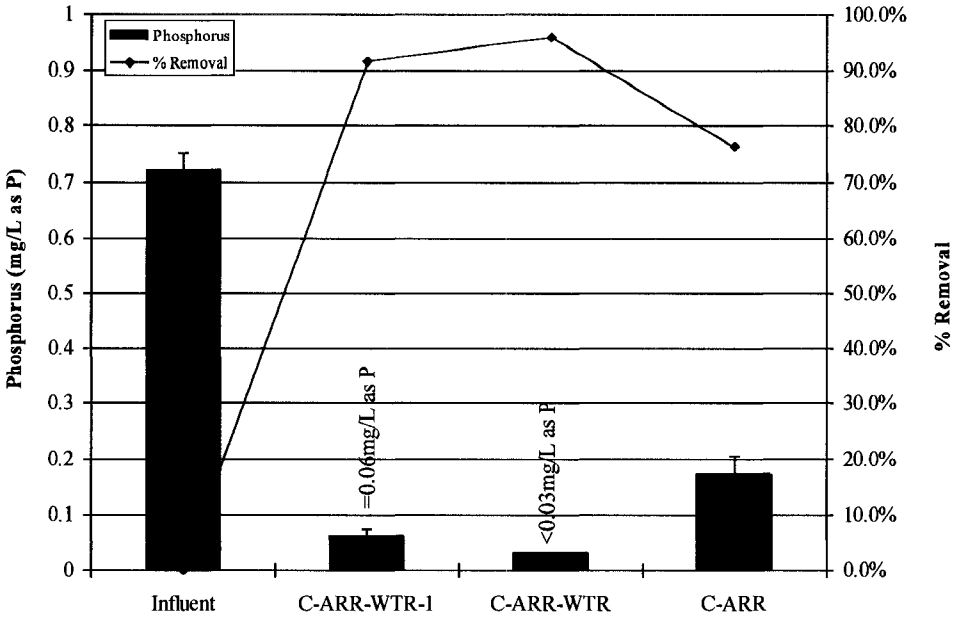


Figure III.20: Sequential RBF and WTR amended ARR column simulation study: Average phosphorus levels.

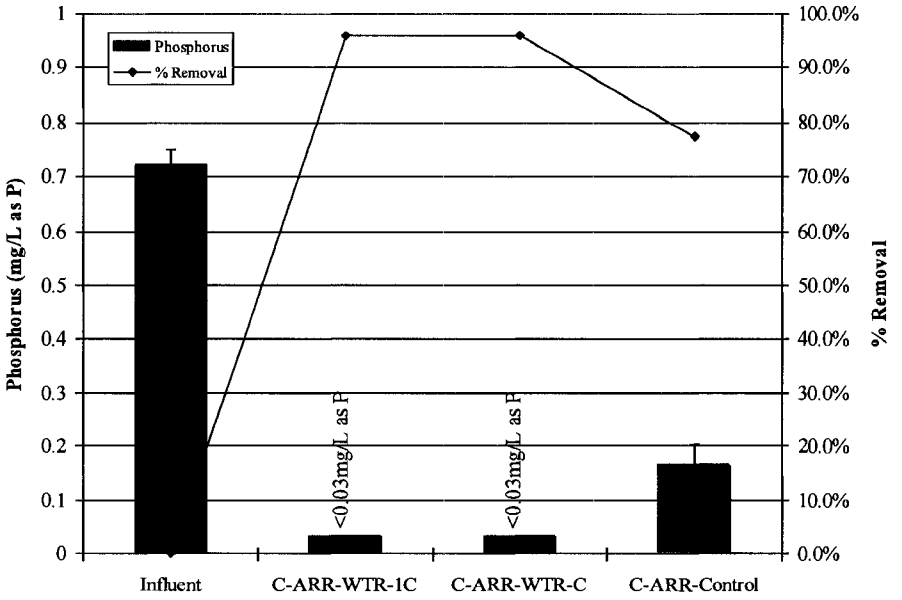


Figure III.21: Sequential RBF and WTR amended ARR column simulation study: Average phosphorus levels for control setup

III.3.5. Phosphorus Sorption Capacity of WTR:

Wellington Water Treatment Plant WTR (Table II.2) has a pH of 7.4 It has a high carbon content of 163.3g/kg and most of it is associated with the organic carbon content (160.7g/kg) coming from sediment organic matter, coagulation of algal cells, activated carbon, and organic polymers (Dayton et al. 2003). Total Al and Fe content of WTR is 150.8 and 5.86 g/kg, respectively. Low total Fe can be explained since an Al based coagulant is used in the treatment plant. Oxalate extractable (amorphous) Al and Fe content (Al_{ox} and Fe_{ox}) are 144.7 and 0.887 g/kg. The phosphorus level measured in the WTR is 0.123g/kg which is associated with the phosphorus removed during the water treatment processes. All chemical properties of Wellington Water Treatment Plant WTR are within the ranges previously reported by other studies except the oxalate extractable Al content which was higher than the values reported by Dayton et al. (2003) (Dayton et al., 2003; Makris et al., 2005).

The sorption capacity of WTR was monitored through out all column simulation studies. Essentially, 1 foot 30% (v/v) WTR amended media has decreased phosphorus concentrations to less then the method detection limit of 0.03 mg/L as P for approximately 2 years. The Figure III.22 shows the cumulative P removed vs. cumulative P applied during 2-year monitoring efforts. The graph has not reached a plateau, thus implying that the WTR has not reached its maximum sorption capacity. The calculation of WTR sorption capacity was calculated by using the mass of WTR in 1 ft media since complete phosphorus removal had been observed in the 1 ft media during the life span of the study. During the lifespan of the studies (Table III.7), 827.34mg of phosphorus has

been removed from the feed water and the calculated phosphorus sorption is 302.5 mg P/kg WTR.

Dayton et al. (2003) reported that the maximum phosphorus sorption capacities (P_{max}) of 21 Al based WTRs with Al_{ox} contents within the same size fraction (<2mm) we used in this study. The reported 15 hour batch test P_{max} and Al_{ox} values were ranging between 0.3 – 5.14 g/kg WTR and 1.33 – 48.7 g/ kg WTR, respectively. They reported a correlation between amorphous Al content. They reported a quadratic correlation between the P_{max} and Al_{ox} with R^2 of 0.69. Based on this relation P_{max} of the Wellington Water Treatment Plant WTR was calculated as 33.23 g P/kg WTR. Ippolito et al., (2003), reported 211 day batch test P_{max} values of 2.18-12.50 g/kg with Englewood Water Treatment Plant (CO) WTR containing total Al of 64.1 g/kg.

Even though extrapolating our Al_{ox} values from the previous studies may not be a reliable method to estimate a P_{max} value for Wellington WTR but it clearly indicates that the maximum sorption capacity of Wellington WTR has not been reached (302.5 mg P/kg WTR) within the 2 year life span of the study. Moreover, the 30% v/v amendment ratio and 1 ft media depth can be optimized in order to achieve a reliable and a long term phosphorus removal in sequential RBF-ARR system.

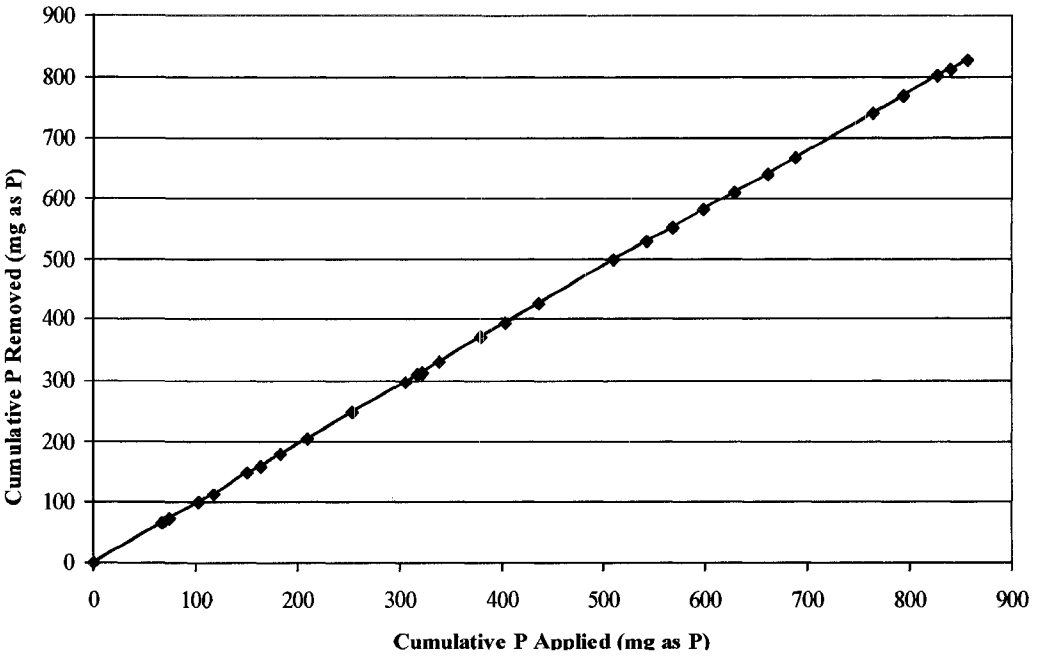


Figure III.22: Overall column simulation studies: Cumulative phosphorus removed vs. cumulative phosphorus applied.

Table III.7: Phosphorus sorption with WTR

Column	C-RBF-WTR (1ft media)
Column Media	Alluvial Sand (70%) WTR (30%)
Mass of Alluvial Sand (kg)	5.40
Mass of WTR (kg)	2.65
Media Mass (kg)	8.05
Run Time (hrs)	14064
Bed Volume (L)	37.94
Cumulative P Removed (mg)	827.34
Sorption Capacity of Sand (mg P/kg Sand)	4.46
Biological Uptake (mg P/kg Sand)	0.30
Sorption by WTR (mg P/kg WTR)	302.50
Total Sorption Capacity (mg P/kg Media)	102.78

III.4. CONCLUSION:

This study was conducted to understand the phosphorus removal efficiencies of natural semi-passive treatment approaches RBF and ARR in series. The RBF system was examined with pilot scale field and column simulation studies to understand the removal efficiency and mechanisms of phosphorus removal through the system. The ARR system was also examined with column simulation studies to estimate the phosphorus removal capability of the system. The benefits of using a WTR as a phosphorus sorbing media was also studied as an alternative amendment approach to sequential RBF – ARR treatment system. The following conclusions were drawn in the study;

- The pilot scale RBF field system was achieved an average phosphorus removal of 69% within 19-month monitoring effort.
- The phosphorus removal mechanism in the RBF field system was sorption on the alluvial sand and biological uptake by microbiota. The sorption capacity of the alluvial sand in RBF field study was reaching its maximum with the indication of increasing effluent phosphorus levels. To understand capacity and the extent of the sorption and biological uptake mechanisms, column simulation studies were conducted.
- The RBF simulation column, C-RBF, achieved an average phosphorus removal of 28% with the retention time of 5 days. This result was similar to the removal efficiency observed at the first monitoring well (PTMW-2) in RBF field study with the retention time of 10 days. C-RBF had reached its maximum sorption capacity of 4.76mg/kg sand within 4872 hours of monitoring effort.

- The RBF abiotic control column, C-RBF-Control, achieved an average phosphorus removal of 12% with the retention time of 5 days. The difference between the removal efficiencies of C-RBF and C-RBF-Control was due to the biological phosphorus uptake in C-RBF. The C-RBF-Control had reached its maximum phosphorus sorption capacity of 4.47 mg/kg sand within 4008 hours of monitoring effort. The sorption difference of 0.3 mg/kg sand between C-RBF and C-RBF-Control was associated with the microbial phosphorus uptake in C-RBF.
- 30% WTR amended RBF column, C-RBF-WTR, showed removal of phosphorus close to the method detection limit of 0.03 mg/L even with 1 ft media depth and 1.25 days of retention time.
- The RBF field and column simulation studies indicated that RBF itself cannot be a barrier for sustainable phosphorus removal.
- The ARR column simulation study indicated phosphorus removals of 3.4% and 17.5% for C-ARR and C-ARR-Control, respectively. The high errors associated with these results indicated that a clear comparison about the removal efficiencies of C-ARR and abiotic control, C-ARR-Control, may not be made. However, low removal efficiencies proved that RBF system followed by ARR application cannot be an efficient and sustainable barrier for phosphorus.
- 30% WTR amended ARR column, C-WTR-ARR, showed complete phosphorus removal with levels of less than the method detection limit of 0.03 mg/L even with the 1 ft media depth and retention time of 1.25 days.

- Sequential RBF – WTR amended ARR column simulation studies showed that after a 1 ft depth of 30% WTR amended media, influent phosphorus levels were decreased close to the method detection limit of 0.03 mg/L. When this water fed to C-ARR columns with the retention time of 25 days, 0.16-0.17 mg/L of phosphorus levels were observed. This was due to the redox sensitive dissolution/desorption mechanisms associated with the alluvial sand media in the column since these columns were used in previous experiments and the media had reached its maximum phosphorus sorption capacities.
- During the overall column simulation study, Wellington WTR had sorbed 302.5 mg P/kg WTR and had not reached its maximum sorption capacity. Previous studies indicated that 302.5 mg P/kg WTR is far less than the actual sorption capacity of Wellington WTR with high Al_{ox} content of 144.7 g/kg WTR.
- The overall study proves that sequential RBF-ARR cannot be a barrier for phosphorus loads in the South Platte River. Amending the system with WTR, once optimized, is a promising and cost effective approach to achieve efficient and sustainable phosphorus removals.

CHAPTER IV: SEQUENTIAL NATURAL TREATMENT: IMPACTS ON CARBON AVAILABILITY AND MICROBIAL PROCESSES

(PAPER WILL BE SUBMITTED TO A JOURNAL)

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Abstract

A labile organic carbon source is needed for natural bioremediation processes. Two such techniques, riverbank filtration (RBF) and aquifer recharge and recovery (ARR), are envisioned as a multi-barrier treatment approach to produce high quality potable water. The study showed that RBF can achieve 50.5% DOC removal being independent of influent concentrations and seasonality. The ARR system in sequential RBF-ARR application suffers from the lack of labile organic carbon and therefore microbially mediated treatment processes are limited. Amending the infiltration of the ARR system with organic carbon rich WTR can promote biological activity, thus allowing further biodegradation of contaminants. Once amended with WTR, the ARR system showed a removal of 71% of the organic carbon that was introduced by the WTR amendment. The type, source, and amount of WTR are important criteria to optimize an efficient and successful WTR amendment implementation to ARR systems. A strong linear correlation ($R^2 = 0.96$) between the amount of WTR and organic carbon leach was observed. For WTRs from different sources, there was no observable correlation between the organic carbon leach and the amount of WTR (5, 10, 20%), except the application ratio of 30% which showed a strong correlation ($R^2 = 0.998$), indicating that below a particular application ratio, the source of WTR is not important and the amount of organic carbon leach mainly controlled by the application ratio.

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IV.1. INTRODUCTION:

The organic matter content of surface waters is composed of an extremely diverse set of organic compounds originating from plants, microbial activities, animals, as well as wastewater treatment discharges and agricultural runoff, varying in structure, chemical reactivity and biodegradability (Wetzel, 2001, Williams, 2001). The organic carbon content of surface waters consists of dissolved organic carbon (DOC) and particulate organic carbon (POC). DOC exists in larger amounts compared to POC with the ratio of 6:1 to 10:1 in lakes and streams (Wetzel, 2001). Living organisms constitute a small portion of POC and a significant amount is composed of detrital organic matter (Wetzel, 2001).

The organic matter content of fresh waters is classified into two major groups, labile organic compounds (non-humic substances) and recalcitrant compounds (humic substances) (Wetzel, 2001). Non-humic substances are low-molecular-weight easily biodegradable organic substances, such as carbohydrates, proteins, amino acids, fats, waxes, resins, and pigments. Humic substances are naturally occurring compounds, high in molecular weight and recalcitrant to rapid biological degradation (Wetzel, 2001).

DOC is transported by water and it may adsorb to inorganic and organic particulate matter. By polymerization on the sorption surfaces, DOC may transform to particulate form, even though, only a small portion of DOC transforms to colloidal and particulate states. POC can be degraded by microorganisms with the release of DOC in soils and hydrosoils (Wetzel, 2001).

The riverbank filtration (RBF) and aquifer recharge and recovery (ARR) processes are similar natural, semi-passive treatment approaches. Both techniques have been used for centuries in primitive ways (Baker, 1948; Pyne, 1995). Modern RBF

technique has been successfully used for the production of drinking water more than a hundred years in Europe and in the last 50 years in the US. (Kuenhn and Mueller, 2000; Ray et al., 2002a). ARR applications are still in use in the United States, Canada, Israel, England, The Netherlands, and Australia (Pyne, 1995).

The fate of various chemical and biological impurities through RBF and ARR has been studied (Ray et al., 2002a; Pyne, 1995). The efficient and consistant removal of DOC with RBF and ARR was shown being independent of temperature and varying influent DOC levels (Eckert and Irmscher, 2006; Grunheid et al., 2005). Under reasonably high oxygen levels DOC was oxidized as an energy source, while in oxygen deficient environments it was used as an electron donor and carbon source by various types of bacteria (Eckert and Irmscher, 2006; Grunheid et al., 2005).

The organic carbon loads to RBF and ARR systems are crucial since they promote the biological activity in the system. The microbial community uses easily biodegradable organic carbon first, within the first couple of meters of the water-aquifer interface, and then biodegradation depends on the chemical characteristics of the compound (Eckert and Irmscher, 2006).

The City of Aurora is developing an innovative approach to utilize South Platte River water downstream of the Denver metropolitan area. With the Prairie Water Project, Aurora envisions the application of sequential riverbank filtration (RBF) and aquifer recharge and recovery (ARR) as a semi-passive, multi-barrier preliminary treatment technique before collecting the treated water in a terminal reservoir (Figure IV.1). One of the city's major concerns is the efficiency of the sequential RBF – ARR application in

terms of the removal of nutrients, such as phosphorus, nitrogen, and carbon before storing the water.

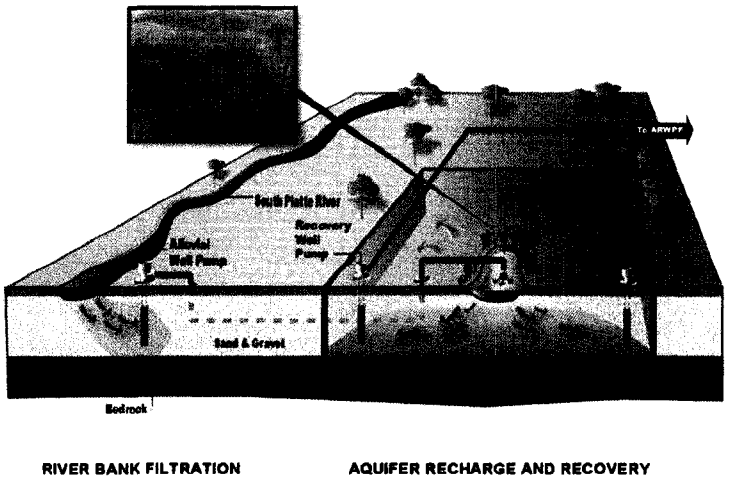


Figure IV.1: Sequential riverbank filtration (RBF) and aquifer recharge and recovery (ARR) (Courtesy of CH2MHill, Denver, CO)

Multiple studies were conducted to evaluate either RBF or ARR as independent treatment approaches. Apart from those associated with this project, application of RBF-ARR system in series has not been studied. The overall project focuses on the advantages and disadvantages of implementing a water treatment strategy of RBF followed by ARR as a two-barrier preliminary treatment step for the production of high quality drinking water.

A concern about the system is that the quality and quantity of organic carbon in RBF treated water may not promote biological degradation of contaminants during the ARR stage. Amending the system with WTR in the infiltration gallery of ARR was evaluated due to the low removal rates of phosphorus throughout the overall system. Besides improving phosphorus removal, organic carbon rich WTR (Dayton and Basta,

2003; Makris et al., 2004; Markis et al., 2005), once optimized, can contribute labile carbon to the carbon limited ARR system, thus promoting further bioremediation.

This study focuses on evaluating; (i) the removal efficiency of natural organic matter through RBF and ARR (ii) possible benefits of WTR amendment on carbon limited ARR to promote biological degradation, and (iii) the effect of type, source, and amount of WTR on carbon contribution to the ARR system.

IV.2. MATERIALS AND METHODS:

IV.2.1. Riverbank Filtration Field Study:

The RBF field study site is located north of the City of Brighton, CO, between the South Platte River and a non-operational gravel mine. The gravel mine is surrounded by a slurry wall to keep groundwater and river water out of the site, isolating the west shore from surrounding groundwater, thus, creating a convenient study site. The production well (PTW-1) and the monitoring wells (PTMW-2, PTMW-3, PTMW-4) are located on the west shore between the slurry wall and the river. PTMW-1 is an imaginary well where the river samples were collected. Production and monitoring wells were installed in November 2004 and the RBF system has been in continuous operation since December 2004 except for short periods of time during the power outages. Figure IV.2 shows the riverbank filtration site, the gravel mine, and production and monitoring wells.

The production well, PTW1, is 18 inches in diameter and is constructed with a stainless steel casing, and pumps water with the flow rate of 450 gpm. All monitoring wells are 2.0-inch, PVC wells. Construction details for production and monitoring wells are given in Table IV.1 below.

South Platte River, monitoring wells, and the production well were monitored twice a month between February 2005 and September 2006 for phosphorus. River samples were collected via grab samples. Monitoring wells were sampled by using an EPA approved low-flow method with dedicated Teflon tubing, and a peristaltic pump. The production well was sampled from a port that is installed in the discharge piping near the well. Samples were collected in HDPE bottles and kept in a cooler during the transport. Samples were filtered with 0.45μm glass fiber filters and kept at 4°C before analysis.



(a) (b)

Figure IV.2: (a) Aerial photo of RBF field study site generated using Google Earth (Newton,2007) (b) RBF field study site with production and monitoring wells, photo by Tetra Tech RMC (Longmont, CO)

Table IV.1: RBF field study well construction details

Well ID	Well Diameter (in)	Total Well Depth (ft)	Depth of Water (ft)	Distance form River (ft)	Residence Time (days)
PTMW-2	2	32	17	137.15	10
PTMW-3	2	30	14	257.89	15
PTMW-4	2	30	14	373.81	22
PTW-1	18	45	33	417.58	25

IV.2.2. Pilot Scale Column Studies:

For the pilot scale studies, 4-foot acrylic columns with an internal diameter of 6 inches were used. Each column has 3 sampling ports, which are 1 foot apart, on the side of the column. Sampling ports are made from stainless steel tubing and they reach to exactly the center of the column cross section for representative sample collection. Each sampling port is screened at the end to prevent column media loss from the ports. To distribute the inflow equally to the column, column caps are built with multiple injection points (Figure IV.3). During the course of the study, all columns were kept at 60° F and wrapped with aluminum foil to prevent photosynthetic microbial activity.

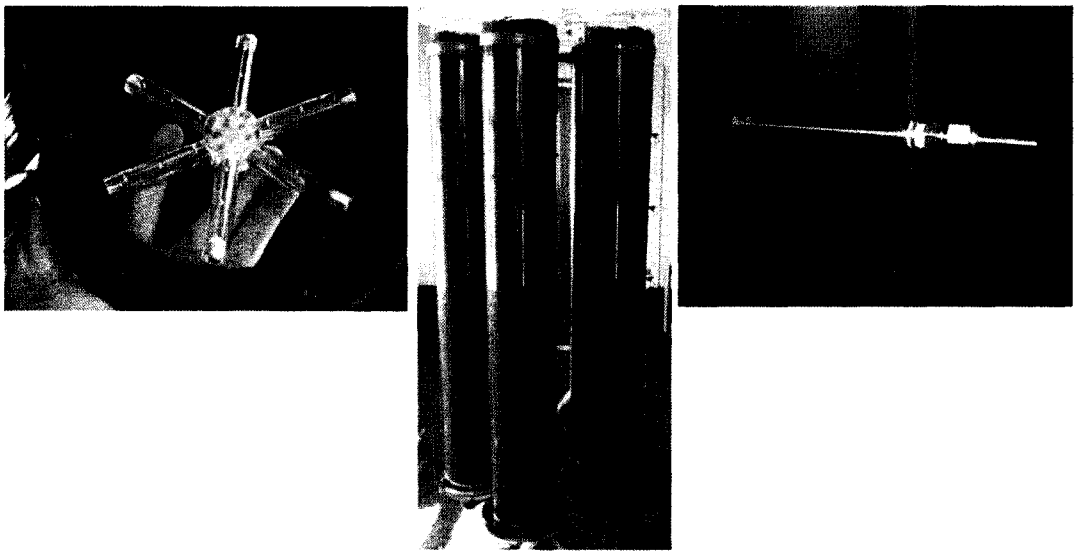


Figure IV.3: Column setup for RBF and ARR simulation studies.

Alluvial sand that was used in the column media was obtained from the west river bank at the RBF field study site approximately 2 feet under the surface. Alluvial sand was sieved with no.10 (<2mm) sieve to obtain uniform particle size. Water treatment residual (WTR) that was used in the column simulation studies was obtained from the City of Wellington Water Treatment Plant, CO (Table IV.2). Aluminum based WTR was first dried in the oven at 180°C overnight then ground and sieved with no.10 (<2mm) to be consistent with the alluvial sand size distribution.

The media was bio-acclimated by feeding the columns with a flowrate of 1mL/min from bottom to top for 15 days, followed by 3mL/min of top to bottom flow for 30 days. Feed water was different for each specific study. Preconditioning steps were repeated before each column simulation study. To feed the columns, peristaltic pumps were used with Teflon tubing throughout the study.

Samples were collected in HDPE bottles and kept in a cooler during the column simulation studies. Samples were filtered with 0.45μm glass fiber filters and kept at 4°C before analysis.

RBF Column Simulation Study:

The RBF column (C-RBF) was built to observe the fate of DOC through the RBF column. C-RBF was monitored biweekly between December 2005 and February 2006 from the effluent. Table IV.2 summarizes the content of the column media and the operating conditions. Figure IV.4 gives a sketch of the experimental column setup. Following the initial preconditioning step described above, C-RBF was fed with 0.2mL/min (25 days of hydraulic residence time) of river water.

Table IV.2: RBF column simulation study: Column media content and operating conditions.

	RBF Column (C-RBF)
Media	Natural alluvial sand (sieved with no.10 sieve)
Condition	wet/saturated
Media Mass in Column	Sand = 32.5kg
Feed water	South Platte River
Flow Rate	0.2 mL/min
HRT	25 days

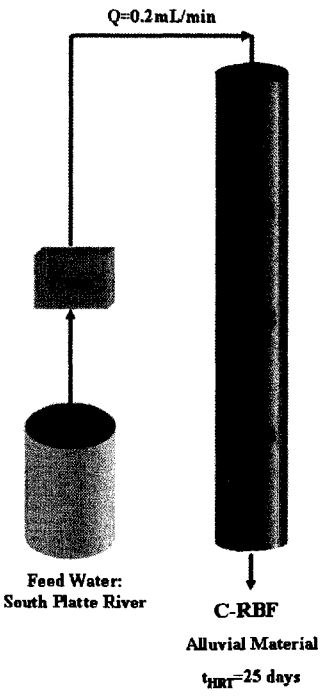


Figure IV.4: RBF column simulation study experimental setup

ARR Column Simulation Study:

An ARR column simulation study was conducted by using RBF treated production well (PTW-1) water as the feed source. Columns that were used for RBF column simulation studies were acclimated with production well water according to the procedure described above and were used in this study. Columns (C-ARR, C-ARR-Control, C-ARR-WTR) were sampled monthly between February 2006 and October 2006. The content of the column media and the operating conditions are summarized in Table IV.3 below. Figure IV.5 shows a sketch of the experimental column setup. The C-ARR column was used to simulate ARR conditions and the column was fed with

0.2mL/min of production well water. With this flow rate, the hydraulic retention time was 25 days. To observe the removal efficiency of DOC under abiotic conditions, the C-ARR-Control column was fed with 0.2mL/min of 2mM sodium azide spiked production well water. Under these feed conditions, the hydraulic retention time was 25 days. To understand the effect of alum based water treatment residual DOC levels, column C-ARR-WTR was fed with 1mL/min of production well water. C-ARR-WTR was sampled from all sampling ports and the effluent, whereas, C-ARR and C-ARR-Control were sampled from the effluent port only.

Table IV.3: ARR column simulation study: Column media content and operating conditions.

	ARR Column (C-ARR)	**Abiotic Control Column (C-ARR-Control)**	**ARR Column amended w/ WTR (C-ARR-WTR)**
Media	Natural alluvial sand (sieved with no.10 sieve)	Natural alluvial sand (sieved with no.10 sieve)	70% v/v natural alluvial sand and 30% v/v WTR (sieved with no.10 sieve)
Condition	wet/saturated	wet/saturated	wet/saturated
Media Mass in Column	Sand = 32.5kg	Sand = 32.5kg	Sand = 21.6kg WTR = 10.6kg Total = 32.2kg
Feed water	Production Well Water (PTW-1)	Production Well Water (PTW-1) Spiked with 2mM Sodium Azide	Production Well Water (PTW-1)
Flow Rate	0.2mL/min	0.2 mL/min	1mL/min
HRT	25 days	25 days	5 days

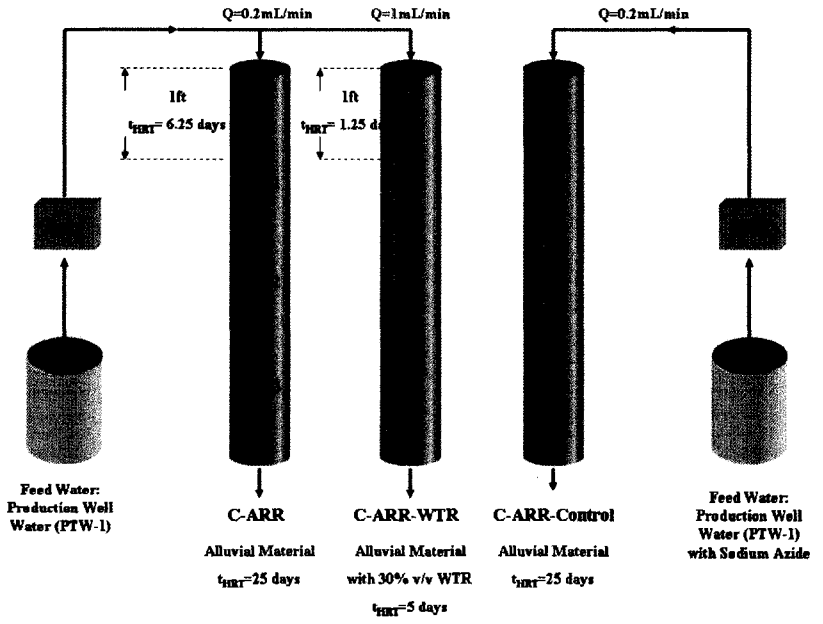


Figure IV.5: ARR column simulation study experimental setup

Sequential RBF – WTR Amended ARR Column Simulation Study:

A sequential RBF – WTR amended ARR column simulation study was conducted to understand the occurrence and fate of DOC throughout the system. During this study RBF treated production well (PTW-1) water was used as the feed. Columns that were used for ARR column simulation studies were acclimated with production well water as the procedure described above and were used in this study. An additional amended abiotic control column (C-ARR-WTR-Control) was built from scratch and was acclimated as others. Operation of columns (C-ARR-WTR, C-ARR, C-ARR-WTR-Control, C-ARR-Control) began in March 2007 and columns were sampled monthly between May 2007 and July 2007. The composition of the column media and the

operating conditions are summarized in Table IV.4. Figure IV.6 shows a sketch of the experimental column setup. The top 1 foot media of C-ARR-WTR column was used to simulate the amended ARR infiltration basin and the C-ARR column was used to simulate the alluvial sand ARR part. C-ARR-WTR was fed with 1mL/min of production well water. After a foot media depth (port 1, C-ARR-WTR-1) water was withdrawn with a flow rate of 0.2 mL/min and fed to the C-ARR column. Hydraulic retention times were 1.25 days and 25 days for C-ARR-WTR-1 and C-ARR, respectively.

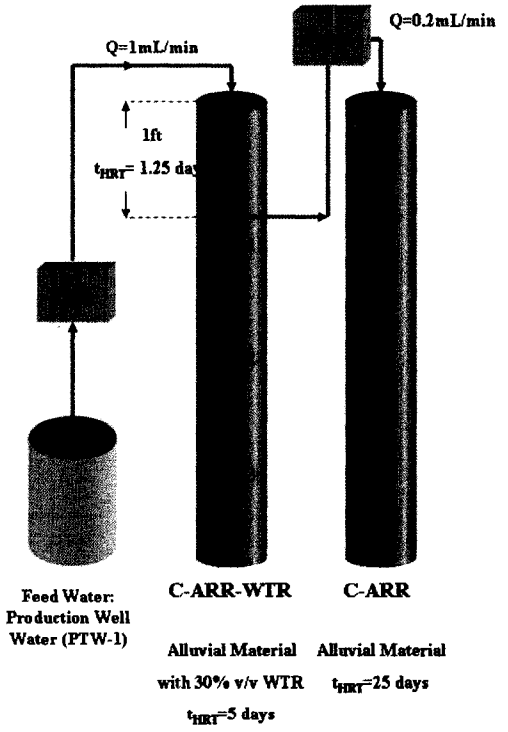


Figure IV.6: Sequential RBF- WTR amended ARR column simulation study experimental setup.

Table IV.4: Sequential RBF – WTR amended ARR column simulation study: Column media content and operating conditions

	ARR Column amended w/ WTR (C-WTR-1) 1 ft media depth	**ARR Column amended w/ WTR (C-WTR-4) 4 ft media depth**	**ARR Column (C-ARR)**	**ARR Column amended w/ WTR Control (C-WTR-1C) 1 ft media depth**	**ARR Column amended w/ WTR Control (C-WTR-4C) 4 ft media depth**	**ARR Column Control (C-ARR-C)**
Media	70% v/v natural alluvial sand and 30% v/v WTR (sieved with no.10 sieve)	70% v/v natural alluvial sand and 30% v/v WTR (sieved with no.10 sieve)	Natural alluvial sand (sieved with no.10 sieve)	70% v/v natural alluvial sand and 30% v/v WTR (sieved with no.10 sieve)	70% v/v natural alluvial sand and 30% v/v WTR (sieved with no.10 sieve)	Natural alluvial sand (sieved with no.10 sieve)
Condition	wet/saturated	wet/saturated	wet/saturated	wet/saturated	wet/saturated	wet/saturated
Mass in Column	Sand = 5.4kg WTR = 2.65kg Total = 8.05kg	Sand = 21.6kg WTR = 10.6kg Total = 32.2kg	Sand = 32.5kg	Sand = 5.4kg WTR = 2.65kg Total = 8.05kg	Sand = 21.6kg WTR = 10.6kg Total = 32.2kg	Sand = 32.5kg
Feed water	Production Well (PTW-1) (spiked with 2mM sodium azide)	Production Well (PTW-1) (spiked with 30ug/L of perchlorate)	C-WTR-1 Water	Production Well (PTW-1) (spiked with 2mM sodium azide)	Production Well (PTW-1) (spiked with 2mM sodium azide)	C-WTR-1C Water
Flow Rate	1mL/min	1mL/min	0.2 mL/min	1mL/min	1mL/min	0.2 mL/min
HRT	1.25 days	5 days	25 days	1.25 days	5 days	25 days

IV.2.3. WTR Carbon Leaching Tests:

To test the influence of the type, source, and amount of WTR on carbon leach, three different aluminum based WTRs were obtained from Aurora, Denver, and Wellington water treatment facilities. The WTRs were dried, ground, and sieved (<2mm). One foot acrylic columns were set with WTR contents of 5%, 10%, 20%, and 30% v/v with <2mm sieved alluvial sand for all three WTRs. A control column containing alluvial sand was also prepared to determine DOC leach from the alluvial material. All columns were preconditioned with 1mL/min bottom to top flow for a week with RBF treated water. The preconditioned columns then were fed with RBF finished water from top to bottom with the flow rate of 0.05mL/min to obtain an infiltration rate of 1ft/day. The effluents of all columns were tested for DOC. All three WTRs were tested for their general physical and chemical characteristics (Table IV.5).

DOC Analyses:

The DOC and WTR characterization analyses were conducted by Soil-Water-Plant Testing Laboratory of Colorado State University. For DOC analysis EPA Method 415.2 was used.

The chemical characterization of WTR was conducted by Soil-Plant-Water Testing Laboratory of Colorado State University. The chemical characterization of WTR was conducted by EPA Method 3050 "Acid Digestion of Sediments, Sludges, and Soils" and EPA Method 6010 "Iductively Coupled Plasma Atomic Emission Spectroscopy".

Table IV.5: Physical and chemical characteristics of WTRs

WTR Source	Total (%) P	Al	Fe	Ca	Mg	K	Oxalate Extractable (%) P	Fe	Al	Saturation Paste pH	EC mmhos/cm
Aurora	0.166	10.25	2.324	0.785	0.241	0.528	0.0363	0.3118	8.623	7.2	0.8
Denver	0.054	10.32	1.719	0.493	0.046	0.724	0.0114	0.1672	9.931	6.8	8.6
Wellington	0.113	15.08	0.586	0.861	0.043	0.161	0.0123	0.0887	14.47	7.4	1.2

WTR Source	(%) Sand	Silt	Clay	Texture	Total (%) C	TOC	$CaCO_3$	CO_3-C
Aurora	98	2	0	Sand	17.28	17.12	1.36	0.16
Denver	93	3	4	Sand	3.669	3.59	0.68	0.08
Wellington	96	2	2	Sand	16.33	16.07	2.21	0.26

IV.3. RESULTS AND DISCUSSION:

IV.3.1. Riverbank Filtration Field Study:

The riverbank filtration field study involved monitoring of the South Platte River, three monitoring wells and the production well for approximately 19 months. The Figure IV.7 summarizes the 19 month study findings from the RBF field study for DOC concentration.

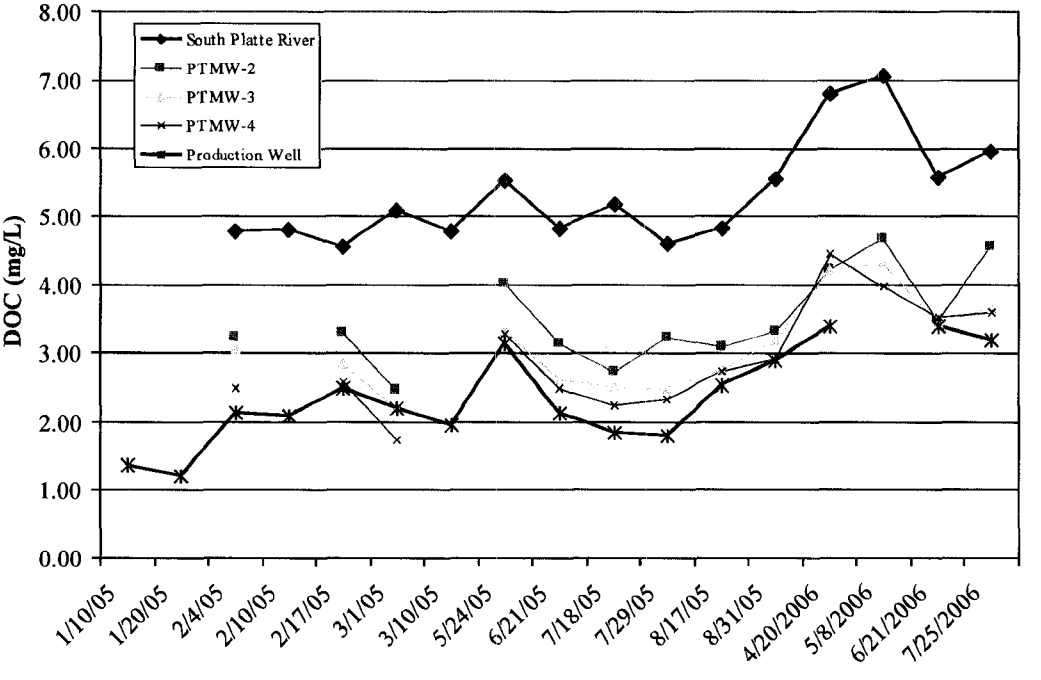


Figure IV.7: RBF field monitoring study for DOC concentration.

The DOC levels in the river were between 4.7 to 7.0 mg/L (Figure IV.7). The lowest DOC concentration in the river was detected in February and the highest was observed in May 2006. Between February 2005 and August 2005, river DOC levels were maintained around 5mg/L. Between April 2006 and May 2006, the DOC concentration

increased and reached a maximum level of 7 mg/L, most likely due to runoff from mountain snowmelt. The background DOC level of natural groundwater was measured as 1.36 mg/L and 1.20 mg/L in January 2005. The DOC levels of RBF treated water was maintained between 2 to 2.5 mg/L except the peak (3.15 mg/L) observed in May 2005. The high flow rate observed in runoff season could be the reason due to the flooding event and shortened travel times. Eckert and Irmscher (2006) reported similar incidents and effects of flooding events on removal efficiencies of various contaminants by shortening the travel time between the river and the production well. The DOC concentration changes following the April 2006 sampling event, the RBF finished water maintained DOC levels of 3-3.5 mg/L. The DOC levels observed in the first monitoring well (PTMW-2) indicates that most of the DOC is degraded between the river and the monitoring well. The easily biodegradable fraction of DOC would be consumed up to PTMW-2. Limited DOC removal continued after the first monitoring well, likely explained by the increased contact time with the microbial community to degrade the moderately biodegradable fraction. The formation of an anaerobic zone and complementary degradation of other contaminants (i.e. nitrate) by using DOC as the electron donor and carbon source might also be the reason further DOC reduction is observed after the first monitoring well.

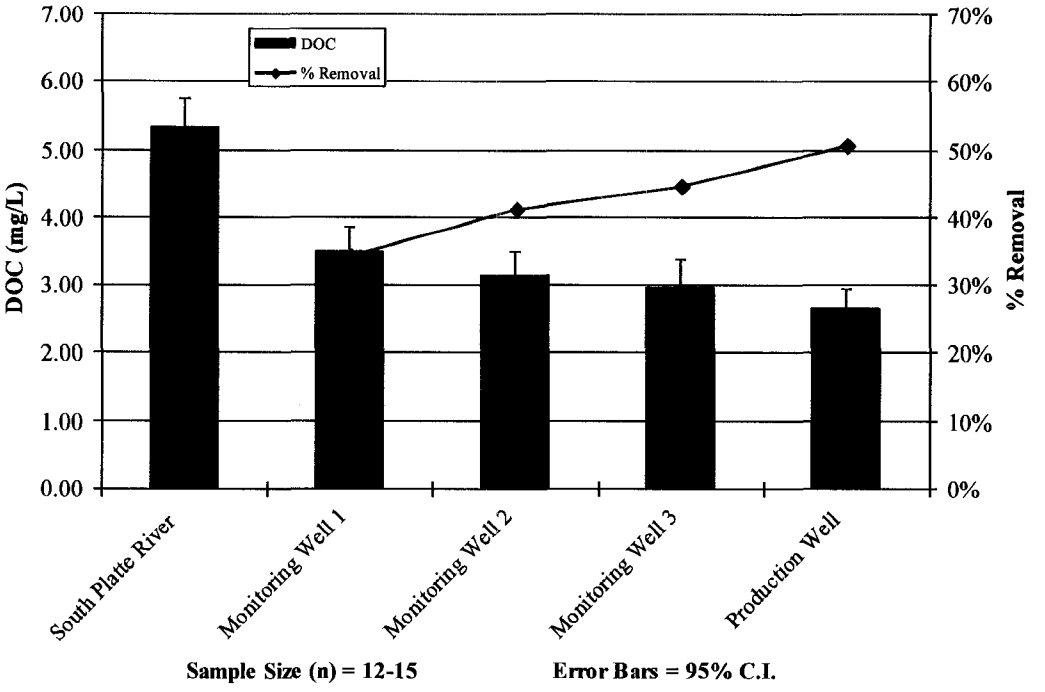


Figure IV.8: Riverbank filtration field study: Average DOC levels.

The average DOC concentration profile (Figure IV.8) across the RBF process shows that 5.32 mg/L of DOC was reduced to 2.63 mg/L after treatment. It was also observed that the majority of the DOC reduction was accomplished between the river and the first monitoring well due to the degradation of easily biodegradable fraction of DOC. Overall, the RBF process results in a DOC reduction of 50.5%.

IV.3.2. Riverbank Filtration Column Simulation Study:

The RBF simulation column (C-RBF) was monitored biweekly between December 2005 and February 2006 including five monitoring events (Figure IV.10). The hydraulic residence time of 25 days was accomplished by feeding the column with 0.2mL/min of river water. The study indicated the DOC degradation from 3.59 to 3.16

mg/L with a removal efficiency of 12%. The low removal efficiency observed in the study compared to RBF field study (50.5%) could be due to the nature of the DOC that was fed to C-RBF column during the monitoring efforts. The lower initial concentration of DOC (average of 3.59 mg/L) compared with the field study (average 5.32 mg/L) likely indicates that the easily biodegradable fraction was less in the column influent than in the river water during the field monitoring.

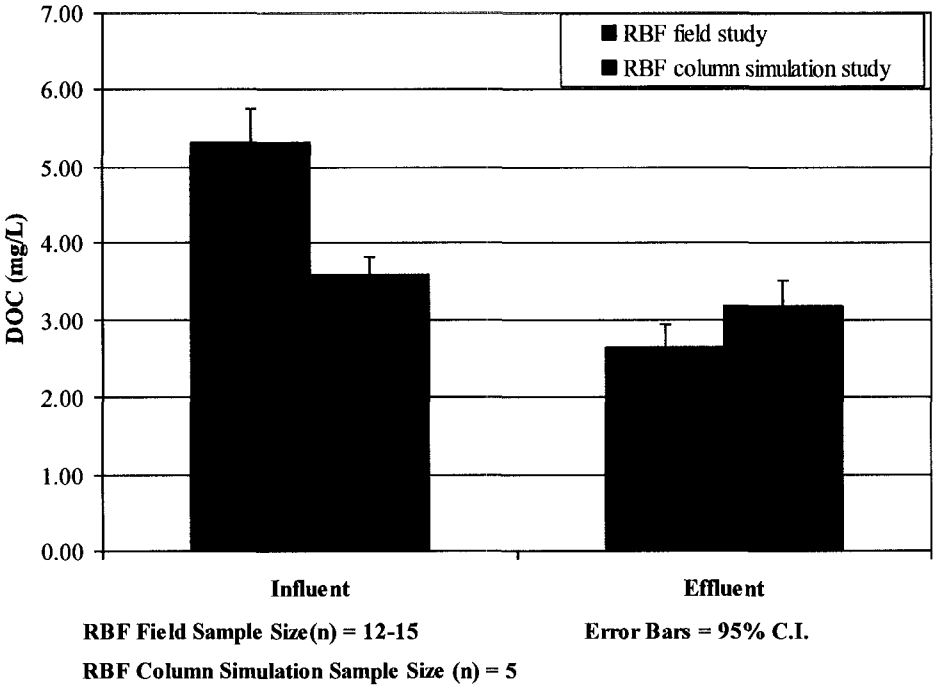


Figure IV.9: RBF field and column simulation study influent and effluent DOC levels.

IV.3.3. Aquifer Recharge and Recovery (ARR) Column Simulation Study:

Three columns, C-ARR, C-ARR-Control, and C-ARR-WTR were fed with RBF finished water and were monitored to understand the DOC removal under ARR conditions. The C-ARR and C-ARR-Control columns were operated with retention times

of 25 days and the effluents were monitored for DOC concentration. Since the C-ARR-WTR column was the treatment set-up to simulate WTR-amended infiltration the total retention time of was only 5 days since we not expect an infiltration travel time greater than this. This column was monitored at all sampling ports and the effluent with retention times of 1.25, 2.5, 3.75, and 5 days. Figure IV.10 shows the average DOC monitoring results for this study.

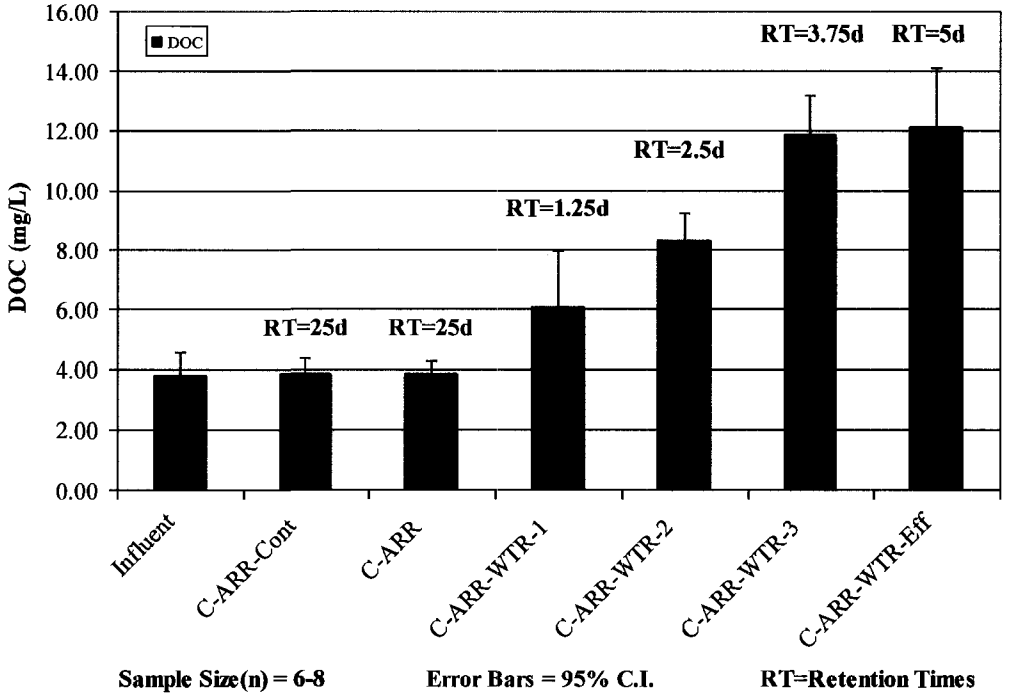


Figure IV.10: ARR column simulation study: Average DOC results.

The C-ARR-Control and C-ARR columns show similar effluent DOC levels close to influent DOC levels of around 4 mg/L. Similar levels in the abiotic control column and ARR column clearly indicate that the influent DOC fraction is not biodegradable and therefore does not promote microbial activity in the system. Additional tests that were

conducted on nitrate (unpublished data) and perchlorate (Chapter V) support the fact that biodegradation and use of organic carbon as an electron donor and carbon source is limited under unamended ARR conditions.

The WTR that was obtained from the Wellington Water Treatment Facility contains a total carbon fraction of 16.3% w/w (163.3 g/kg WTR) (Table IV.5). The organic carbon fraction (16.1% w/w, 160.7g/kg) of the WTR is almost all of the carbon content. The high organic carbon content of various WTRs was reported in numerous studies (Dayton et al., 2003, Makris et al., 2004). The column, C-WTR, shows excessive carbon leach from all the ports and the effluent. At the effluent of the column (5 day exposure time) the DOC concentration reaches 12.1 mg/L (Figure IV.10). The results of this study clearly indicate that amending the infiltration gallery of ARR with WTR can contribute organic carbon to the electron donor limited ARR system. Even though DOC levels of 12.1 mg/L is unacceptable for groundwater applications and surface storage, by simply changing the amount and the ratio of WTR applicaiton, the organic carbon contribution of WTR can be controlled.

Figure IV.11 shows the average DOC concentration that is leached from the WTR in samples collected across column C-ARR-WTR. The influent concentration was subtracted from the average DOC measured from each port, thus, showing the amount of DOC leach versus media depth. There is a linear relation (r^2=0.96) between the 30% WTR amended media depth versus the DOC leach. This linear relation could be useful to estimate and optimize the DOC introduction to carbon limited ARR. The linear relation indicates that the average of 2 mg/L of DOC is leached per foot of 30% WTR amended media. The 4-foot C-ARR column contains total of 10.6 kg of WTR, therefore, each foot

of media contains 2.65 kg of WTR. To help the optimization of WTR amount in amending the ARR, it can be assumed that 0.76 mg/L DOC leaches per kg of Wellington WTR. This result may not be extrapolated different types of WTRs since the organic carbon content varies between WTRs produced by different facilities.

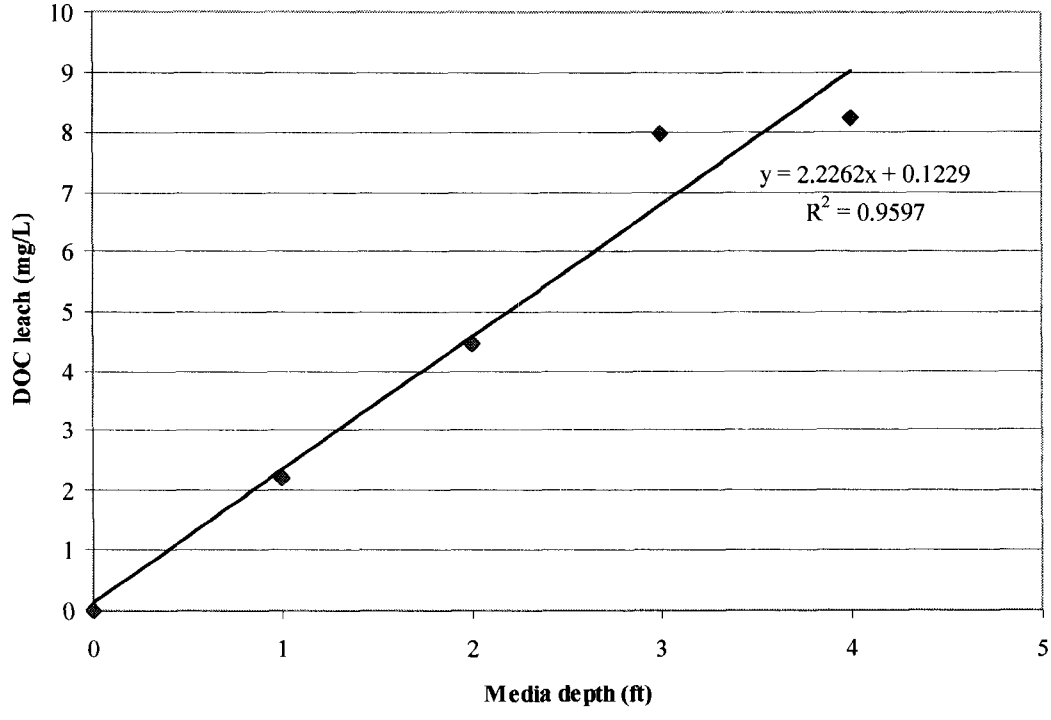


Figure IV.11: WTR amended ARR column DOC leach.

IV.3.4. Sequential RBF and WTR Amended ARR Column Simulation Study:

To evaluate the fate of organic carbon in RBF and WTR amended ARR in series, the column C-ARR-WTR was fed with river water and after a travel time of 1.25 days in C-ARR-WTR, the water was diverted to the C-ARR column for a subsequent travel time of 25 days through alluvial sand. The average level DOC level of 4.01 mg/L was increased to 4.75 mg/L with the average DOC leach of 0.74 mg/L from the first port of

the 30% WTR amended column. This water is introduced to C-ARR and after 25 days of travel time, an average final concentration of 4.22 mg/L of DOC was observed (Figure IV.12). Even though C-ARR was not able to remove the DOC coming from the RBF finished water, it could be noted that it removed 71% of the DOC introduced by the WTR amendment. By using the results of this study, it can be stated that the DOC content of RBF finished water is not biodegradable, however, the DOC introduced during the WTR amended infiltration can be used by microbiota to achieve further degradation processes in the ARR environment. The perchlorate (Chapter V) and nitrate (unpublished data) analysis clearly indicates that the DOC leached from WTR amendment is used as an electron donor and carbon source for microorganisms It is also worthwhile noting that compared to the ARR simulation study, the average amount of DOC leach was decreased from 2.2 mg/L to 0.74 mg/L. The sequential RBF – WTR amended ARR study was concluded approximately 24 months from the initial setup of C-WTR column. The clear decrease in the amount of DOC leach should be considered in the actual design since the DOC exploited from WTR is depleting with time.

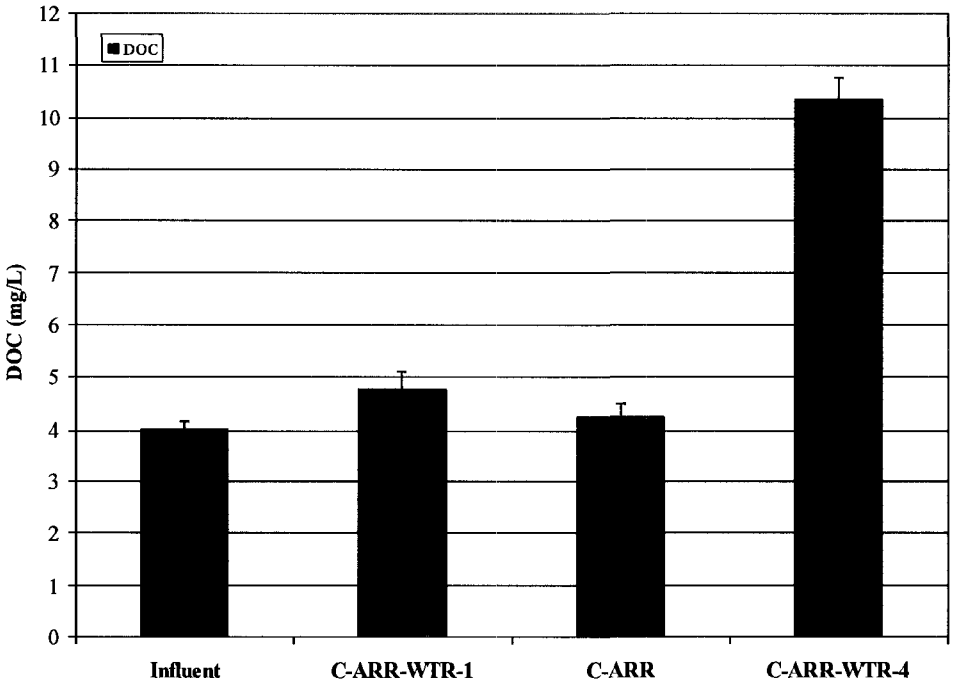


Figure IV.12: Sequential RBF - WTR amended ARR column DOC monitoring.

IV.3.5. WTR Carbon Leaching Tests:

To better understand the effect of the type, source, and amount of WTR amendment, three different WTRs from Aurora, Denver, and Wellington Water Treatment Facilities were tested in terms of physical and chemical characteristics as well as DOC leach. The Al_{ox} and Fe_{ox} contents of the WTRs are the most important properties since they are directly related to the phosphorus adsorption capacities, which is the main reason that WTR was considered as an amendment to ARR system (Chapter III). To promote the biological activity during ARR, the carbon content in the WTR is crucial since this will control the amount of DOC leach from the WTR.

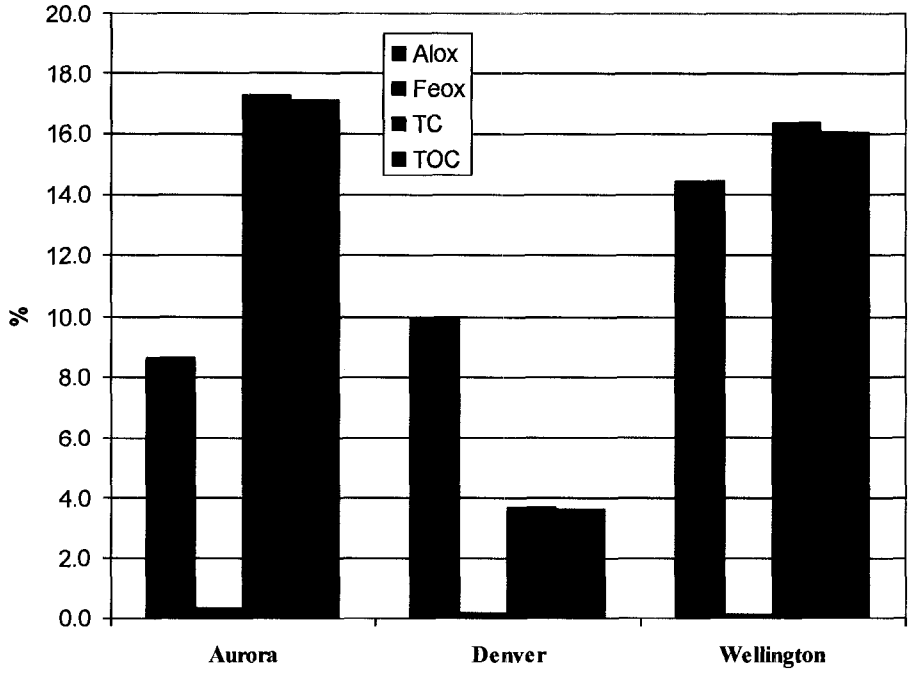


Figure IV.13: Physical and chemical properties of WTRs.

All three WTRs are aluminum based with varying organic carbon contents as shown in Table IV.5 and Figure IV.13. The Aurora WTR has the highest total and organic carbon content followed by Wellington and Denver WTRs. To understand the amount of organic carbon leaching from these WTRs (Aurora, Denver, Wellington) with different application ratios (5, 10, 20, 30%) 1 ft acrylic columns were built with given WTRs and percentages and alluvial sand. The retention time of 20 hours was established and DOC levels were monitored. The relation between the DOC leach and % WTR applied for different types of WTRs show a reasonably linear relation (Figure IV.14). The best linear fit is for Aurora WTR with the $r^2 = 0.977$. This linear relation could be useful to estimate the DOC leach from the WTR before the application to ARR site.

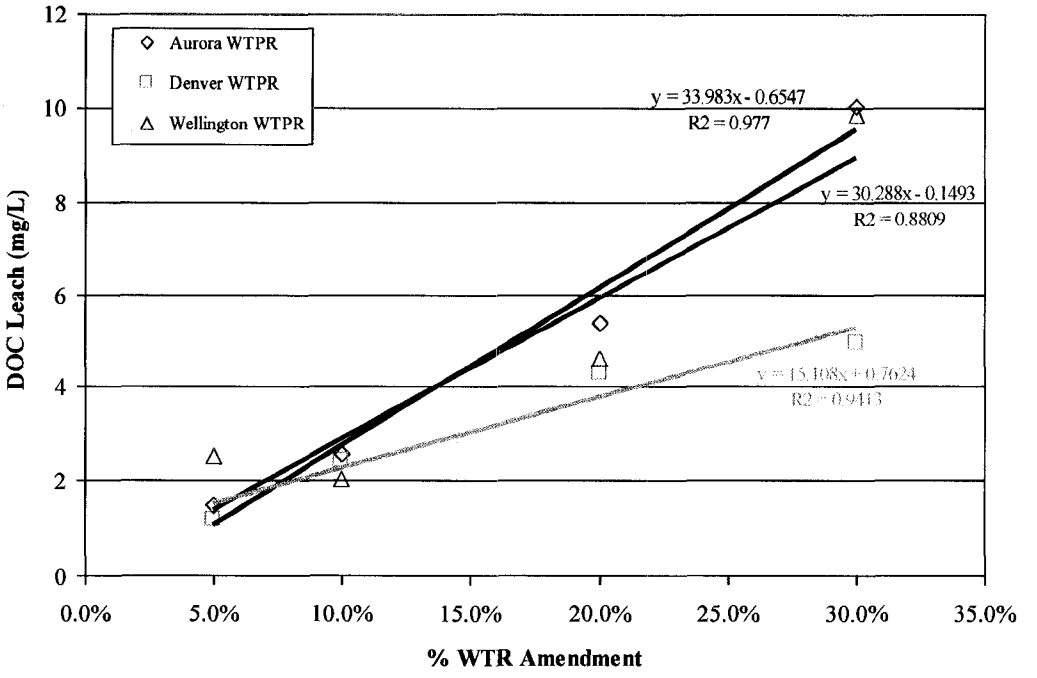


Figure IV.14: DOC leach vs. % WTR amendment.

Another approach was developed to understand the relation between the amounts of DOC leach (mg/L) versus the TOC content (g/kg) of different WTRs (Figure IV.15). The correlations of organic matter fraction in the WTR versus leached TOC were weak except for the 30% WTR application which showed a good linear relation ($R^2 = 0.998$). The lower application ratios shown in Figure IV.15 (20%, 10%, 5% v/v) had a flat response to increased organic matter concentration in the WTR (Aurora> Wellington>Denver). These results seem to indicate that below a particular application ratio (30% v/v in this study), the source of WTR is not very important and the amount of DOC leach will be controlled mostly by the application ratio.

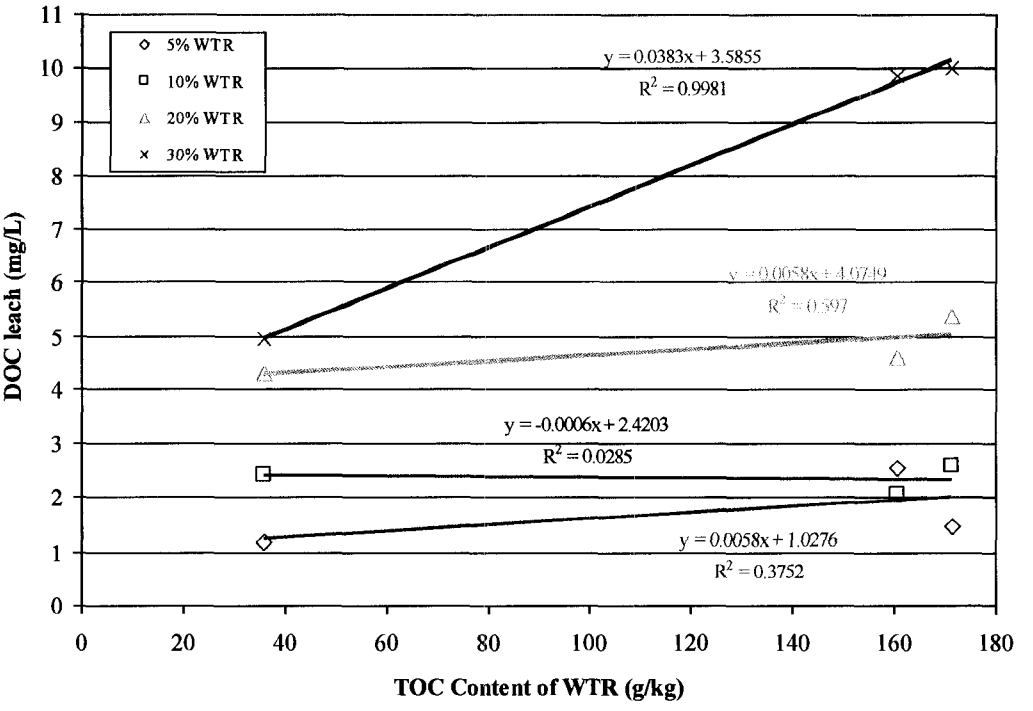


Figure IV.15: DOC leach vs. TOC content of different types of WTRs

IV.4. CONCLUSION:

The overall study was conducted to evaluate the efficiency of RBF and ARR systems on DOC removal. Despite the fact that the presence of NOM in the water can cause important health concerns as a precursor to DBP formations, it is also important for the microbial remediation in natural treatment systems.

Conclusions from the study include:

- The RBF field study showed 50.5% overall DOC removal being independent of the influent DOC concentrations and the seasonal temperature changes.
- RBF column simulation studies showed very low DOC removal efficiencies (11.9%) compared to RBF field study due to the low and non-biodegradable carbon level and content of the source water

- The ARR column simulation study suggested that the remaining organic carbon after RBF treatment is not easily biodegradable for the microbiota. The abiotic control column C-ARR-Control and C-ARR showed almost no difference compared to the feed water. The 30% WTR amended ARR column C-WTR contributes great amounts of liable carbon to the system indicating that WTR amendment can promote biological activity in ARR system and prevails the microbial degradation of variety of contaminants and, thus, improves the ability of ARR system as a barrier for contaminants.
- A linear relation ($r^2 = 0.96$) between the DOC leach and column media depth was developed for 30% WTR amended ARR column suggesting that for a fixed amount of WTR amendment changing media depth can be a possible DOC leach control to ARR system.
- The sequential RBF – WTR amended ARR study was showed that ARR is not able to degrade organic carbon coming from the RBF treated water however it can successfully remove (71%) of the leached DOC from WTR. It is a very useful finding since biodegradable organic carbon is needed by the microbiota to further remediate contaminants following the RBF step.
- WTR carbon leaching tests were conducted to understand the relation between the amount/type of WTR and DOC leach. The study suggested relatively strong correlation between the DOC leach and the amount of WTR amendment for separate WTRs. However, a correlation between different WTRs' DOC leach and TOC content could not be established except one application percentage of 30% which showed a strong correlation with r^2 of 0.998, indicating that below a

particular application ratio (30% v/v in this study), the source of WTR is not very important and the amount of DOC leach is controlled mostly by the application ratio.

CHAPTER V: REMOVAL OF PERCHLORATE THROUGH RIVERBANK FILTRATION AND AQUIFER RECHARGE AND RECOVERY: BENEFITS OF WATER TREATMENT RESIDUAL

(Paper Submitted to AWWA WQTC 2007)

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ABSTRACT

Limited water supply and increasing water demand are key problems facing highly populated areas. If the source of water is highly polluted, treatment applications may be costly. To overcome this problem, passive, on-site treatment techniques such as river bank filtration and aquifer recharge and recovery increasingly attract interest. The scope of a current, on-going project envisions the use of South Platte River as a water source for the City of Aurora in Colorado. Water treatment alternatives include the application of river bank filtration (RBF) and aquifer recharge and recovery (ARR) in series as the initial steps of a multi-barrier treatment approach. This study consists of examining removal efficiencies and kinetics of observed macro and micro pollutants in the South Platte River. An important and potentially soon-to-be regulated contaminant, perchlorate, was studied in terms of the removal mechanism, efficiency and kinetics through RBF and ARR. An analytical method using HPLC/MS TOF was modified from findings of previous studies for quantifying perchlorate. Field and column studies were conducted to simulate RBF and ARR. Column studies also examined the possible benefits of water treatment residual as an amendment to ARR for increasing biodegradability and adsorption. Results of the study showed that both RBF and ARR can be used as an appropriate treatment for perchlorate removal as long as sufficient electron donating compounds (e.g. organic carbon) are present in the environment.

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V.1. INTRODUCTION:

Widespread use of perchlorate (ClO_4^-) in high quantities and not having standards or regulations for disposal in addition to the possible health impacts has resulted in significant environmental interest, especially since more sophisticated detection technologies, have been developed. The physical and chemical nature of perchlorate provides challenges in detection, assessment of health impacts and treatment.

The perchlorate ion consists of one Cl atom in the center and a tetrahedral group of four oxygen atoms. This molecular structure results in the negative charge being dispersed evenly and therefore hard to combine with positively charged metallic ions. Perchlorate salts are extremely soluble, the ion is unreactive thus perchlorate is not reduced or precipitated by common reducing agents and cations. (Urbansky, 1998) Once perchlorate is released to the environment, its fate and transport is very similar to other dissolved minerals. Perchlorate is biologically stable although in anaerobic environments, some bacteria have evolved enzymes that can reduce perchlorate to choride. Also, its concentration is generally 10^3 to 10^5 times less than other dissolved minerals in the environment. (Bull et al., 2004)

Although perchlorate has both natural and man-made sources, the majority of perchlorate contamination is attributed to industrial applications. As a strong oxidant, perchlorate is used in explosives such as rocket fuel, missile propellant and fireworks in oxygen deficient environments. Perchlorate is also used in air bag initiators for vehicles, flash powder for photography, bleaching agents, leather tanning, chemical laboratories for analytical testing, oxygen generators, ejection seats, paints and enamels, electroplating operations, perchloric acid production, electropolishing, production of matches, engine oil testing, etching of brass and copper, and road flares. (U.S. EPA,

2005) Fertilizers, which are used as a nitrate source, may also contain perchlorate. In particular, Chilean caliche is a fertilizer that has been identified as a source of naturally occurring perchlorate. (Bull et al., 2004) Also perchlorate is formed in the atmosphere during electrical discharges and deposited to the ground by precipitation naturally. (Dasgupta et al., 2006) Considering that 65% of all groundwater and surface water perchlorate contamination is related primarily to defense and aerospace activities in the USA, fertilizers and atmospheric perchlorate deposition are not considered major concerns. (Dasgupta et al., 2006; U.S. GAO, 2005; Sanchez et al., 2005)

In 1985 perchlorate contamination was detected for the first time in the state of California. In 1997, more perchlorate contaminated water sources were found when analytical technology allowed the detection limit to be decreased to less than 4 ppb. Discovery of the existence of perchlorate in drinking water proved that people were exposed to perchlorate by water consumption. This concern initiated many studies and occurrence research has been conducted in the states of California, Massachusetts, Texas and Arizona, which were suspected to be subject to high perchlorate contamination. (Tikkanem, 2006) According to the nationwide studies, perchlorate was detected in at least 26 States' and 2 Territories' in 160 drinking water sources, which serve approximately 16.8 million people. The average occurrence was 9.85 μg/L and the median value was 6.40 μg/L with no significant difference in concentration between ground and surface water sources. (U.S. EPA, 2006)

Perchlorate has been known as an endocrine disruptor that interferes with the function of thyroid glands. Thyroid glands produce T_3 and T_4 hormones, which regulate growth and development. The thyroid gland receives iodide which is a component of T_3

and T_4. Perchlorate competes with iodide and inhibits iodide transport and causes hypothyroidism which is a condition in which the body lacks sufficient thyroid hormone (NRC, 2005). Perchlorate uptake may cause skeletal and nervous system development problems, a significant concern especially for pregnant women and fetuses.

Due to the increasing concerns, perchlorate has been under review for determining the occurrence, possible health effects and federal regulatory safe drinking water limits. In 1998, perchlorate was included on Contaminant Candidate List (CCL) by USEPA as the primary basis for selecting contaminants for future monitoring under the Unregulated Contaminants Monitoring Rule (UCMR) (U.S. EPA, 1998). Although there have been many studies to collect more data and review perchlorate, the USEPA still has not set a maximum contamination level (MCL) for perchlorate. This is likely due to the uncertainties in the toxicological database, inconsistencies between health impact studies, the complex nature of endocrine disruptors, and the nature of the debate between the defense industry, federal government and rational scientific risk assessments. Nevertheless, the EPA has established an official RfD of 0.0007 mg/kg/day. (NRC, 2005; U.S. EPA, 2002; U.S. EPA, 2007) Although there is not a nationwide regulation, a number of states have advisory limits for perchlorate ranging from 1 to 51μg/L. (U.S. EPA, 2005)

As the regulatory advisory limits imply, even in very low levels, precise detection of perchlorate is also important. Analytical technology has become advanced enough to detect low levels of perchlorate. In 1999 the USEPA approved method 314.0 with a minimum reporting level (MRL) of 4 μg/L to determine perchlorate in drinking water using ion chromatography. (U.S. EPA, 1999) Although method 314.0 was acceptable for

most drinking water, in lower (< 4μg/L) concentrations, results were not reliable. (Bull et al., 2004) It was inadequate when the concentrations are low, also inadequate in detecting perchlorate in food and in complex matrices having common anions which elute at close retention time with perchlorate. In order to overcome these issues, some studies have been made using evaporative preconcentration techniques and ion chromatography with electrospray ionization mass spectrometric detection (IC-ESI-MS) and IC-ESI-MS-MS techniques were developed in some laboratories. However, even using IC-ESI-MS-MS has some limitations such as co-elution of contaminants with ions having the same m/z as perchlorate, high background noise and low signal-to-noise ratio, loss of sensitivity over time and suppression of gas phase ion formation at high contaminant concentrations. (Hedrick and Munch, 2004) Evaporative preconcentration techniques helped to lower the MDL to 0.2μg/L. (Jackson et al., 1999) Considering these problems, in 2005 EPA released Method 314.1 "Determination of Perchlorate in Drinking Water Using Inline Column Concentration/Matrix Elimination Ion Chromatography with Suppressed Conductivity Detection". This method is a sample pre-concentration, matrix elimination ion chromatographic (IC) method using suppressed conductivity detection for the determination of perchlorate in raw and finished drinking waters. This method has an improved MDL with a reported value for the single laboratory Lowest Concentration Minimum Reporting Level (LCMRL) of 0.14 μg/L. (U.S. EPA, 2005) Also in 2005, EPA released Method 332.0 "Determination of Perchlorate in Drinking Water by Ion Chromatography with Suppressed Conductivity and Electrospray Ionization Mass Spectrometry" applicable for identifying and quantifying perchlorate in raw and finished drinking water. (U.S. EPA, 2005)

Although Method 314.1 has been used successfully in the past, improved sensitivity and specificity was required since in complex matrices, the MDL may be as high as 4 μg/L and the IC method does not precisely prove existence of perchlorate if species with adequate specific conductivity also exists. (Winkler et al., 2004) Therefore, there have been studies using HPLC/MS/MS with lower method detection limits. In one of them, Winkler et. al. successfully reduced the MDL to 0.05 μg/L for aqueous samples. (Winkler et al., 2004) Also for perchlorate detection in complex matrices such as surface waters, Backus et. al. were able to reduce the MDL to as low as 0.2 μg/L by using HPLC/MS/MS. (Backus et al., 2005)

Currently, most effective perchlorate treatment methods are ion exchange and biological reduction. On-going studies show that reverse osmosis (RO), chemical reduction through catalysis and GAC can be used for perchlorate removal; however these methods seem to not be cost effective near-term and more research and development is needed. (Bull et al., 2004) Furthermore, oxidation cannot be used as a treatment method since perchlorate already has the highest oxidation state. (Catton, 1999)

As one of the current applicable methods, ion exchange removes perchlorate with the same principle of having a packed bed of synthetic, strong base, anionic resin in the chloride form and anions such as perchlorate, nitrate and sulfate are attached to the resin when Cl^- is released. This technology has the disadvantage of disposing highly concentrated sulfate, nitrate and perchlorate when the resin capacity is exhausted. In order to regenerate the resin, concentrated sodium chloride (NaCl) is used to wash the resin and reverse the exchange process so that Cl^- again can be attached by the resin while other anions are released (Bull et al.,2004).

Recent developments improved our understanding of bacterial perchlorate degradation thus it is known that select bacteria have evolved enzymes to catalyze the reduction of perchlorate (Xu et al., 2003). The reduction occurs by a chain reaction with a relatively high rate in soil (Robles, 2000). Also both autotrophs and heterotrophs can accomplish these transformations when organic carbon and CO_2 are present, respectively. (Bull et al., 2004)

Riverbank filtration (RBF) and aquifer recharge and recovery (ARR) are similar natural, semi-passive treatment approaches. Both techniques have been used for centuries in primitive ways (Baker, 1948, Pyne, 1995). Modern RBF technique has been successfully used for the production of drinking water for more than a hundred years in Europe and in the last 50 years in the US. (Kuhen and Mueller, 2000). Also, modern ARR applications are in use in the United States, Canada, Israel, England, The Netherlands, and Australia (Payne, 1995). Physical, chemical and biological processes all play an important role to improve the water quality in RBF and ARR applications.

The primary physical process that is involved during RBF is filtration. Physical removal occurs at the soil pores as well as the electrostatic attachments to soil particles (Ray et al, 2002a). The major chemical processes that occur during riverbank filtration include adsorption, ion exchange, and chemical reactions (Kuhen and Mueller, 2000; Ray et al., 2002b; Kelly and Rydlund, 2006). Physical and chemical characteristics of the soil influence ion exchange capacities causing some soil types to have an unlimited capacity for ion exchange and adsorption, while others are very limited (Kuhen and Mueller, 2000). Varying pH and oxygen concentrations affects acid/base dissociation reactions as well as the oxidation state of many compounds (Kuhen and Mueller, 2000; Ray et al.,

2002b). Microbiological activities involve the degradation of hydrophobic compounds that are adsorbed to soil surfaces and the consumption of organic carbon through various heterotrophic metabolic activities. Most of the microbial activity takes place at the interface between the riverbed and the aquifer (Kuhen and Mueller, 2000; Ray et al., 2002b). The nutrients in the river water encourage the growth of a biofilm on the border between the riverbed and the aquifer. Flow rates in through the riverbank can be similar to those of slow sand filters which means that riverbank filtration may be comparable to or more effective than a slow sand filtration process (Kelly and Rydlund, 2006). The biofilm is responsible for the initial degradation and removal of organic carbon, nutrients, and pathogens as well as micronutrients (Kuhen and Mueller, 2000; Ray et al., 2002b; Kelly and Rydlund, 2006).

As in the RBF, physical, chemical, and biological processes are the key elements of ARR applications. Microorganisms are present in aquifers to depths of at least 1500 feet (Pyne, 1995), therefore, ARR can stimulate biological degradation of organic and redox-active contaminants providing there are sufficient electron donors. The major advantages of RBF and ARR applications are; seasonal changes influent water quality due to concentration and temperature do not alter the RBF efficiency (Kuhen and Mueller, 2000). RBF and ARR systems achieve pathogen removal, particle removal, dissolved organic matter reduction, thus, reduction in disinfection by-product formation, and production of biologically stable water. Finally, recent studies stated that the application of RBF and/or ARR is efficient in biodegradation of trace organic materials, such as, pesticides and antibiotics (Ray et al., 2002b).

V.1.1. Project Description and Goals:

This on-going study was part of the City of Aurora's Prairie Waters Project. Limited water supplies have caused the city to consider the use of South Platte River as a future source of drinking water. The approach for purifying this water includes the application of riverbank filtration and aquifer recharge and recovery in series as a multi-barrier, semi-passive preliminary treatment technique. Following the indirect draw of South Platte River water through RBF with the residence time of approximately 20 days, water will be pumped to an ARR infiltration basin to percolate back into a controlled groundwater system. After a residence time of 25-30 days, water will be recovered by a series of production wells located at the periphery of the ARR basin. Water from the ARR site will be pumped to a storage reservoir and then be treated in an advanced drinking water treatment plant in Aurora, Colorado (Figure V.1).

Multiple studies were conducted to evaluate either RBF or ARR as independent treatment approaches. Apart from those associated with this project, application of RBF-ARR system in series has not been studied. The overall project focuses on the advantages and disadvantages of implementing a water treatment strategy of RBF followed by ARR as a natural, two-barrier treatment step for the production of high quality drinking water.

Preliminary results of the project showed that the macronutrient phosphorus was not removed efficiently through the multi-barrier RBF-ARR approach. To overcome this problem, water treatment residual (WTR) was applied as an adsorbent during the ARR percolation process. This paper presents the results of research on the removal mechanism, kinetics, and efficiency of perchlorate, through the RBF-ARR multi-barrier

treatment process. The secondary objective was to assess the benefits of amending the ARR infiltration process with WTR in terms of perchlorate removal.

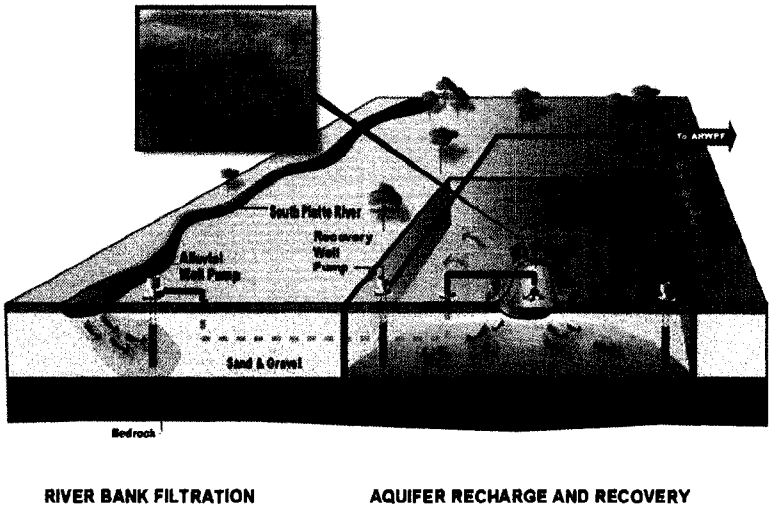


Figure V.1: Application of RBF and ARR in series.

V.2. MATERIALS AND METHODS:

V.2.1. Riverbank Filtration Field Study:

The riverbank filtration field study site is located on the north of City of Brighton, CO, between the South Platte River and a non-operational gravel mine. The gravel mine is surrounded by a slurry wall to keep groundwater and river water out of the site, limiting groundwater intrusion to the RBF field. The production well (PTW-1) and the monitoring wells (PTMW-2, PTMW-3, PTMW-4) are located on the west shore of the river and PTW-1 is the well where the RBF samples were taken. Production and monitoring wells were installed in November 2004 and the RBF system has been in continuous operation since December 2004 except for short periods of times during

power outages. Figure V.2 shows the RBF site with the Brighton Wastewater Plant, gravel mine, and the production and monitoring wells.

The production well, PTW1, is 18 inches in diameter and was constructed with a stainless steel casing, and pumps water with the flow rate of 450gpm. All monitoring wells are 2.0-inch, PVC wells. Construction details for production and monitoring wells are given in Table V.1 below.



(a) **(b)**

Figure V.2: (a) Aerial photo of RBF field study site generated using Google Earth. (b) RBF field study site with production and monitoring wells, photo by Tetra Tech RMC (Longmont, CO).

Table V.1: RBF field study well construction details.

Well ID	Well Diameter (in.)	Total Well Depth (ft)	Depth of Water (ft)	Distance form River (ft)	Residence Time (days)
PTMW-2	2	32	17	137	10
PTMW-3	2	30	14	257	15
PTMW-4	2	30	14	373	22
PTW-1	18	45	33	417	25

The South Platte River (PTMW-1) and the production well were monitored monthly between June 2006 and July 2007 for perchlorate. Water samples from the production well, PTW-1, and the South Platte River were sampled via grab samples. The river water was sampled through direct withdrawls while water from PTW-1 was obtained via a port installed in the discharge piping near the production well and was designated as the RBF treated water. Samples were collected in HDPE bottles and kept in a cooler during transport. Samples were then filtered with 0.45μm glass fiber filters and kept at 4°C until analysis.

V.2.2. Pilot Scale Column Studies:

Pilot scale studies were conducted with 4-foot acrylic columns with an internal diameter of 6 inches. Each column had 3 sampling ports, 1 foot apart, on the side of the column. Sampling ports were made from stainless steel tubing and reached the center of the column cross section for a representative sample collection. Each sampling port was screened at the end to prevent the column media lost from the ports. To distribute the inflow equally to the column, column caps are built with multiple injection points. Detailed column photos are shown in Figure V.3. During the course of the study all

columns were kept at 60° F and wrapped with aluminum foil to prevent photosynthetic microbial growth in the columns.

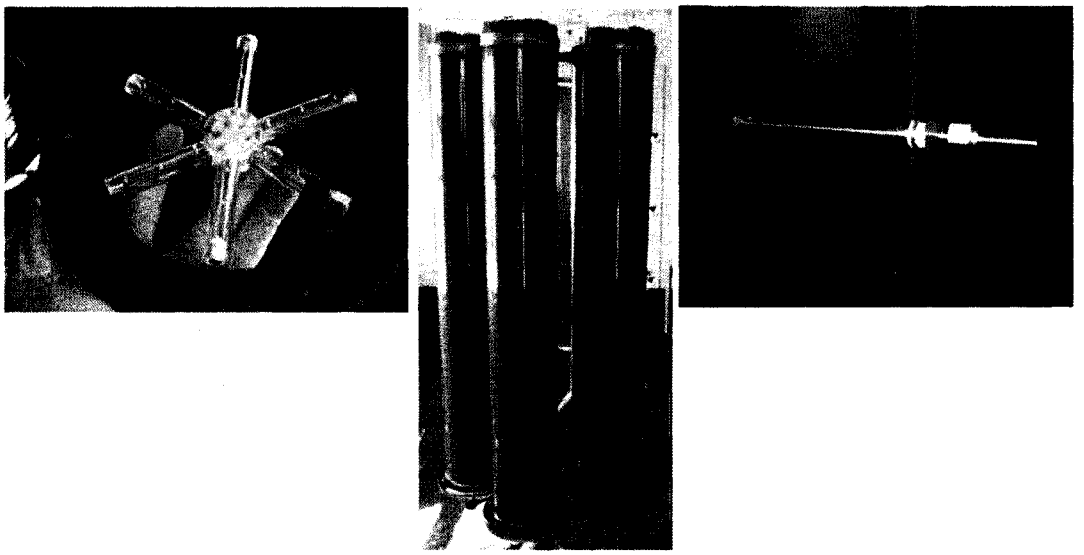


Figure V.3: Column setup for pilot scale RBF and ARR studies.

All columns were preconditioned with 3mL/min of bottom to top flow for 30 days and 1mL/min top to bottom flow for 30 days with the feed water that was different for each specific study. To feed the columns, peristaltic pumps were used with Teflon tubing throughout the study.

V.2.3. RBF Column Studies:

The column set-up to simulate RBF (C-RBF) (Table V.2) was built by using alluvial sand that was obtained from the west river bank at the field study site approximately 2 feet under the surface. Alluvial sand was sieved with a no.10 (2mm) sieve to obtain uniform particle size in the column. Following the initial preconditioning step described above, the column was fed with the flow rate of 1mL/min (5 days of

hydraulic residence time) of river water to simulate RBF conditions. Since perchlorate does not always exist in the river water and/or close to the method detection limit, the water was spiked with 30μg/L of perchlorate. The influent and effluent to the column was sampled every two weeks for 3 months.

V.2.4. ARR Column Studies:

Pilot scale ARR column studies were conducted by using RBF production well (PTW-1) water as the feed. Column preparation was the same as with RBF column setup. For the ARR column study, a control column was set up and the feed solution, production well water, was spiked with 2mM of sodium azide to prevent microbial activity in the column. To observe the possible benefits of the alum based water treatment plant residual (WTR), one of the ARR columns was amended with 30% v/v WTR. WTR was obtained from City of Wellington Water Treatment Plant that is located north of Fort Collins. WTR was dried in the oven at 180°C overnight ground and sieved with no.10 (2mm) sieve to achieve uniform size distribution. Detailed column preparation and operating conditions are summarized in Table V.2 below.

Table V.2: Pilot scale RBF and ARR column study preparation and operating conditions.

	RBF Column (C-RBF)	ARR Column (C-ARR)	ARR Control Column (C-ARR-Cont)	ARR Column amended w/ WTR (C-ARR-WTR)
Media	Natural alluvial sand (sieved with no.10 sieve)	Natural alluvial sand (sieved with no.10 sieve)	Natural alluvial sand (sieved with no.10 sieve)	70% natural alluvial sand and 30% WTR (sieved with no.10 sieve)
Condition	wet/saturated	wet/saturated	wet/saturated	wet/saturated
Mass in Column	Sand = 32.5kg	Sand = 32.5kg	Sand = 32.5kg	Sand = 21.6kg WTR = 10.6kg Total = 32.2kg
Feed water	South Platte River (spiked with 30ug/L of perchlorate)	Production Well (PTW-1) (spiked with 30ug/L of perchlorate)	Production Well (PTW-1) (spiked with 2mM of sodium azide and 30ug/L of perchlorate)	Production Well (PTW-1) (spiked with 30ug/L of perchlorate)
Flow Rate	1mL/min	0.2 mL/min	0.2 mL/min	1mL/min
HRT	5 days	25 days	25 days	5 days

V.2.5. Sequential RBF and WTR Amended ARR Column Study:

To simulate the RBF and WTR amended ARR in series field application, RBF production well (PTW-1) water was fed to a WTR amended ARR column with the flow rate of 1mL/min which provides a residence time of 5 days for the 4-foot column and provides an infiltration rate of 0.8 ft/day. Water was drawn from the first sample port of the WTR amended ARR column which provided a 1 foot media depth with the residence time of approximately 1.25 days. This water was fed to an ARR column (C-ARR) which has 100% alluvial material as the column media. The flow rate was kept at 0.2mL/min to create a residence time of 25 days. The same setup was used for the control process with a difference of 2mM of sodium azide spike to the feed water. Table V.3 provides the study setup details.

Table V.3: Pilot scale RBF and amended ARR in-series column study; preparation and operating conditions.

	ARR Column amended w/ WTR (C-WTR-1) 1 ft media depth	ARR Column (C-ARR)	ARR Column amended w/ WTR (C-WTR-4) 4 ft media depth	ARR Column amended w/ WTR Control (C-WTR-1C) 1 ft media depth	ARR Column Control (C-ARR-C)	ARR Column amended w/ WTR Control (C-WTR-4C) 4 ft media depth
Media	70% natural alluvial sand and 30% WTR (sieved with no.10 sieve)	Natural alluvial sand (sieved with no.10 sieve)	70% natural alluvial sand and 30% WTR (sieved with no.10 sieve)	70% natural alluvial sand and 30% WTR (sieved with no.10 sieve)	Natural alluvial sand (sieved with no.10 sieve)	70% natural alluvial sand and 30% WTR (sieved with no.10 sieve)
Condition	wet/saturated	Wet/saturated	wet/saturated	wet/saturated	wet/saturated	wet/saturated
Mass in Column	Sand = 5.4kg WTR = 2.65kg Total = 8.05kg	Sand = 32.5kg	Sand = 21.6kg WTR = 10.6kg Total = 32.2kg	Sand = 5.4kg WTR = 2.65kg Total = 8.05kg	Sand = 32.5kg	Sand = 21.6kg WTR = 10.6kg Total = 32.2kg
Feed water	Production Well (PTW-1) (spiked with 30ug/L of perchlorate)	C-WTR-1 Water	Production Well (PTW-1) (spiked with 30ug/L of perchlorate)	Production Well (PTW-1) (spiked with 2mM of sodium azide and 30ug/L of perchlorate)	C-WTR-1C Water	Production Well (PTW-1) (spiked with 2mM of sodium azide and 30ug/L of perchlorate)
Flow Rate	1mL/min	0.2 mL/min	1mL/min	1mL/min	0.2 mL/min	1mL/min
HRT	1.25 days	25 days	5 days	1.25 days	25 days	5 days

V.2.6. Perchlorate Analysis:

Sample Preparation

After filtering the samples with 0.45μm fiber glass filters, pretreatment was conducted. Dionex OnGuard® II barium, silver, and hydrogen cartridges were used to remove sulfate, halides, and alkali- and alkaline earth metals, cationic transition metals, and acidify the samples, respectively. Cartridges were eluted with 10mL of HPLC grade water and 6mL of sample was fed through the cartridges. After discarding the first 3mL, the rest of the sample was collected. 18O labeled perchlorate was used as an internal standard. 3mL of sample was concentrated to 150μL and analyzed with HPLC TOF.

HPLC TOF Analyses

An Agilent 1200 Series HPLC with a Dionex AG16 ion exchange column was used for the separation. 95/5 50mM ammonium hydroxide solution was used as an eluant with the flow rate of 0.5mL/min. Under these conditions, the retention time of perchlorate was 3 minutes. An Agilent 6210 Time of Flight (TOF) mass spectrometer was used for the detection of perchlorate using Analyst QS software. To provide an optimum signal the following conditions were used: ion polarity: negative, ion source gas temperature: 325° C, drying gas: 10L/min, nebulizer: 35psig, capillary voltage: 3000V.

V.3. RESULTS AND DISCUSSION

V.3.1. RBF Field Study:

An RBF field site was sampled monthly form June 2006 to July 2007. Figure 4 shows the results of the perchlorate analysis from the South Platte River (PTMW-1) and production well (PTW-1) throughout the study with a retention time estimated to be approximately 25 days. Perchlorate occurrence greater than the method detection level (MDL) of 0.25μg/L was observed mostly during the low flow conditions (flow data is not shown). The monitoring study indicates that perchlorate concentrations of less than 3μg/L can be efficiently removed in the RBF process with the lowest removal efficiency of 72% (Figure V.4). When the river concentration of perchlorate was measured at 6.5μg/L in September 2006, the removal efficiency decreased to less than 65%. This result indicates that the RBF process studied does not completely reduce perchlorate.

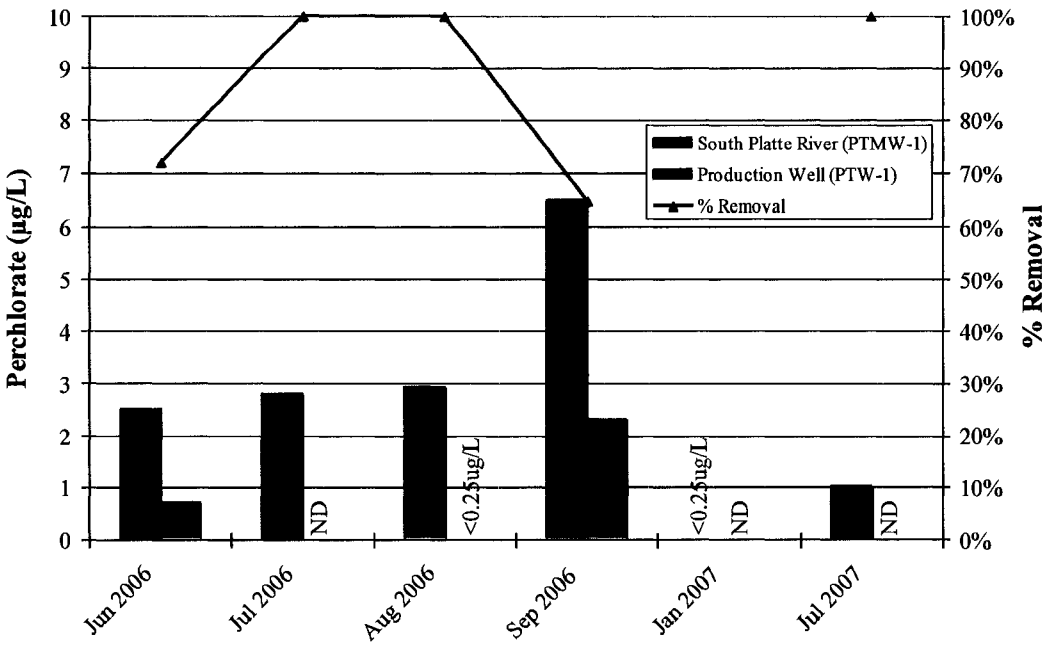


Figure V.4: RBF field monitoring study for perchlorate. Samples were collected and analyzed once per month for 14 months. This figure shows only detects.

The removal mechanism of perchlorate in an RBF process is expected to be a microbiologically mediated chemical reduction. It has been previously reported that perchlorate has limited sorption on sand and other sorption media such as GAC (U.S. EPA, 2005). Microbiological reduction of perchlorate requires low-oxygen, reducing conditions with an available carbon and electron donating sources. Under these conditions, perchlorate can be used as an electron acceptor and reduced to ClO_3^-, ClO_2^-, and finally to Cl^- (Xu et al., 2003; Rikken et al., 1996). Zimmerman (2006) studied microbiological nitrate removal in the same RBF system for a 21 month period in 2005-2006. The study indicated that a significant amount of organic carbon was utilized within approximately 10 days of travel time as shown in Figure V.5 below. Nitrate removal efficiencies (data not shown) indicated that a considerable amount of denitrification was

achieved within the first 10 days of travel time. It is also reported that most of the biologically available organic carbon was used between the river and the first monitoring well. Another study (Xu et al., 2003) reported that in water matrices where nitrate and perchlorate coexist, nitrate is the primary electron acceptor. Following the nitrate removal perchlorate is used as an electron acceptor and reduced. In terms of perchlorate removal it is believed that efficient perchlorate removal is achieved after the first monitoring well.

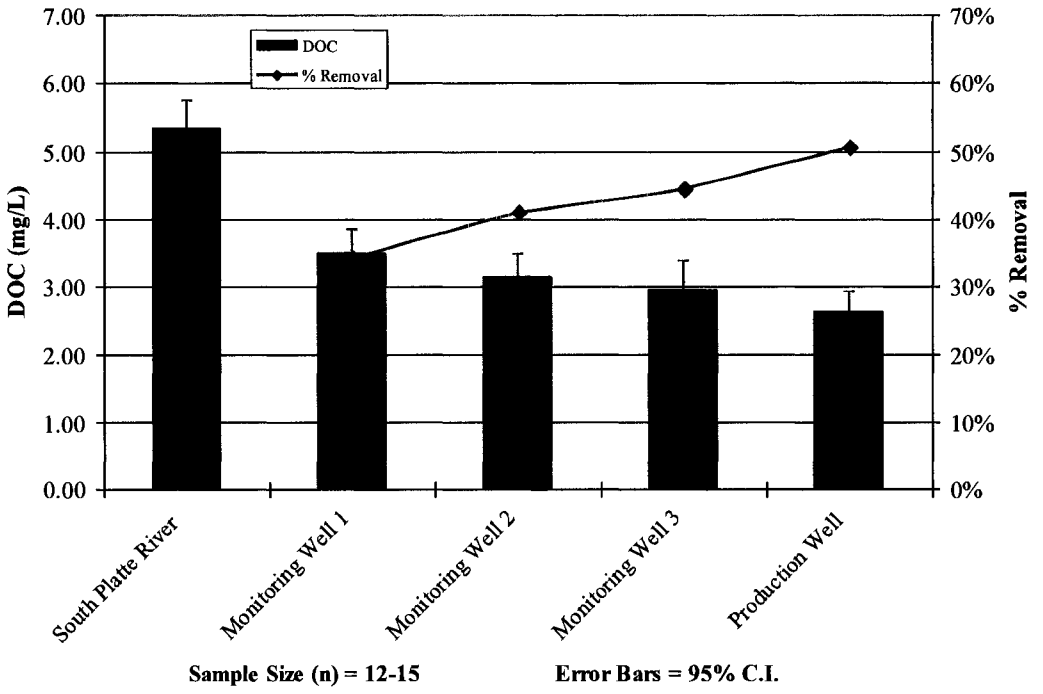


Figure V.5: DOC reduction observed in field RBF system (Sampling events 1/2005-7/2006).

V.3.2. RBF Column Study:

A pilot scale RBF column study was conducted to understand RBF removal characteristics of perchlorate under more controlled conditions than the field study. The column set-up to simulate RBF was composed of natural alluvial sand and fed with South Platte River water with a retention time of 5 days. The retention time of 5 days was chosen as the first testing condition for RBF column study and additional times of 10, 15, 20, and 25 days are currently being studied. At the end of the study, removal kinetics of perchlorate will be estimated.

Figure V.6 summarizes the RBF column monitoring study which was conducted for three months. Source water was collected from the river and spiked with approximately 40 μg/L of perchlorate to assure and an adequate influent signal. The initial concentration of perchlorate was reduced by approximately 19% to an average of 33 μg/L during the 5 days of travel time. Relatively inefficient perchlorate removal can be explained by the fact that the nitrate is primarily used as an electron acceptor (Xu et al., 2003). It is expected that after nitrate removal, perchlorate will be used as an electron acceptor and more efficient perchlorate removal will be observed.

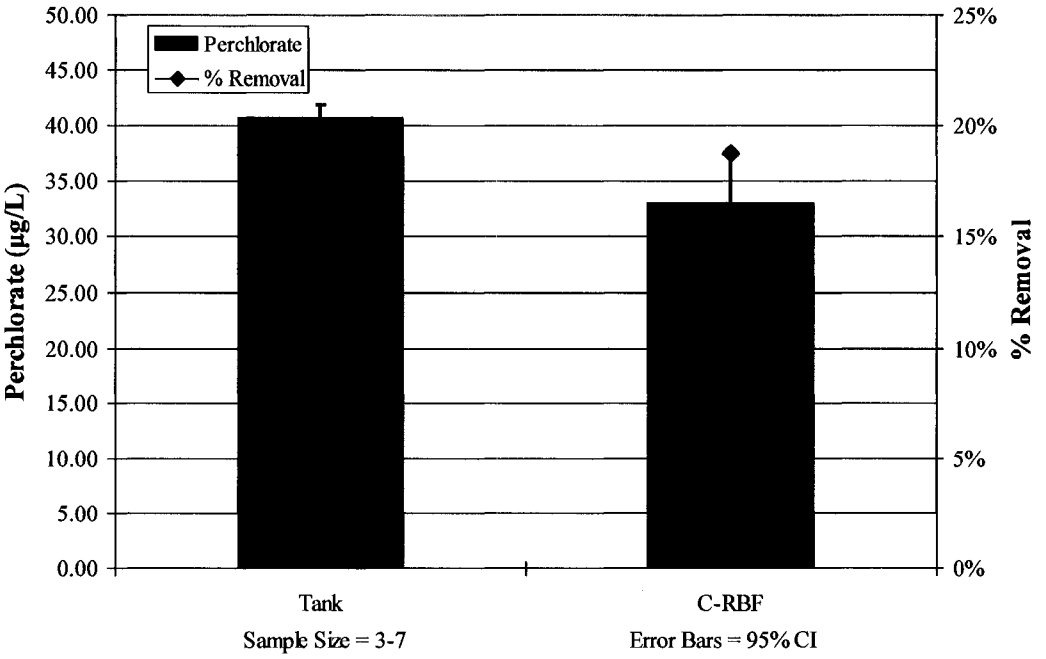


Figure V.6: Perchlorate removal during column-simulated RBF

V.3.3. ARR Column Studies:

ARR conditions were established by feeding the ARR columns with RBF production well (PTW-1) water that had been spiked with 30 µg/L perchlorate. The improved quality of feed water is the major difference between ARR and RBF columns, especially in terms of organic carbon and nitrate. To better understand the removal mechanism of perchlorate through the columns, a control column was used. Microbial activity in the control column was inhibited by the addition of 2mM of sodium azide. Also to examine the possible benefits of water treatment residual on perchlorate removal, a column amended with 30% aluminum-based WTR was studied. As seen in Figure V.7, the removal efficiency of perchlorate in the simulated ARR process was found to be

about 13%, slightly higher than the removal efficiency observed in the control column, 11%. Since the biological activity in the control column was inhibited, the decrease in the perchlorate concentration may be due to sorption on the alluvial sand surface. The relatively low perchlorate removal in the simulated ARR column indicates that even with a residence time of 25 days, assimilable organic carbon is needed for perchlorate degradation. As shown in Figure V.8, organic carbon concentration coming from the production well water (PTW-1) and the carbon levels in the -ARR effluent are the same. Nitrate monitoring results (Yarkin, 2007) (data is not shown) supports the same conclusion that either the DOC levels in the feed water was not sufficient or the nature of the remaining organic carbon after RBF is not suitable for microorganisms to carry out biological degradation.

The WTR amended column showed a high amount of organic carbon leach from residual, an unexpected result (Figure V.8). Apparently, this organic matter promotes significant microbiological activity and the corresponding reduction of perchlorate (Figure V.7). This result is similar to observations of nitrate removal in a previous study (Yarkin, 2007). Figure V.9 shows the TOC levels observed and the amount of TOC leach per foot of column media. An average of 2 mg/L of DOC leaches per foot of column media. If optimized, the WTR amendment can act as an additional organic carbon source and can promote further microbiological activity in ARR for the biodegradation of perchlorate and other trace contaminants.

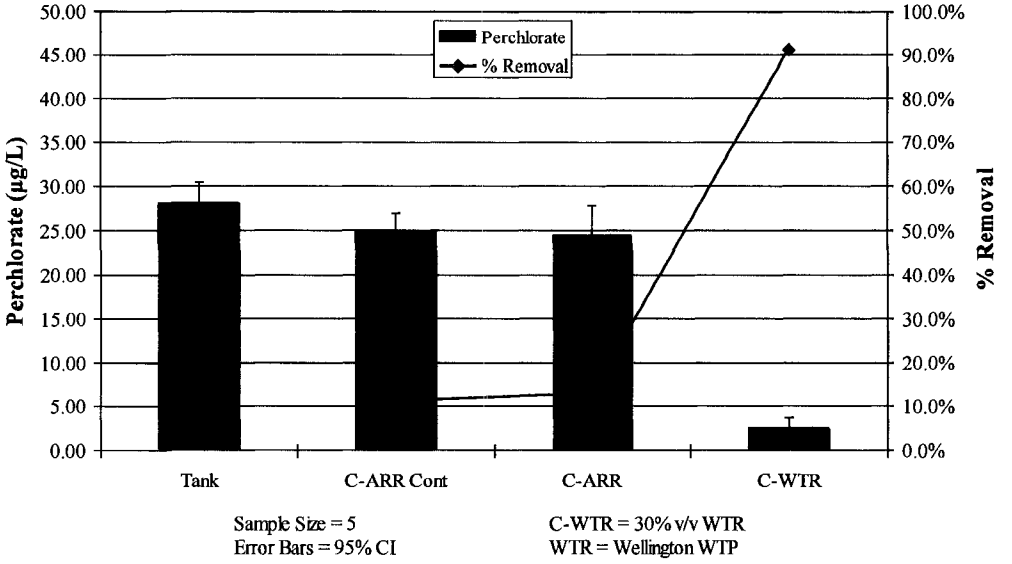


Figure V.7: Perchlorate removal during column-simulated ARR.

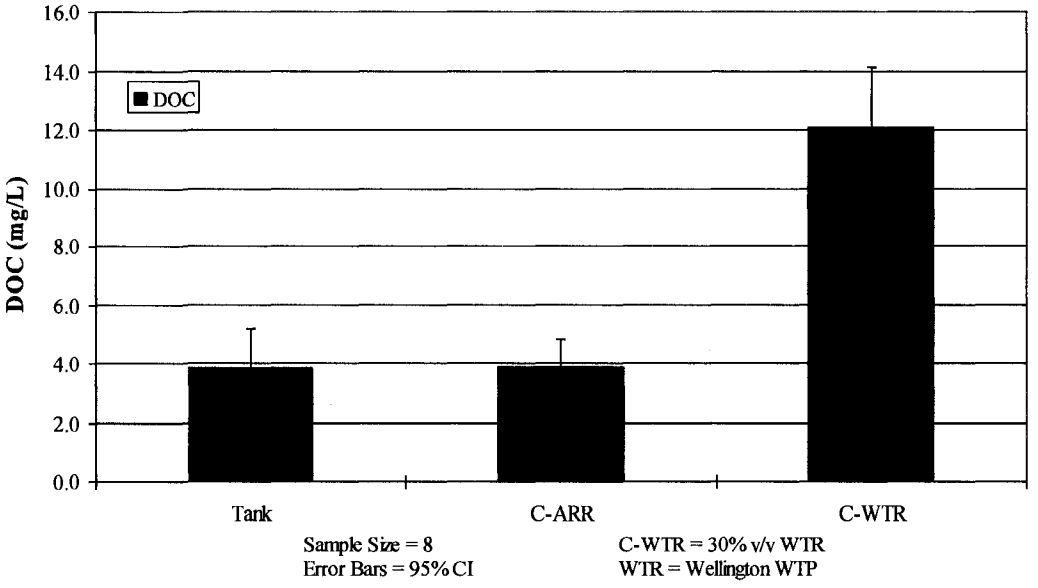


Figure V.8: DOC leaching in ARR columns.

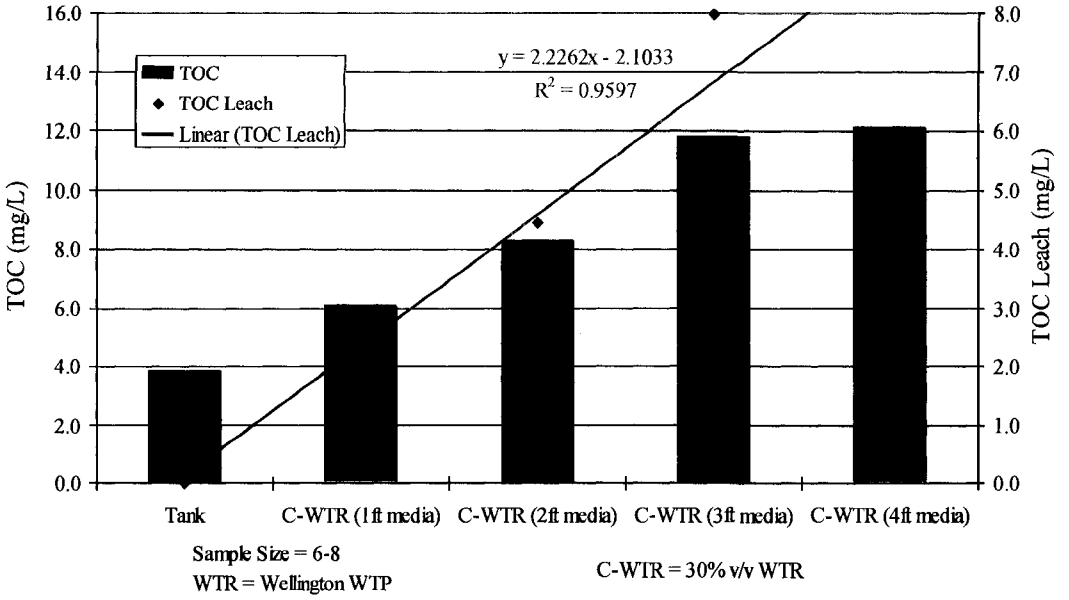


Figure V.9: DOC leaching in WTR-amended column as a function of depth.

V.3.4. Sequential RBF and WTR Amended ARR Column Study:

To observe the fate of perchlorate in the amended infiltration basin and 25 days of ARR treatment a series of column studies were conducted. This study involved the amendment of 1ft sand with 30% v/v WTR to simulate infiltration basin amendment. The infiltration rate was controlled at approximately 1 0.8 ft/day and the retention time in this amended zone was roughly 1.25 days. Perchlorate was spiked at a concentration of 40μg/L into RBF production well (PTW-1) water and fed to the WTR-amended column. Following infiltration through the 1 ft amended zone the water was fed to a simulated ARR column with a flow rate of 0.2mL/min resulting in about 25 days of retention time in the alluvial sand. The same setup was used as a control experiment with a spike of 2mM of sodium azide to the feed water being the only difference. Figure V.10 shows the

results of this study. Exposure to the 1ft WTR column media shows 14.6% removal within 1.25 days. When this water was passed through the ARR column for additional anaerobic reduction, only an additional 30% of perchlorate was removed. However, when the spiked water was passed through the whole 4 ft WTR-amended column, complete removal of perchlorate was observed. Based on this result, it appears that perchlorate reduction is limited by electron donors and that we can control the removal by the amount and/or exposure time to the WTR amended soil. The abiotic control column results (Figure V.11) indicate that perchlorate removal is mostly accomplished through microbial reduction and sorption was not statistically significant.

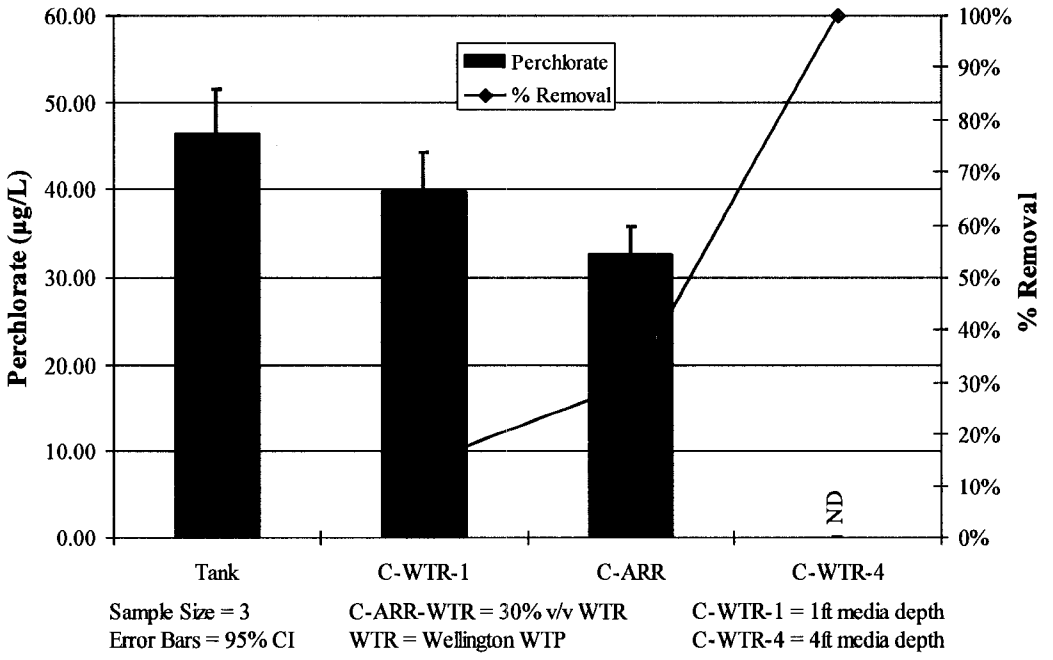


Figure V.10: Sequential RBF- WTR amended ARR column study.

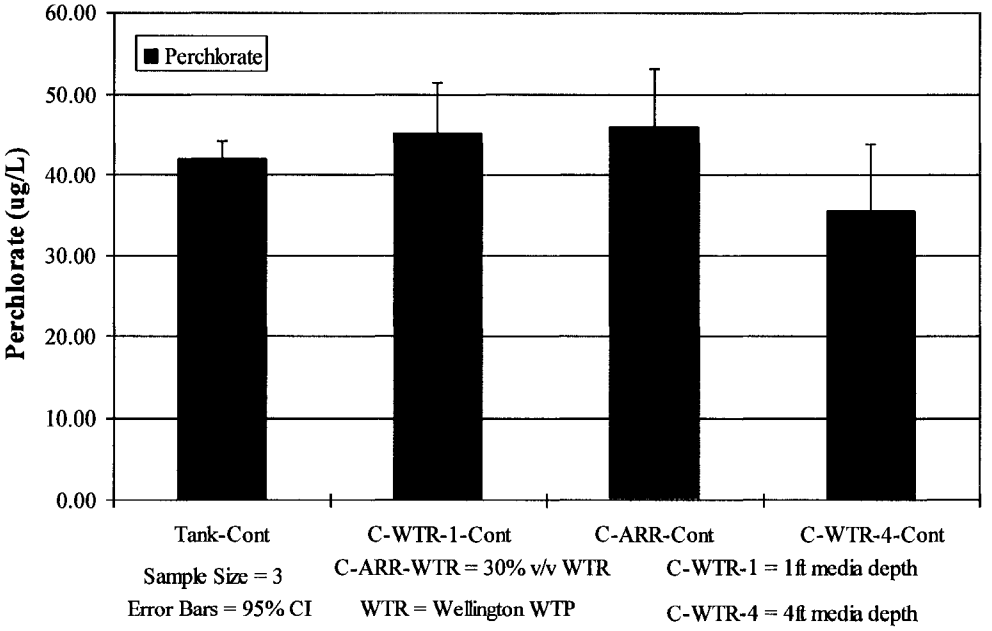


Figure V.11: Sequential RBF- WTR amended ARR column study, abiotic control conditions.

V.4. CONCLUSIONS

RBF and ARR are effective, semi-passive, microbiological treatment options for producing potable water. Their efficiencies in removing nutrients, organic carbon, and trace organic contaminants have been reported by various studies. A study sponsored by the City of Aurora, CO as part of the Prairie Waters Project examined the use of RBF and ARR in series as a multi-barrier pre-treatment approach to supply water to an advanced water treatment facility. One of the specific concerns was the fate of a soon to be regulated contaminant, perchlorate. This specific part of the project tested the removal efficiency, kinetics and the mechanism of perchlorate removal during RBF and ARR using field and column tests. When adequate electron donating substances were present,

perchlorate was readily removed. In un-amended ARR which has been shown to be carbon and electron-donor limited, WTR amendments in the infiltration basin was required to achieve significant removal. It appears that we can alter the design of the WTR-amendment layer to accomplish different objectives.

CHAPTER VI: REMOVAL OF NITRATE DURING RIVERBANK FILTRATION (RBF) AND AQUIFER RECHARGE AND RECOVERY (ARR): BENEFITS OF WATER TREATMENT RESIDUAL (WTR) AMENDMENT

(PAPER WILL BE SUBMITTED TO A JOURNAL)

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Abstract

Riverbank filtration (RBF) and aquifer recharge and recovery (ARR) are well known natural, semi-passive, treatment techniques. An on-going municipal project envisions the implementation of these systems in series to obtain high quality water for long-term storage in a reservoir. This study focuses on the removal efficiency, kinetics, and mechanism of nitrate through a multi-barrier, sequential RBF and ARR system. The study includes the monitoring of a pilot scale field RBF system and column simulation studies. Results of the study indicated that the RBF system is a sustainable barrier for nitrate removal while labile carbon limited ARR cannot achieve significant nitrate removal. To use the ARR system as a secondary barrier for nitrate, a labile carbon source should be introduced to the system. Water treatment residual (WTR) was used as a supplier of organic carbon to the ARR system and the experimental studies indicated that, once optimized, WTR can promote biological significant denitrification through the ARR system.

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VI.1. INTRODUCTION:

The increasing contamination of drinking water sources with nitrate has been a chronic problem throughout the world and the United States. Numerous studies reported that the nitrate levels in surface waters and groundwaters have been increasing in the United States, European Union, and the rest of the world (Spalding and Exner, 1991; 1993; Fried, 1991; Nixon, 1992; Gillham 1991; Faillat; 1990, Kapoor and Viraraghavan, 1997). A survey that was conducted by American Water Works Association in 1985 indicated that 23% of drinking water standard violations were due to excessive nitrate levels (Montgomery, 1985). The U.S. EPA's survey in 1990 revealed that 1,130 public and around 250,000 private domestic water supplies have exceeded the maximum contaminant level for nitrate (Briskin, 1991).

The major inputs of nitrate to surface waters and ground waters are mainly from agricultural runoff due to the excessive application of fertilizers, wastewater discharges, animal manure applications, and urban runoff (Wetzel, 2001). It was reported that the urban sewage effluents can contribute up to 40% of the nitrate contamination in surface waters (Wild, 1977).

The excessive nitrate levels in drinking waters and surface waters can cause significant health issues and environmental problems. A disease known as methaemoglobinaemia or blue-baby syndrome is one of the major health risks that is associated with high nitrogen levels in drinking water. The disease influences infants by decreasing the ability of hemoglobin to carry oxygen (Winton, 2002). Also the formation of n-nitroso compounds during the chlorination of nitrate rich treated waters or in the digestive track due to the consumption of high nitrate containing waters is a potential health risk for humans. The direct link between the digested system cancers and the

consumption of n-nitroso compounds has been reported (Mitch et al., 2003). There is also epidemiologic evidence suggesting that animals exposed to elevated nitrate or nitrite levels experienced negative reproductive effects (Manassaram et al., 2006). High nitrate concentrations reaching surface waters can also cause eutrophication depending on the presence of other nutrients such as phosphorus.

Due to the known adverse health effects on human, the nitrate level in drinking water has been regulated by the U.S. EPA. The established maximum contaminant level for nitrate in drinking water is 10 mg/L NO_3-N.

Nitrate is a negatively charged, small and stable ion with high solubility. Due to these properties, nitrate has a low potential for coprecipitation or adsorption thus it is hard to remove with conventional treatment techniques (Kapoor and Viraraghavan, 1997). Ion exchange, reverse osmosis, and biological denitrification are the major advanced techniques that are used for nitrate removal. Even though these techniques have been applied successfully for nitrate removal, various drawbacks with these technologies such as high concentration brine formation, high operational cost, decrease in efficiency due to the presence of similar ions, and possible breakthrough problems has led to the development of more cost effective and reliable techniques.

Riverbank filtration is a process in which the river water and the water from the surrounding aquifer infiltrates through the porous alluvial media into the collection wells by the hydraulic gradient created. Physical, chemical, and biological processes play an important role in improving water quality as the surface water is subjected to subsurface flow prior to extraction from vertical or horizontal wells (Ray et al., 2002a; Eckert and Irmscher, 2006). The biological process, namely heterotrophic denitrification, is the key

removal mechanism for nitrate removal through RBF. Heterotrophic denitrification requires anaerobic conditions, the presence of a carbon source, and an electron donor. When the environmental conditions are suitable, denitrifying bacteria reduce nitrate to the final product of nitrogen gas by multiple sequential steps to produce energy. The organic carbon in the river water is used as the external carbon source as well as the electron donor while using nitrate as an electron acceptor during this dissimilatory process. Since the denitrifying bacteria are facultative anaerobes, the presence of oxygen inhibits the process, thus anaerobic or anoxic conditions are needed for the denitrification. Eckert and Irmscher (2006) indicated that anaerobic conditions occur in the RBF system few centimeters below the river sediment interface. Wu et al. (2007) reported high nitrogen removal efficiencies (over 95%) from highly nitrate contaminated river by saturated RBF systems.

ARR systems include the natural purification of water through confined or unconfined aquifers. Water is diverted to an infiltration gallery where it percolates into an aquifer and is recovered from collection wells thus creating a residence time through the aquifer's alluvial media. Biological removal of various contaminants has been reported by ARR systems under aerobic and anaerobic conditions (Eckert and Irmscher; 2006). If a sufficient organic carbon source is provided and if anaerobic conditions are established, ARR can achieve nitrate removal by heterotrophic denitrification.

The City of Aurora, CO, envisions an innovative preliminary water purification technique by using RBF and ARR systems in series before collecting the treated water in a terminal reservoir (Figure VI.1). The source water, South Platte River, passes through the Denver downtown area and is impacted by industrial and wastewater treatment plant

discharges as well as agricultural runoff. The city expects the sequential RBF-ARR application as the primary barrier for nitrate contamination before supplying the water to consumers.

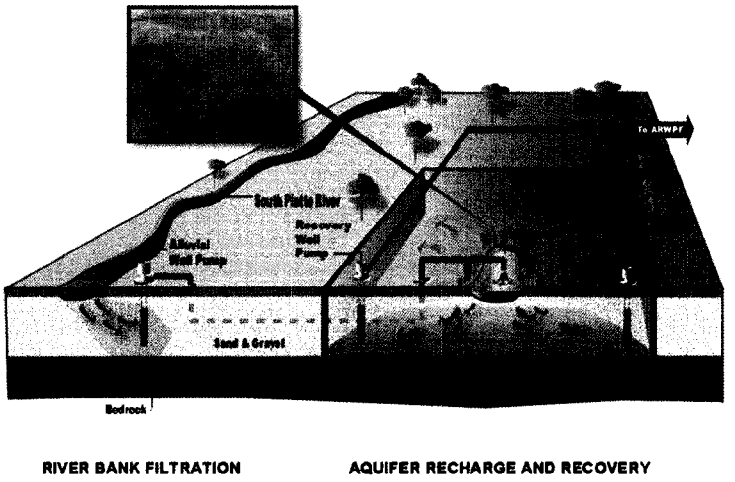


Figure VI.1: Sequential riverbank filtration (RBF) and aquifer recharge and recovery (ARR) (Courtesy of CH2MHill, Denver, CO)

Since most of the biologically available organic carbon would be used during the RBF step (Chapter IV), amending the infiltration basin with water treatment residual (WTR) has been considered beside other alternatives. The high organic carbon content of the WTR from various sources has been reported (Dayton and Basta, 2003; Makris et al., 2004; Markis et al., 2005). It has been envisioned that once optimized, WTR amendment can contribute labile carbon to the carbon limited ARR system, thus promoting further bioremediation of various contaminants as well as nitrate.

This study focuses on evaluating; (i) the removal efficiency of nitrate trough RBF and ARR, and (ii) possible benefits of WTR amendment on carbon limited ARR to promote denitrification.

VI.2. MATERIALS AND METHODS:

VI.2.1. Riverbank Filtration Field Study:

The RBF field study site is located north of the City of Brighton, CO, between the South Platte River and a non-operational gravel mine. The gravel mine is surrounded by a slurry wall to keep groundwater and river water out of the site, isolating the west shore from surrounding groundwater, thus, creating a convenient study site. The production well (PTW-1) and the monitoring wells (PTMW-2, PTMW-3, PTMW-4) are located on the west shore between the slurry wall and the river. PTMW-1 is an imaginary well where the river samples were collected. Production and monitoring wells were installed in November 2004 and the RBF system has been in continuous operation since December 2004 except for short periods of time during the power outages. Figure VI.2 shows the riverbank filtration site, the gravel mine, and production and monitoring wells.

The production well, PTW1, is 18 inches in diameter and is constructed with a stainless steel casing, and pumps water with the flow rate of 450 gpm. All monitoring wells are 2.0-inch PVC wells. Construction details for production and monitoring wells are given in Table VI.1 below.

South Platte River, monitoring wells, and the production well were monitored biweekly between January 2005 and October 2005 for nitrate. River samples were collected via grab samples. Monitoring wells were sampled by using an EPA approved low-flow method with dedicated Teflon tubing, and a peristaltic pump. The production well was sampled from a port that is installed in the discharge piping near the well. Samples were collected in HDPE bottles and kept in a cooler during the transport. Samples were filtered with 0.45μm glass fiber filters and kept at 4°C before analysis.



(a) (b)

Figure VI.2: (a) Aerial photo of RBF field study site generated using Google Earth (Newton,2007) (b) RBF field study site with production and monitoring wells, photo by Tetra Tech RMC (Longmont, CO)

Table VI.1: RBF field study well construction details

Well ID	Well Diameter (in)	Total Well Depth (ft)	Depth of Water (ft)	Distance form River (ft)	Residence Time (days)
PTMW-2	2	32	17	137.15	10
PTMW-3	2	30	14	257.89	15
PTMW-4	2	30	14	373.81	22
PTW-1	18	45	33	417.58	25

VI.2.2. Pilot Scale Column Studies:

For the pilot scale studies, 4-foot acrylic columns with an internal diameter of 6 inches were used. Each column has 3 sampling ports, which are 1 foot apart, on the side of the column. Sampling ports are made from stainless steel tubing and they reach to

exactly the center of the column cross section for representative sample collection. Each sampling port is screened at the end to prevent column media loss from the ports. To distribute the inflow equally to the column, column caps are built with multiple injection points (Figure VI.3). During the course of the study, all columns were kept at 60° F and wrapped with aluminum foil to prevent photosynthetic microbial activity.

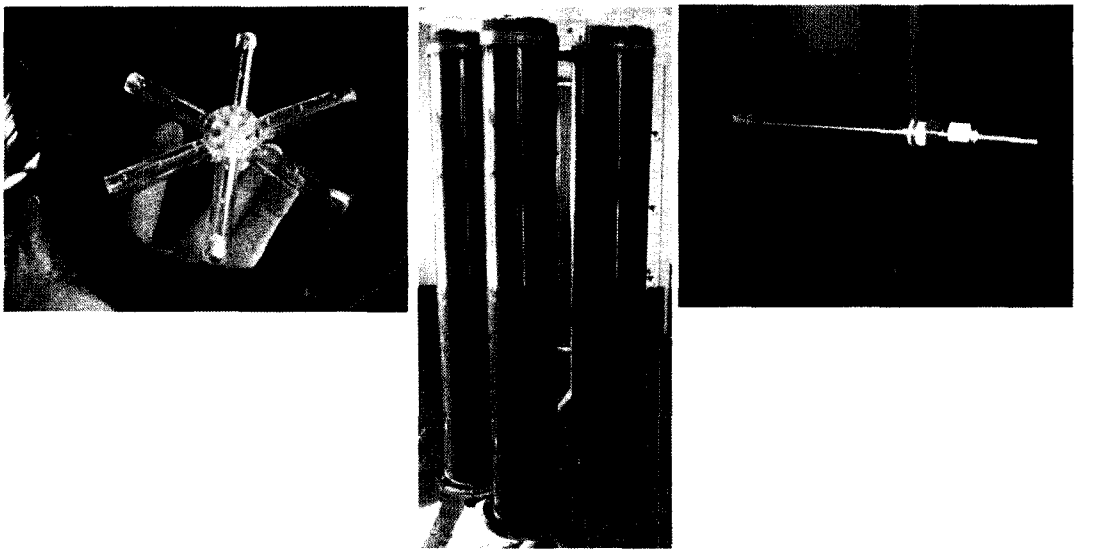


Figure VI.3: Column setup for RBF and ARR simulation studies.

Alluvial sand that was used in the column media was obtained from the west river bank at the RBF field study site approximately 2 feet under the surface. Alluvial sand was sieved with no.10 (<2mm) sieve to obtain uniform particle size. Water treatment residual (WTR) that was used in the column simulation studies was obtained from the City of Wellington Water Treatment Plant, CO (Table VI.2). Aluminum based WTR was first dried in the oven at 180°C overnight then ground and sieved with no.10 (<2mm) to be consistent with the alluvial sand size distribution.

Table VI.2: Physical and chemical characteristics of WTRs

WTR Source	Total (%) P	Al	Fe	Ca	Mg	K	Oxalate Extractable (%) P	Fe	Al	Saturation Paste pH	EC mmhos/cm
Aurora	0.166	10.25	2.324	0.785	0.241	0.528	0.0363	0.3118	8.623	7.2	0.8
Denver	0.054	10.32	1.719	0.493	0.046	0.724	0.0114	0.1672	9.931	6.8	8.6
Wellington	0.113	15.08	0.586	0.861	0.043	0.161	0.0123	0.0887	14.47	7.4	1.2

WTR Source	Sand (%)	Silt	Clay	Texture	Total (%) C	TOC	$CaCO_3$	CO_3-C
Aurora	98	2	0	Sand	17.28	17.12	1.36	0.16
Denver	93	3	4	Sand	3.669	3.59	0.68	0.08
Wellington	96	2	2	Sand	16.33	16.07	2.21	0.26

The media was bio-acclimated by feeding the columns with a flow rate of 1mL/min from bottom to top for 15 days, followed by 3mL/min of top to bottom flow for 30 days. Following the acclimation, columns were fed with different feed waters depending on the needs of each specific study. Preconditioning steps were repeated before each column simulation study. To feed the columns, peristaltic pumps were used with Teflon tubing throughout the study.

Samples were collected in HDPE bottles and kept in a cooler during the column simulation studies. Samples were filtered with 0.45μm glass fiber filters and kept at 4°C before analysis.

RBF Column Simulation Study:

The RBF columns (C-RBF) were built to observe the denitrification kinetics during riverbank filtration. Five air-tight columns were connected in series to achieve 25 days of hydraulic residence time. C-RBF columns were monitored from the sampling ports located on the first column as well as the effluents of each column biweekly between August 2005 and December 2005. Table VI.3 summarizes the content of the column media and the operating conditions. Figure VI.4 gives a sketch of the experimental column setup. Following the initial preconditioning step described above, five C-RBF columns in series were fed with 1mL/min (25 days of total hydraulic residence time) of the South Platte water. The abiotic control column (C-RBF-Control) was fed with the South Platte water that was spiked with 2mM of sodium azide to observe the fate of nitrate without microbiological activity. Following the preconditioning step described above, the column was fed with a flow rate of 1mL/min (5

days of hydraulic residence time) and sampled biweekly from the sampling ports and the effluent.

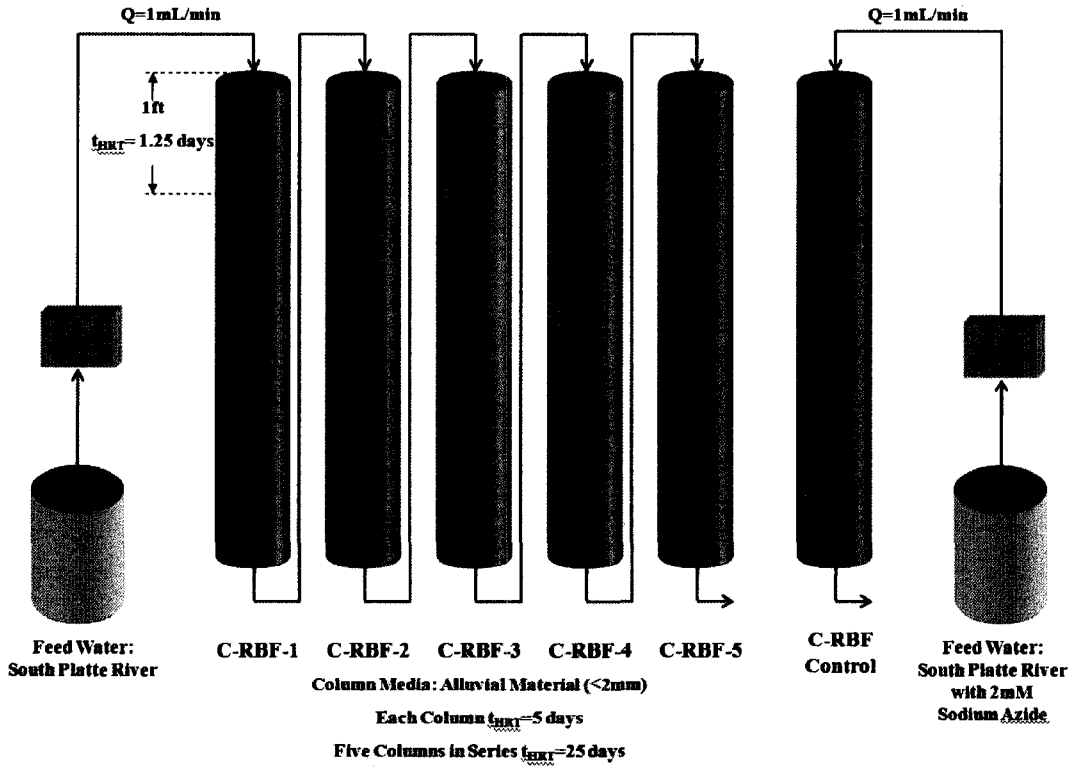


Figure VI.4: RBF column simulation study experimental setup

Table VI.3: RBF column simulation study: Column media content and operating conditions.

	RBF Columns (C-RBF) (Five Columns in Series)	**RBF Control Column (C-RBF-Control)**
Media	Natural Alluvial Sand (Sieved with no.10 sieve)	Natural Alluvial Sand (Sieved with no.10 sieve)
Condition	Wet/Saturated	Wet/Saturated
Media Mass in the Column	Sand = 32.5kg (one column)	Sand = 32.5kg
Feed Water	South Platte Water	South Platte Water Spiked with 2mM of Sodium Azide
Flow Rate	1mL/min	1mL/min
HRT	5 days (one column) 25 days (five columns)	5 days

ARR Column Simulation Study:

An ARR column simulation study was conducted by using RBF treated production well (PTW-1) water that was spiked with 10mg/L NO_3-N as the feed source. Columns that were used for RBF column simulation studies were acclimated with production well water according to the procedure described above and were used in this study. Columns (C-ARR, C-ARR-Control, C-ARR-WTR) were sampled monthly between April 2006 and November 2006. The content of the column media and the operating conditions are summarized in Table VI.4 below. Figure VI.5 shows a sketch of the experimental column setup. The C-ARR column was used to simulate ARR conditions and the column was fed with 0.2mL/min of production well water. With this flow rate, the hydraulic retention time was 25 days. To observe the removal efficiency of nitrate under abiotic conditions, the C-ARR-Control column was fed with 0.2mL/min of

2mM sodium azide and 10 mg/L NO_3-N spiked production well water. Under these feed conditions, the hydraulic residence time was 25 days. To understand the effect of alum based water treatment residual on nitrate removal, column C-ARR-WTR was fed with 1mL/min of production well water spiked with 10 mg/L NO_3-N. All columns were sampled from the effluent port.

Table VI.4: ARR column simulation study: Column media content and operating conditions.

	ARR Column (C-ARR)	**Abiotic Control Column (C-ARR-Control)**	**ARR Column amended w/ WTR (C-ARR-WTR)**
Media	Natural alluvial sand (sieved with no.10 sieve)	Natural alluvial sand (sieved with no.10 sieve)	70% v/v natural alluvial sand and 30% v/v WTR (sieved with no.10 sieve)
Condition	wet/saturated	wet/saturated	wet/saturated
Media Mass in Column	Sand = 32.5kg	Sand = 32.5kg	Sand = 21.6kg WTR = 10.6kg Total = 32.2kg
Feed water	Production Well Water (PTW-1) spiked with 10 mg/L NO_3-N	Production Well Water (PTW-1) Spiked with 2mM Sodium Azide and 10 mg/L NO_3-N	Production Well Water (PTW-1) spiked with 10 mg/L NO_3-N
Flow Rate	0.2mL/min	0.2 mL/min	1mL/min
HRT	25 days	25 days	5 days

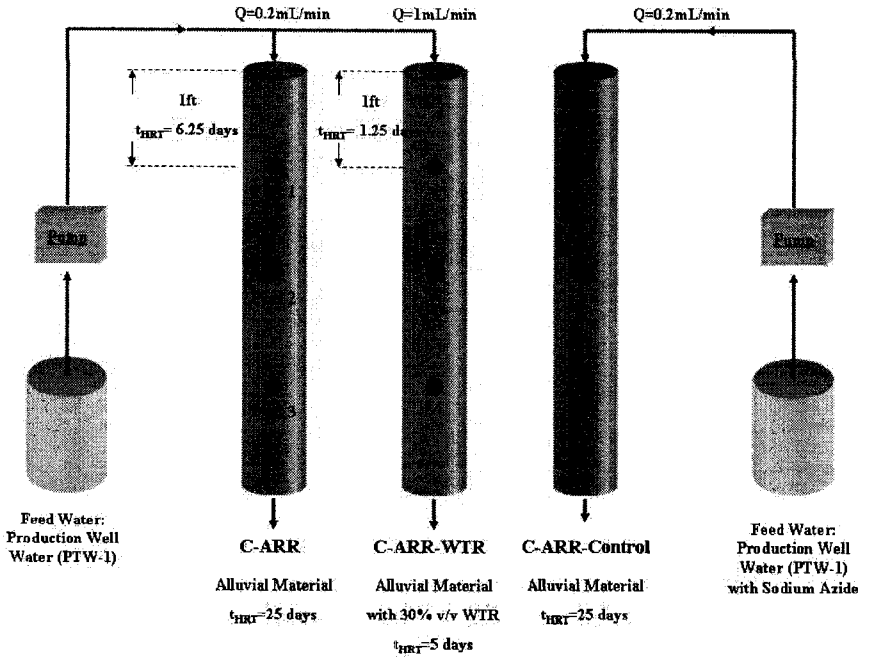


Figure VI.5: ARR column simulation study experimental setup

Sequential RBF – WTR Amended ARR Column Simulation Study:

A sequential RBF – WTR amended ARR column simulation study was conducted to understand the removal efficiency and kinetics of nitrate throughout the system. During this study RBF treated production well (PTW-1) water spiked with 10mg//L NO_3-N was used as the feed. Columns that were used for ARR column simulation studies were acclimated with production well water as the procedure described above and were used in this study. An additional amended abiotic control column (C-ARR-WTR-Control) was built from scratch and was acclimated as others. Operation of columns (C-ARR-WTR, C-ARR, C-ARR-WTR-Control, C-ARR-Control) began in March 2007 and columns were sampled monthly between May 2007 and July 2007. The composition of the column

media and the operating conditions are summarized in Table VI.5. Figure VI.6 shows a sketch of the experimental column setup. The top 1 foot media of C-ARR-WTR column was used to simulate the amended ARR infiltration basin and the C-ARR column was used to simulate the alluvial sand ARR part. C-ARR-WTR was fed with 1mL/min of production well water. After a foot media depth (port 1, C-ARR-WTR-1) water was withdrawn with a flow rate of 0.2 mL/min and fed to the C-ARR column. Hydraulic retention times were 1.25 days and 25 days for C-ARR-WTR-1 and C-ARR, respectively.

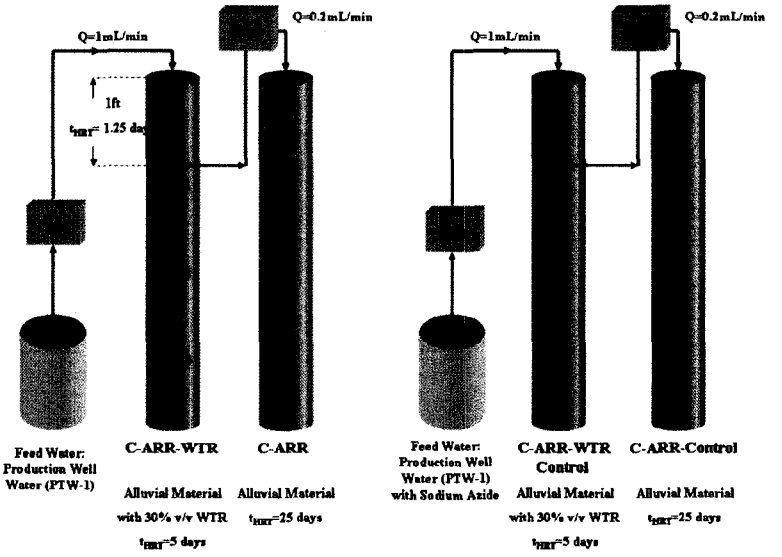


Figure IV.6: Sequential RBF- WTR amended ARR column simulation study experimental setup.

Table VI.5: Sequential RBF – WTR amended ARR column simulation study: Column media content and operating conditions

	ARR Column amended w/ WTR (C-WTR-1) 1 ft media depth	**ARR Column amended w/ WTR (C-WTR-4) 4 ft media depth**	**ARR Column (C-ARR)**	**ARR Column amended w/ WTR Control (C-WTR-1C) 1 ft media depth**	**ARR Column amended w/ WTR Control (C-WTR-4C) 4 ft media depth**	**ARR Column Control (C-ARR-C)**
Media	70% v/v natural alluvial sand and 30% v/v WTR (sieved with no.10 sieve)	70% v/v natural alluvial sand and 30% v/v WTR (sieved with no.10 sieve)	Natural alluvial sand (sieved with no.10 sieve)	70% v/v natural alluvial sand and 30% v/v WTR (sieved with no.10 sieve)	70% v/v natural alluvial sand and 30% v/v WTR (sieved with no.10 sieve)	Natural alluvial sand (sieved with no.10 sieve)
Condition	wet/saturated	wet/saturated	wet/saturated	wet/saturated	wet/saturated	wet/saturated
Mass in Column	Sand = 5.4kg WTR = 2.65kg Total = 8.05kg	Sand = 21.6kg WTR = 10.6kg Total = 32.2kg	Sand = 32.5kg	Sand = 5.4kg WTR = 2.65kg Total = 8.05kg	Sand = 21.6kg WTR = 10.6kg Total = 32.2kg	Sand = 32.5kg
Feed water	Production Well (PTW-1) (spiked with 10 mg/L NO_3-N)	Production Well (PTW-1) (spiked with 10 mg/L NO_3-N)	C-WTR-1 Water	Production Well (PTW-1) (spiked with 2mM sodium azide and 10 mg/L NO_3-N)	Production Well (PTW-1) (spiked with 2mM sodium azide and 10 mg/L NO_3-N)	C-WTR-1C Water
Flow Rate	1mL/min	1mL/min	0.2 mL/min	1mL/min	1mL/min	0.2 mL/min
HRT	1.25 days	5 days	25 days	1.25 days	5 days	25 days

Nitrate Analyses:

Samples were analyzed for nitrate by the Soil-Water-Plant Testing Laboratory of Colorado State University. Flow Injection Analysis utilizing an OI Analytical (College Station, TX) Flow Solution 3000 was used to analyze the samples according to the U.S. EPA Method 353.2.

DOC Analyses:

The DOC and analyses were conducted by the Soil-Water-Plant Testing Laboratory of Colorado State University. For DOC analysis EPA Method 415.2 was used.

VI.3 RESULTS AND DISCUSSION:

VI.3.1 Riverbank Filtration Field Study:

The riverbank filtration field study involved monitoring of the South Platte River, three monitoring wells and the production well for approximately 10 months for nitrate levels and DOC concentration. Figure VI.7 summarizes the 10 month study nitrate levels from the RBF field study.

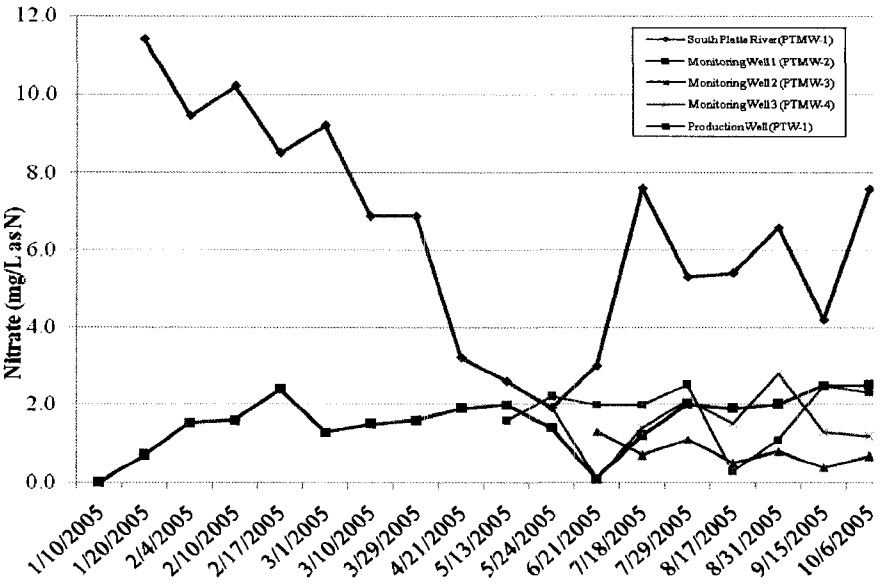


Figure VI.7: RBF field monitoring study for nitrate

The nitrate concentrations in the South Platte River fluctuate throughout the year. The flow rate of the river is one of the major factors that affect the nitrate levels. The runoff season when the nitrate transportation occurs from the agricultural lands to the river directly affect the flow rate and nitrate levels in the river. Also, the flowrate of the river is mostly regulated by the water treatment plant discharges, especially by Brighton WWTP. Brighton WWTP directly affects the nitrate levels in the river during the dry seasons. The background groundwater nitrate level was measured as <0.01mg/L NO_3-N in January 2005 before the production well was activated. During the monitoring study the highest and lowest nitrate concentrations in the river were recorded as 11.4 mg/L NO_3-N in January 2005 and 1.9 mg/L NO_3-N in May 2005, respectively.

Highly fluctuating nitrate concentrations in the river directly influence the nitrate levels in the monitoring wells as well as the finished water nitrate levels. However, even

with the varying nitrate levels in the river, finished water nitrate levels never exceeded 2.5 mg/L NO_3-N. Even the highest effluent nitrate concentration is considerably less than the U.S. EPA's drinking water nitrate criteria of 10 mg/L NO_3-N. The RBF system showed approximately 100% nitrate removal (Figure VI.7) when the nitrate level in the river was less than 2 mg/L NO_3-N with the lag time of 27 days which is approximately equal to the hydraulic residence time of 25 days that was calculated by the groundwater flow model.

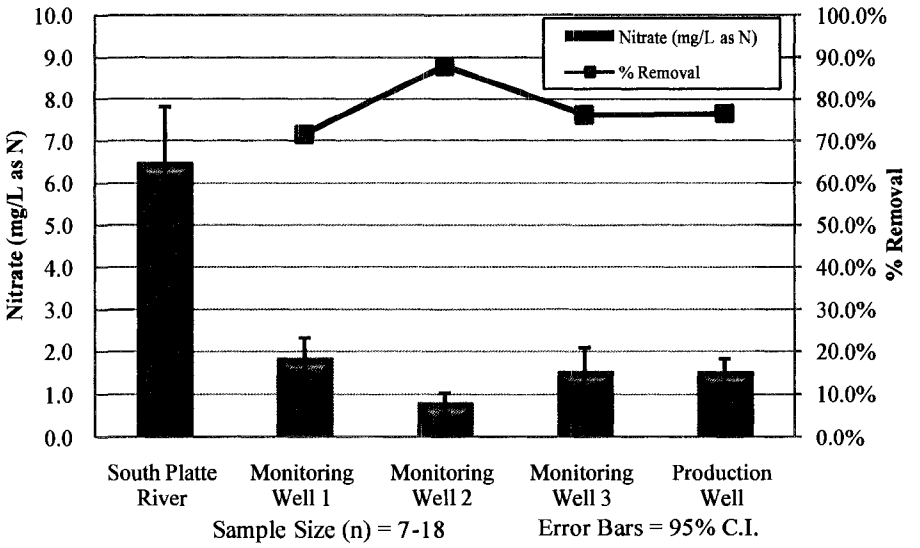


Figure VI.8: RBF field study: Average nitrate levels and percent removal

During the 10 months of the study, the average influent nitrate level of 6.5 mg/L NO_3-N was reduced to 1.53 mg/L NO_3-N with a removal efficiency of 76.4% (Figure VI.8). The monitoring well 2 shows (Figure VI.8) a better removal with the nitrate concentration of 0.78 mg/L NO_3-N and 88% removal. The higher concentrations that were observed in the monitoring well 3 and the production well compared to the

monitoring well 2 is caused by the influence of the nitrate rich surrounding ground water. Newton (2007) reported nitrate levels in the monitoring wells, PTMW-8, and PTMW-9 (Figure VI.2b), which are parallel to the river, ranging between 1.7 to 2.6 mg/L NO_3-N. Also the groundwater flow model developed by CH2MHill indicated that there is groundwater flow from the southwest corner of the slurry wall toward the production well. The higher nitrate concentrations that were observed in the monitoring well 3 and the production well are attributed to the mixing of nitrate rich natural groundwater and the RBF treated river water.

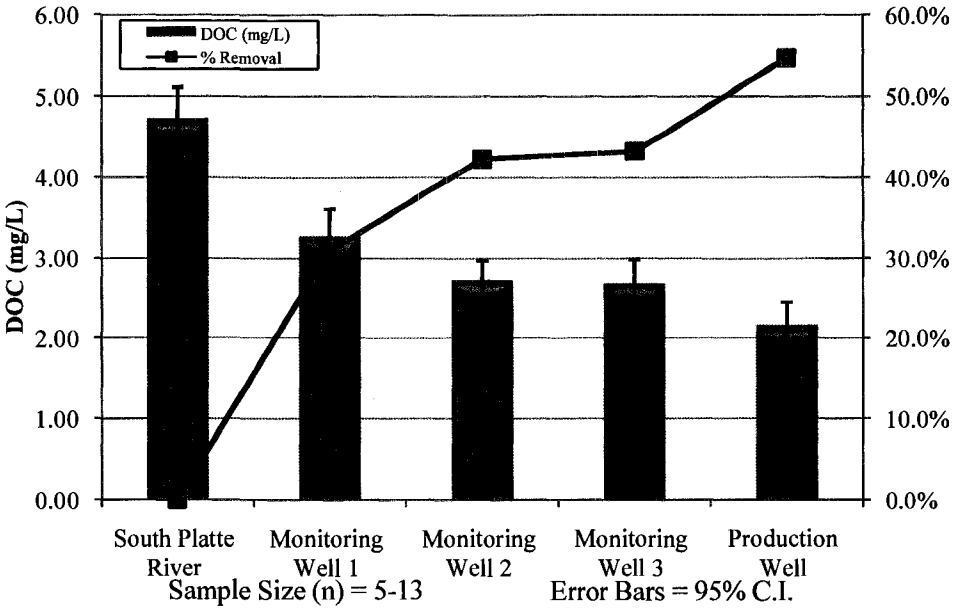


Figure VI.9: RBF field study: Average DOC levels

DOC monitoring (Figure VI.9) indicates that the easily biodegradable portion of the DOC was consumed between the river and monitoring well 2, therefore, this region is where the majority of the denitrification takes place. The decrease in DOC concentration

also continues to a lesser extent after monitoring well 2 indicating additional denitrification occurs up to the production well.

Even though the nitrate levels in the South Platte River rarely exceeds the drinking water criteria of 10 mg/L NO_3-N, the RBF system reduces the average nitrate levels from 6.5 mg/L as NO_3-N to 1.53 NO_3-N with the removal efficiency of 76.4%. The data obtained from the study also indicates that nitrate removal continuously occurs and keeps the effluent nitrate concentrations around 2 mg/L NO_3-N being independent of the seasonal temperature variations.

VI.3.2. Riverbank Filtration Column Simulation Study:

The RBF columns, C-RBF, with five serially connected air-tight columns were monitored from the three sampling ports on C-RBF-1 and effluents of all five columns as biweekly for 4 months. Figure VI.10 shows the average nitrate levels monitored during the RBF column simulation study.

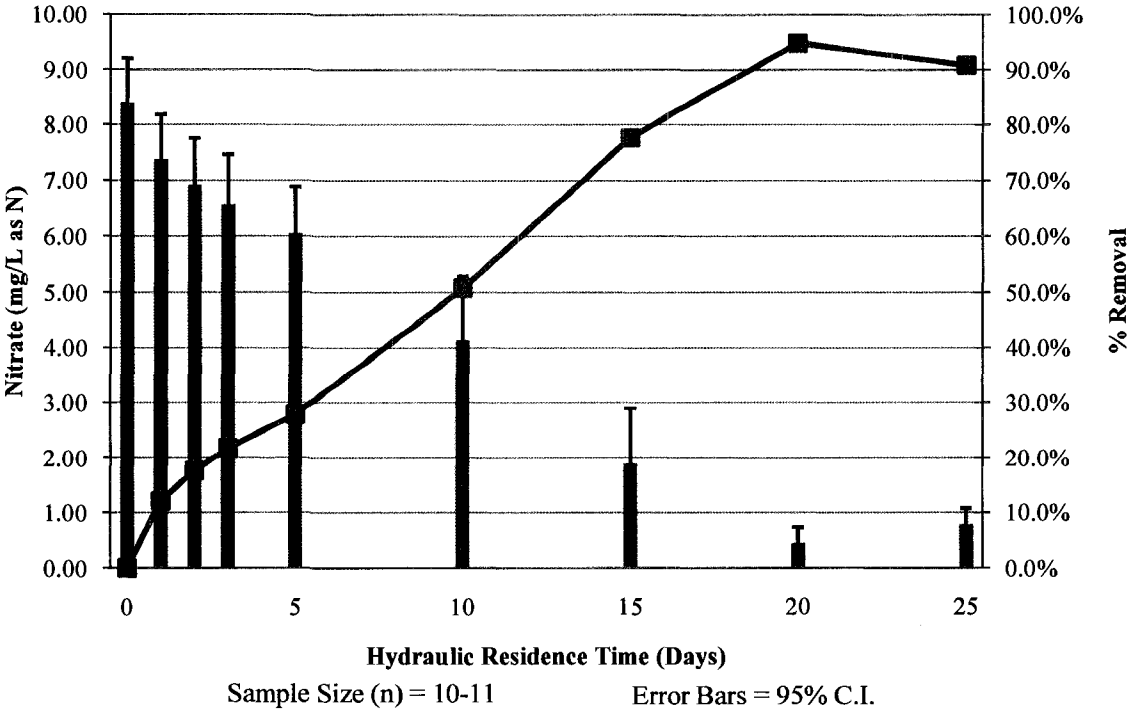


Figure VI.10: RBF column simulation study: Average nitrate levels

The initial average nitrate concentration that was fed to the simulation columns (8.37 mg/L NO_3-N) was higher than the average river nitrate level (6.5 mg/L NO_3-N). The removal efficiencies that were observed in the simulation columns were slightly higher than what was observed in the RBF field study with respect to the hydraulic residence time. Overall, the RBF columns achieved 90.9% removal by reducing the nitrate level from 8.37 mg/L NO_3-N to 0.77 mg/L NO_3-N within 25 days while the field monitoring study showed 76.4% removal by reducing the nitrate levels from 6.5 mg/L NO_3-N to 1.53 mg/L NO_3-N. The lower removal efficiency is attributed to the influence of nitrate rich groundwater.

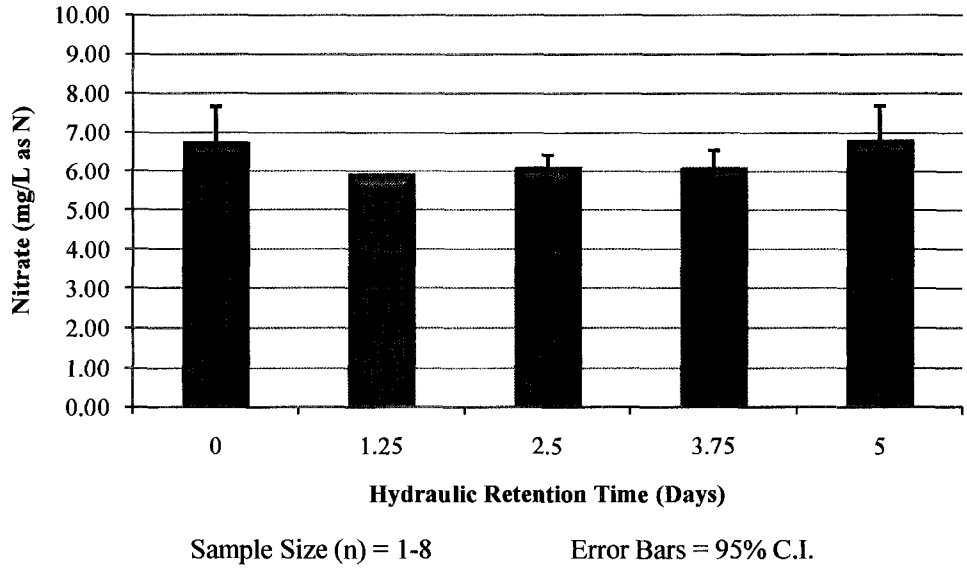


Figure VI.11: RBF column simulation study: C-RBF-Control average nitrate levels

To understand the effect of microbial denitrification, the abiotic RBF simulation control column C-RBF-Control was monitored for 4 months from all sampling ports and the effluent with the hydraulic residence time of 1.25, 2.5, 3.75, and 5 days (Figure VI.11). The abiotic control column shows that there is no nitrate removal when the biological activity is minimized.

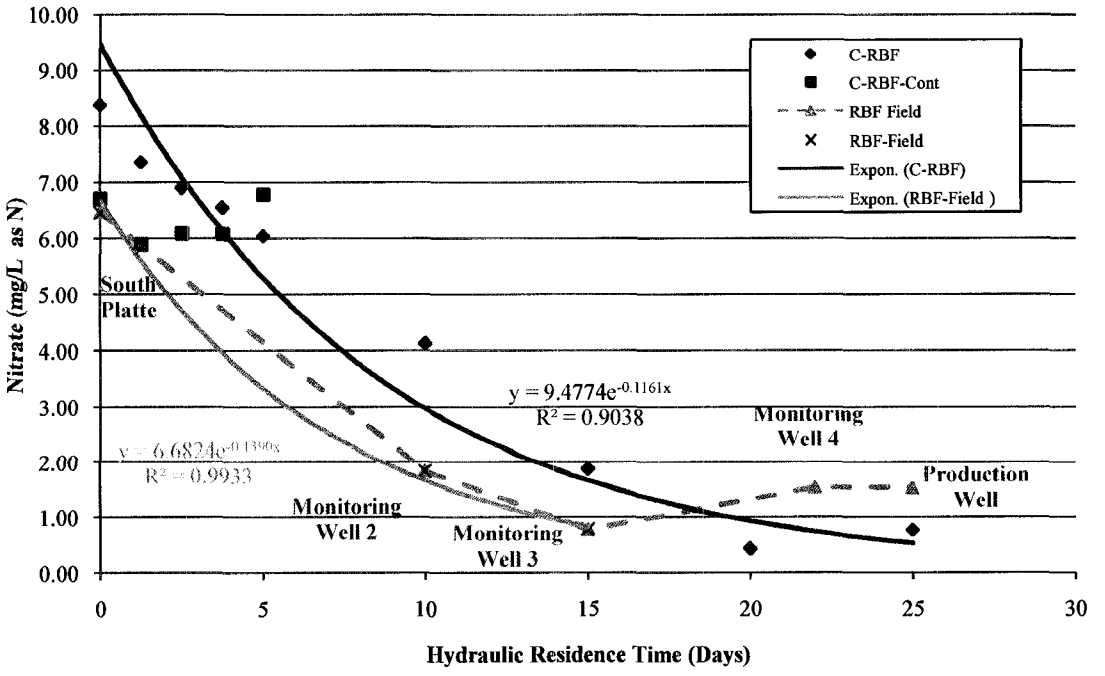


Figure VI.12: RBF column simulation study: Comparison with the field study

Figure VI.12 compares the findings of the RBF column simulation study with the field RBF study. The field and the column simulation studies show that the nitrate removal follows a similar pattern except the fact that the nitrate levels observed between the residence time of 20 to 25 days are slightly higher in the field due to the influence of the natural groundwater. The nitrate data observed in the RBF simulation data fits a first order exponential decay with the correlation coefficient of 0.9038. The first order decay coefficient k was obtained as 0.1161 with the half life of 5.97 days. When the nitrate levels in the river, monitoring well 2, and monitoring well 3 are considered, similarly data fits a first order exponential decay with the correlation coefficient of 0.9933. The first order decay coefficient k for the RBF field was obtained as 0.1390 with the half life is calculated as 4.97 days.

The results of the RBF column simulation study also indicates that the RBF system is capable of reducing nitrate concentration well below the drinking water criteria of 10 mg/L NO_3-N.

VI.3.3 Aquifer Recharge and Recovery (ARR) Column Simulation Study

The ARR columns C-ARR, C-ARR-Control and C-WTR-ARR were fed with RBF finished water with 10 mg/L NO_3-N spike. All columns were monitored monthly for eight months from effluents with the retention times of 25 days for C-ARR and C-ARR-Control, and 5 days for C-ARR-WTR. Figure VI.13 shows the average nitrate results for this study.

The feed solution was spiked with nitrate to reach the concentration of 10 mg/L NO_3-N to simulate a scenario in which the RBF system fails and the ARR system is the only barrier for nitrate before water is pumped for surface storage. Also the column C-ARR-WTR was monitored to see the possible beneficial use of WTR on nitrate removal since WTRs are reported to contain high organic carbon levels (Dayton et al., 2003, Makris et al., 2004) and high amount of DOC leach occurs from the WTR amended columns (Chapter IV).

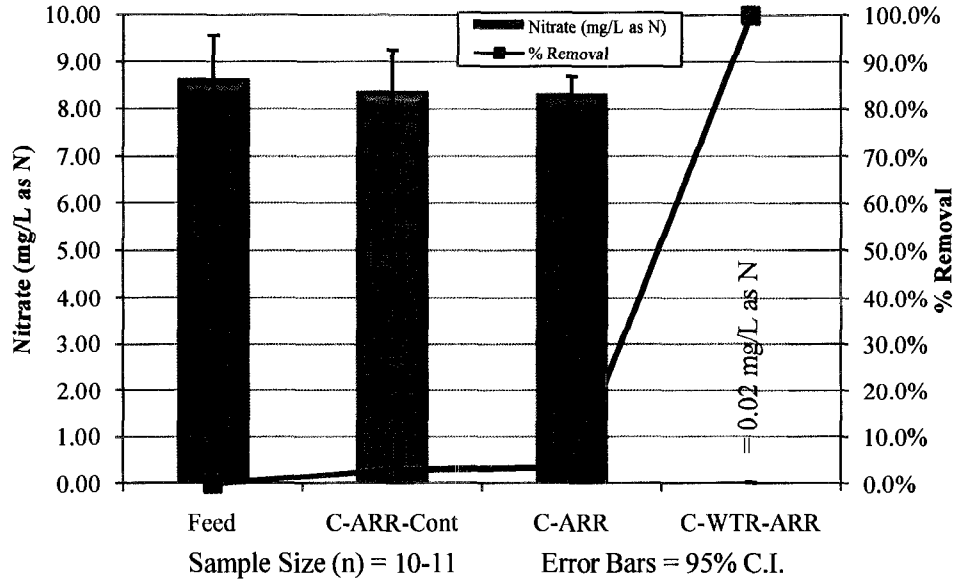


Figure VI.13: ARR column simulation study: Average nitrate levels

The nitrate level was reduced from 8.52 to 8.31 mg/L NO_3-N through the C-ARR column indicating that most of the biologically available carbon was used during the RBF process. Since the biologically available DOC is the major carbon source and electron donor for the heterotrophic denitrification in the column, the low denitrification efficiency (3.5%) can be explained by the lack of organic carbon source. The abiotic control column shows the removal of the nitrate level from 8.52 to 8.36 mg/L NO_3-N (2.9%) indicating that the removal mechanism of nitrate is biological denitrification.

The WTR amended ARR column C-ARR-WTR reduces the nitrate level of 8.52 to 0.02 mg/L NO_3-N with the removal efficiency of 99.8%. Essentially the complete removal of nitrate with the residence time of 5 days can be due to the promoted biological activity with the organic carbon leach from the WTR amendment. Another removal mechanism could be a chemical reduction of nitrate to ammonia due to the anoxic and

highly reducing environment created by the WTR amendment. Also the conversion of nitrate to ammonia under strong reducing conditions by variety of bacteria, including *Geobacter metallireducens*, *Desulfovibrio* spp., and *Clostridium* through dissimilatory reduction has been reported(Prescott et al., 2005). The ARR column simulation study experimental plan is insufficient to explain the removal mechanism of nitrate through WTR amended column. The following study was also conducted to explain the removal mechanism of nitrate through the WTR amended media.

VI.3.4. Sequential RBF and WTR Amended ARR Column Simulation Study

To evaluate the fate of nitrate in RBF and WTR amended ARR in series, the column C-ARR-WTR was fed with RBF finished with the nitrate spike of 10mg/L NO_3-N and after a travel time of 1.25 days in C-ARR-WTR, the water was diverted to the C-ARR column for a subsequent travel time of 25 days through alluvial sand. To confirm the nitrate removal mechanism, exactly the same experimental setup was prepared and fed with the RBF finished water that was spiked with 10mg/L NO_3-N and 2mM sodium azide to prevent biological activity.

Figure VI.12 shows the average nitrate levels throughout the sequential RBF – WTR amended ARR column simulation study. 1-foot WTR amended column reduces the nitrate level form 12.6 to 11.17 mg/L NO_3-N (11% removal) with the residence time of 1.25 days. Following the 1-foot WTR amended column, C-WTR-1, ARR simulation column reduces the nitrate concentration from 11.17 to 8.23 mg/L NO_3-N with the residence time of 25 days. The total nitrate removal at the effluent of C-ARR column was monitored as 35%. The organic carbon addition from the 1-foot WTR amended column

provides additional 24% removal. The nitrate level at the effluent of WTR amended column was monitored as 1.04 mg/L NO_3-N with 92% removal.

The abiotic experimental setup (Figure VI.14) shows a reduction of nitrate level from 11.73 to 10.93 mg/L NO_3-N through the WTR amended control column with the residence time of 1.25 days. Following the C-WTR-1 the nitrate concentration was reduced to 10.47 mg/L NO_3-N with the residence time of 25 days. The 4-foot (residence time of 5 days) WTR amended control column was reduced the nitrate level to 0.01 mg/L NO_3-N with essentially 100% removal.

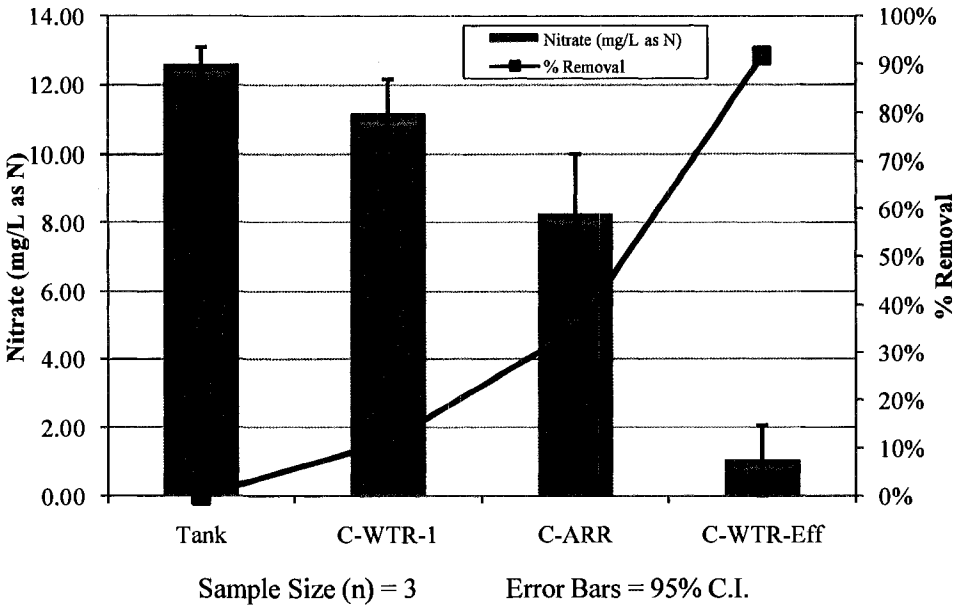


Figure VI.14: Sequential RBF - WTR amended ARR column nitrate monitoring

When the results of the actual setup is compared to the results of the abiotic control setup (Figure VI.15), slightly better nitrate removal was observed in the 1-foot WTR amended column of the actual setup (11%) compared to the control setup (7%)

with the residence time of 1.25 days. Following the 1-foot WTR amended column, C-ARR achieved additional 24% removal compared to the 4% removal that was achieved in C-ARR-Control. This result is a clear indication of promoted heterotrophic denitrification that occurs under a biotic condition due to the leach of biologically available organic carbon from the WTR amendment.

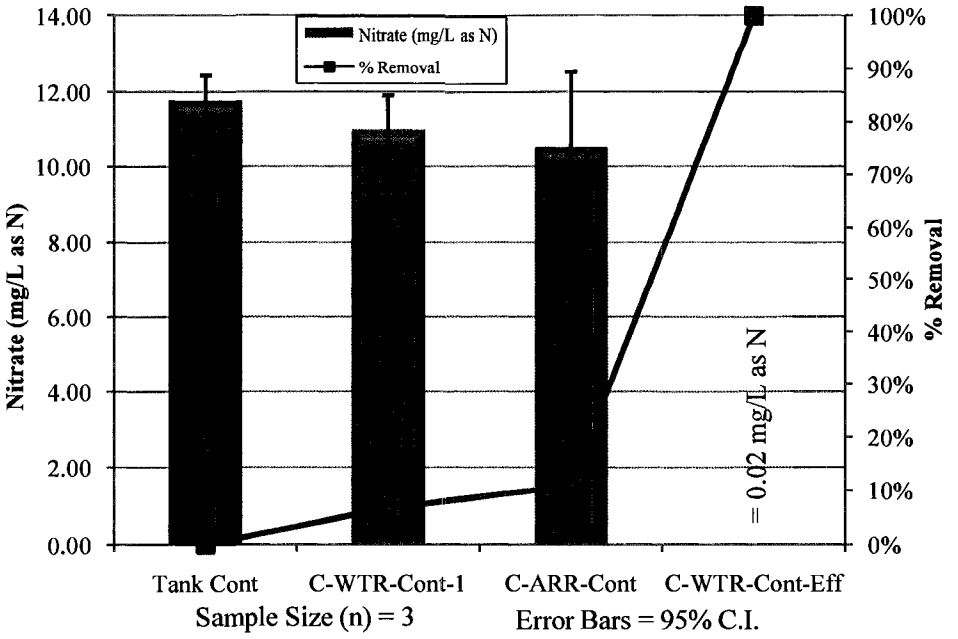


Figure VI.15: Sequential RBF - WTR amended ARR control column nitrate monitoring

The removal mechanism of nitrate through the abiotic WTR amended column could be a chemical reduction of nitrate to ammonia. Li et al., (2007) indicated that the chemical nitrate reduction to ammonia occurs under strong reducing environment created by amending a column system with zero valent iron (ZVI). Chi et al., (2004) also

observed the chemical reduction of nitrate to ammonia with ZVI amended system under acidic conditions.

VI.4. CONCLUSION:

This study was conducted to understand the nitrate removal efficiencies and kinetics of natural semi-passive treatment approaches RBF and ARR. The RBF system was examined with pilot scale field and column simulation studies to understand the removal efficiency and mechanisms of nitrate removal through the system. The ARR system was also examined with column simulation studies to estimate the nitrate removal capability of the system. The benefits of using a WTR as media to supply additional biologically available carbon as a carbon and electron donor source was also studied as an alternative amendment approach to sequential RBF – ARR treatment system. The following conclusions were drawn in the study;

- The pilot scale RBF field system was achieved an average nitrate removal of 76.4% within 10-month monitoring effort.
- The nitrate removal mechanism in the RBF field system was biological denitrification by using DOC in the river water as carbon and electron donor source for heterotrophic denitrification.
- The RBF simulation column, C-RBF, achieved an average nitrate removal of 90.9% with the retention time of 25 days. This result was slightly higher than RBF field monitoring study due to the possible influence of the nitrate rich surrounding groundwater. The half-life of nitrate calculated for the RBF field

(4.97 days) and the RBF simulation column (5.97 days) indicates that the RBF column simulation study can be successfully used to estimate the removal kinetics of nitrate through the RBF system.

- The RBF abiotic control column, C-RBF-Control, achieved no nitrate removal with the retention time of 25 days, thus indicating that the biological heterotrophic denitrification is the mechanism of nitrate removal through the RBF process.
- The RBF field and column simulation studies indicated that RBF itself can achieve significant nitrate removal and can be a sustainable barrier for nitrate being independent of the temperature variations due to seasonality.
- The ARR column simulation study indicated phosphorus removals of 3.5% and 2.9% for C-ARR and C-ARR-Control, respectively. These results indicate that the ARR system is biologically available carbon limited thus cannot be a barrier for nitrate removal unless a proper carbon source is introduced to the system.
- 4 foot, 30% WTR amended ARR column, C-WTR-ARR, showed complete nitrate removal with levels of close to the method detection limit of 0.01 mg/L. The removal mechanism was concluded as either promoted biological denitrification due to the introduction of biologically available organic carbon from the WTR amendment or chemical reduction of nitrate to ammonia due to the formation of strongly reducing environment.
- Sequential RBF – WTR amended ARR column simulation studies showed that after a 1 ft depth of 30% WTR amended media, 11% and 7% nitrate removal

achieved with C-ARR-WTR and C-ARR-WTR-Control columns, respectively. Leaching biologically available carbon from the 1-foot C-ARR-WTR promoted additional 24% nitrate removal through the C-ARR column while abiotic control column C-ARR-Control did not achieve significant nitrate removal. This result indicates that WTR amendment can improve the nitrate removal rates through the ARR system.

- Both WTR amended biotic and abiotic columns achieved significant nitrate removal within 5 days of residence time indicating that after 1-foot of media depth, strongly reducing conditions occur and nitrate was removed by chemical reduction.
- The overall study suggests that RBF system can be a sustainable barrier for nitrate loads in the South Platte River. To apply the ARR system as a secondary barrier in sequential RBF-ARR system, some sort of labile carbon source is needed. WTR, once optimized, is a promising and cost effective amendment alternative for nitrate removal through ARR system

CHAPTER VII: REMOVAL OF PESTICIDES DURING RIVERBANK FILTRATION (RBF) AND AQUIFER RECHARGE AND RECOVERY (ARR): BENEFITS OF WATER TREATMENT RESIDUAL (WTR)

(PAPER WILL BE SUBMITTED TO A JOURNAL)

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Abstract

Riverbank filtration (RBF) and aquifer recharge and recovery (ARR) are well known natural, semi-passive, treatment techniques. An on-going municipal project envisions the implementation of these systems in series to obtain high quality water for long-term storage in a reservoir. Presence of the pesticides in the source water, South Platte River, at high concentrations during the runoff season necessitates the removal of these contaminants with the sequential RBF – ARR application. This study focuses on the removal efficiency of three commonly applied pesticides atrazine, alachlor, and metolachlor through a multi-barrier, sequential RBF and ARR system. The study includes the monitoring of a pilot scale field RBF system and column simulation studies. Results of the study indicated that the ability of the RBF and ARR systems to remove alachlor and metolachlor is limited by the biodegradation through the alluvial sand. As a sorbent and an organic carbon source, aluminum based water treatment residual (WTR) was tested as an amendment for the ARR infiltration basin. Concentrations of selected pesticides were reduced to the method detection limit of 0.3 μg/L during 1-foot 30% WTR amended column treatment with the residence time of 1.25 days under both abiotic and biotic conditions. The removal mechanism was suggested as a sorption on the aluminum (hydr)oxide particles in the WTR media with subsequent biodegradation. The study indicates that once optimized, WTR can be used as an amendment for the sequential RBF –ARR system to successfully remove pesticide contamination in the source water.

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VII.1. INTRODUCTION:

By the early 1960s, pesticides started to be used widely for agricultural applications across the United States (Battaglin et al., 2003). Pesticide use increased by more than 800 percent between 1960 and 1980 (Lin et al., 1995; Aspelin and Grube, 1999; Battaglin et al., 2003). As a result of this increase, pesticides have become one of the most important contaminants in ground and surface waters. Their recurrent detection in ground water (Barbash and Resek, 1996), surface water (Larson et al., 1997), aquatic biota and sediment (Nowell et al., 1999), the atmosphere (Majewski and Capel, 1995), and their impacts on human health have forced state and federal agencies to develop monitoring and management programs (Barbash et al., 2001).

Dennehy et al. (1998) studied the water quality in the South Platte River between 1992 and 1995. The authors reported that more than 2 million pounds of active pesticide ingredients were applied to the South Platte River Basin. Atrazine was detected in 90% of the surface water samples and 6 percent of the groundwater samples with the maximum concentration of 100μg/L. Alachlor was detected in 21% of the surface water samples and 1% of the groundwater samples with the maximum concentration of 30μg/L. Metolachlor detections were observed in 50% of the surface water samples and 10% of the groundwater samples with the maximum concentration of 100μg/L. It was reported that the highest concentrations were observed in June during the three year monitoring effort.

Due to the adverse health effects on humans, atrazine and alachlor were regulated by the U.S. EPA under National Primary Drinking Water Regulations. The U.S. EPA regulated the atrazine and alachlor with the maximum contaminant levels of 3.0 μg/L and

2 µg/L, respectively. Metolachlor has not been regulated yet with an MCL however this pesticide is on the Candidate Contaminant List in which the U.S. EPA lists the soon to be regulated contaminants.

Presence of pesticides in water sources is a problem and requires advance treatment techniques since conventional drinking water treatment applications cannot remove these contaminants (U.S. EPA, 2001). Advance treatment techniques such as powdered activated carbon (PAC), granular activated carbon (GAC), membrane treatment technologies reverse osmosis (RO), and nanofiltration (NF) have been showed as successful methods to treat pesticide contaminated waters. However, high operational cost associated with these techniques leads authorities and scientific community to consider alternative cost effective techniques.

The riverbank filtration (RBF) and aquifer recharge and recovery (ARR) processes are similar natural, semi-passive treatment approaches. Both techniques have been used for centuries in primitive ways (Baker, 1948; Pyne, 1995). Modern RBF technique has been successfully used for the production of drinking water for more than a hundred years in Europe and in the last 50 years in the US. (Kuenhn and Mueller, 2000; Ray et al., 2002a). ARR applications are still in use in the United States, Canada, Israel, England, The Netherlands, and Australia (Pyne, 1995).

Physical, chemical and biological processes play an important role to improve the water quality through RBF. Physical removal occurs at the soil pores as well as electrostatic attachment to soil particles (Ray et al., 2002b). The major chemical processes include adsorption, ion exchange, and chemical reactions (Kuenhn and Mueller, 2000; Ray et al., 2002b; Kelly and Rydlund, 2006). The biofilm is responsible

for the initial degradation and removal of organic carbon, nutrients, and pathogens as well as micronutrients (Kuenhn and Mueller, 2000; Ray et al., 2002b; Kelly and Rydlund, 2006). Ray et al. (2000b) reported pesticide removal with the RBF system located in Elbe River, Germany. Atrazine concentrations in Elbe River was reduced from 0.42 μg/L to less than 0.04 μg/L. Biological degradation of atrazine was reported as the removal mechanism for atrazine and other pesticides that were monitored (Ray et al., 2002b).

As in RBF, physical, chemical, and biological processes are the key elements of ARR applications. Microorganisms are present in aquifers to depths of at least 1500 feet (Pyne, 1995), therefore, ARR can result in biological degradation, as well as physical and chemical removal mechanisms, providing there are sufficient electron donors.

Drinking water treatment process byproducts, either dried solids or sludge, are broadly classified as water treatment residuals (WTR) and primarily consist of sediment, aluminum and/or iron (hydr)oxides, activated carbon and polymer (Elliott and Dempsey, 1991). Even though removal of pesticides with WTR has not been reported in the literature, adsorption of pesticides to iron (hydr)oxides were reported by many studies (Singh et al., 1998; Chew et al., 1998; Eykholt and Davenport, 1998; Dombek et al., 2001) Also aluminum salts were reported to be used to improve the pesticide removal in unsaturated soils (Gaber et al., 2002). The high organic carbon content of the WTR has been reported by many studies (Dayton and Basta, 2003; Makris et al., 2004; Markis et al., 2005). With the high organic carbon content, WTR can also contribute labile carbon to the carbon limited systems thus promotes further bioremediation.

The City of Aurora is developing an innovative approach to utilize South Platte River water downstream of the Denver metropolitan area. Under the Prairie Waters

Project, the city envisions the application of sequential riverbank filtration (RBF) and aquifer recharge and recovery (ARR) as a semi-passive, multi-barrier preliminary treatment technique before collecting the treated water in a terminal reservoir (Figure VII.1). One of the city's major concerns is the efficiency of the sequential RBF – ARR application in terms of the removal of pesticides before storing in the terminal reservoir.

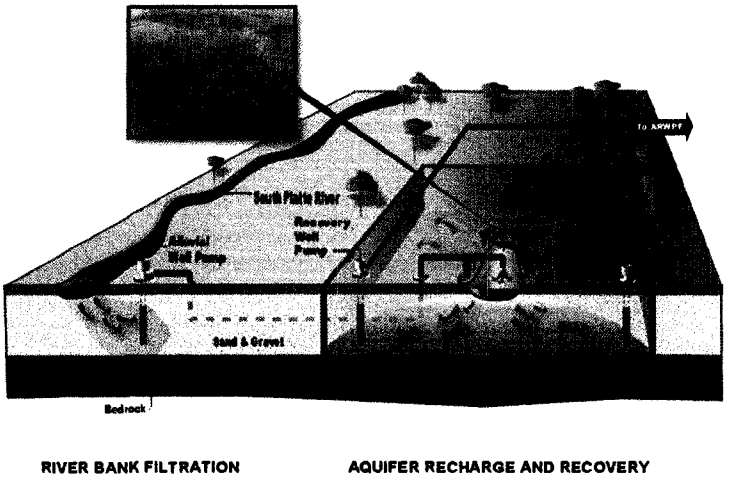


Figure VII.1: Sequential riverbank filtration (RBF) and aquifer recharge and recovery (ARR) (Courtesy of CH2MHill, Denver, CO)

Multiple studies were conducted to evaluate either RBF or ARR as independent treatment approaches. Apart from those associated with this project, application of RBF-ARR system in series has not been studied. The overall project focuses on the advantages and disadvantages of implementing a water treatment strategy of RBF followed by ARR as a two-barrier preliminary treatment step for the production of high quality drinking water. A concern about the system is that the quality and quantity of organic carbon in RBF treated water may not promote biological degradation of contaminants during the

ARR stage. Amending the system with WTR in the infiltration gallery of ARR was evaluated to improve the treatment efficiency through the ARR system.

This study focuses on evaluating; (i) the removal efficiency of three commonly used pesticides, atrazine, alachlor, and metolachlor trough RBF and ARR (ii) possible benefits of WTR amendment on carbon limited ARR to promote biological degradation as well as capability to serve as an adsorbent.

VII.2. MATERIALS AND METHODS:

Riverbank Filtration Field Study

The RBF field study site is located north of City of Brighton, CO, between the South Platte River and a non-operational gravel mine. The gravel mine is surrounded by a slurry wall to keep groundwater and river water out of the site, isolating the west shore from surrounding groundwater, thus, creating a convenient study site. The production well (PTW-1) and the monitoring wells (PTMW-2, PTMW-3, PTMW-4) are located on the west shore between the slurry wall and the river. PTMW-1 is an imaginary well where the river samples were collected. Production and monitoring wells were installed in November 2004 and the RBF system has been in continuous operation since December 2004 except for short periods of time during the power outages. Figure VII.2 shows the riverbank filtration site, the gravel mine, and production and monitoring wells.

The production well, PTW1, is 18 inches in diameter and is constructed with a stainless steel casing, and pumps water with the flow rate of 450gpm. All monitoring wells are 2.0-inch, PVC wells. Construction details for production and monitoring wells are given in Table VII.1 below.

The South Platte River and the production well were monitored twice a month between July 2005 - September2006 and monthly between April 2006 – August 2006 for atrazine, alachlor, and metolachlor. River samples were collected via grab samples. Monitoring wells were sampled by using an EPA approved low-flow method with dedicated Teflon tubing, and a peristaltic pump. The production well was sampled from a port that is installed in the discharge piping near the well. Samples were collected in amber glass bottles and kept in a cooler during the transport. Samples were filtered with 0.45μm glass fiber filters and kept at 4°C before analysis.

Pilot Scale Column Studies:

For all column studies, 4-foot acrylic columns with an internal diameter of 6 inches were used. Each column has 3 sampling ports, which are 1 foot apart, on the side of the column. Sampling ports are made from stainless steel tubing and they reach to the center of the column cross section for representative sample collection. Each sampling port is screened at the end to prevent column media loss from the ports. To distribute the inflow equally to the column, column caps are built with multiple injection points (Figure VII.3). During the course of the study, all columns were kept at 60° F and wrapped with aluminum foil to prevent photosynthetic microbial activity.

Table VII.1: RBF field study well construction details.

Well ID	Well Diameter (in)	Total Well Depth (ft)	Depth of Water (ft)	Distance form River (ft)	Residence Time (days)
PTMW-2	2	32	17	137	10
PTMW-3	2	30	14	258	15
PTMW-4	2	30	14	374	22
PTW-1	18	45	33	418	25



(a) (b)

Figure VII.2: (a) Aerial photo of RBF field study site generated using Google Earth (Newton,2007) (b) RBF field study site with production and monitoring wells, photo by Tetra Tech RMC (Longmont, CO).

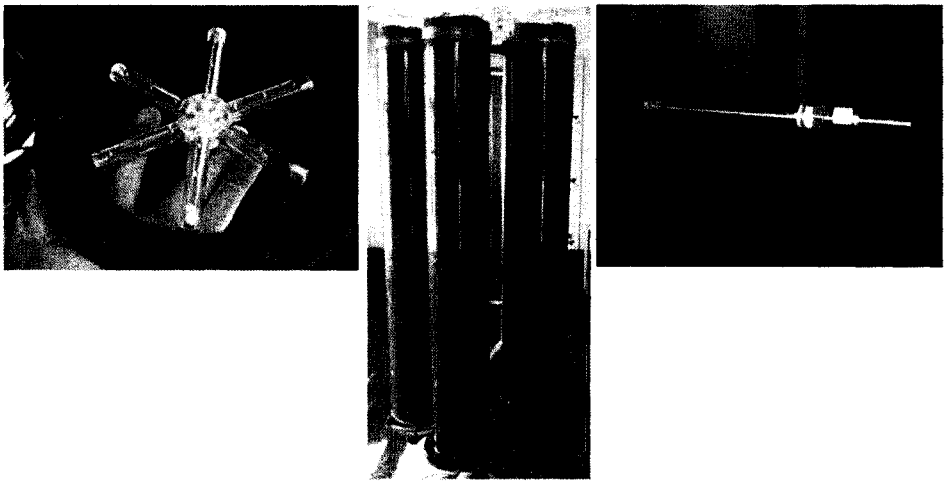


Figure VII.3: Column setup for column simulation studies.

Alluvial sand that was used in the column media was obtained from the west river bank at the RBF field study site approximately 2 feet under the surface. Alluvial sand then was sieved with no.10 (<2mm) sieve to obtain uniform particle size. Water treatment residual (WTR) that was used in the column simulation studies was obtained from the City of Wellington Water Treatment Plant, CO (Table VII.2). Aluminum based WTR was first dried in the oven at 180°C overnight then ground and sieved with no.10 (<2mm) to be consistent with the alluvial sand size distribution.

All columns were acclimated by feeding the columns with a flowrate of 1 mL/min from bottom to top for 15 days, followed by 3 mL/min of top to bottom flow for 30 days. Feed water was different for each specific study. Preconditioning steps were repeated before each column simulation studies. To feed the columns, peristaltic pumps were used with Teflon tubing throughout the study.

Table VII.2: General chemical properties of WTR.

			Total						Oxalate Extractable		
WTR Source	**pH**	**EC**	**P**	**Al**	**Fe**	**Ca**	**Mg**	**K**	**P**	**Fe**	**Al**
		mmhos/cm	**%**	**%**	**%**	**%**	**%**	**%**	**%**	**%**	**%**
	7.4	1.2	0.113	15.08	0.586	0.861	0.043	0.161	0.0123	0.0887	14.47

					Total			
Wellington Water Treatment Plant Wellington, CO	**Sand**	**Silt**	**Clay**	**Texture**	**C**	**TOC**	**$CaCO_3$**	**CO_3-C**
	%	**%**	**%**		**%**	**%**	**%**	**%**
	96	2	2	Sand	16.33	16.07	2.21	0.26

Samples were collected in amber glass bottles and kept in a cooler during the column simulation studies. Samples were filtered with 0.45μm glass fiber filters and kept at 4°C before analysis.

ARR Column Simulation Study:

An ARR column simulation study was conducted by using RBF treated production well (PTW-1) water spiked with 50 µg/L of all three pesticides as the feed water. Columns (C-ARR, C-ARR-Control, C-ARR-WTR) were sampled monthly between May 2006 and July 2006. The content of the column media and the operating conditions are summarized in Table VII.3 below. Figure VII.4 shows a sketch of the experimental column setup. The C-ARR column was used to simulate ARR conditions and the column was fed with 0.2mL/min of production well water. With this flow rate, the hydraulic retention time was 25 days. To observe the removal efficiency of the three selected pesticides under abiotic conditions, the C-ARR-Control column was fed with 0.2mL/min of 50 µg/L of the pesticides and 2mM sodium azide spiked production well water. Under these feed conditions, the hydraulic retention time was 25 days. To understand the benefits of alum based water treatment residual on pesticide removal, column C-ARR-WTR was fed with 1mL/min of production well water. C-ARR-WTR was sampled from all sampling ports and the effluent, whereas, C-ARR and C-ARR-Control were sampled from the effluent port only.

Table VII.3: ARR column simulation study: column media content and operating conditions.

	ARR Column (C-ARR)	Abiotic Control Column (C-ARR-Control)	ARR Column amended w/ WTR (C-ARR-WTR)
Media	Natural alluvial sand (sieved with no.10 sieve)	Natural alluvial sand (sieved with no.10 sieve)	70% v/v natural alluvial sand and 30% v/v WTR (sieved with no.10 sieve)
Condition	wet/saturated	wet/saturated	wet/saturated
Media Mass in Column	Sand = 32.5kg	Sand = 32.5kg	Sand = 21.6kg WTR = 10.6kg Total = 32.2kg
Feed water	Production Well Water (PTW-1) spiked w/ 50µg/L of atrazine, alachlor, and metolachlor	Production Well Water (PTW-1) Spiked w/ 2mM Sodium Azide and 50µg/L of atrazine, alachlor, and metolachlor	Production Well Water (PTW-1) spiked w/ 50µg/L of atrazine, alachlor, and metolachlor
Flow Rate	0.2mL/min	0.2 mL/min	1mL/min
HRT	25 days	25 days	5 days

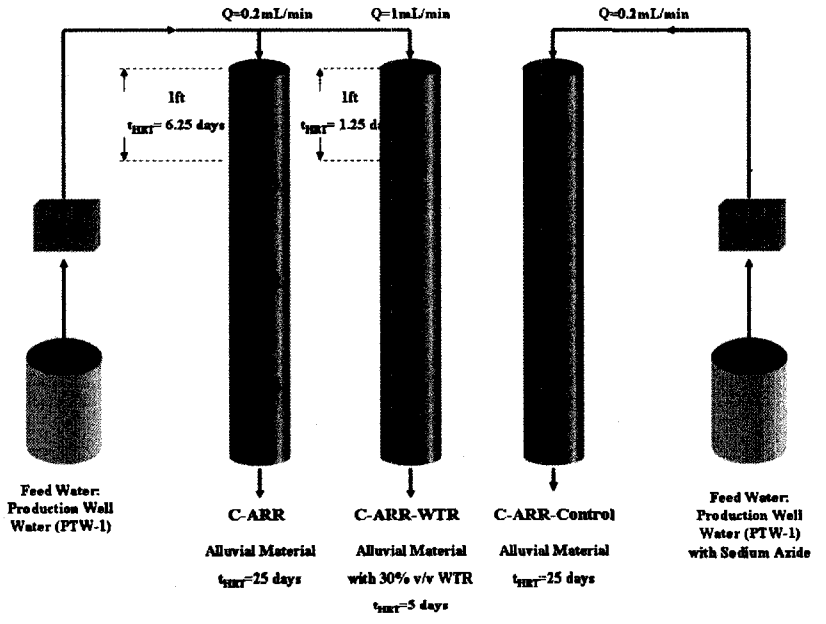


Figure VII.4: ARR column simulation study experimental setup

Sequential RBF – WTR Amended ARR Column Simulation Study:

A sequential RBF – WTR amended ARR column simulation study was conducted to understand the efficiency of the system in terms of pesticide removal. During this study, RBF treated production well (PTW-1) water spiked with 50µg/L of all three pesticides was used as the feed. Columns that were used for ARR column simulation studies were acclimated with production well water as the procedure described above and were used in this study. An additional amended abiotic control column (C-ARR-WTR-Control) was built and was acclimated as others. Operation of columns (C-ARR-WTR, C-ARR, C-ARR-WTR-Control, C-ARR-Control) began in March 2007 and columns were sampled monthly between May 2007 and July 2007. The composition of the column media and the operating conditions are summarized in Table VII.4 below. Figure VII.5 shows a sketch of the experimental column setup. The top 1 foot media of C-ARR-WTR column was used to simulate the amended ARR infiltration basin and the C-ARR column was used to simulate the alluvial sand ARR part. C-ARR-WTR was fed with 1mL/min of production well water. After a foot media depth (port 1, C-ARR-WTR-1) water was withdrawn with a flowrate of 0.2mL/min and fed to the C-ARR column. Hydraulic retention times were 1.25 days and 25 days for C-ARR-WTR-1 and C-ARR, respectively. To observe the removal efficiency of pesticides under abiotic conditions, an identical column set was used and fed with 50 µg/L of selected pesticides and 2 mM of sodium azide spiked production well water. Samples were collected from C-ARR-WTR-1, C-ARR-WTR-4, C-ARR, C-ARR-WTR-1C, C-ARR-WTR-4C, and C-ARR-Control for both biotic and abiotic column setups.

Table VII.4: Sequential RBF – WTR amended ARR column simulation study: Column media content and operating conditions

	ARR Column amended w/ WTR (C-WTR-1) 1 ft media depth	**ARR Column amended w/ WTR (C-WTR-4) 4 ft media depth**	**ARR Column (C-ARR)**	**ARR Column amended w/ WTR Control (C-WTR-1C) 1 ft media depth**	**ARR Column amended w/ WTR Control (C-WTR-4C) 4 ft media depth**	**ARR Column Control (C-ARR-C)**
Media	70% v/v natural alluvial sand and 30% v/v WTR (sieved with no.10 sieve)	70% v/v natural alluvial sand and 30% v/v WTR (sieved with no.10 sieve)	Natural alluvial sand (sieved with no.10 sieve)	70% v/v natural alluvial sand and 30% v/v WTR (sieved with no.10 sieve)	70% v/v natural alluvial sand and 30% v/v WTR (sieved with no.10 sieve)	Natural alluvial sand (sieved with no.10 sieve)
Condition	wet/saturated	wet/saturated	wet/saturated	wet/saturated	wet/saturated	wet/saturated
Mass in Column	Sand = 5.4kg WTR = 2.65kg Total = 8.05kg	Sand = 21.6kg WTR = 10.6kg Total = 32.2kg	Sand = 32.5kg	Sand = 5.4kg WTR = 2.65kg Total = 8.05kg	Sand = 21.6kg WTR = 10.6kg Total = 32.2kg	Sand = 32.5kg
Feed water	Production Well (PTW-1) (spiked w/ 50µg/L of atrazine, alachlor, and metolachlor)	Production Well (PTW-1) (spiked w/ 50µg/L of atrazine, alachlor, and metolachlor)	C-WTR-1 Water	Production Well (PTW-1) (spiked with 2mM sodium azide and 50µg/L of atrazine, alachlor, and metolachlor)	Production Well (PTW-1) (spiked with 2mM sodium azide and 50µg/L of atrazine, alachlor, and metolachlor)	C-WTR-1C Water
Flow Rate	1mL/min	1mL/min	0.2 mL/min	1mL/min	1mL/min	0.2 mL/min
HRT	1.25 days	5 days	25 days	1.25 days	5 days	25 days

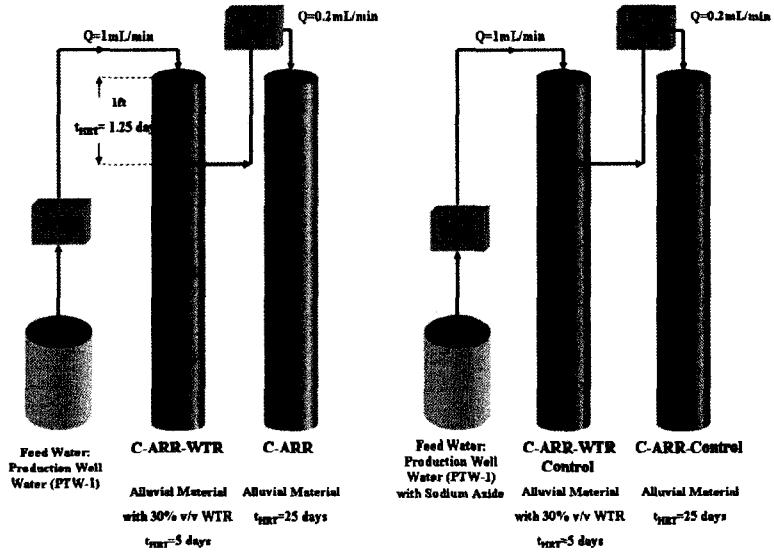


Figure VII.5: Sequential RBF- WTR amended ARR column simulation study experimental setup.

Solid Phase Extraction Procedure:

For solid phase extractions and GC/MS analysis, EPA Method 525.2, was modified. Solid phase extractions were achieved by using C18 cartridges (Waters Co., Sep-Pak® Vac. 3cc 200mg C-18 Cartridges) and a vacuum manifold (Fisher Scientific, Fisher PrepSep 12-Port Vacuum Manifold). Cartridges were preconditioned by eluting 3mL of ethyl acetate (Fisher Scientific, Acros Pesticide Residue Analysis Grade), followed by 3mL methylene chloride (Fisher Scientific, Pesticide Grade). After each flush, the cartridges were drain-dried and then eluted with 6 mL of methanol and 6 mL of deionized water. Before samples were transferred to the cartridges 2 mL of methanol and the internal standard, Phenanthrene-D_{10} (Ultra Scientific), were added to sample flasks. Samples were eluted through cartridges with a slight vacuum of approximately 5in. of mercury within 30 minutes. After all samples were passed through the cartridges, air was

allowed to flow for 10 minutes. Cartridges were eluted with 3 mL of ethyl acetate followed by 3mL of methylene chloride, and extracts were collected in collection vials. To remove the small amount of residual water, extracts were passed through a drying column. The drying column was prepared by using 2g of anhydrous sodium sulfate (Fisher Scientific, Acros Organics, Anhydrous 99%). After the extract was passed through a drying column and collected in another collection vial, sodium sulfate was washed with 2 mL of methylene chloride and collected in the same vial. The final solution was concentrated to 0.25 mL in a warm water bath under a gentle stream of high purity nitrogen.

Gas Chromatography / Mass Spectrometry:

An Agilent 6890 series gas chromatograph (GC) equipped with an Agilent 7683 autosampler and interfaced to an Agilent 5973 Network mass selective detector was used for all analyses. Samples of 1μL were injected by pulsed, splitless injection mode at 295°C into the Agilent 6890 gas chromatograph equipped with a 30m x 0.25mm Supelco SPB-1 methyl silicone capillary column (0.25μm film thickness). The Agilent 5973 Network mass selective detector was operated with a source temperature of 230°C and the interface temperature held at 300°C. GC oven temperature was held at 100°C for 2 min, ramped at a rate of 25°C/min. to 200°C, at which point the rate was decreased to 10°C/min. to a temperature of 250°C. The temperature was then increased to 290°C with a rate of 15°C/min and held at 290°C for 3 minutes. The helium carrier gas flow rate was 1.0mL/min. Mass spectral data acquisition was started at 4 minutes and acquired throughout the run from m/z 45-450.

VII.3. RESULTS AND DISCUSSION:

VII.3.1. Riverbank Filtration Field Study:

The occurrence and the fate of the pesticides atrazine, alachlor, and metolachlor in the South Platte River and through the pilot RBF study site were monitored biweekly between July 2005 – September 2005 and monthly between April 2006 – August 2006. Samples were collected from the river and the production well only.

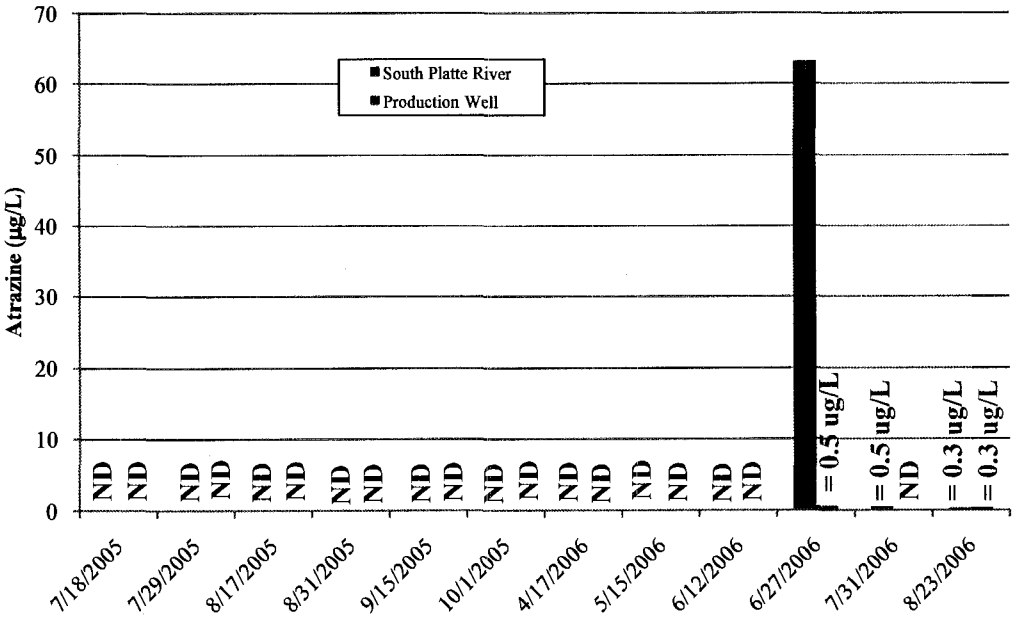


Figure VII.6: RBF field monitoring atrazine levels

Figure VII.6 summarizes the atrazine levels in the river and production wells throughout the RBF field monitoring study. Atrazine pesticide had not been detected until the end of June 2006. A high atrazine level of 63µg/L was detected on 6/27/2006. The detection of atrazine at the high level was most probably due to the runoff after the application of the pesticide to agricultural land upstream of the study site. The following

two months, the atrazine level was measured between 0.3 and 0.5 μg/L in the river. The data indicates the highly transient nature of the contamination.

The RBF system efficiently reduced atrazine levels and the highest atrazine level was observed in the production well was 0.5 μg/L that is below the MCL of 3 μg/L. The removal mechanism was assumed to be biological degradation since atrazine is considerably soluble in water (solubility = 240 mg/L) and does not tend to adsorb on soil (K_{oc} = 100 g/mL) (Goolsby and Pereira, 1995).

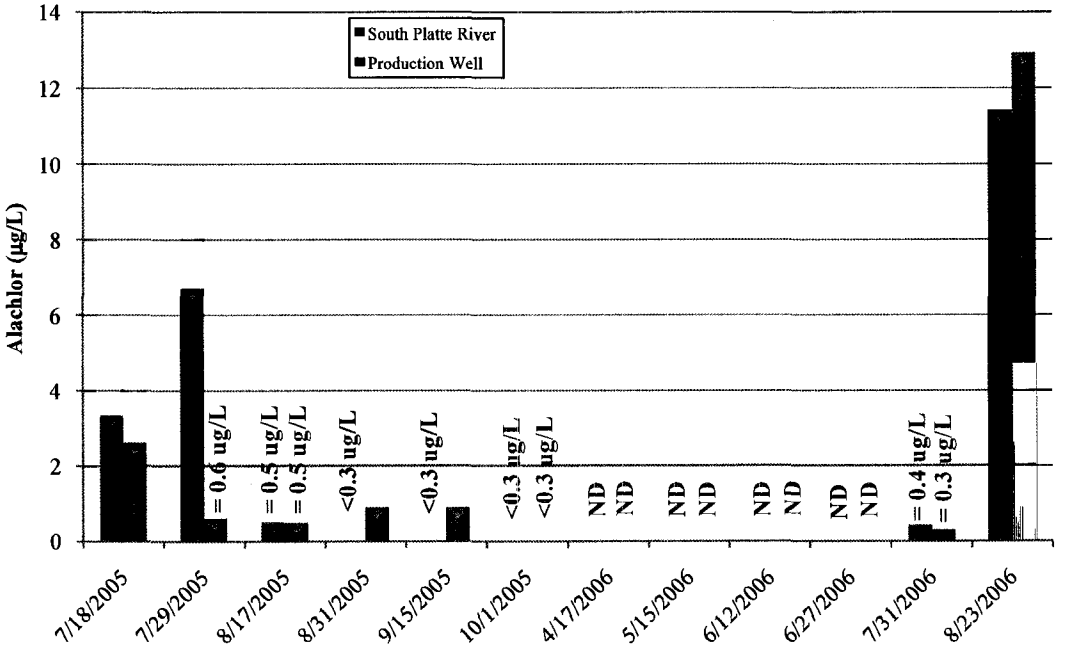


Figure VII.7: RBF field monitoring alachlor levels

FigureVII.7 summarizes the alachlor levels in the river and production wells throughout the RBF field monitoring study. Alachlor levels that are exceeding the MCL of 2 μg/L were detected in July and August of 2005 and 2006 in river samples. The

maximum alachlor concentration in the river was detected as 11.4 µg/L throughout the study. Except July and August occurrences, alachlor levels were less than 0.5 µg/L indicating that the alachlor contamination is connected to the application and following runoff events in agricultural fields. The RBF finished water alachlor levels were generally less than 0.6 µg/L however the sampling events July 2005 and August 2006 indicates that higher levels of alachlor can be observed in the production well. Even though the data is inconclusive to evaluate the removal efficiency of alachlor through the RBF system, the occurrence of high alachlor levels that were observed in the production well indicates that RBF itself is not an adequate barrier for alachlor contamination.

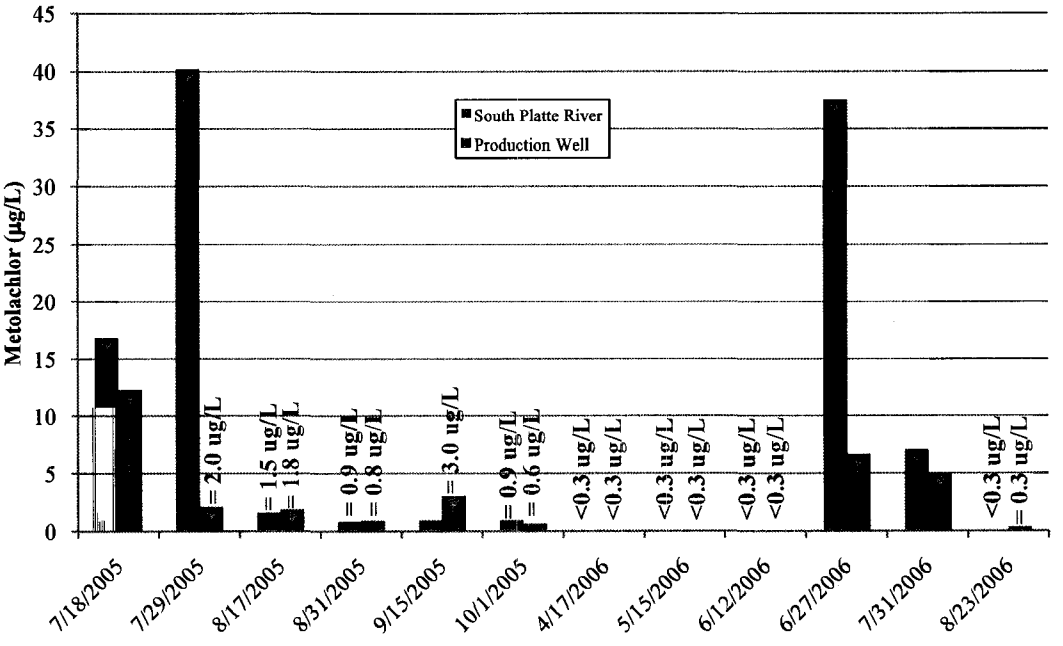


Figure VII.8: RBF field monitoring metolachlor levels

FigureVII.8 summarizes the metolachlor levels in the river and production wells throughout the RBF field monitoring study. High metolachlor levels (7.0-40.1µg/L) were

detected in June and July in river samples during the monitoring study. High concentrations that were observed at the beginning of summer season are attributed to pesticide application followed by agricultural runoff. The highest metolachlor concentrations observed in the production well were also during June and July with the levels ranging between 2 μg/L and 12.3 μg/L. Except the runoff season the highest metolachlor concentrations in the river and the production well were observed as 1.5 μg/L and 3.0 μg/L, respectively. Even though the metolachlor concentration in the drinking water has not been regulated yet, the presence of metolachlor with considerable concentrations in the RBF finished water during the runoff season indicates that the RBF system itself is not an effective barrier for metolachlor.

VII.3.2 ARR Column Studies:

To simulate ARR conditions, three columns, C-ARR, C-ARR-Control, and C-ARR-WTR were fed with RBF finished water that was spiked with 50 μg/L of atrazine, alachlor and metolachlor. The feed solution of the abiotic control column C-ARR-Control was also spiked with 2 mM of sodium azide to prevent biological activity in the column. The RBF finished water was spiked with all three pesticides to obtain detectable pesticide levels in the feed and effluent thus to evaluate the removal efficiencies of the pesticides.

Figure VII.9 shows the atrazine levels in the feed and the effluents of the three columns. The abiotic control column shows a removal efficiency of 6.6% with a residence time of 25 days indicating that the adsorption of atrazine on alluvial sand is insignificant as a removal mechanism. 56.3% removal of atrazine was observed in the biotic ARR simulation column C-ARR with the residence time of 25 days indicating that microbial activity can degrade atrazine with significant amounts. 30% WTR amended

ARR column, C-ARR-WTR, decreased the atrazine concentration from 49.9 μg/L to 1.1 μg/L with a residence time of 5 days. Adsorption of atrazine on metal oxide surfaces were reported by various studies (Chew et al., 1998; Dombek et al., 2001; Ghauch and Suptil, 2000). The adsorption of atrazine on iron oxide and hydroxide surfaces and following reductive dechlorination mechanism under acidic (Dombek et al., 2001) and ambient pH (Chew et al., 1998; Ghauch and Suptil, 2000) were reported with the formation of dechlorinated atrazine by-products. Ghauch and Suptil (2000) reported that complete atrazine removal with the initial atrazine concentration of 20 g/L during the 60 minute lab scale study. The by-products formed after the reductive dechlorination were reported to be easily biodegradable compared to atrazine (Chew et al., 1998). The possible removal mechanism observed in the WTR amended ARR column was biological degradation as well as the adsorption on aluminum oxide and hydroxide surfaces followed by the reductive dechlorination.

The results of the ARR column simulation study indicates that the ARR system can act as a second barrier for the removal of atrazine. Atrazine removal efficiencies can be improved by amending the infiltration basin of the ARR system with aluminum based WTR to get essentially complete removal of atrazine.

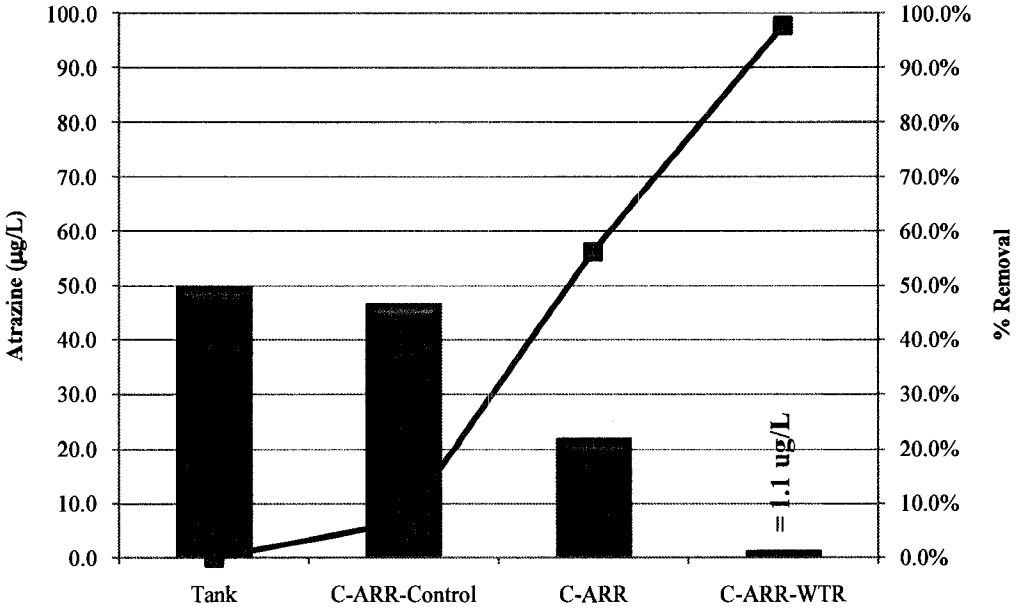


Figure VII.9: ARR column simulation study atrazine levels

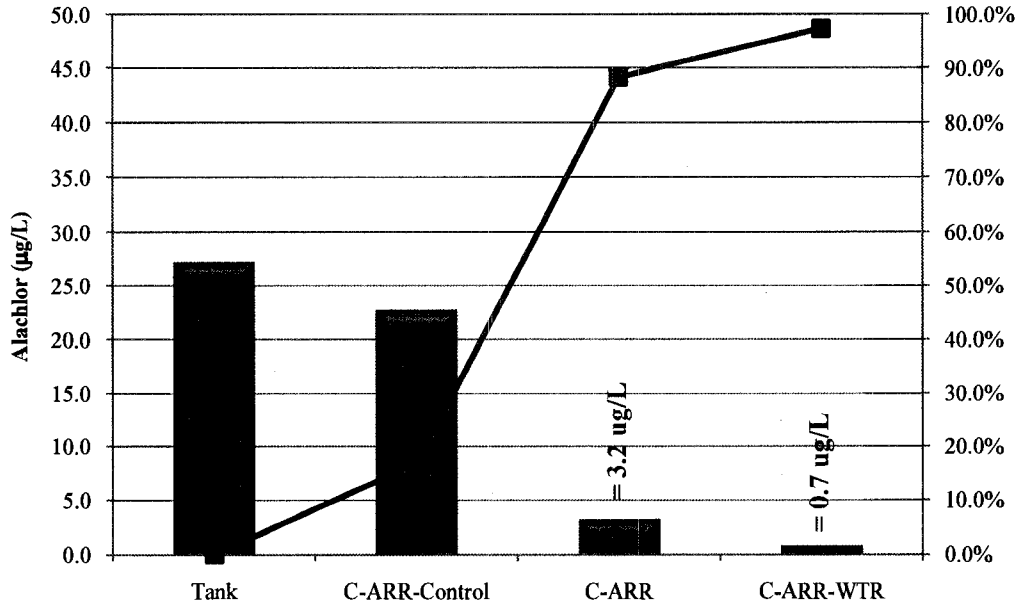


Figure VII.10: ARR column simulation study alachlor levels

Figure VII.10 shows the alachlor levels in the feed and the effluents of three columns. The abiotic control column shows a removal of 16.7% with the residence time of 25 days. Compared to atrazine, the higher removal of alachlor with adsorption on the sand media can be explained by the sorption coefficients (K_{oc}). Atrzine and alachlor have K_{oc} values of 100 g/mL and 170 mg/mL, respectively, indicating that alachlor has a higher tendency to adsorb onto sand surface compared to atrazine. Biotic ARR simulation column C-ARR shows a removal efficiency of 88.3% indicating that biological activity in the column decreases the alachlor concentration drastically within the residence time of 25 days. The ARR system that follows the RBF treatment can be an additional barrier for alachlor even with the limited biologically available organic carbon content. 30% WTR amended ARR column, C-ARR-WTR, decreased the alachlor concentration from 27.2 μg/L to 0.7 μg/L with the residence time of 5 days. Eykholt and Davenport (1998) reported an initial sorption followed by a reductive dechlorination as a removal mechanism for alachlor with iron oxide and hydroxides. The possible removal mechanism within the WTR amended ARR column was attributed to the adsorption on the aluminum oxide and hydroxide surfaces and promoted biological activity due to the leach of biologically available organic carbon from the WTR amendment.

The results of the ARR column simulation study indicates that the ARR system can act as a second barrier for alachlor removal. Alachlor removal efficiencies can be improved by amending the infiltration basin of the ARR system with aluminum based WTR.

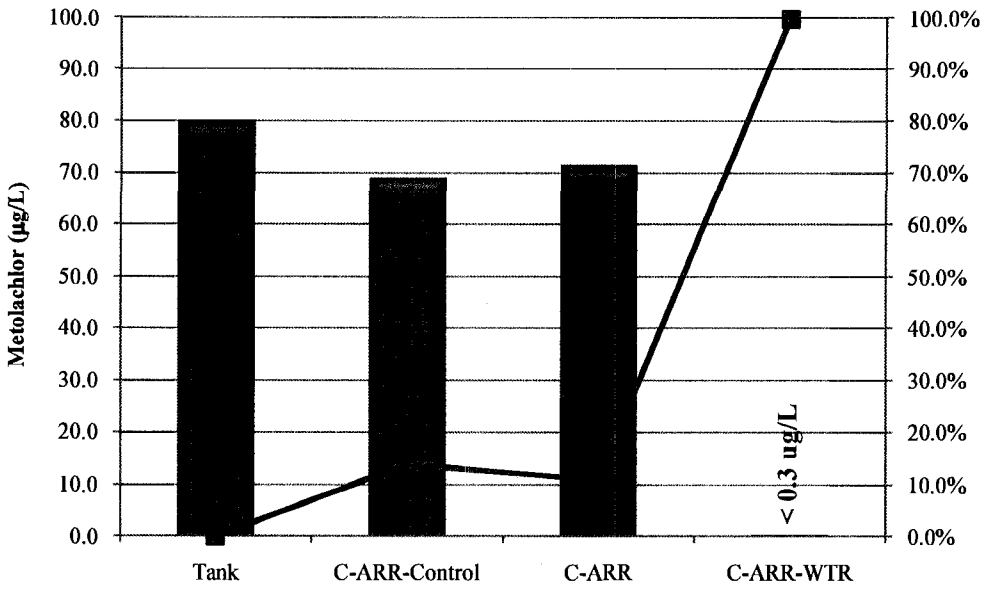


Figure VII.11: ARR column simulation study metolachlor levels

Figure VII.11 shows the metolachlor levels in the feed and the effluents of three columns. The C-ARR and C-ARR-Control columns show low removal efficiencies of 10.9% and 14%, respectively. The insignificant biological degradation of metolachlor under ARR condition was observed during the ARR column simulation study. Essentially 100% metolachlor removal was observed in WTR amended column C-ARR-WTR with the residence time of 5 days. Effluent level was monitored as less than the method detection limit of 0.3 µg/L. Comfort et al (2000) reported field scale remediation of a metolachlor contaminated spill site with zerovalent iron and aluminum salt. They reported that in their batch experiments, metolachlor is absorbed on the iron surface during the first 2 hours. After 2 hours, dechlorination of metolachlor was observedwith the dechlorinated by-product formation. They concluded that addition of aluminum salts greatly increases metolachlor removal. In our study, metolachlor removal in C-ARR-

WTR was attributed to the adsorption of metolachlor onto aluminum oxide and hydroxide particles and followed by the possible reductive dechlorination.

The ARR column simulation study indicated that under biotic ARR conditions, metolachlor removal is limited and the ARR system cannot be a secondary barrier for metolachlor during sequential RBF – ARR application. Amending the ARR system with WTR can drastically improve the removal efficiency for metolachlor.

VII.3.3. Sequential RBF and WTR Amended ARR Column Study:

The sequential RBF and WTR amended ARR column simulation study was conducted to observe the removal efficiencies and mechanisms of three selected pesticides, atrazine, alachlor, and metolachlor, during the scenario of WTR amendment of ARR infiltration gallery. The RBF finished water was used as feed water and spiked with 50 μg/L of all three pesticides. The control column was run with the same conditions except the feed water was spiked with 2mM of sodium azide to prevent biological activity in the columns.

Figure VII.12 shows the pesticide levels at the feed tank and the effluents of 1-foot WTR amended column, C-ARR column, and 4-foot WTR amended column. Drastic pesticide removal efficiencies were observed even after the 1-foot WTR amended ARR column. The atrazine concentration decreased from 39.6 μg/L to 0.43 μg/L after the C-WTR-1 and following C-ARR treatment decreased the concentration further to less than the method detection limit of 0.3 μg/L. The initial average alachlor level of 38.8 μg/L decreased to 1.23 μg/L after C-WTR-1 and additional removal was observed with the final concentration of 0.87 μg/L after C-ARR treatment. All metolachlor levels were observed as less than the method detection limit of 0.3μg/L at and after C-WTR-1.

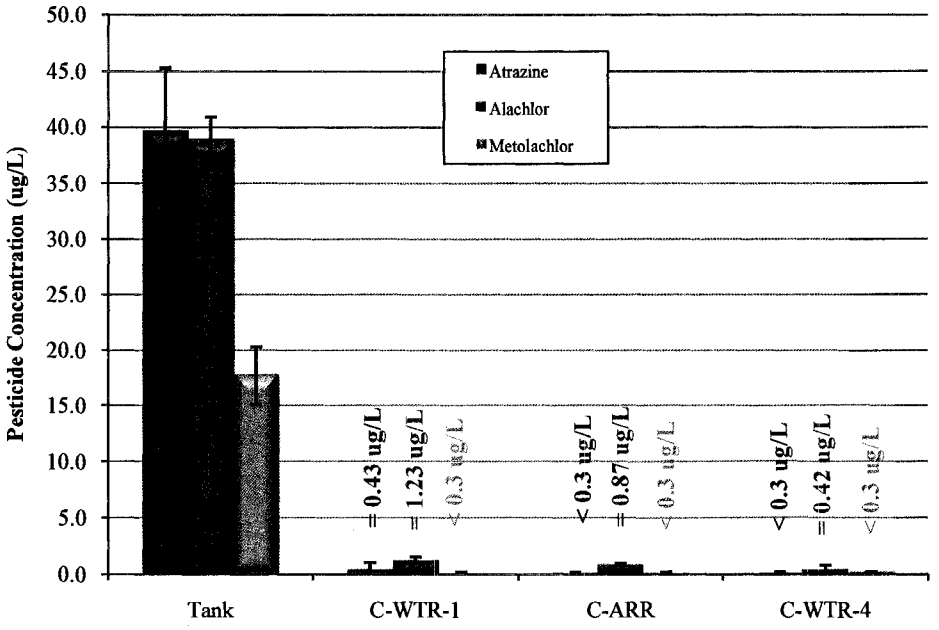


Figure VII.12: Sequential RBF – WTR amended column simulation study: Pesticide levels

The control column setup (Figure VII.13) showed similar or less levels of pesticide at all sampling points indicating that the biological activity is less significant compared to the adsorption mechanism on the WTR media. All pesticide levels after 1 foot WTR amended media were less than the maximum contaminant levels for drinking water reported by the U.S. EPA ($MCL_{atrazine}$ = 3 μg/L, $MCL_{alachlor}$ = 2 μg/L).

Sequential RBF- WTR amended ARR column simulation study indicated that once optimized, amending the infiltration basin of the ARR system can be successfully used to create a barrier for the three selected pesticides.

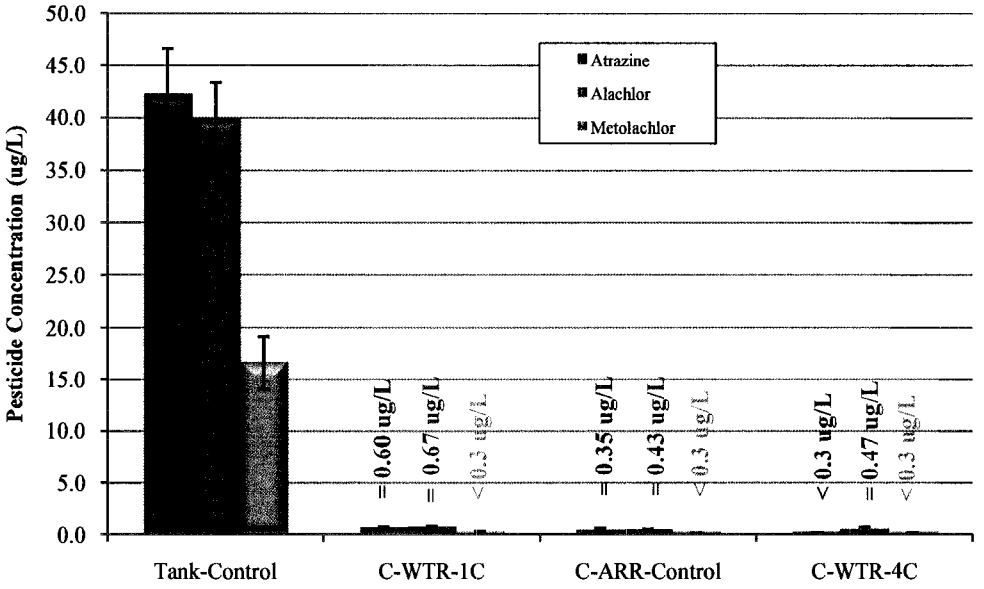


Figure VII.13: Sequential RBF – WTR amended column simulation control study: Pesticide levels

VII.4 CONCLUSIONS

The overall study was conducted to evaluate the efficiency of RBF and ARR systems on the removal of three selected pesticides, atrazine, alachlor, and metolachlor. Conclusions from the study include:

- The RBF field study showed the pesticides were detected with high levels in the river following their applications and agricultural runoff events in June, July, and August.
- The highest atrazine, alachlor, and metolachlor concentrations were monitored as 63 µg/L, 11.4 µg/L, 40.1 µg/L, respectively. These concentrations were higher than the U.S. EPA's reported MCLs of 3 µg/L for atrazine, and 2 µg/L for alachlor.

- The RBF field monitoring study indicated that the atrazine levels in the production well were below the MCL during all the monitoring events, thus it is concluded that RBF itself can be a barrier for atrazine contamination.
- Alachlor levels above the MCL were detected twice in the production well implying that the RBF system cannot be a sustainable barrier for alachlor especially following the runoff events where high alachlor levels were observed in the river.
- Metolachlor concentrations in the production well ranged between 4.9 µg/L and 12.3 µg/L indicating that the RBF system cannot efficiently remove metolachlor following the runoff events.
- The ARR column simulation study suggested that under abiotic conditions the removals of all three pesticides are limited. While alachlor was the most easily biodegradable pesticide with the removal efficiency of 88.3% under biotic ARR conditions, metolachlor removal was monitored as 10.9% which indicates that the biodegradation was limited for metolachlor.
- WTR amended ARR column showed essentially complete removal for all pesticides with the suggested removal mechanism of adsorption on the aluminum hydr(oxide) surfaces and biodegradation with lesser extent.
- The sequential RBF – WTR amended ARR study was showed that WTR amended ARR essentially removes all pesticides even with 1-foot media depth under biotic and abiotic conditions. Complete removal with WTR amended ARR column under abiotic conditions indicates that the removal mechanism is dominated by the adsorption on the aluminum hydr(oxide) particles in the WTR media.

CHAPTER VIII: CONCLUSIONS AND FUTURE RESEARCH

CONCLUSIONS:

The research described in this report relates to an application of riverbank filtration (RBF) and aquifer recharge and recovery (ARR) in series as preliminary treatment steps of a multi-barrier treatment approach for the City of Aurora's Prairie Waters Project. The city of Aurora plans to store the water in a terminal reservoir following preliminary sequential RBF – ARR treatment. Water stored in the reservoir will be further treated with softening, advanced UV–peroxide oxidation and UV disinfection. The source water, South Platte River, is impacted by wastewater and industrial wastewater treatment plant discharges as well as runoff from agricultural fields and thus it is expected that the sequential RBF-ARR system should improve the water quality so that it is suitable for surface storage.

The primary focus of the project is the removal of phosphorus, nitrogen, and carbon from the source water thus producing biologically stable water that can be stored in the terminal reservoir. In addition to nutrients, the removal efficiencies of perchlorate and three commonly used pesticides (atrazine, alachlor, and metolachlor) has been studied using pilot scale and field RBF and ARR systems.

Due to the limited and unsustainable phosphorus removal expected through the RBF and ARR systems, aluminum based water treatment residual was considered as an amendment to enhance treatment. The objectives of the study were extended to test the possible benefits of WTR on the removal of other contaminants of concern. The experimental studies included the monitoring of a RBF field site and pilot columns that

simulate RBF and ARR systems. Possible benefits of WTR amendment were tested by amending a column with 30% WTR under RBF and ARR conditions. Also an application scenario of RBF followed by a WTR amended ARR infiltration basin and ARR was simulated with a column study.

The phosphorus monitoring study at the pilot scale RBF site indicated that the phosphorus levels in the South Platte River ranged between 0.55 mg/L and 2.21 mg/L as P. In contrast to highly varying phosphorus levels in the river, more stable phosphorus levels were observed in the production well of the RBF field system with the average removal efficiency of 69%. An increasing trend (from the minimum level of 0.2 mg/L to the maximum level of 0.8 mg/L) in the production well phosphorus levels indicated that the phosphorus removal was not sustainable thus the RBF system cannot be considered a phosphorus barrier over the long term. The RBF column simulation studies under biotic and abiotic conditions indicated that the adsorption on the alluvial sand was the dominant removal mechanism and biological uptake had a minor effect on the phosphorus removal efficiency. The adsorption capacity of the columns was reached after about 5000 hours with a residence time of 5 days. The WTR amended RBF column resulted in a 100% P removal with a residence time of 1.25 days. The removal was attributed to adsorption of phosphorus on aluminum (hydr)oxide particles in the WTR media.

The ARR column simulation study indicated that a limited removal of phosphorus (up to 17.5%) can be achieved through the ARR system with the residence time of 25 days due to the limited sorption capacity of the alluvial sand media. The results of the study suggested that the ARR system cannot be a sustainable barrier for phosphorus contamination. A 100% phosphorus removal efficiency was achieved with the WTR

amended ARR column with 1.25 days of residence time indicating that amending the infiltration basin of the ARR system can be an effective approach to eliminate phosphorus contamination.

The sequential RBF- WTR amended ARR study indicated that the WTR amended 1-foot media is enough to decrease phosphorus concentrations to less than the method detection limit of 0.03mg/L as P. This study clearly pointed out that amending the infiltration basin of the ARR system reduces phosphorus concentrations to a level that the treated water is suitable for surface storage. The removal of phosphorus with WTR was attributed to the aluminum content of the WTR. The testing resulted in a P loading on the WTR of 302.5 mg P/ kg WTR which is significantly lower than the adsorption capacities reported in the literature. The highest adsorption capacity reported in the literature was 12.5 g/kg WTR indicating that breakthrough of our column set-up will not occur for a long period of time.

The fate of organic carbon through the RBF and ARR systems was monitored by the field and column tests. In spite of the highly fluctuating DOC levels in the river (4.7 to 7.0 mg/L), more stable DOC levels were observed in the production well (2.0 to 2.5 mg/L) with the average removal efficiency of 50.5% during the RBF field monitoring study. The remaining portion of the DOC after the RBF treatment was attributed to the non-biodegradable (humic) portion of the DOC in the river.

The ARR column simulation studies indicated that insignificant organic carbon removal under both biotic and abiotic conditions. High amount of organic carbon leach from the WTR amended column was detected with a linear relationship (r^2=0.96) between the column media depth and the amount of DOC leach. An average of 2mg/L

DOC leach was detected per foot of a 30% (v/v) WTR amended column depth. The sequential RBF – WTR amended ARR column simulation study indicated that the ARR column can successfully remove 71% of the leaching DOC from the 1 foot WTR amended column. It clearly suggests that most of the organic carbon contribution to the ARR system from the WTR amended infiltration gallery can and will increase the biological activity and thus help to improve biological degradation of the contaminants of concern.

The removal of nitrate through the RBF and ARR systems were tested by field and column simulation studies. Highly fluctuating nitrate levels (1.9 – 11.4 mg/L NO_3-N) were observed in the South Platte River. The production well nitrate levels were very stable with the maximum nitrate concentration of 2.5 mg/L NO_3-N. During the course of the study, the RBF system achieved an average removal efficiency of 76.4% indicating that the RBF system can provide sustainable nitrate removal by biological denitrification while utilizing the organic carbon in the source water as an electron donor and a carbon source.

The RBF column simulation study showed 90.9% nitrate removal under biotic conditions with the residence time of 25 days. The nitrate removal kinetics was observed as a first order decay ($r^2 = 0.904$) with the calculated half life of 5.97 days. No significant nitrate removal was observed with the abiotic control column indicating that the dominant removal mechanism is biological denitrification.

The ARR column simulation study indicated that no significant nitrate removal can be achieved under organic carbon limited ARR conditions with the residence time of 25 days. The WTR amended ARR column showed almost complete nitrate removal with

a residence time of 5 days indicating that either the carbon leaching from the WTR amendment can significantly promote biological denitrification under carbon limited ARR conditions or the chemical reduction of nitrate to ammonia can happen due to the highly reducing condition that occurs in the WTR amended column.

The sequential RBF- WTR amended ARR column simulation study indicated that the organic carbon leach from the WTR media (media depth of 1-foot with the residence time of 1.25 days) can promote biological activity and additional denitrification of nitrate. The abiotic control study indicated that no significant nitrate removal can be achieved when the biological activity is suppressed. The column simulation studies suggest that amending the infiltration basin of the ARR system with aluminum based WTR can significantly improve nitrate removal efficiencies by promoting biological activity.

Perchlorate concentrations up to 6.5 μg/L were observed in the South Platte River during the RBF field monitoring study between June and September. The RBF system achieved more than 72% removal with the river water perchlorate levels of 3 μg/L. A decrease in the removal efficiency was observed with the perchlorate levels above 3 μg/L and the minimum removal efficiency was monitored as 65% with the perchlorate level of 2.3 μg/L. The removal mechanism through the RBF system was suggested as a microbiologically mediated chemical reduction. During the biochemical reduction, perchlorate was used as an electron acceptor after the chemical contaminants that are upper in the redox ledder such as nitrate. The organic carbon was used as an electron donor during the reduction process. The RBF column simulation study showed a 19% removal of perchlorate due to the short residence time of 5 days and possible use of other electron acceptors such as nitrate before perchlorate.

The ARR column simulation studies showed no significant perchlorate removal under biotic and abiotic conditions with the residence time of 25 days. The limited perchlorate removal under typical ARR conditions was attributed to the limited easily biodegradable organic carbon content of the source water following the RBF treatment. The WTR amended ARR column showed 91% removal efficiency with the residence time of 5 days. The high removal efficiency was attributed to the promoted biological activity due to organic carbon leach from the WTR media.

The sequential RBF-WTR amended ARR study indicated that under biotic conditions the WTR amended 1-foot media achieved 14.7% removal. The following ARR simulation column achieved an additional 15.1% removal suggesting that the additional organic carbon supplied by the WTR amendment promotes the biological activity thus perchlorate removal efficiency. No perchlorate removal was observed with the abiotic control study indicating that the removal mechanism of perchlorate through the WTR amended ARR and ARR columns is predominantly biological reduction.

The RBF field study showed the pesticides were detected with high levels in the river following their applications and agricultural runoff events in June, July, and August. The highest atrazine, alachlor, and metolachlor concentrations were monitored as 63 μg/L, 11.4 μg/L, 40.1 μg/L, respectively. These concentrations were higher than the U.S. EPA's reported MCLs of 3 μg/L for atrazine, and 2 μg/L for alachlor. The RBF field monitoring study indicated that the atrazine levels in the production well were below the MCL during all the monitoring events, thus it is concluded that RBF itself can be a barrier for atrazine contamination. Alachlor levels above the MCL were detected twice in the production well implying that the RBF system cannot be a sustainable barrier for

alachlor especially following the runoff events where high alachlor levels were observed in the river. Metolachlor concentrations in the production well ranged between 4.9 μg/L and 12.3 μg/L indicating that the RBF system cannot efficiently remove metolachlor following the runoff events.

The ARR column simulation study suggested that under abiotic conditions the removals of all three pesticides are limited. While alachlor was the most easily biodegradable pesticide with a removal efficiency of 88.3% under biotic ARR conditions, metolachlor removal was monitored as 10.9% which indicates that the biodegradation was limited for metolachlor. The WTR amended ARR column showed essentially complete removal for all pesticides with the suggested removal mechanisms of adsorption on the aluminum hydr(oxide) surfaces and subsequent biodegradation.

The sequential RBF – WTR amended ARR study showed that WTR amended ARR essentially removes all pesticides even with 1-foot media depth under biotic and abiotic conditions. Complete removal with a WTR amended ARR column under abiotic conditions indicates that the removal mechanism is dominated by the adsorption on the aluminum hydr(oxide) particles in the WTR media.

The overall studies indicated that biological removal of contaminants such as nitrate, perchlorate, and pesticides in the source water can be achieved by the application of RBF system especially under anaerobic conditions that occur during the passage of water through the alluvial media. The organic carbon source is crucial since microorganisms use the available organic carbon as a carbon source and an electron donor during the biological removal processes. When the organic carbon limited conditions occur such as the ARR system, the ability of the system to achieve biological

remediation processes reduces. Labile organic carbon contribution to such systems by an external source (in our case WTR) can promote the biological activity thus enhance remedial processes within the system. For the contaminants that can be removed by adsorption mechanism, the RBF and ARR systems have a limited capacity due to the limited adsorption capacity of the alluvial material. The WTR amendment can also enhance the remediation of such contaminants through the RBF and ARR systems by simply creating effective sorption surfaces. All in all, the remediating capability of natural, semi-passive treatment techniques such as RBF and ARR can be enhanced by using WTR, a cost-free waste product, for biologically stable high quality water production.

FUTURE RESEARCH:

To maximize the benefits of WTR amendment further research is needed. The source of the WTR, mixing ratio, amended media depth, and media size are the major points that needed to be optimize the sequential RBF – WTR amended ARR system to produce high quality water.

The source of the WTR amendment influences the adsorption mechanism and capacity with changing coagulant such as aluminum or iron based and aluminum and iron (hydr)oxide content. A strong linear relation between the oxalate extractable aluminum and iron content (Al_{ox} and Fe_{ox}) and adsorption capacity of WTR (especially for phosphorus) was reported by previous studies. The amount of coagulant that is used and the source water quality directly affects the chemical characteristics of the WTR. After choosing the water treatment facility that the WTR will be obtained, the relationship

between the Al_{ox} and/or Fe_{ox} and sorption capacity of the contaminants (phosphorus and pesticides) can be established. This will be useful to estimate the life time of the WTR amendment and to schedule the time frame to replace the WTR amended infiltration gallery of the ARR. As the future research, first the water treatment facility where the WTR will be obtained should be decided. The WTR should be monitored in terms of the Al_{ox} and/or Fe_{ox} content and the relationship between the Al/Fe content and the maximum sorption capacity for the contaminants of concern should be established. This will be useful a design criteria to determine the replacing time interval for the WTR amended infiltration basin media.

The organic carbon content of the WTR is also important and depends on the source water quality of the water treatment facility. Since organic carbon leach from the WTR is the only carbon source to promote biological activity in the ARR system, a relation between the organic carbon content of the WTR and the amount of organic carbon that leaches should be developed. Our study indicated that less than the application ratio of 30% the source of WTR is not very important. However, above the application ratio of 30%, establishing a relationship between the WTR carbon content and the amount of carbon leach will be critical to optimize the carbon contribution to the ARR system. Also our study indicated that the amount of carbon leach from the WTR decreases by time, therefore, the time frame in which the leaching carbon depletes should be studied to decide when to replace the WTR amended layer from the ARR infiltration gallery.

The application ratio directly affects the amount of WTR in the infiltration basin. The adsorption capacity is directly related to the application ratio thus an optimum

application ratio should be decided by testing different WTR mixing ratios for the removal efficiencies and adsorption kinetics for the contaminants of concern.

The media depth directly affects the hydraulic residence time thus it should should be adjusted to achieve the removal efficiencies that are targeted for the contaminants in concern.

Finally, the media size is also one of the most important criteria to optimize the WTR amendment. The media size directly affects the amount of available sorption surfaces thus the adsorption capacity. Different media sizes should be tested in terms of the adsorption efficiencies and the hydraulic conductivity that achieves the optimum removal of the contaminants and hydraulic residence time.

The WTR that is obtained from the water treatment facilities usually has high moisture content and in the form of lump. Direct application of WTR to alluvial sand with this form affects the available surface area for sorption as well as creates short circuiting of water through the mixture thus decreases removal efficiencies of contaminants. The suggested application technique is drying and grinding the WTR followed by sieving it to a desired media size. For an infiltration basin with a defined surface area, volumetric mixing of WTR amendment and alluvial sand can be achieved by using the ratio of sand media depth and WTR media depth (to obtain 10% WTR amended media, mixing of 9-foot deep alluvial sand and 1-foot WTR spread over the sand will be required).

CHAPTER IX: REFERENCES

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APPENDIX

Table A.1: Riverbank filtration field study phosphorus measurements

Sampling Event	South Platte River (PTMW-1)	Monitoring Well 1 (PTMW-2)	Monitoring Well 2 (PTMW-3)	Monitoring Well 3 (PTMW-4)	Production Well (PTW-1)
	mg/L as P	mg/L as P	mg/L as P	mg/L as P	mg/L as P
2/4/2005	1.66	0.64	0.28	0.25	0.22
2/10/2005	1.37	n/a	n/a	n/a	0.21
2/17/2005	1.52	0.97	0.31	0.25	0.23
3/1/2005	1.56	0.92	0.34	0.22	0.23
3/10/2005	1.46	n/a	n/a	n/a	0.23
3/29/2005	1.52	0.40	0.22	0.17	0.19
4/21/2005	n/a	n/a	n/a	n/a	0.33
5/13/2005	1.47	0.35	0.35	0.29	0.26
5/24/2005	0.66	1.13	0.38	0.32	0.38
6/21/2005	0.55	0.75	0.36	0.29	0.35
7/18/2005	1.26	0.64	0.39	0.36	0.37
7/29/2005	1.01	0.65	0.45	0.45	0.37
8/17/2005	0.87	n/a	0.46	0.35	0.33
8/31/2005	1.10	0.60	0.39	0.34	0.36
9/15/2005	1.34	0.71	0.41	0.38	0.38
10/6/2005	1.53	0.92	0.40	0.36	0.61
10/25/2005	1.42	0.85	0.39	0.36	0.47
1/10/2006	1.68	1.35	0.57	0.37	0.54
2/14/2006	1.51	1.36	0.59	0.76	0.48
3/28/2006	2.21	1.71	0.96	1.13	0.67
4/20/2006	1.50	2.16	1.03	1.25	0.73
5/8/2006	1.95	1.42	0.90	0.99	n/a
6/21/2006	1.01	1.10	1.45	1.12	0.81
7/25/2006	1.22	0.93	0.63	0.96	0.77
8/31/2006	1.03	0.88	0.60	0.87	0.71
9/27/2006	2.13	1.11	0.65	0.81	0.65
Average	1.38	0.98	0.54	0.55	0.44
St Dev	0.40	0.43	0.29	0.34	0.20
95% C.I.	0.16	0.17	0.11	0.13	0.08
% Removal	n/a	29.1%	60.6%	60.3%	68.5%

Table A.2: Riverbank filtration column simulation study: RBF column (C-RBF) phosphorus measurements

Sampling Event	Run Time (hrs)	Feed Volume (L)	Bed Volume (L)	Influent (mg/L as P)	Port-1 (mg/L as P)	Port-2 (mg/L as P)	Port-3 (mg/L as P)	Effluent (mg/L as P)
5/9/2005	0	0.00	0.00	n/a	n/a	n/a	n/a	n/a
5/13/2005	96	5.76	0.26	1.47	n/a	n/a	n/a	n/a
5/24/2005	360	21.60	0.97	0.66	n/a	n/a	n/a	n/a
6/21/2005	1032	61.92	2.78	0.55	n/a	n/a	n/a	n/a
7/18/2005	1680	100.80	4.53	1.26	n/a	n/a	n/a	n/a
7/21/2005	1776	106.56	4.79	0.99	0.85	n/a	n/a	0.68
7/30/2005	1992	119.52	5.37	1.16	0.99	0.69	0.66	0.64
8/26/2005	2640	158.40	7.12	1.09	n/a	n/a	n/a	n/a
9/7/2005	2928	175.68	7.90	1.07	0.95	0.85	0.83	0.72
9/21/2005	3264	195.84	8.81	1.66	1.07	0.97	0.93	0.87
9/28/2005	3432	205.92	9.26	1.54	1.09	1.08	0.93	0.81
10/22/2005	4008	240.48	10.81	1.53	1.48	1.35	1.01	0.94
10/30/2005	4200	252.00	11.33	1.08	1.51	1.44	1.19	0.95
11/2/2005	4272	256.32	11.53	1.05	1.35	1.54	1.19	0.90
11/9/2005	4440	266.40	11.98	1.01	1.12	1.34	1.29	0.98
11/16/2005	4608	276.48	12.43	1.94	1.08	1.13	1.27	1.02
11/27/2005	4872	292.32	13.14	1.56	1.35	1.10	1.19	1.16
12/13/2005	5256	315.36	14.18	1.53	1.34	1.19	1.03	1.10
Average				1.24	1.18	1.15	1.05	0.90
St Dev				0.37	0.22	0.26	0.20	0.16
95% C.I.				0.17	0.12	0.15	0.12	0.09
% Removal				0.0%	5.0%	7.3%	15.9%	28.0%

Table A.3: Riverbank filtration column simulation study: RBF column (C-RBF) phosphorus loadings and removal

Sampling Event	Run Time (hrs)	Feed Volume (L)	C_{Port1}/C_{Ave}	C_{Port2}/C_{Ave}	C_{Port3}/C_{Ave}	C_{Eff}/C_{Ave}	P Applied (mg)	Cumulative P Applied (mg)	P Removed (mg)	Cumulative P Removed (mg)
5/9/2005	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5/13/2005	96	5.76	n/a	n/a	n/a	n/a	8.48	8.48	n/a	n/a
5/24/2005	360	21.60	n/a	n/a	n/a	n/a	10.49	18.97	n/a	n/a
6/21/2005	1032	61.92	n/a	n/a	n/a	n/a	22.37	41.34	n/a	n/a
7/18/2005	1680	100.80	n/a	n/a	n/a	n/a	49.10	90.44	54.57	54.57
7/21/2005	1776	106.56	0.69	n/a	n/a	0.55	5.68	96.11	1.77	56.34
7/30/2005	1992	119.52	0.79	0.56	0.53	0.51	14.97	111.08	6.72	63.07
8/26/2005	2640	158.40	n/a	n/a	n/a	n/a	42.38	153.46	n/a	n/a
9/7/2005	2928	175.68	0.77	0.69	0.67	0.58	18.50	171.95	19.79	82.86
9/21/2005	3264	195.84	0.86	0.78	0.75	0.70	33.55	205.50	16.05	98.91
9/28/2005	3432	205.92	0.88	0.87	0.74	0.65	15.53	221.03	7.37	106.28
10/22/2005	4008	240.48	1.19	1.09	0.81	0.76	53.00	274.03	20.53	126.80
10/30/2005	4200	252.00	1.21	1.16	0.96	0.77	12.41	286.44	1.43	128.23
11/2/2005	4272	256.32	1.09	1.24	0.96	0.72	4.53	290.96	0.63	128.86
11/9/2005	4440	266.40	0.90	1.08	1.03	0.79	10.13	301.09	0.26	129.13
11/16/2005	4608	276.48	0.87	0.91	1.02	0.82	19.60	320.70	9.34	138.47
11/27/2005	4872	292.32	1.09	0.89	0.95	0.93	24.71	345.41	6.31	144.78
12/13/2005	5256	315.36	1.07	0.95	0.83	0.88	35.34	380.74	10.07	154.85

Table A.4: Riverbank filtration column simulation study: RBF control column (C-RBF-Control) phosphorus measurements

Sampling Event	Run Time (hrs)	Feed Volume (L)	Bed Volume (L)	Influent (mg/L as P)	Port-1 (mg/L as P)	Port-2 (mg/L as P)	Port-3 (mg/L as P)	Effluent (mg/L as P)
5/9/2005	0	0.00	0.00	n/a	n/a	n/a	n/a	n/a
5/13/2005	96	5.76	0.26	1.47	n/a	n/a	n/a	n/a
5/24/2005	360	21.60	0.97	0.66	n/a	n/a	n/a	n/a
6/21/2005	1032	61.92	2.78	0.55	n/a	n/a	n/a	n/a
7/18/2005	1680	100.80	4.53	1.26	n/a	n/a	n/a	n/a
7/21/2005	1776	106.56	4.79	0.99	0.78	n/a	n/a	n/a
7/30/2005	1992	119.52	5.37	1.16	1.03	0.89	0.76	0.79
8/26/2005	2640	158.40	7.12	1.18	1.14	1.13	0.93	0.81
9/7/2005	2928	175.68	7.90	1.19	1.23	1.12	1.05	0.86
9/21/2005	3264	195.84	8.81	n/a	n/a	n/a	n/a	0.87
9/28/2005	3432	205.92	9.26	1.53	n/a	n/a	n/a	1.02
10/22/2005	4008	240.48	10.81	1.65	n/a	n/a	n/a	1.37
11/9/2005	4440	266.40	11.98	n/a	n/a	n/a	n/a	1.54
11/16/2005	4608	276.48	12.43	1.94	n/a	n/a	n/a	1.47
11/27/2005	4872	292.32	13.14	1.80	n/a	n/a	n/a	1.46
12/13/2005	5256	315.36	14.18	1.66	n/a	n/a	n/a	1.34
Average				1.31	1.05	1.05	0.92	1.15
St Dev				0.42	0.20	0.13	0.14	0.31
95% C.I.				0.26	0.22	0.17	0.19	0.22
% Removal				0.0%	20.3%	20.2%	30.2%	12.1%

Table A.5: Riverbank filtration column simulation study: RBF control column (C-RBF-Control) phosphorus loadings and removal

Sampling Event	Run Time (hrs)	Feed Volume (L)	C_{Port1}/C_{Ave}	C_{Port2}/C_{Ave}	C_{Port3}/C_{Ave}	C_{Eff}/C_{Ave}	P Applied (mg)	Cumulative P Applied (mg)	P Removed (mg)	Cumulative P Removed (mg)
5/9/2005	0	0.00	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
5/13/2005	96	5.76	n/a	n/a	n/a	n/a	8.48	8.48	n/a	n/a
5/24/2005	360	21.60	n/a	n/a	n/a	n/a	10.49	18.97	n/a	n/a
6/21/2005	1032	61.92	n/a	n/a	n/a	n/a	22.37	41.34	n/a	n/a
7/18/2005	1680	100.80	n/a	n/a	n/a	n/a	49.10	90.44	n/a	n/a
7/21/2005	1776	106.56	0.59	n/a	n/a	n/a	5.68	96.11	65.32	65.32
7/30/2005	1992	119.52	0.79	0.68	0.58	0.60	14.97	111.08	4.74	70.06
8/26/2005	2640	158.40	0.87	0.86	0.71	0.62	45.93	157.01	14.46	84.52
9/7/2005	2928	175.68	0.94	0.85	0.80	0.66	20.53	177.54	5.64	90.16
9/21/2005	3264	195.84	n/a	n/a	n/a	0.67	n/a	n/a	n/a	n/a
9/28/2005	3432	205.92	n/a	n/a	n/a	0.78	46.18	223.72	15.20	105.35
10/22/2005	4008	240.48	n/a	n/a	n/a	1.04	57.06	280.78	9.70	115.05
11/9/2005	4440	266.40	n/a	n/a	n/a	1.17	n/a	n/a	n/a	n/a
11/16/2005	4608	276.48	n/a	n/a	n/a	1.12	70.01	350.80	17.15	132.20
11/27/2005	4872	292.32	n/a	n/a	n/a	1.11	28.53	379.33	5.48	137.68
12/13/2005	5256	315.36	n/a	n/a	n/a	1.02	38.34	417.67	7.52	145.20

Table A.6: Riverbank filtration column simulation study: WTR amended RBF column (C-RBF-WTR) phosphorus measurements

Sampling Event	Run Time (hrs)	Feed Volume (L)	Bed Volume (L)	Influent (mg/L as P)	Port-1 (mg/L as P)	Port-2 (mg/L as P)	Port-3 (mg/L as P)	Effluent (mg/L as P)
5/9/2005	0	0.00	0.00	n/a	n/a	n/a	n/a	n/a
6/24/2005	1104	66.24	2.98	1.01	n/a	n/a	n/a	0.03
7/1/2005	1272	76.32	3.43	0.76	0.01	n/a	0.03	n/a
7/21/2005	1752	105.12	4.73	0.99	0.01	n/a	n/a	n/a
7/30/2005	1968	118.08	5.31	1.16	0.01	n/a	n/a	n/a
8/19/2005	2448	146.88	6.60	1.17	0.06	n/a	n/a	n/a
8/26/2005	2616	156.96	7.06	1.25	0.03	0.03	n/a	n/a
9/7/2005	2904	174.24	7.83	1.12	0.03	n/a	n/a	n/a
9/21/2005	3240	194.40	8.74	1.34	0.02	n/a	n/a	0.04
9/28/2005	3408	204.48	9.19	1.44	0.02	n/a	n/a	0.04
10/22/2005	3984	239.04	10.75	1.52	0.04	0.05	0.03	0.04
10/30/2005	4176	250.56	11.27	1.04	0.03	0.02	0.04	0.05
11/2/2005	4248	254.88	11.46	0.96	0.03	0.03	0.03	0.03
11/9/2005	4416	264.96	11.91	1.59	0.02	0.03	0.02	0.03
11/16/2005	4584	275.04	12.37	2.01	0.02	0.01	n/a	0.03
11/27/2005	4848	290.88	13.08	1.57	0.01	0.01	0.03	0.02
12/13/2005	5232	313.92	14.12	1.42	0.01	n/a	n/a	0.02
1/7/2006	5832	349.92	15.73	2.04	0.04	0.04	0.02	0.02
Average				1.32	0.02	0.03	0.03	0.03
St Dev				0.36	0.01	0.01	0.01	0.01
95% C.I.				0.19	0.01	0.01	0.01	0.01
% Removal				0.0%	98.3%	98.1%	98.0%	97.8%

Table A.7: Riverbank filtration column simulation study: WTR amended RBF column (C-RBF-WTR) phosphorus loadings and removals

Sampling Event	Run Time (hrs)	Feed Volume (L)	P Applied (mg)	Cumulative P Applied (mg)	P Removed (mg)	Cumulative P Removed (mg)
5/9/2005	0	0.00	0.00	0.00	0.00	0.00
6/24/2005	1104	66.24	66.90	66.90	65.17	65.17
7/1/2005	1272	76.32	7.63	74.53	7.33	72.50
7/21/2005	1752	105.12	28.38	102.92	27.52	100.02
7/30/2005	1968	118.08	14.97	117.89	14.58	114.60
8/19/2005	2448	146.88	33.83	151.72	32.97	147.57
8/26/2005	2616	156.96	12.63	164.35	12.33	159.90
9/7/2005	2904	174.24	19.28	183.63	18.77	178.66
9/21/2005	3240	194.40	27.01	210.65	26.22	204.89
9/28/2005	3408	204.48	43.62	254.26	42.33	247.22
10/22/2005	3984	239.04	52.55	306.82	51.09	298.31
10/30/2005	4176	250.56	12.03	318.85	11.50	309.81
11/2/2005	4248	254.88	4.14	322.99	4.02	313.84
11/9/2005	4416	264.96	16.03	339.02	15.72	329.56
11/16/2005	4584	275.04	40.52	379.54	39.93	369.49
11/27/2005	4848	290.88	24.81	404.35	24.45	393.94
12/13/2005	5232	313.92	32.63	436.98	32.17	426.11
1/7/2006	5832	349.92	73.42	510.40	72.60	498.71

Table A.8: Aquifer recharge and recovery column simulation study phosphorus measurements

Sampling Event	Run Time (hrs)	Feed Volume (L)	Bed Volume (L)	Influent (mg/L as P)	C-ARR (mg/L as P)	C-ARR-Control (mg/L as P)	C-ARR-WTR-1 (1ft Media)	C-ARR-WTR-2 (2ft Media)	C-ARR-WTR-3 (3ft Media)	C-ARR-WTR Effluent (4ft Media)
2/3/2006	0	0	0	0.62	0.54	n/a	<0.03	<0.03	<0.03	<0.03
3/10/2006	864	51.84	2.33	0.52	0.58	n/a	<0.03	<0.03	<0.03	<0.03
4/13/2006	1680	100.80	4.53	0.66	0.73	0.28	<0.03	<0.03	<0.03	<0.03
5/15/2006	2448	146.88	6.60	0.74	0.6	0.4	<0.03	<0.03	<0.03	<0.03
6/12/2006	3120	187.20	8.42	0.79	0.68	0.4	<0.03	<0.03	<0.03	<0.03
7/10/2006	3792	227.52	10.23	0.88	0.6	0.52	<0.03	<0.03	<0.03	<0.03
8/1/2006	4320	259.20	11.65	0.73	0.75	0.74	<0.03	<0.03	<0.03	<0.03
10/12/2006	6048	362.88	16.32	1.23	1.48	1.48	<0.03	<0.03	<0.03	<0.03
Average				0.77	0.75	0.64	0.03	0.03	0.03	0.03
St Dev				0.22	0.31	0.44	n/a	n/a	n/a	n/a
95% C.I.				0.17	0.24	0.40	n/a	n/a	n/a	n/a
% Removal				0.0%	3.4%	17.5%	96.1%	96.1%	96.1%	96.1%

Table A.9: Aquifer recharge and recovery column simulation study: WTR amended ARR column (C-ARR-WTR) phosphorus loadings and removals

Sampling Event	Run Time (hrs)	Feed Volume (L)	P Applied (mg)	Cumulative P Applied (mg)	P Removed (mg)	Cumulative P Removed (mg)
2/3/2006	0	0	0.00	0.00	0.00	0.00
3/10/2006	864	51.84	32.14	32.14	30.59	30.59
4/13/2006	1680	100.80	25.46	57.60	23.99	54.58
5/15/2006	2448	146.88	30.41	88.01	29.03	83.61
6/12/2006	3120	187.20	29.84	117.85	28.63	112.23
7/10/2006	3792	227.52	31.85	149.70	30.64	142.88
8/1/2006	4320	259.20	27.88	177.58	26.93	169.80
10/12/2006	6048	362.88	75.69	253.27	72.58	242.38

Table A.10: Sequential RBF – WTR amended ARR column simulation study phosphorus measurements

Sampling Event	Run Time (hrs)	Feed Volume (L)	Bed Volume (L)	Influent (mg/L as P)	C-ARR-WTR-1 (mg/L as P)	C-ARR-WTR Effluent (4ft Media)	C-ARR (mg/L as P)	C-ARR-WTR-1C (mg/L as P)	C-ARR-WTR-C Effluent (4ft Media)	C-ARR-Control (mg/L as P)
3/29/2007	0	0	0	0.68	n/a	n/a	n/a	n/a	n/a	n/a
4/29/2007	744	44.64	2.01	0.71	n/a	n/a	n/a	n/a	n/a	n/a
5/31/2006	1512	90.72	4.08	0.72	0.05	0.03	0.18	0.03	0.03	0.13
6/13/2007	1824	109.44	4.92	0.73	0.06	0.03	0.14	0.03	0.03	0.17
6/28/2007	2184	131.04	5.89	0.76	0.06	0.03	0.19	0.03	0.03	0.19
Average				0.72	0.06	0.03	0.17	0.03	0.03	0.16
StDev				0.03	0.01	0.00	0.03	0.00	0.00	0.03
95% CI				0.03	0.01	n/a	0.03	n/a	n/a	0.04
% Removal				0.0%	92.1%	95.8%	76.4%	95.8%	95.8%	77.3%

Table A.11: WTR phosphorus adsorption capacity during column simulation studies

Column Simulation Study	Sampling Event	Run Time (hrs)	Feed Volume (L)	P Applied (mg)	Cumulative P Applied (mg)	P Removed (mg)	Cumulative P Removed (mg)
RBF Column Simulation Study	5/9/2005	0	0	0.00	0.00	0.00	0.00
	6/24/2005	1104	66.24	66.90	66.90	65.17	65.17
	7/1/2005	1272	76.32	7.63	74.53	7.33	72.50
	7/21/2005	1752	105.12	28.38	102.92	27.52	100.02
	7/30/2005	1968	118.08	14.97	117.89	14.58	114.60
	8/19/2005	2448	146.88	33.83	151.72	32.97	147.57
	8/26/2005	2616	156.96	12.63	164.35	12.33	159.90
	9/7/2005	2904	174.24	19.28	183.63	18.77	178.66
	9/21/2005	3240	194.4	27.01	210.65	26.22	204.89
	9/28/2005	3408	204.48	43.62	254.26	42.33	247.22
	10/22/2005	3984	239.04	52.55	306.82	51.09	298.31
	10/30/2005	4176	250.56	12.03	318.85	11.50	309.81
	11/2/2005	4248	254.88	4.14	322.99	4.02	313.84
	11/9/2005	4416	264.96	16.03	339.02	15.72	329.56
	11/16/2005	4584	275.04	40.52	379.54	39.93	369.49
	11/27/2005	4848	290.88	24.81	404.35	24.45	393.94
	12/13/2005	5232	313.92	32.63	436.98	32.17	426.11
	1/7/2006	5832	349.92	73.42	510.40	72.60	498.71
ARR Column Simulation Study	3/10/2006	6696	401.76	32.14	542.54	30.59	529.29
	4/13/2006	7512	450.72	25.46	568.00	23.99	553.29
	5/15/2006	8280	496.8	30.41	598.42	29.03	582.32
	6/12/2006	8952	537.12	29.84	628.25	28.63	610.94
	7/10/2006	9624	577.44	31.85	660.10	30.64	641.59
	8/1/2006	10152	609.12	27.88	687.98	26.93	668.51
	10/12/2006	11880	712.8	75.69	763.67	72.58	741.09
Sequential RBF-WTR Amended ARR Column Simulation Study	4/29/2007	12624	757.44	30.36	794.02	29.02	770.11
	5/31/2006	13392	803.52	32.72	826.74	30.41	800.52
	6/13/2007	13704	822.24	13.48	840.22	12.36	812.87
	6/28/2007	14064	843.84	15.77	855.99	14.47	827.34

Table A.12: RBF field monitoring study DOC measurements

Sample Date	South Platte River PTMW-1 DOC mg/L	Monitoring Well 1 PTMW-2 DOC mg/L	Monitoring Well 2 PTMW-3 DOC mg/L	Monitoring Well 3 PTMW-4 DOC mg/L	Production Well PTW-1 DOC mg/L
1/10/05	n/a	n/a	n/a	n/a	n/a
1/20/05	n/a	n/a	n/a	n/a	n/a
2/4/05	4.76	3.23	3.07	2.50	2.15
2/10/05	4.79	n/a	n/a	n/a	2.10
2/17/05	4.55	3.30	2.86	2.58	2.50
3/1/05	5.08	2.47	2.20	1.73	2.20
3/10/05	4.77	n/a	n/a	n/a	1.97
5/24/05	5.52	4.02	3.32	3.28	3.15
6/21/05	4.82	3.15	2.64	2.50	2.14
7/18/05	5.17	2.74	2.52	2.26	n/a
7/29/05	4.59	3.24	2.49	2.35	n/a
8/17/05	4.81	3.10	2.77	2.74	2.53
8/31/05	5.54	3.32	3.18	2.93	2.89
4/20/2006	6.79	4.22	4.21	4.44	3.39
5/8/2006	7.07	4.65	4.31	3.97	n/a
6/21/2006	5.57	3.49	3.43	3.53	3.40
7/25/2006	5.95	4.55	3.67	3.60	3.20
Average	5.32	3.50	3.13	2.95	2.63
St Dev	0.77	0.67	0.65	0.76	0.54
95% CI	0.43	0.37	0.36	0.43	0.30
% Removal	0.0%	34.2%	41.2%	44.5%	50.5%

Table A.13: Riverbank filtration column simulation study: RBF column (C-RBF) DOC measurements

Sample Date	South Platte River DOC (mg/L)	C-RBF Effluent DOC (mg/L)
12/4/2005	3.53	3.32
12/18/2005	3.53	2.95
1/6/2006	3.43	3.17
1/16/2006	3.44	2.74
1/23/2006	4.02	3.64
Average	3.59	3.16
St Dev	0.25	0.35
95% CI	0.25	0.35
% Removal	0.0%	11.9%

Table A.14: Aquifer recharge and recovery column simulation study: DOC measurements

Sampling Date	Influent DOC (mg/L)	C-ARR-Cont DOC (mg/L)	C-ARR DOC(mg/L)	C-ARR-WTR-1 DOC (mg/L)	C-ARR-WTR-2 DOC (mg/L)	C-ARR-WTR-3 DOC (mg/L)	C-ARR-WTR-Eff DOC (mg/L)
4/13/2006	n/a	2.84	4.11	5.26	9.27	13.10	15.80
5/15/2006	7.27	2.81	4.33	9.31	8.46	12.80	9.09
6/12/2006	3.60	4.37	3.49	6.12	9.07	12.40	13.50
6/27/2006	3.12	4.36	4.15	4.76	7.63	10.90	14.50
7/10/2006	3.11	4.04	3.13	4.80	7.03	9.97	12.70
8/1/2006	5.23	4.07	4.30	7.60	6.82	9.69	12.30
10/12/2006	3.65	4.06	3.53	3.96	6.22	8.74	9.27
11/3/2006	4.17	4.22	n/a	4.72	6.89	7.57	9.52
Average	4.31	3.85	3.86	6.05	8.29	11.83	12.09
St Dev	0.80	0.64	0.47	1.90	0.95	1.34	2.55
95% CI	0.73	0.51	0.40	1.91	0.95	1.35	2.02

Table A.15: Sequential RBF – WTR amended ARR column simulation study DOC measurements

Sampling Date	Influent DOC (mg/L)	C-ARR-WTR-1 DOC (mg/L)	C-ARR-WTR-4 DOC (mg/L)	C-ARR DOC (mg/L)
4/29/2007	4.10	n/a	n/a	n/a
5/31/2007	n/a	4.74	10.30	4.18
6/13/2007	4.05	4.48	10.10	4.44
6/28/2007	3.89	5.03	10.70	4.03
Average	4.01	4.75	10.37	4.22
St Dev	0.11	0.28	0.31	0.21
95% CI	0.14	0.36	0.40	0.27

Table A.16: DOC leach tests with WTRs from different sources (small column tests)

Samples (% v/v mixing ratio)	Sampling 1 DOC (mg/L)	Sampling 2 DOC (mg/L)	Sampling 3 DOC (mg/L)	Average DOC (mg/L)	St Dev	95% CI	Leach DOC (mg/L)
Tank	3.57	3.57	3.57	3.57	0.00	n/a	n/a
Control	4.78	3.91	4.63	4.44	0.47	0.60	n/a
Aurora 5%	4.86	6.77	6.11	5.91	0.97	1.26	1.48
Aurora 10%	6.87	7.43	7.20	7.17	0.28	0.36	2.57
Aurora 20%	10.14	10.10	10.03	10.09	0.06	0.07	5.40
Aurora 30%	13.47	13.58	14.65	13.90	0.65	0.84	10.02
Denver 5%	5.38	5.70	5.82	5.63	0.23	0.29	1.19
Denver 10%	6.94	7.49	7.05	7.16	0.29	0.38	2.42
Denver 20%	9.68	9.22	8.94	9.28	0.37	0.48	4.31
Denver 30%	9.16	9.50	9.58	9.41	0.22	0.29	4.95
Wellington 5%	6.67	7.24	7.17	7.03	0.31	0.40	2.54
Wellington 10%	7.36	6.77	6.68	6.94	0.37	0.48	2.05
Wellington 20%	9.42	9.82	9.26	9.50	0.29	0.37	4.63
Wellington 30%	15.71	16.44	14.50	15.55	0.98	1.27	9.87

Table A.17: RBF field monitoring study nitrate measurements

Sampling Date	South Platte River (PTMW-1)	Monitoring Well 1 (PTMW-2)	Monitoring Well 2 (PTMW-3)	Monitoring Well 3 (PTMW-4)	Production Well (PTW-1)
	mg/L NO_3-N	mg/L NO_3-N	mg/L NO_3-N	mg/L NO_3-N	mg/L NO_3-N
1/10/2005	n/a	n/a	n/a	n/a	<0.01
1/20/2005	11.4	n/a	n/a	n/a	0.7
2/4/2005	9.4	n/a	n/a	n/a	1.5
2/10/2005	10.2	n/a	n/a	n/a	1.6
2/17/2005	8.5	n/a	n/a	n/a	2.4
3/1/2005	9.2	n/a	n/a	n/a	1.3
3/10/2005	6.9	n/a	n/a	n/a	1.5
3/29/2005	6.9	n/a	n/a	n/a	1.6
4/21/2005	3.2	n/a	n/a	n/a	1.9
5/13/2005	2.6	1.6	n/a	n/a	2.0
5/24/2005	1.9	2.2	n/a	1.9	1.4
6/21/2005	3.0	2.0	1.3	0.1	0.1
7/18/2005	7.6	2.0	0.7	1.4	1.2
7/29/2005	5.3	2.5	1.1	2.1	2.0
8/17/2005	5.4	0.3	0.5	1.5	1.9
8/31/2005	6.6	1.1	0.8	2.8	2.0
9/15/2005	4.2	2.5	0.4	1.3	2.5
10/6/2005	7.6	2.3	0.7	1.2	2.5
Average	6.47	1.84	0.78	1.53	1.53
St Dev	2.83	0.73	0.33	0.79	0.61
95% CI	1.34	0.48	0.24	0.54	0.29
% Removal	0.0%	71.6%	88.0%	76.3%	76.4%

Table A.18: Riverbank filtration column simulation study: RBF column (C-RBF) nitrate measurements

	Influent	**C-RBF-1-1**	**C-RBF-1-2**	**C-RBF-1-3**	**C-RBF-1**	**C-RBF-2**	**C-RBF-3**	**C-RBF-4**	**C-RBF-5**
	mg/L NO_3-N	mg/L NO_3-N	mg/L NO_3-N	mg/L NO_3-N	mg/L NO_3-N	mg/L NO_3-N	mg/L NO_3-N	mg/L NO_3-N	mg/L NO_3-N
Hydraulic Residence Time (days)	0	1.25	2.5	3.75	5	10	15	20	25
8/18/2005	5.00	5.60	6.23	n/a	5.00	n/a	n/a	0.05	0.04
9/7/2005	7.60	6.60	5.70	5.10	4.40	0.54	0.09	0.01	0.14
9/19/2005	8.5	7.6	7.4	7.0	6.3	2.2	0.4	0.3	1.1
9/28/2005	9.4	8.6	7.4	6.7	6.2	4.6	0.27	1.1	1.3
10/12/2005	9.74	7.85	7.39	7.64	8.12	4.86	0.68	1.20	1.25
10/26/2005	9.78	9.45	9.15	8.49	7.82	5.20	3.31	0.005	1.14
11/2/2005	7.08	5.13	4.41	3.97	4.49	6.67	3.24	0.005	0.38
11/9/2005	8.91	7.65	6.88	5.50	4.57	2.95	4.62	0.005	0.005
11/17/2005	8.49	8.64	9.09	8.39	7.6	3.32	1.74	1.27	1.11
11/30/2005	8.84	7.9	6.88	5.75	5.13	4.85	3.38	0.26	0.96
12/21/2005	8.75	5.90	5.34	6.93	6.83	6.06	1.00	0.51	0.99
Average	8.37	7.36	6.90	6.55	6.04	4.13	1.87	0.43	0.77
% Removal	0.0%	12.1%	17.6%	21.8%	27.8%	50.7%	77.6%	94.9%	90.9%
St Dev	1.39	1.38	1.45	1.46	1.41	1.86	1.63	0.52	0.51
95% C.I	0.82	0.81	0.86	0.91	0.83	1.16	1.01	0.30	0.30

Table A.19: Aquifer recharge and recovery column simulation study: nitrate measurements

Sampling Date	Feed mg/L NO_3-N	C-ARR-Cont mg/L NO_3-N	C-ARR mg/L NO_3-N	C-WTR-ARR mg/L NO_3-N
4/13/2006	8.52	8.35	n/a	0.01
5/15/2006	9.19	8.6	8.53	0.01
6/12/2006	6.22	5.99	n/a	0.01
6/27/2006	8.94	8.58	7.91	0.01
7/10/2006	8.17	8.78	8.1	0.005
8/1/2006	8.38	7.97	7.86	0.05
10/12/2006	8.96	8.64	8.69	0.02
11/3/2006	10.5	9.99	8.76	0.01
Average	8.61	8.36	8.31	0.02
% Removal	0.0%	2.9%	3.5%	99.8%
St Dev	1.20	1.12	0.40	0.01
95% CI	0.95	0.89	0.37	0.01

Table A.20: Sequential RBF – WTR amended ARR column simulation study nitrate measurements

Sampling Date	Tank	C-WTR-1	C-ARR	C-WTR-Eff	Tank Cont	C-WTR-Cont-1	C-ARR-Cont	C-WTR-Cont-Eff
	mg/L NO3-N	mg/L NO3-N	mg/L NO3-N	mg/L NO3-N	mg/L NO3-N	mg/L NO3-N	mg/L NO3-N	mg/L NO3-N
5/31/2007	13.10	11.90	6.50	1.70	11.60	10.60	12.30	0.01
6/13/2007	12.40	11.40	8.70	1.40	12.40	11.90	8.70	0.01
6/28/2007	12.30	10.20	9.50	0.01	11.20	10.30	10.40	0.01
Average	12.60	11.17	8.23	1.04	11.73	10.93	10.47	0.01
St Dev	0.44	0.87	1.55	0.90	0.61	0.85	1.80	0.00
95% C.I.	0.49	0.99	1.76	1.02	0.69	0.96	2.04	
% Removal	0%	11%	35%	92%	0%	7%	11%	100%

Table A.21: RBF field monitoring study perchlorate measurements

Sampling Date	South Platte River ug/L	Production Well ug/L	% Removal
Jun 2006	2.5	0.7	72.0%
Jul 2006	2.8	ND	100.0%
Aug 2006	2.9	<0.25	100.0%
Sep 2006	6.5	2.3	64.6%
Jan 2007	<0.25	ND	
Jul 2007	1	ND	100.0%

Table A.22: Riverbank filtration column simulation study: RBF column (C-RBF) perchlorate measurements

Sampling Date	Perchlorate Concentration (ug/L)	
	Tank	C-RBF
4/29/2007	40.66	
510/2007		35.75
5/21/2007		33.30
5/31/2007	39.83	36.60
6/18/2007		34.54
6/28/2007	41.56	20.71
7/20/2007		35.43
7/31/2007		35.05
Average	40.68	33.05
% Removal	0.0%	18.8%
St Dev	0.87	5.54
95% CI	1.12	4.69

Table A.23: Aquifer recharge and recovery column simulation study: perchlorate measurements

Sampling Date	Perchlorate Concentration (ug/L)			
	Tank	C-ARR Cont	C-ARR	C-ARR-WTR
4/13/2006	25.40	26.20	ND	ND
5/15/2006	29.70	26.10	22.20	3.40
6/12/2006	26.20	24.40	26.80	<0.25
7/10/2006	28.70	26.50	28.00	1.60
8/1/2006	30.60	21.60	21.00	ND
Average	28.12	24.96	24.50	2.50
%Removal		11.2%	12.9%	91.1%
St Dev	2.24	2.05	3.42	1.27
95% CI	2.25	2.06	3.43	1.28

Table A.24: Sequential RBF – WTR amended ARR column simulation study perchlorate measurements

Sampling Time	Perchlorate Concentration (ug/L)							
	Tank	C-WTR-1	C-ARR	C-WTR-4	Tank-Cont	C-WTR-1-Cont	C-ARR-Cont	C-WTR-4-Cont
4/29/2007	47.25	n/a	n/a	n/a	41.85	n/a	n/a	n/a
5/31/2007	n/a	38.93	34.48	ND	n/a	39.67	52.17	36.07
6/13/2007	42.2	36.56	29.84	ND	43.65	45.82	44.07	28.4
6/28/2007	49.77	43.44	33.49	ND	40.18	49.41	41.48	41.48
Average	46.41	39.64	32.60	n/a	41.89	44.97	45.91	35.32
% Removal	0.0%	14.6%	29.7%	100.0%	0.0%	-7.3%	-9.6%	15.7%
St Dev	3.85	3.50	2.44	n/a	1.74	4.93	5.58	6.57
95% CI	4.99	4.52	3.16	n/a	2.25	6.37	7.22	8.51

Table A.25: RBF field monitoring study atrazine measurements

Sampling Date	South Platte River PTMW-1 ug/L	Production Well PTW-1 ug/L
7/18/2005	ND	ND
7/29/2005	ND	ND
8/17/2005	<0.3	ND
8/31/2005	ND	ND
9/15/2005	ND	ND
10/1/2005	ND	ND
4/17/2006	ND	ND
5/15/2006	ND	<0.3
6/12/2006	ND	ND
6/27/2006	63	0.5
7/31/2006	0.5	<0.3
8/23/2006	0.3	0.3

Table A.26: RBF field monitoring study alachlor measurements

Sampling Date	South Platte River PTMW-1 ug/L	Production Well PTW-1 ug/L
7/18/2005	3.3	2.6
7/29/2005	6.7	0.6
8/17/2005	0.5	0.5
8/31/2005	<0.3	0.9
9/15/2005	<0.3	0.9
10/1/2005	<0.3	<0.3
4/17/2006	ND	ND
5/15/2006	ND	ND
6/12/2006	ND	ND
6/27/2006	ND	ND
7/31/2006	0.4	0.3
8/23/2006	11.4	12.9

Table A.27: RBF field monitoring study metolachlor measurements

Sampling Date	South Platte River PTMW-1 ug/L	Production Well PTW-1 ug/L
7/18/2005	16.8	12.3
7/29/2005	40.1	2.0
8/17/2005	1.5	1.8
8/31/2005	0.8	0.9
9/15/2005	0.9	3.0
10/1/2005	0.9	0.6
4/17/2006	<0.3	<0.3
5/15/2006	<0.3	<0.3
6/12/2006	<0.3	<0.3
6/27/2006	37.4	6.6
7/31/2006	7.0	4.9
8/23/2006	<0.3	0.3

Table A.28: ARR column simulation study atrazine measurements

Sample	5/15/2006	6/12/2006	7/10/2006	Average	% Removal
Tank	31.7	76.6	41.3	49.9	0.0%
C-ARR-Control	29.4	67.3	43.1	46.6	6.6%
C-ARR	28.9	19.2	17.3	21.8	56.3%
C-ARR-WTR	0.15	0.15	3.1	1.1	97.7%

Table A.29: ARR column simulation study alachlor measurements

Sample	5/15/2006	6/12/2006	7/10/2006	Average	% Removal
Tank	5.4	54.7	21.4	27.2	0.0%
C-ARR-Control	3.1	38.2	26.6	22.6	16.7%
C-ARR	0.4	0.3	8.8	3.2	88.3%
C-ARR-WTR	0.15	0.15	1.8	0.7	97.4%

Table A.30: ARR column simulation study metolachlor measurements

Sample	5/15/2006	6/12/2006	7/10/2006	Average	% Removal
Tank	92.6	65.9	81.36	80.0	0.0%
C-ARR-Control	91.4	67.4	47.5	68.8	14.0%
C-ARR	133.6	43.4	36.8	71.3	10.9%
C-ARR-WTR	0.15	0.15	0.15	0.2	99.8%

Table A.31: Sequential RBF – WTR amended ARR column simulation study pesticide measurements

Pesticide	Date	Tank	C-WTR-1	C-ARR	C-WTR-4	Tank-Control	C-WTR-1C	C-ARR-Control	C-WTR-4C
	5/31/2007	40.50	0.15	0.15	0.15	43.30	0.50	0.30	0.15
	6/13/2007	34.20	1.00	0.15	0.15	45.40	0.70	0.60	0.15
	6/28/2007	44.10	0.15	0.15	0.15	37.90	0.60	0.15	0.15
Atrazine	Average	39.60	0.43	0.15	0.15	42.20	0.60	0.35	0.15
	St Dev	5.01	0.49	0.00	0.00	3.87	0.10	0.23	0.00
	95% C.I.	5.67	0.56	n/a	n/a	4.38	0.11	0.26	n/a
	% Removal	0.0%	98.9%	99.6%	99.6%	0.0%	98.6%	99.2%	99.6%
	5/31/2007	40.7	1	0.9	0.4	41.5	0.8	0.4	0.7
	6/13/2007	38.6	1.2	0.9	0.7	36.3	0.6	0.4	0.4
	6/28/2007	37.1	1.5	0.8	0.15	41.8	0.6	0.5	0.3
Alachlor	Average	38.80	1.23	0.87	0.42	39.87	0.67	0.43	0.47
	St Dev	1.81	0.25	0.06	0.28	3.09	0.12	0.06	0.21
	95% C.I.	2.05	0.28	0.07	0.31	3.50	0.13	0.07	0.24
	% Removal	0.0%	96.8%	97.8%	98.9%	0.0%	98.3%	98.9%	98.8%
	5/31/2007	16.5	0.15	0.15	0.15	16.9	0.15	0.15	0.15
	6/13/2007	20.3	0.15	0.15	0.15	18.7	0.3	0.15	0.15
	6/28/2007	16.2	0.15	0.15	0.15	14.2	0.15	0.15	0.15
Metolachlor	Average	17.67	0.15	0.15	0.15	16.60	0.20	0.15	0.15
	St Dev	2.29	0.00	0.00	0.00	2.26	0.09	0.00	0.00
	95% C.I.	2.59	n/a	n/a	n/a	2.56	0.10	n/a	n/a
	% Removal	0.0%	99.2%	99.2%	99.2%	0.0%	98.8%	99.1%	99.1%