IMPACT OF SOIL PROPERTIES ON REMOVAL OF EMERGING CONTAMINANTS FROM WASTEWATER EFFLUENT DURING SOIL AQUIFER TREATMENT

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TITLE: Impact of Soil Properties on Removal of Emerging Contaminants from Wastewater Effluent During Soil Aquifer Treatment

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ABSTRACT

Impact of Soil Properties on Removal of Emerging Contaminants from Wastewater Effluent During Soil Aquifer Treatment

Lauren Riley

This study evaluates soil properties that impact the effectiveness of soil aquifer treatment (SAT) as a polishing step to the remove two classes of ECs from wastewater effluent: pharmaceuticals and personal care products (PPCPs), and engineering nanomaterials (ENMs). In recent years, it has been determined that elevated levels of emerging contaminants (ECs) are being released into the environment with wastewater effluent. ECs are proven to cause adverse environmental and health effects as a result of long-term exposure. It is important to evaluate sustainable solutions to improve the current methods of wastewater treatment to address these ECs.

Soil aquifer treatment (SAT) is a sustainable, cost effect treatment alternative to advanced treatment at a wastewater treatment plant. SAT replenishes local groundwater supplies while allowing for indirect potable reuse, if contaminants of concern such as ECs can be effectively removed from the water. Since wastewater effluent can contain a variety of contaminants with myriad physical and chemical properties, understanding the potential of the aquifer itself to provide EC removal is a key step in establishing SAT as a viable treatment alternative. Peer-reviewed research studies were analyzed to determine the soil properties that affect the fate and transport of ECs in the aquifer environment. The data was complied to produce recommendations for an effective SAT site.

Physical and chemical properties of the soil facilitate contaminant removal as the groundwater flows through the aquifer. This study determined that removal of ECs from effluent had a correlation with (1) high clay content, (2) small Darcy Velocity, (3) high soil organic matter content, and (4) low sand content. Based on the 6 peer-reviewed research studies reviewed, the removal of nanomaterials is affected by clay content and sand content, but not soil organic matter content. Conversely, the removal of PPCPs is affected by clay content and soil organic mater content, but not sand content. It can be concluded that two different removal mechanisms facilitate the removal of nanomaterials versus PPCPs; physical removal for nanomaterials and chemical removal (sorption) for PPCPs. Clay facilitates the removal of both contaminants. The small soil diameter of clay forms smaller pores in the soil media. This causes increased pore straining, while also restricting the flow through the soil, which increases the contact time between the soil particle and the ECs. Additionally, clay has a large surface area, which increases surface interactions, such as sorption, of the EC to the surface of the clay particle.

Keywords: Emerging contaminants, pharmaceuticals and personal care products, nanomaterials, soil aquifer treatment, indirect potable reuse

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CHAPTER 1

INTRODUCTION

The demand for water is increasing across the world due to many factors including population growth, climate change, and urbanization (Kapley, 2019). Meanwhile, both surface and groundwater water supplies are declining as a result of these same forces. Concurrently, pollution in water systems is contaminating critical surface and groundwater supplies and exacerbating the demand and supply imbalance (Kapley, 2019). Because of the decline in water supply, the use of reclaimed or recycled water to augment potable and non-potable supplies is becoming the norm in some parts of the world (Asano T., 2002). While recycling effluent for reuse applications can address the water scarcity problem, it can also introduce and/or concentrate certain contaminants in the water supply and environment.

A rising population yields larger quantities of wastewater production and consequently increases wastewater discharge into the environment. As a result of the high concentrations of organic and inorganic contaminants in the wastewater, river systems and other discharge points cannot effectively absorb the poor water quality (Kapley, 2019). Thousands of man-made contaminants from wastewater have been discovered in the drinking water supply, which could have potential negative effects on both people and the surrounding environment (Kapley, 2019). Therefore, wastewater treatment will be continually evolving to develop alternative solutions to address these emerging threats.

In 2002, Takashi Asano identified water reuse as "the greatest challenge of the 21st century" and stated that it will require special attention in the upcoming years. This statement is even more relevant today as the problems discussed then have only been exacerbated since. Dr. Asano, a professor emeritus at the University of California, Davis, suggested that the increased quantity of wastewater can be used as a resource to address the challenges of water scarcity and environmental pollution (Asano T., 2002). Dr. Asano's primary conclusion was that wastewater can be used for all purposes, as long as it is treated to the necessary water quality requirements for the anticipated use (Asano T., 2002).

The traditional wastewater treatment process utilizes primary and secondary treatment technologies that produce "clean" water, which is then discharged into the environment as treated effluent. The primary treatment process removes the physical constituents in the wastewater entering the treatment plant via gravity sedimentation. The secondary treatment process eliminates the remaining suspended solids and about 85% of the remaining organic and inorganic matter (EPA, 1998). Municipalities must then find an acceptable method of disposing of or discharging the treated effluent, from releasing it into local waterways, utilizing it as irrigation, or releasing it into the ocean via marine outfalls if the treatment plant is near the coast.

Depending on the requirements associated with the method of discharge or the plans for reuse of the effluent, various additional treatment processes may be used. After primary and secondary treatment, the wastewater can go through tertiary treatment, which is primarily characterized by filtration. This treatment step is capable of removing particles that are larger than about 3 μm by passing the effluent through a filter media (Mujeriego, 1999). The wastewater can be treated to even higher levels with the use of advanced treatment. Typical advanced treatment steps include chemical treatments or reverse osmosis. The goal of this additional treatment step is to remove the remaining organic materials to produce water suitable for non-potable reuse (Abdel-Raouf et al., 2012). Current advanced treatment is extremely effective, but is often too expensive to implement in many locations because of required materials and energy usage (Abdel-Raouf et al., 2012).

Advanced treatment of effluent can make "indirect potable reuse" (IPR) feasibly. IPR produces high quality recycled drinking water from wastewater, but requires some sort of an environmental buffer, such as lakes, rivers, or a groundwater aquifer, as a final step before it is suitable as a drinking water source (Rodriguez et al., 2009). It is currently illegal in the state of California to produce drinking water directly from a wastewater treatment plant without the addition of an environmental buffer (US EPA, 2017). However, IPR utilizing an environmental buffer is used to transform highly-treated effluent into drinking-water where the conditions of the environment are suitable.

A treatment process known as "soil aquifer treatment" (SAT) has become increasingly popular as a means of creating this environmental buffer. SAT is the artificial recharge of wastewater effluent into the unsaturated zone of a groundwater aquifer (Sharma, S. K., & Kennedy, M. D., 2017). The groundwater aquifer has natural properties that filter out contaminants in the effluent and improve the water quality, while also replenishing the local groundwater supply. SAT is an extremely efficient wastewater treatment alternative because it augments groundwater while creating a safe drinking water supply for communities. SAT can represent a valuable solution to communities facing water supply and water quality challenges as a result of increased demand, drought or climate change.

One significant challenge in developing advanced water treatment processes for IPR is the relatively recent discovery of emerging contaminants (ECs) in urban effluent. ECs may include pharmaceuticals, personal care products, nanomaterials and other materials. ECs are proven to cause adverse environmental impacts, but all the potential consequences have yet to be fully understood (Matamoros, V., & Salvadó, V., 2012).

For most municipalities, conventional wastewater treatment does not effectively remove ECs so the water recycling process can cause a continual increase in ECs in the environment (Díaz-Garduño et al., 2017). There are advanced water reclamation facilities which include ozonization, photo-fenton, and reverse osmosis that can degrade or remove ECs, but these treatment technologies require large inputs of energy and are expensive to build and maintain (Matamoros, V., & Salvadó, V. 2012).

SAT systems are a reliable, cost effective, low energy treatment method to remove pollutants when compared to other advanced treatment techniques. Ideally, SAT treatment could supplement or replace advanced treatment to safely and efficiently remove ECs and keep them from entering aquifer systems during IPR. However, the efficiency of SAT for removing ECs requires additional research. This study presents an analysis on the fate and transport of ECs during SAT. Since wastewater effluent can contain a wide variety of ECs with myriad chemical and physical characteristics, this study will focus on the soil characteristics that affect EC removal, with the goal of determining key soil characteristics that increase the efficacy of SAT as a polishing step for EC removal. This information will facilitate selection of appropriate sites for SAT to increase viability of IPR as a supplement to diminishing freshwater sources.

CHAPTER 2

MATERIALS AND METHODS

Literature review techniques were exercised by this study to draw formal conclusions regarding the effectiveness of soil properties for removal of ECs from effluent during SAT. The selection process for the articles used for this study was governed by specific search parameters and research limitations. The six steps of conducting literature review-based research studies, as outlined by Paré, et. al. (2015) are:

1. Formulating research questions and objectives
2. Searching the extant literature
3. Screening for inclusion
4. Assessing the quality of primary studies
5. Extracting data
6. Analyzing data

The details of the literature review process as they pertain to this study are discussed below.

2.1 Formulating Research Questions and Objectives

ECs are a significant concern regarding the production of clean water and the protection of our environment. Over the recent years, new and improved monitoring techniques have allowed for the detection of ECs in effluent and drinking water (Yan, S. et. al., 2010). Since adverse health and environmental effects are linked with EC ingestion, advanced water treatment practices to remove ECs will be critical in the future (Kapley, 2019; Matamoros & Salvadó, 2012; Yan et al., 2010). Soil aquifer treatment is an extremely low-cost effluent polishing method, but the fate and transport of ECs through soil needs the further research. The purpose of this study is to advance the collected research that analyzes whether soil aquifer treatment could provide a sustainable and cost-effective solution to the increasing prevalence of ECs in our water. Accordingly, an objective was formulated that incorporated the fate and transport of the ECs through soil media. The established research question became: “what soil media properties are effective at removing ECs from recharged effluent?”

2.2 Searching the Extant Literature

California Polytechnic State University’s Unified Library Management System, OneSearch, was used to access the literature used in this study. The databases used for the literature review searches predominantly included Elsevier ScienceDirect, ProQuest and Springer Link. The resource type of interest was primarily limited to peer-reviewed journals, although sometimes the search was extended to articles, white papers, books, book chapters, government studies, and reports. The initial search was to determine if enough research has been done on the topic of ECs to produce conclusions and an informative thesis. The search topic used on OneSearch was “fate and transport of emerging contaminants in soil media”. From that search, most of the research presented was on PPCPs, so the search was refined to the following two phrases: “fate and transport of pharmaceuticals and personal care products in soil media” and “fate and transport of nanomaterials in soil media”. The articles were selected that appeared to have information which could be of interest, based on abstract review.

2.3 Screening for Inclusion

After the studies were assembled, they were evaluated to see if they had relevant content which could be used in the research. Figure 1 illustrates the process which was followed in reviewing and selecting the peer-reviewed journals to be included in this study

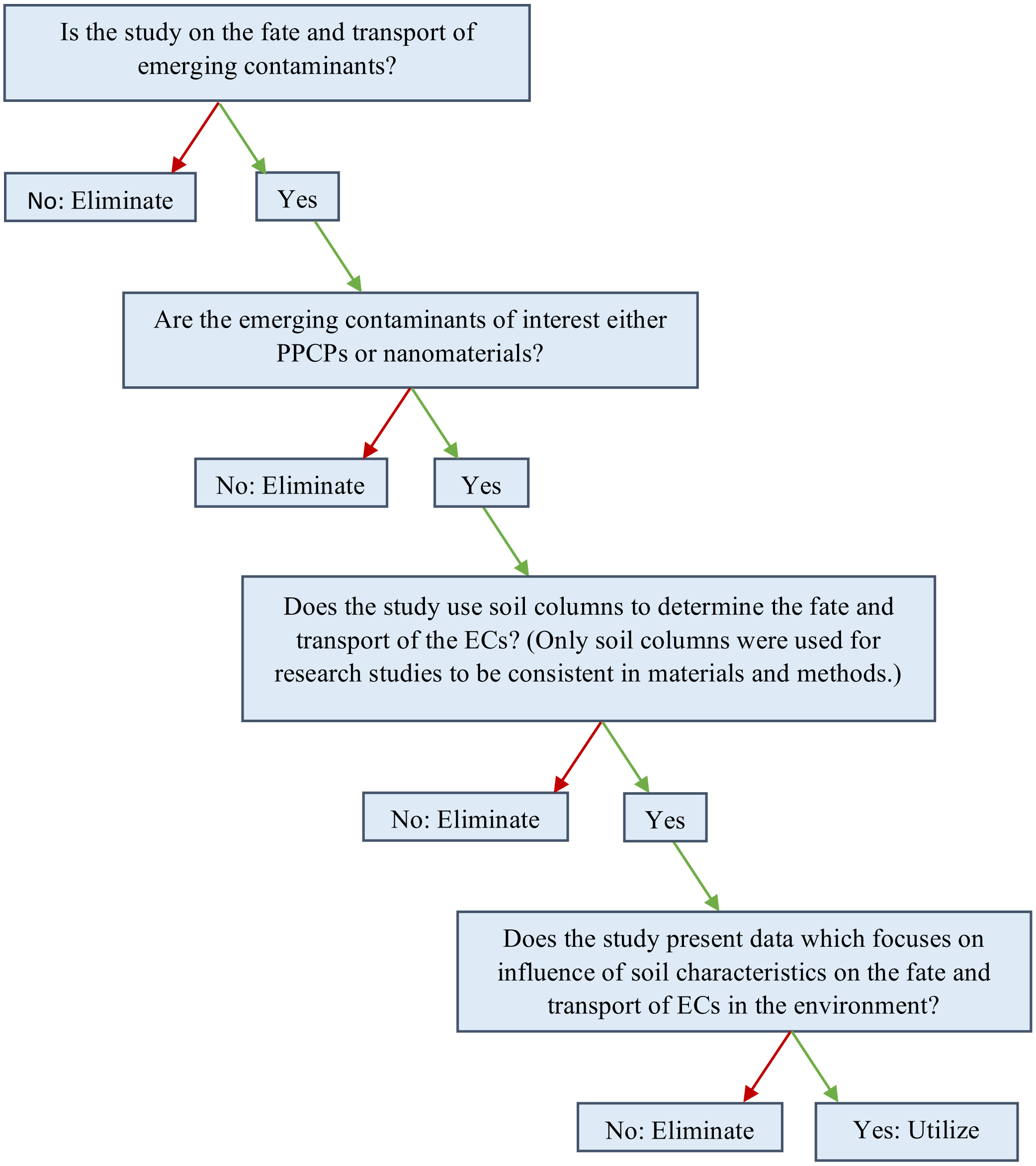


Figure 1: Screening process flow chart for inclusion of literature in this study.

2.4 Assessing the Quality of Primary Studies

After the screening process was complete, the quality of the studies was assessed to determine if the studies were acceptable sources. Specifically, the experimental methods employed in the studies were considered to determine if the conclusions were valid considering the procedures utilized in the soil column experiment(s). For example, when constructing a soil column for an experiment, one must compact the soil correctly to ensure the soil closely represents soil in the environment.

The initial search for this study yielded 30 articles. Of these 30 articles, 13 were eliminated due to the fact they were not relevant to my study of interest. An additional 11 were removed upon review because the results of the studies were not usable in the context of this study. The remaining 6 articles were used as the sources for my data analysis on the soil column studies and yielded the results for this study. Additional studies were the selected for background information and additional context necessary for this study.

2.5 Extracting Data

Data was extracted from the peer-reviewed journals that qualified as information of interest, credibility, and validity based on the initial research question. The specific characteristics of the soil media, the EC(s), and the groundwater flow that affect the removal ECs from effluent in soil media were researched.

2.6 Analyzing Data

Ultimately the data collected from the selected articles was analyzed. The studies of interest were compared, and overall conclusions were drawn regarding the effectiveness of soil aquifer treatment for removal of ECs from effluent. The analysis of the data is presented in the Chapter 4 of this study, and the overall conclusions are presented in Chapter 5.

CHAPTER 3

LITERATURE REVIEW

This thesis reviewed various literature studies and drew conclusions based off the collected findings. This section reviews emerging contaminants and the applications of soil aquifer treatment. This material provides background for the more in-depth discussion in the next chapter regarding effect of soil characteristics on emerging contaminant removal during soil aquifer treatment.

3.1 Emerging Contaminants Introduction

Emerging contaminants (ECs) can be found globally in aquatic systems and include many chemicals and their breakdown products. ECs are predominantly unregulated in the United States, despite having the ability to cause environmental damage and harmful effects on human health (Kapley, 2019; Yan et al., 2010). They are unregulated due the vast number of contaminants produced, ongoing research into human and environmental toxicology, and the large cost required to monitor. The 1996 Safe Drinking Water Act requires the EPA to release a list of no more than 30 unregulated contaminants to be monitored in public waters (EPA, 2016). The production and disposal of ECs is ahead of the monitoring capabilities of the EPA. Thousands of categories of ECs exist in air, water, soil food, and human and animal tissue (Yan, S. et. al., 2010). The list of current ECs in the environment is extensive and will continue to grow with the introduction of new chemicals. This study focuses on two important classes of ECs: engineered nanomaterials (ENMs) and pharmaceuticals and personal care products (PPCPs).

3.1.1 Nanomaterials

Nanotechnology has become one of the most valuable technologies in the science and engineering field. Consequently, Engineered Nanomaterials (ENMs) can be found in some of the newest advancements such as automotive, medical, energy, cosmetic, paint, nutrition and electronic products (D. Lin et al., 2010; M. Wang et al., 2016). The National Science Foundation estimated that ENMs would generate a global economic impact of of about $3 trillion in the year 2020 alone (M. Wang et al., 2016). Nanomaterials are anticipated to be used even more extensively in the future, which will lead to inevitable and inadvertent introduction of these materials into the environment from the manufacturing, conveyance, product use, and disposal processes (D. Lin et al., 2010). Despite their attention and use in industry, the fate and transport mechanisms for ENMs within the environment remains uncertain, as does their potential ecotoxicity.

Nanomaterials are defined as particles that include at least one dimension that is below 100 nm in size (M. Wang et al., 2016). ENM's that are discharged into the environment will eventually make their way into the air, surface water, groundwater, and/or soil. Nanomaterials typically enter the environment from wastewater, waste gas, or industrial residues (M. Wang et al., 2016). The sources of nanomaterials in the environment are displayed in Figure 2.

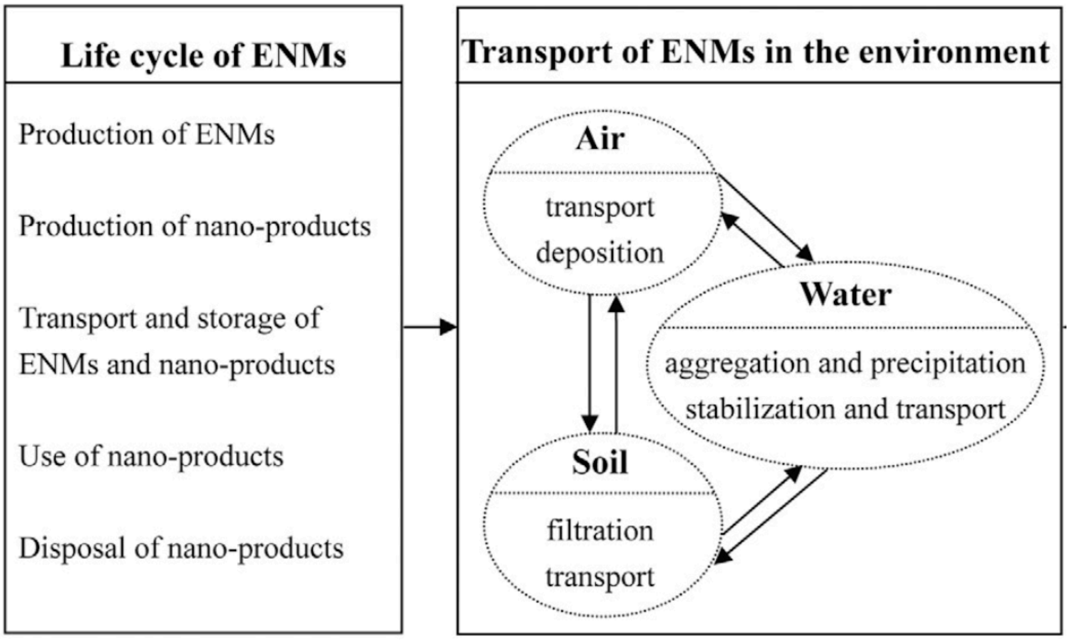


Figure 2: Sources of nanomaterials in the environment (D. Lin et al., 2010)

3.1.2 Effects of Nanomaterials

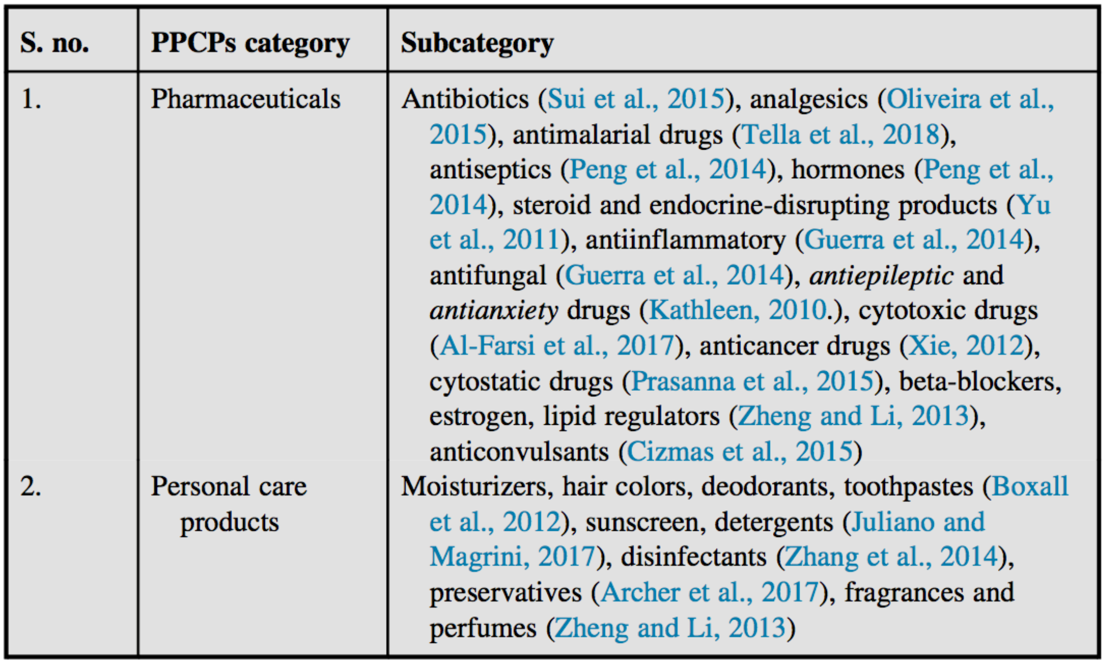
If ingested or inhaled, nanomaterials can have extremely harmful effects on humans. Studies have shown that exposure can cause genetic disease, lung and pleural fibrosis and carcinogenesis, and systemic immune disorders (M. Wang et al., 2016). Nanomaterials exhibit unconventional pathways in humans and they can even penetrate the skin, which makes them potentially very dangerous (Abbott & Maynard, 2010). Nanomaterials are also capable of entering the bloodstream after inhalation because they are so small (Abbott & Maynard, 2010).

Additionally, nanomaterials can be harmful to plants, causing a decrease in seed germination and formation of leaves (M. Wang et al., 2016). There could be numerous other health and environmental effects caused by nanomaterials, but since they are a relatively new technology, it is difficult to predict their impacts (Abbott & Maynard, 2010).

3.1.3 Pharmaceuticals and Personal Care Products

Pharmaceuticals and personal care products (PPCPs) are primarily found in materials that are used for personal health and cosmetic purposes (Yan, S., et al. 2010). Examples of common PPCPs include antibiotics, soaps, detergents, domestic cleaners, disinfectants and biocides, and cosmetics (Kapley, 2019). Table 1 shows an extended list of PPCPs.

Table 1: Pharmaceuticals and personal care product list (Jamil, 2019)



S. no.	**PPCPs category**	**Subcategory**
1.	Pharmaceuticals	Antibiotics (Sui et al., 2015), analgesics (Oliveira et al., 2015), antimalarial drugs (Tella et al., 2018), antiseptics (Peng et al., 2014), hormones (Peng et al., 2014), steroid and endocrine-disrupting products (Yu et al., 2011), antiinflammatory (Guerra et al., 2014), antifungal (Guerra et al., 2014), ***antiepileptic*** and ***antianxiety*** drugs (Kathleen, 2010.), cytotoxic drugs (Al-Farsi et al., 2017), anticancer drugs (Xie, 2012), cytostatic drugs (Prasanna et al., 2015), beta-blockers, estrogen, lipid regulators (Zheng and Li, 2013), anticonvulsants (Cizmas et al., 2015)
2.	Personal care products	Moisturizers, hair colors, deodorants, toothpastes (Boxall et al., 2012), sunscreen, detergents (Juliano and Magrini, 2017), disinfectants (Zhang et al., 2014), preservatives (Archer et al., 2017), fragrances and perfumes (Zheng and Li, 2013)

Since there are so many PPCPs, they are difficult to track. Additionally, monitoring can be a challenge because the concentrations of PPCPs can span between μg/L to a few ng/L and sometimes can exist below detection levels. Over the last decade PPCPs have received relatively little attention despite the fact they are considered the most common EC found in both surface and groundwater systems (Kapley, 2019).

PPCPs can enter the environment through hundreds of pathways due to the wide usage of these contaminants globally. They are commonly consumed by a host and then discharged into water bodies via wastewater and disposal of effluent (Kapley, 2019; Naidu et al., 2016). The source of PPCPs in the environment can be grouped into either a point source or a non-point source (Naidu, R., 2016). The United States Environmental Protection Agency (EPA) defines a point source as “any discernible, confined and discrete conveyance, including but not limited to any pipe, ditch, channel…from which pollutants are or may be discharged” (Clean Water Act, 1972). Human consumption is considered a point source. Sometimes the body does not break down PPCPs and the contaminant can be directly discharged into a treatment plant. However, typically the body breaks down PPCPs, producing by-products called metabolites, which continue to transform in the wastewater treatment facility (Kapley, 2019). Many PPCPs can survive the wastewater treatment process, then are discharged as effluent and collect in receiving water bodies, such as rivers, streams, lakes and oceans (Kapley, 2019). Furthermore, metabolites may themselves be pharmaceutically active or may transform back into their harmful parent state while in the environment (Kapley, 2019).

A nonpoint source refers to pollution which originates from an indistinguishable source and usually over a considerable area (Naidu, R., 2016). A common example of a nonpoint source is the large scale application of manure and bio solids to land (Naidu, R., 2016). In this example, the PPCPs in the manure can be washed away as runoff during a large storm event, and then contaminate clean bodies of water downstream. Figure 3 displays the various pathways that PPCPs take to enter the environment, from either a point source or a nonpoint source.

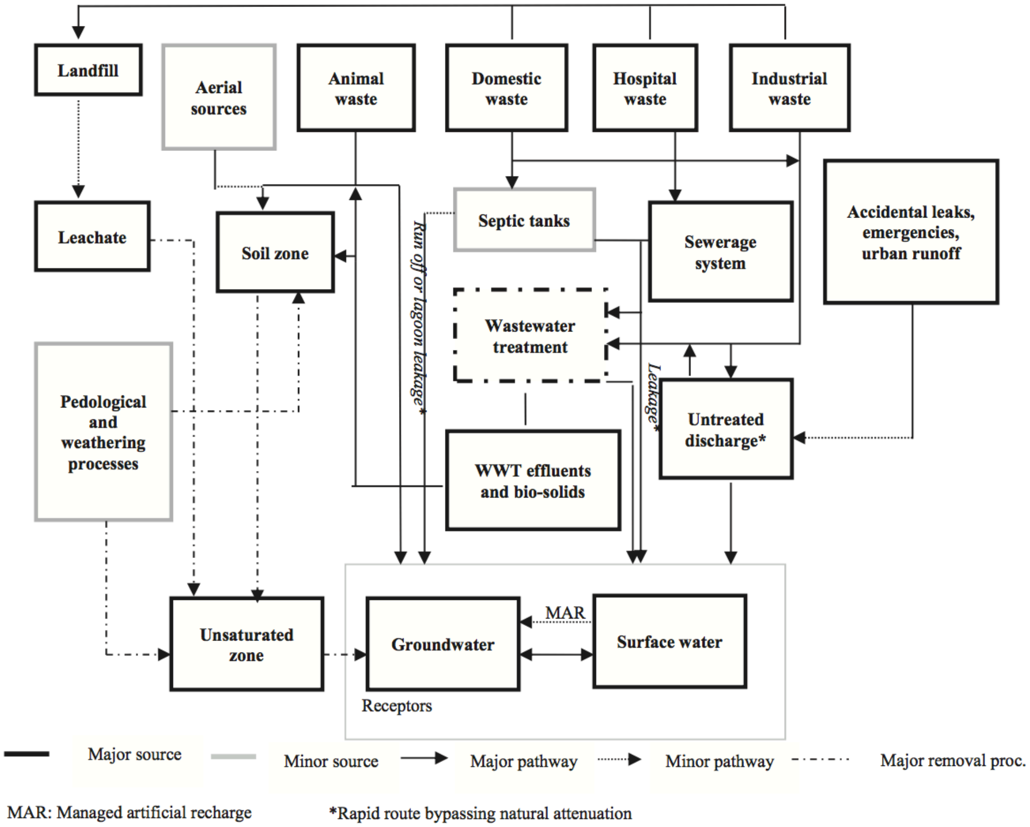


Figure 3: Source of PPCPs in the environment (Naidu, R. et al., 2016)

3.1.4 Effects of PPCPs

Recent studies have raised concerns about the presence of PPCPs in the drinking water supply and environment because of the potential negative health effects if ingested by vertebrates and invertebrates (Archer et al., 2017; Yang et al., 2017). Even extremely low concentrations can have serious health impacts (Yang et al., 2017). A 2009 research study conducted by the Environmental Working Group of the US (EWG) determined that the organic compound 1,4-dioxane, which is a known carcinogen, was found in 28% of the 27,000 PPCPs under investigation (Yang et al., 2017). The EWG also conducted a study on 20 mid-teen girls and concluded that 16 unsafe PPCPs were present due to use of cosmetic products (Yang et al., 2017).

Many PPCPs are qualified as endocrine disrupting chemicals (EDCs), which are pollutants that affect the endocrine system of humans and animals (Yan et al., 2010). EDCs can affect multiple functions including respiration, metabolism, sexual development, growth, behavior and reproduction (Yan et. al., 2010). The discharge of PPCPs is so widespread that the contaminants can be found in a large number of rivers, streams, and lakes. Global studies have shown the EDCs found within PPCPs are causing feminization of fish and frogs (Archer et al., 2017; McLachlan et al., 2006). If exposed to EDCs, male fish produce the protein that is typically produced by a female before she lays her eggs (McLachlan et al., 2006). This “egg yolk protein” is not characteristically generated by a male unless they are given estrogen (McLachlan et al., 2006). Frogs subjected to EDCs can become infertile due to the development of ovaries (McLachlan et al., 2006).

Mammals are even showing signs of reproductive adverse effects as a result of EDC ingestion (McLachlan et al., 2006).   For example, sheep who consume clover irrigated with water containing large concentrations of subterranean EDCs have been found to become infertile (McLachlan et al., 2006). This problem may be more widespread than realized; the plants above an aquifer contaminated with PPCPs can draw up the water containing the contaminants, and can sometimes become toxic themselves (McLachlan et al., 2006).

The extent of the negative effects caused by PPCPs and the risk to animals and the environment is not completely understood. The current research regarding the adverse health effects of PPCPs leads to the conclusion that a long-term exposure to PPCPs poses risks of harm to the environment and human health (Jamil, K., 2019). PPCPs are extremely valuable and can save lives, but we must figure out a way to reduce the discharge of these contaminants into our environment.

3.2 Soil Aquifer Treatment

Soil aquifer treatment (SAT) is a water treatment process that relies on the natural filtering properties of the soil to remove contaminants from water. The application of SAT under consideration in this study is polishing of tertiary wastewater effluent via groundwater recharge (Saroj K. Sharma & Kennedy, 2017). Groundwater recharge has been utilized for decades for underground storage of surface water supplies and for some water treatment purposes. Recent studies highlight the significant benefits of SAT as a low cost and effective advanced treatment process capable of producing high quality drinking water from highly-treated wastewater effluent (S. K. Sharma et al., 2008; Saroj K. Sharma & Kennedy, 2017).

SAT is accomplished by releasing treated effluent into an infiltration basin, where the effluent percolates through the soil and eventually recharges the underlying groundwater aquifer (Saroj K. Sharma & Kennedy, 2017). As the effluent passes through the aquifer, various mechanisms such as filtration though the pores of the soil, sorption to the soil particles, and biodegradation of the contaminants occur (Saroj K. Sharma & Kennedy, 2017). The aquifer "polishes" the applied effluent, removing the contaminants either through retention in the soil or biological degradation.

Groundwater aquifers contain both a vadose zone and a saturated zone. The vadose zone begins directly below the ground surface, and represents the segment of the aquifer that is unsaturated. This zone is characterized by three elements: soil media, water, and air. The depth of the vadose zone depends on the setting. It can range from less than 1 meter to depths over 100 meters (Doods, 2002). The saturated zone is where the water table begins, and constitutes the portion of the aquifer that has no air in the soil media voids; it is completely saturated with groundwater. Different contaminant removal mechanisms may dominate these two different zones of an aquifer.

Figure 4 is a schematic that displays the typical path of effluent in a SAT system. As seen in Figure 4, the treated effluent is recharged into the ground via infiltration basins that allow the water to percolate into the existing soil media. The effluent typically travels vertically through the vadose zone and then meets the existing saturated groundwater table. The effluent flow transitions to a horizontal direction and decreases in velocity.

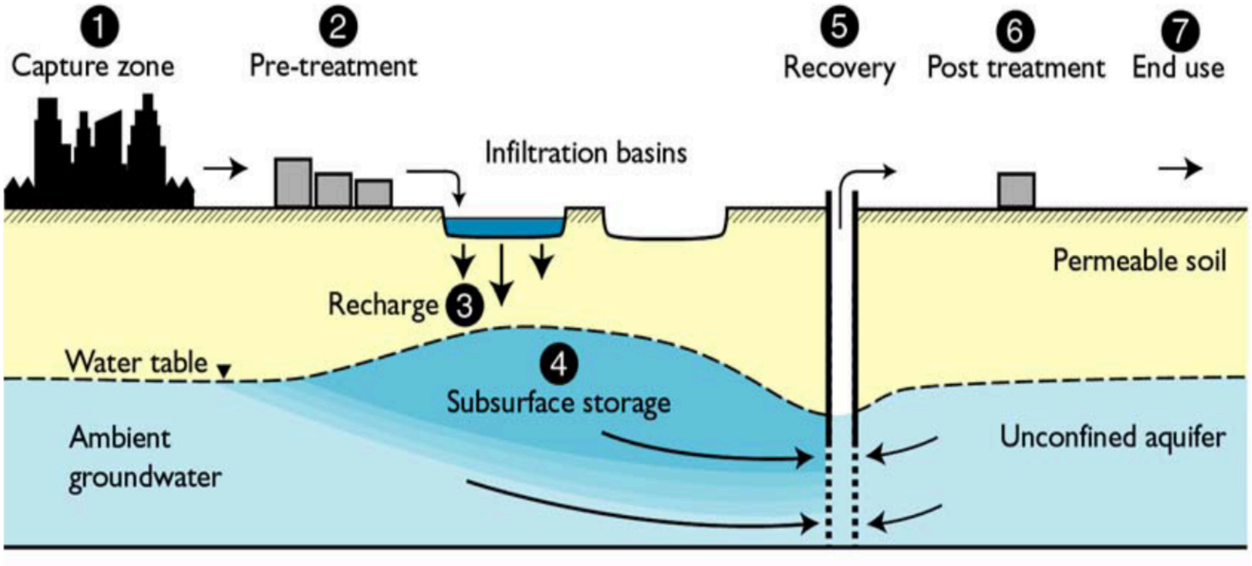


Figure 4: SAT system schematic of water flow (Page, et al., 2018)

Groundwater recharge has long been used to store water underground to augment the groundwater supply – for water quantity purposes only. This type of recharge is referred to as "artificial recharge" (Dillon et al., 2019). A more recent best management practice called "managed aquifer recharge" also involves the intentional recharge of water into aquifers, but it focuses on both the quantity and quality of the groundwater (Dillon et al., 2019). Unlike conventional artificial recharge, managed aquifer recharge considers the pollutant levels in the recharge water and the pollutant removal capacity of the soil, and controls recharge rate to achieve or maintain a desired water quality.

SAT is a critical component of properly managing aquifer recharge to produce high quality water. The effectiveness of SAT largely depends on the characteristics of the vadose zone and saturated zone of an aquifer. Accordingly, it is important to identify the media properties of an aquifer to understand the extent of the potential soil treatment.

The advantages of SAT are extensive, but one of the most important aspects is the substantially lower cost when compared to the alternative option of advanced treatment in a wastewater treatment facility. Additionally, SAT enhances the urban water supply, which can be affected by seasonal weather patterns or climate change (Page, et. al., 2018). Furthermore, in costal environments, SAT can prevent seawater intrusion. For instance, the community of Los Osos, CA located on the coast of the Central Valley, is experiencing contamination of its drinking water supply due to seawater intrusion and excess nitrate contaminants in its groundwater aquifer. Localized groundwater pumping has caused seawater to enter the aquifer. The community of Los Osos plans to perform a groundwater replenishment project to enhance the quality of the aquifer with the use of SAT. This application of SAT is widely used, and very effective. Another advantage of SAT is that it allows for storage of large amounts of water without compromising valuable land surface area (Page, et. al., 2018). Storage of water under the ground also reduces the loss of water through evaporation. Finally, the quality of the water is improved via physical, chemical, and biological processes.

Conversely, SAT presents a few disadvantages. Sometimes the soil media is not capable of removing the pollutants, so the contaminated groundwater can travel and pollute water bodies. Additionally, if the soil retains the contaminants via filtration or sorption, the pollutant can be left behind in the soil; this can cause adverse environmental impacts to plants and animals.

There is extensive research on the removal process of familiar wastewater contaminants discharged from a treatment plant, such as bulk organic materials, pathogens, and nitrate species. Emerging contaminants such a PPCPs and nanomaterials have received much less attention, but recent research has begun to focus more on studying fate and transport of these contaminants in groundwater environments.

The efficiency of various soils for SAT can be tested and modeled in a lab using soil column experiments. Columns can range in size: some of the smallest soil columns can measure 1 mm in diameter, while the larger columns can be a large as 2 m x 2 m x 5 m (Lewis & Sjöstrom, 2010). They are typically filled with representative samples of the potential soils under consideration for SAT (Trussell et al., 2018). The columns are either classified as "packed columns," which are comprised of excavated soil that is compacted into the rigid container, or "monolithic columns," which contain extracted, undisturbed soil (Lewis & Sjöstrom, 2010). When using the packed column method, small quantities of soil are loaded into the column incrementally and each layer is compacted to achieve a bulk density similar to the natural environment (Lewis & Sjöstrom, 2010). The vadose zone of an aquifer can be modeled with an unsaturated column experiment, while the saturated zone of an aquifer can be modeled with the use of completely saturated soil in the column (Lewis & Sjöstrom, 2010). Effluent containing ECs can be pumped in the upward direction (more representative of saturated flow), or can percolate through the soil in the downward direction by gravity (more representative of flow in the vadose zone). Common practice for a saturated soil column simulation includes the upward pumping method because it maintains the saturated condition during the total duration of the experiment (Lewis & Sjöstrom, 2010). The concentration of the contaminant of concern in the effluent is assessed before and after it travels through the columns. A soil column experiment can compare different media to determine the most effective soil media type for removing various contaminants. Figure 5 represents a typical schematic of a soil column used for contaminant removal research, using a down flow method.

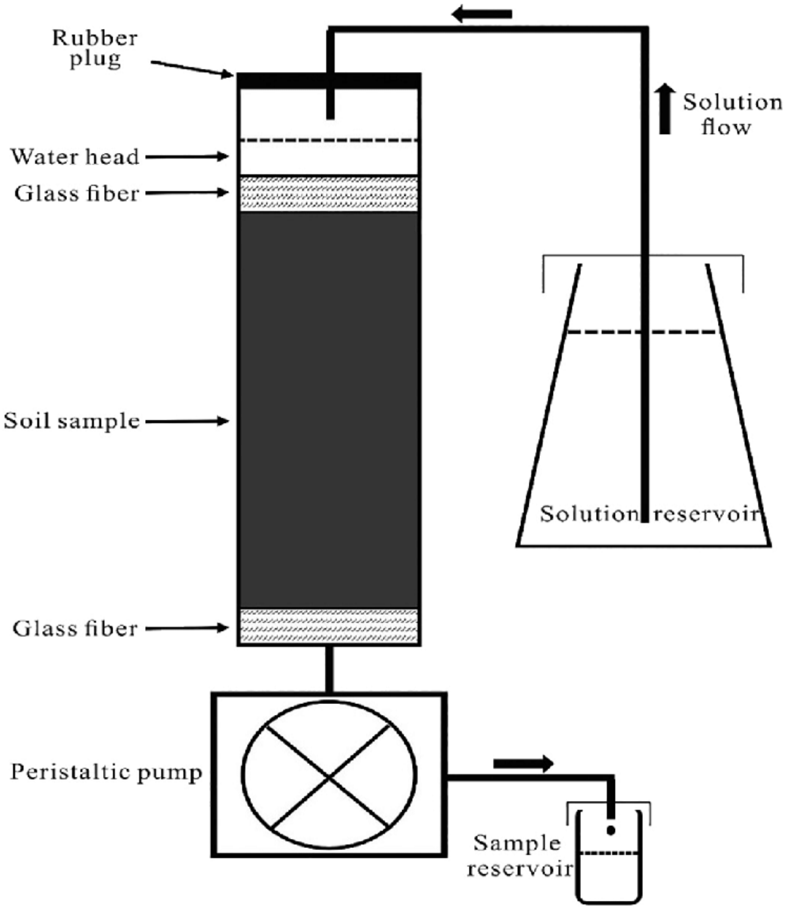


Figure 5: Schematic of typical soil column (Gu et al., 2018)

CHAPTER 4

FATE AND TRANSPORT OF EMERGING CONTAMINANTS THROUGH AN AQUIFER

The effectiveness of SAT to address ECs largely depends on three factors - the properties of the soil media, the properties of the pollutant, and the nature of the groundwater or effluent flow (M. Wang et al., 2016). Each factor has several characteristics which can vary on a case by case or site by site basis. Figure 6 shows the various properties that can affect ECs in porous media.

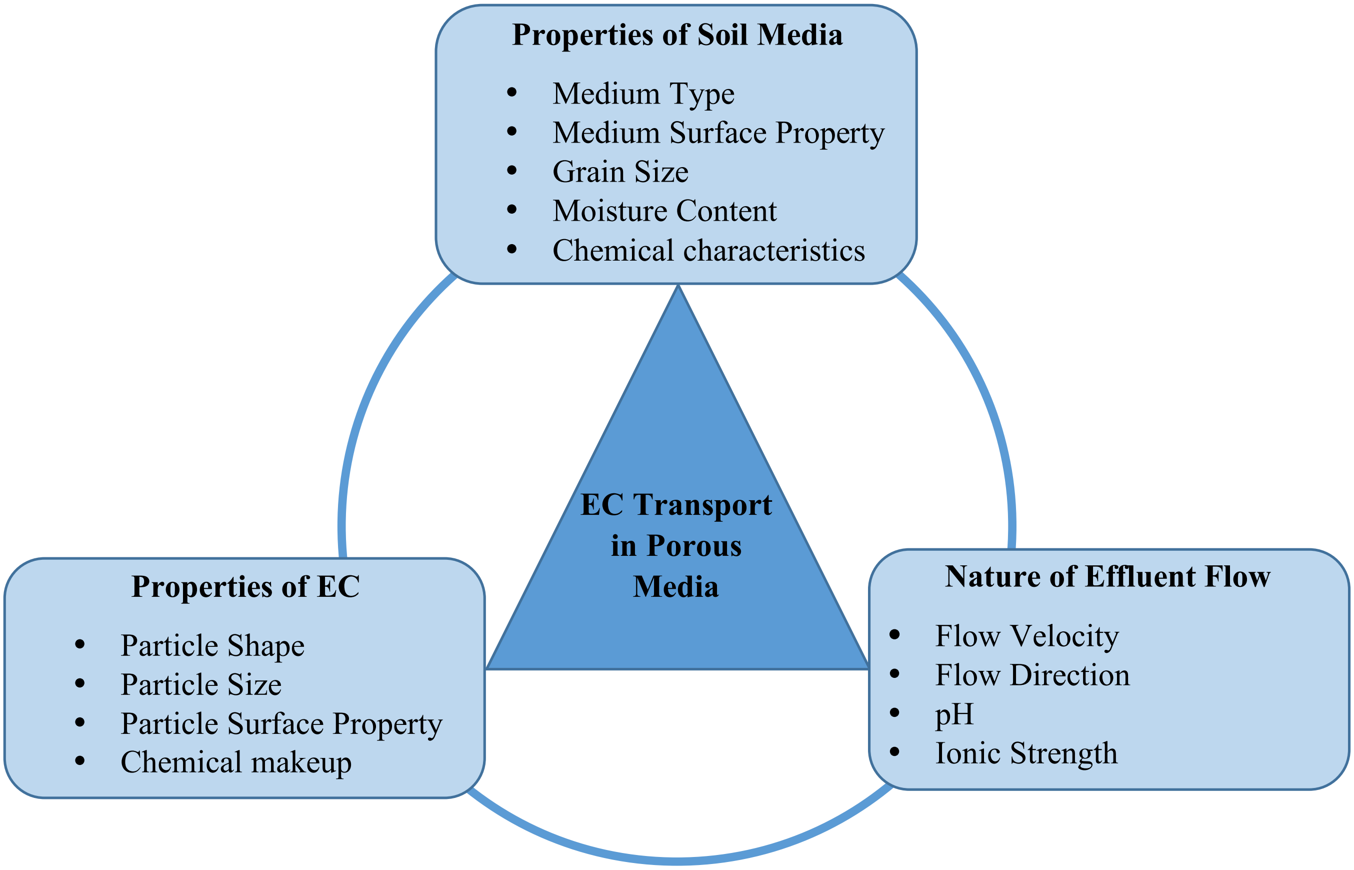


Figure 6: Emerging contaminant's transport in porous media (M. Wang et al., 2016)

While all three factors are related to each other and are all important to consider to determine the fate and transport of an ECs through porous media, this study focuses on the characteristics of the soil media. This section reviews the properties of ECs and the nature of the effluent flow to present context for a more in-depth discussion to determine the effect of soil media characteristics on the fate and transport of ECs.

4.1 PROPERTIES OF EMERGING CONTAMINANTS

Thousands of ECs exist in our environment and are constantly entering our wastewater treatment plants. This large quantity of ECs generates a wide range of possible pollutant properties. Properties of the particle such as shape, size, surface chemistry, and chemical characteristics can all impact the transport of ECs in porous media. Common properties that have the ability to influence the mobility of ECs include charge or surface charge, hydrophobicity, solubility, and the octonol-water partition coefficient (Harbordt, 2016; Wang et al., 2016).

4.1.1 Nanomaterials - Properties of Emerging Contaminant

Fate and transport of nanomaterials through an aquifer are largely driven by properties of the nanomaterials themselves, including shape, size and surface characteristics of the nanomaterial.

4.1.1.1 Particle Shape and Size – Impact on Removal of Nanomaterials

The size and shape of the ENM is an important function to recognize the removal capabilities through SAT. Distinctions in both their shape and size on the nanoscale causes disparities in the mobility of these contaminants. One of the most significant factors contributing to the unpredictability of a nanomaterial's transport in soil is due to their unpredictable mobility is the varying shapes and sizes of these ECs.

Nanomaterials come in various shapes, ranging from "layer, tube, sphere, wire, rod and fiber," as shown in Figure 7 (M. Wang et al., 2016). Graphene has emerged as one of the most common nanomaterials due to the combination of its strength and thin composition (Rao et al., 2009). Graphene can be morphed to become a spherical particle called fullerene (C_{60}). It can also be rolled up into a single-walled carbon nanotube (SWCNT) or a multi-walled carbon nanotube (MWCNT).

A nanomaterial's shape affects its transport through soil media, but there is insufficient research on the extent of the removal capabilities (M. Wang et al., 2016). Several studies which have compared the transport of various nanomaterial allotropes in the same conditions have discovered contradictory conclusions (M. Wang et al., 2016). For example, a study compared the mobility of MWCNTs and C_{60}. The research revealed that C_{60} demonstrated higher mobility than the MWCNTs when the ionic strength was below 10.89 mM. On the other hand, MWCNTs exhibited higher mobility when the ionic strength was higher than 10.89 mM. Further investigation should be completed which compares the transport of various particle shapes of nanomaterials in constant environmental conditions. (M. Wang et al., 2016)

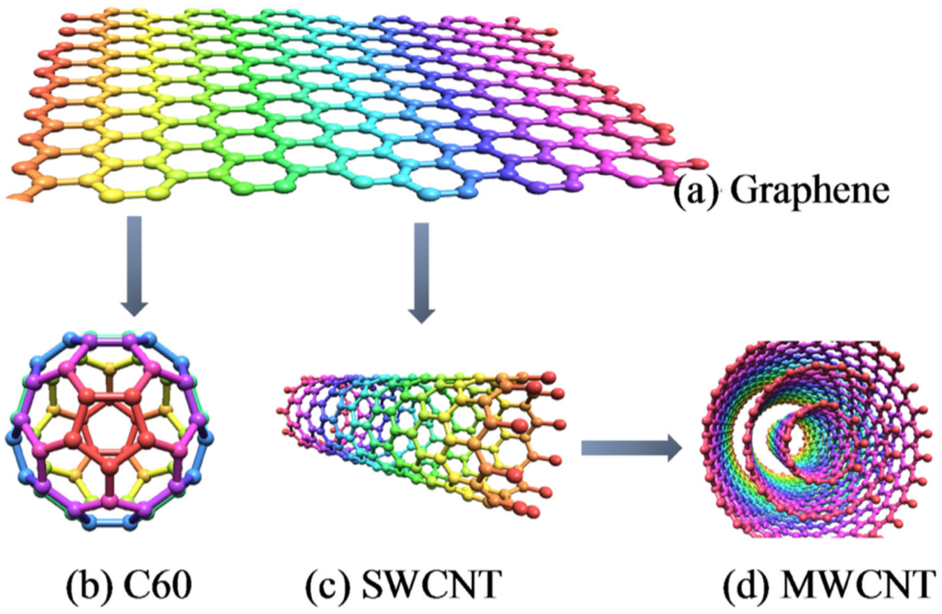


Figure 7: Various nanomaterial particle shapes (M. Wang et al., 2016)

The particle size of nanomaterials is recognized to influence their transport through porous media. Like particle shape, there are contradictory studies on this topic. A research study done by O'Carroll, et. al. compared the transport of various sizes of multi-walled carbon nanotubes (MWCNTs) through sand columns. This study found that smaller diameter MWCNTs are less mobile than larger diameter particles. O'Carroll, et. al. suggested that this occurrence is likely due to Brownian motion, the random movement of particles in a fluid. A smaller particle size is known to typically have a much stronger random displacement, and therefore creates more collision of particles (Hao, 2005). It is possible that the increase in collisions due to smaller particles size leads to higher retention in the soil (O'Carroll et al., 2013).

However, several studies present contrasting conclusions. A study by Wang et. al. showed that the length of SWCNTs affects the retention of that nanomaterial. A shorter SWCNT would have greater transport through soil media, whereas a longer SWCNT has a higher chance of being retained through straining mechanisms because if its irregular and oblong shape (M. Wang et al., 2016). A separate study analyzed the transport of MWCNTs through saturated quartz sand using soil columns. This study found that the retention of MWCNTs increased with an increasing tube length. This column study result is most likely due to soil straining mechanisms; the longer the particle, the easier it is trapped in the soil media (M. Wang et al., 2016; Y. Wang et al., 2012).

The scientific community has opposing opinions as to how the particle size and shape of nanomaterials affects their transport. These contaminants are so diverse that the transport properties are typically analyzed on a case-by-case basis. Further research should be completed to understand this subject more.

4.1.1.2 Particle Surface Properties – Impact on Removal of Nanomaterials

Nanomaterials encompass a wide range of surface properties due to the thousands of varieties that exist. Nanomaterials typically have an extremely high surface area to volume ratio relative to most contaminants (Christian et al., 2008). This mean that the surface chemistry of the nanomaterial is a very important property to consider because the surface of the contaminant occupies the most space. Furthermore, the surface is the first aspect of the nanomaterial exposed to the environment (Christian et al., 2008).

Untreated nanomaterials have the tendency to aggregate, which restricts their beneficial functions. To mitigate the aggregation of nanomaterials, the manufacturer frequently applies surfactant coatings or performs a chemical oxidation treatment to decrease hydrophobicity. The effect of surfactants on nanomaterials in a solution is displayed in Figure 8. These surface treatments can also affect the transport of nanomaterials in soil.

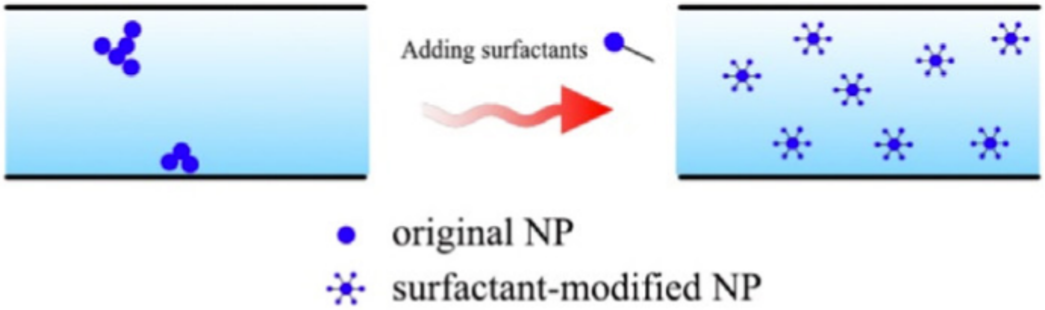


Figure 8: Effect of surfactants on nanomaterials (M. Wang et al., 2016)

The mobility of a nanomaterial due to particle surface properties is largely controlled by the properties of the coating. Coatings can be either negatively or positively charged, which affects the mobility of a nanomaterial (M. Wang et al., 2016). The charge of the particle influences its chemical attraction to or repulsion from the soil media. Soil media is typically negatively charged, so positively charged nanomaterials will be attracted to the soil media and will experience higher retention rates than negatively charged nanomaterials (Tian et al., 2011).

The mobility of a nanomaterial is also controlled by the hydrophobicity of the surface of the particle. Nanomaterials with hydrophilic surfaces typically are more attracted to the water solution than the soil particle, so they will have higher transport rates (Tian et al., 2011). On the other hand, nanomaterials that are hydrophobic will generally experience higher sorption rates to the soil media due to their repulsion from water (Tian et al., 2011).

4.1.2 Pharmaceuticals and Personal Care Products - Properties of Emerging Contaminant

This section evaluates the properties of PPCPs that affect their transport through porous media. PPCP transport is largely governed by chemical and surface properties of the molecule that increase its attraction to or repulsion from soil media.

4.1.2.1 Chemical Properties – Impact on Removal of Pharmaceuticals and Personal Care Products

Properties of the contaminant that affect its mobility include solubility, hydrophobicity, and the octonol-water partition coefficient (K_{ow}) (Harbordt, 2016). Solubility is the ability of a substance to dissolve in a solution (Caliman & Gavrilescu, 2009). Hydrophobicity is defined in the Particle Surface Property of Nanomaterials Section of this thesis. The K_{ow} value of substance is defined as the ratio of its concentration in the octonal phase to its concentration in the aqueous phase at equilibrium (EPA, 2012). It indicates the attraction of a particle to water versus matter containing organic matter such as non-polar fats and lipid, mineral oils, greases and surfactants (Caliman & Gavrilescu, 2009) or, in an aquifer, Soil Organic Matter (SOM). A larger K_{ow} value typically indicates that the PPCP particles are hydrophobic and will tend to have low water solubility (Caliman & Gavrilescu, 2009; Harbordt, 2016). A hydrophobic particle is repulsed from the water, and therefore has a stronger attraction to the soil media. This leads to higher accumulation of PPCPs in the soil media. On the other hand, when the K_{ow} value is smaller, the particles become hydrophilic and tend to attract to the water instead of the soil, so they will not be retained by the soil. Table 2 indicates the effects of various log K_{ow} values.

Table 2: The effect of log K_{ow} values on the solubility of a particle (EPA, 2012)

Log K_{ow} Values	**Solubility**
<1	High solubility in water – hydrophilic
>4	Low solubility in water – hydrophobic
>8	Not readily bioavailable
>10	Difficult to experimentally measure – Not bioavailable

Another chemical property of the contaminant that affects the fate and transport of PPCPs is its tendency to degrade in the environment. The original form of a PPCP can have different transport characteristics than its transformed metabolite or breakdown products. For example, the breakdown product can have a difference charge, K_{ow}, and/or hydrophobicity.

4.2 PROPERTIES AND NATURE OF EFFLUENT FLOW

The flow of groundwater is controlled by many physical factors including media type, porosity, aquifer conditions, hydraulic gradient, volume of groundwater, height of aquifer, confining layers, and presence of existing nearby water bodies. The nature and chemical properties of the groundwater itself also affects the removal capabilities of the soil media. Flow velocity, flow direction, pH, and ionic strength are all flow- or effluent-related properties that influence ECs' transport through soil.

The velocity and direction of groundwater flow is one of the most significant factors affecting the effectiveness of SAT projects to remove ECs. Because flow velocity and direction are dictated by the unique physical properties of the aquifer, SAT projects must assess these aquifer characteristics in siting the location of the project. The state of California requires a minimum residence time, from release to receptor, of two to 12-months for IPR projects (US EPA, 2017). This residence time allows for adequate removal of the contaminants in the recharged groundwater via SAT and is determined by the water velocity in the aquifer between the infiltration point and the nearest extraction well.

The pH of effluent containing ECs can also influence the removal capabilities of SAT. pH affects the charge of the particles in the solution, and therefore can cause either attraction or repulsion of the ECs to the soil media, depending on the surface properties of the soil. The application of SAT will combine the effluent with the existing groundwater. It is important to investigate both the pH of the effluent containing ECs and the pH of the native groundwater to determine if there will be attractive forces between the constituents and the soil media. This will help determine the suitability of a site for the use of SAT.

The ionic strength of a solution refers to the concentration of ions present. A high ionic strength of solution indicates a high total dissolved solids (TDS) content as well. TDS refers to the content of all the dissolved organic and inorganic substances present in the solution. TDS can be measured to help determine the ionic strength of the solution. A high ionic strength causes an attraction between the molecule in the solution and the soil media (Bradford et al., 2011; Braun et al., 2015; P. Sharma et al., 2014; M. Wang et al., 2016). Therefore, a higher ionic strength leads to higher soil retention of the EC particles in the effluent.

4.2.1 Nanomaterials – Properties and Nature of Effluent Flow

This section analyzes the properties and nature of the groundwater flow that control the effectiveness of SAT for nanomaterials. These properties include the velocity and direction of the groundwater flow, the pH of the effluent, and the ionic strength of the effluent.

4.2.1.1 Flow Velocity and Direction – Impact on Removal of Nanomaterials

When all other conditions remain the same, flow velocity dictates the removal capabilities of soil media (M. Wang et al., 2016). Several studies indicate that mobility of nanomaterials increases with increasing flow velocity (Bradford et al., 2011; Braun et al., 2015; P. Sharma et al., 2014; M. Wang et al., 2016). As the velocity of groundwater decreases, the action of diffusion dominates the particle movement, whereas advection dominates higher velocities (Braun et al., 2015). Diffusion refers to the movement of particles in a fluid from a higher concentration to a lower concentration. A particle dominated by advection in fluid will follow the flow of the groundwater. In low velocities, diffusion will allow for longer retention times and which leads to an increase in the contact time of the contaminant with the soil media. Another reason that high retention is correlated to low velocity is that lower flow rates cause a decrease in kinetic energy which allows greater soil retention (P. Sharma et al., 2014). Additionally, a slower groundwater velocity allows greater progress toward equilibrium. Retention mechanisms are often driven by equilibrium relationships, such as sorption.

The direction of groundwater flow also has an impact on the mobility of nanomaterials in soil media. A change in the direction of the groundwater flow can cause previously retained particles to detach from the soil. This is especially common for particles that were retained through pore straining mechanisms. (Tian, Gao, Wang, et al., 2012; M. Wang et al., 2016). The direction of groundwater flow can change seasonally or due to pumping, construction, and large rain events.

4.2.1.2 pH of Solution – Impact on Removal of Nanomaterials

Studies have shown that the pH of the effluent solution in groundwater affects the transport of nanomaterials (M. Wang et al., 2016). The pH can change the zeta potential of the solution, as seen in Figure 9 (M. Wang et al., 2016). This can change the attractive forces between nanomaterial particles, which ultimately affects their transport through porous media. The zeta potential is the repulsive force of charged particles on each other. A neutral pH of the solution can cause a state of zero surface potential (point of zero charge, PZC). The larger the absolute difference between the point of zero charge pH of the nanomaterial and the pH of the solution, the more mobile the particles are. (M. Wang et al., 2016).

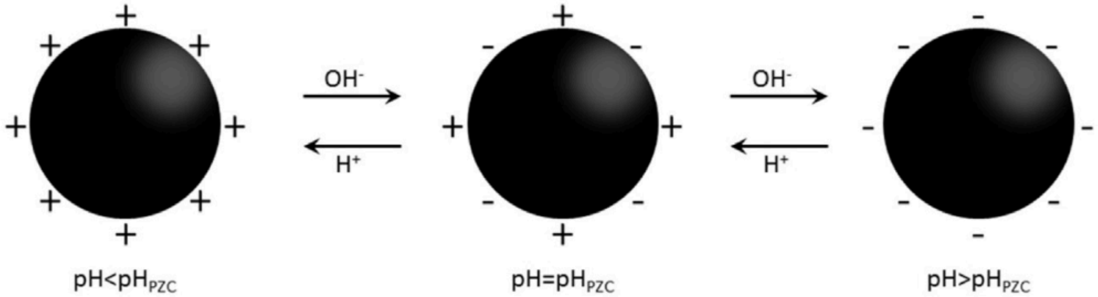


Figure 9: Effects of pH on charge of nanomaterials (M. Wang et al., 2016)

Not only does the pH of the solution affect the attractive forces between nanomaterials, but also between nanomaterials and the soil media. Solution pH can directly alter the surface charges on porous media (M. Wang et al., 2016). Soil media surfaces are typically heterogeneously charged due to minerals and organic materials in the soil. When the pH of the solution is greater than the point of zero charge of the soil, then the heterogeneity of the soil charge reduces, which can decrease favorable attachment sites for negatively charged nanomaterials (M. Wang et al., 2016). Conversely, a lower solution pH will promote retention of nanomaterials in the soil (Chowdhury & Walker, 2012; Tian, Gao, Wang, et al., 2012; M. Wang et al., 2016). The pH of soil typically ranges between 6.0 and 7.0, and the pH of wastewater effluent is normally between 6.0 and 9.0 (EPA, 1998; USDA, 1998). Wastewater with high pH may see reduced SAT efficacy.

4.2.1.3 Ionic Strength – Impact on Removal of Nanomaterials

Several studies have shown that an increase in the ionic strength of a solution reduces the transport of nanomaterials in porous media (Bradford et al., 2011; Braun et al., 2015; P. Sharma et al., 2014; M. Wang et al., 2016). A study completed by Sharma et. al. researched the transport of MWCNTs using quartz sand in glass columns. They compared the mobility the nanomaterials using ionic strength values between 0.1 and 10 mM (millimolar, .001M/L). The research showed that there were high retention rates of the MWCNTs for higher ionic strengths. Additionally, there was less that 10% breakthrough of nanomaterials for an ionic strength of 4 mM and above. Figure 10 shows the trend of the ratio of effluent to influent MWCNTs mass as a function of ionic strength from the research experiment. (P. Sharma et al., 2014).

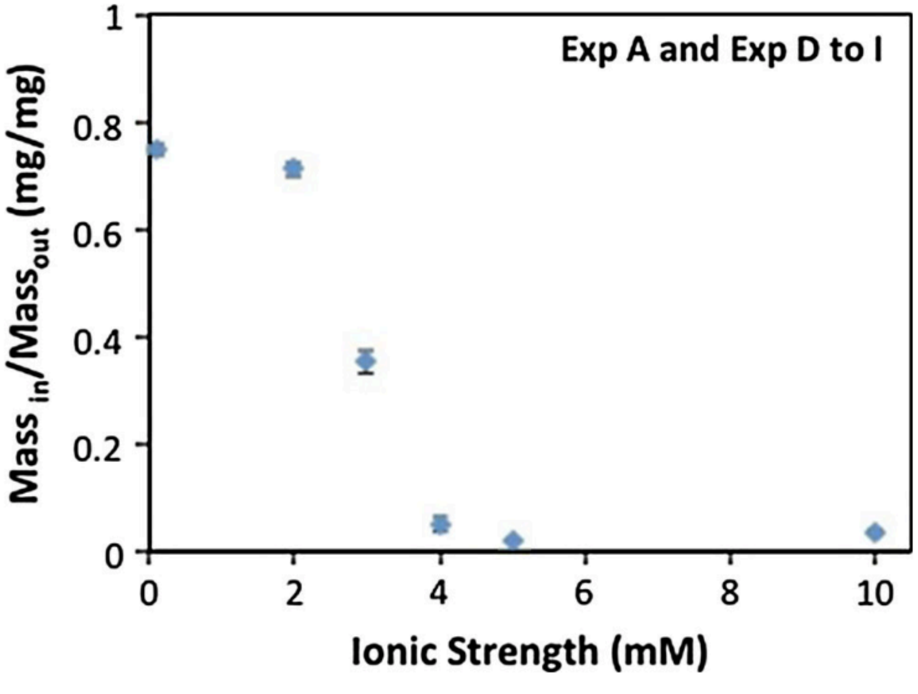


Figure 10: The ratio of influent mass to effluent mass of MWCNTs as a function of ionic strength (P. Sharma et al., 2014)

The authors suggest the reason for this material retention is related to the double-layer theory. An increase in the ionic strength compresses the electrical double layer of the nanomaterial, which forces the two layers closer together (P. Sharma et al., 2014; M. Wang et al., 2016). Formations of double layers around a nanomaterial exist due to electrostatic interactions between the particle and aqueous medium (Hunley & Marucho, 2016). This creates a layer of liquid strongly attracted to the particle on the surface of the nanomaterial (Hunley & Marucho, 2016). Shrinking the double layer reduces repulsive forces of the nanomaterial which then can cause aggregation or deposition in soil media (M. Wang et al., 2016).

4.2.2 Pharmaceuticals and Personal Care Products - Properties and Nature of Effluent Flow

This section analyzes the properties of the groundwater and effluent flow that can affect the removal capabilities of the soil media for PPCPs.

4.2.2.1 Flow Velocity and Direction – Impact on Removal of Pharmaceuticals and Personal Care Products

As described in the "Flow Velocity and Direction – Impact on Removal of Nanomaterials" section of this thesis, a change in flow direction can cause previously retained particles to detach from the soil media. This change in flow direction could be a result of an increase in the flow of groundwater, and it could potentially be clean water. An increase in clean groundwater flow could desorb the PPCPs from the soil media and increase their dissolution into the groundwater aquifer. Furthermore, an increase in flow velocity can cause increased PPCP transport in the aquifer. The increased velocity decreases the contact time between the soil media and the PPCPs, which reduces opportunity for sorption to occur.

4.2.2.2 Ionic Strength – Impact on Removal of Pharmaceuticals and Personal Care Products

Also like nanomaterials, studies have shown that the ionic strength of effluent containing PPCPs influences the mobility of the PPCPs through soil. Xing et al. researched the fate and transport of a PPCP known as ciprofloxacin which is an antibiotic commonly used by humans and animals. The study saw that an increase in the ionic strength of the solution decreased the transport of the PPCPs to the soil media (both sand and clay) (Xing et al., 2016). This occurrence can be explained by the traditional electrochemical theory – "increasing ionic strength is unfavorable to molecular sorption on oppositely charged surfaces" (Xing et al., 2016). In the case of this study, the PPCP had a positive charge, and the soil media was negatively charged, which is typically the case. Since the soil media and the contaminant are oppositely charged, it makes sense that an increase in ionic strength reduced the attraction between the two constituents.

4.2.2.3 pH of Solution – Impact on Removal of Pharmaceuticals and Personal Care Products

The solution pH of effluent in an aquifer can affect the removal capabilities of the soil for PPCPs. Xing et al. suggests that the impact of solution ionic strength on the removal of PPCs changes with varying solution pH. For example, the study determined that an increase in the ionic strength of tetracycline may reduce the mobility of the PPCP in alkaline conditions, but may not have the same effect in either neutral or acidic conditions (Xing et al., 2016). The typical pH of wastewater effluent is neutral (pH = 7.0), but the EPA allows a pH range of 6.0-9.0 (EPA, 1998). It is important to understand all the characteristics of a solution to determine the true the removal potential of the soil media.

4.3 PROPERTIES OF THE SOIL MEDIA

As discussed above, efficacy of SAT caries depending on the nature of the contaminant and physical and chemical characteristics of the effluent and groundwater flow. Wastewater consists of a highly variable mixture of potential contaminants, and the nature of effluent and groundwater flow can also be highly variable by time of day or season. Consequently, these two factors may not play a determining role in the efficacy of a given site for SAT. SAT also relies on the physical and chemical components of the soil to remove contaminants in the wastewater being introduced into an aquifer. These critical physical and chemical soil components include the following properties: soil type, surface properties of the soil particles, grain size and moisture content (M. Wang et al., 2016). As these characteristics are relatively stable compared to the other drivers of SAT efficacy, it is important to understand each of these properties first in considering the potential effectiveness of SAT for removal of ECs at a given site. This section examines research studies that investigate the effects of various soil properties on the removal of both nanomaterials and PPCPs.

The nature of the soil medium is critical to the capability of SAT to remove ECs from wastewater. The total amount of sand, clay, and soil organic matter determines the fate and transport of ECs in soil media. The soil characteristics can affect both physical and chemical removal capabilities of the soil.

The surface properties of the soil media particles also play an important role in the transport of ECs through the soil. Properties such as hydrophobicity, polarity, ionic attractive forces, and roughness of the surface grain affect play a significant role in the attraction of ECs to the soil media.

Soil grain or particle size affects the soil's potential treatment mechanisms. There is a large range of different soil particle sizes *(ASTM D422-63, 2007)*. Typically, the size of a particle is due to the medium type. Table 3 shows various soil sizes based on ASTM's classification. Various entities have different size classifications, but they are all very similar.

Table 3: Soil gran sizes (ASTM D422-63, 2007)

Soil Type	**USCS Symbol**	**Grain Size Range (mm)**			
		USCS	**AASHTO**	**USDA**	**MIT**
Gravel	G	76.2 to 4.75	76.2 to 2	>2	>2
Sand	S	4.75 to 0.075	2 to 0.075	2 to 0.05	2 to 0.06
Silt	M	Fines < 0.075	0.075 to 0.002	0.05 to 0.002	0.06 to 0.002
Clay	C		< 0.002	< 0.002	< 0.002

The moisture content of the soil can also have a large effect on the removal of ECs from effluent in the soil media. The removal mechanisms in the saturated conditions of an aquifer are typically dominated by the solid-to-water interactions and pore straining mechanisms (M. Wang et al., 2016). Conversely, additional removal mechanisms can be present in the vadose zone due to the existence of air within the pores. Numerous studies have concluded that the vadose zone, specifically the first 1.5 meters of vertical flow, is responsible for removing a significant quantity of constituents prior to reaching the groundwater table, either through sorption, flow restriction, or biodegradation (Amy et al., 1993; Essandoh et al., 2011; S. K. Sharma et al., 2008).

4.3.1 Nanomaterials - Properties of Soil Media

Fate and transport of nanomaterials during SAT is highly influenced by key properties of the soil, including the characteristics of the soil media, the surface properties of the soil particles, and moisture content.

4.3.1.1 Soil Media - Impact on Removal of Nanomaterials

The type of soil media can have vastly different effects on the removal of nanomaterials from effluent (D. Lin et al., 2010). A study done by the School of Environmental Science and Engineering in China used soil columns to research the fate and transport of a common nanomaterial called multiwalled carbon nanotubes (MWCNTs) using 14 different soil types (Fang, Shan, et al., 2013). The study concluded that soil with higher sand content allows for additional mobility of the nanomaterial, and in contrast, soil with higher clay content retains the contaminants (Fang, Shan, et al., 2013). Several studies propose that pore space is significant; the pore space of clay is smaller and better retains nanomaterials during transport, while the larger pore space in sand allows more particles to be passed through during transport (Fang, Shan, et al., 2013; M. Wang et al., 2016).

Closely related to pore size, grain size of the soil media directly affects the mobility of nanomaterials in a groundwater aquifer. Studies indicate the smaller the grain size, the more retention associated with the soil (M. Wang et al., 2016). A study by P. Sharma, D. Bao, F. Fagerlund, investigated the transport of nanomaterials through fine sand versus coarse sand. The research revealed that the finer sand retained 15% more of the particles when compared to the coarse sand. This is most likely due to the smaller pore sizes that are produced by small grain sizes, which leads to a more effective straining mechanism. (P. Sharma et al., 2014; M. Wang et al., 2016). Additionally, soil media with smaller grain sizes typically have a high surface area. This produces higher retention rates of the nanomaterials through surface driven-mechanisms such as sorption.

Additionally, the flow velocity of the groundwater through an aquifer depends on the type of soil. A soil with very low hydraulic conductivity will cause the groundwater to flow much slower though the aquifer compared to a more permeable soil. Higher hydraulic conductivities, and therefore a larger flow velocity, can cause nanomaterials to be more mobile in the soil media (M. Wang et al., 2016). A decrease in the velocity of the groundwater will cause an increase in the contact time of the nanomaterial with the soil media (M. Wang et al., 2016). This event will induce increased sorption to the soil media surface area and therefore result in increased nanomaterial removal (M. Wang et al., 2016).

4.3.1.2 Surface Properties - Impact on Removal of Nanomaterials

A study done by Y. Tian, et al. suggests that ionic attractive forces of the soil surface may alter the mobility of nanomaterials through soil media. This study compared the transport of a nanomaterial classified as carbon nanotubes within three different types of sand: acid clean sand, baked sand, and natural sand. The research concluded that the carbon nanotubes were retained in the baked and natural sand, and were highly mobile in the acid cleaned sand. Acid cleaning the sand reduces the metal oxyhydroxide impurities on the sand surfaces and increases the pH of the media. This research suggests that the transport of nanomaterials is affected by the electrostatic and/or hydrogen bonding forces of attraction between the nanomaterial and the impurities on the sand surface. (Tian, Gao, Morales, et al., 2012). In this case, the metal oxyhydroxide provided electrostatic attractive forces that removed the carbon nanotubes from the effluent by sorption to the soil.

The roughness of the surface media can also affect the mobility of nanomaterials through a soil media. A soil with higher roughness tends to produce greater retention because the inconsistencies of the surface weaken the repulsive attractions between the particle and the soil medium (M. Wang et al., 2016). Additionally, smoother particles have a lower friction force between the particle and the surface of the soil, which decreases capillary action allowing for higher transport of the nanomaterials. (Morales et al., 2009; M. Wang et al., 2016).

4.3.1.3 Moisture Content – Impact on Removal of Nanomaterials

The transport of nanomaterials in an unsaturated soil media condition is much more complex than in a saturated soil (M. Wang et al., 2016). Studies have shown that a low moisture content in the soil tends to remove a larger number of nanomaterials, such as graphene oxide, C_{60}, and titanium dioxide (L. Chen et al., 2008; M. Wang et al., 2016; Zhang et al., 2012). A study done by Tian et al. in 2011, concluded that retention of single walled carbon nanotubes (SWCNTs) in unsaturated porous media only occurred when the moisture content was below 0.10.

Studies have also reported that a high mobility of nanomaterials in high moisture content conditions is due to repulsive interactions between the constituent and the negatively charged air-water interface (Fang, Xu, et al., 2013; Tian et al., 2011; M. Wang et al., 2016). The overall conclusion that soil media with moisture content below 0.1 produce the highest removal rates of nanomaterial from the groundwater solution (Tian et al., 2011).

4.3.2 Research Studies for Nanomaterials

The fate and transport of nanomaterials in the environment is influenced by many factors. The following research studies (1-3) analyze the fate and transport of nanomaterials through various soil media to determine the effectiveness of SAT as a polishing step for effluent. All of these studies utilized soil columns under saturated flow conditions, but they represent a variety of soil types and types of nanomaterials.

4.3.2.1 Research Study 1 – Mobility of Tx100 Suspended Multiwalled Carbon Nanotubes

Research Study 1 (Fang, Shan, et al., 2013) investigates the transport behavior of one type of nanomaterial, TX100 suspended multiwalled carbon nanotubes (MWCNTs), through 14 different soils, as seen in Table 4. The MWCNTs had an outside diameter of 28 nm, and a length of the 1-2 µm. The suspension of the nanomaterials was prepared using the surfactant Triton X-100 (TX100).

Column experiments were completed using glass columns 20 cm in length with a 25-mm inner diameter. The soil was packed in the columns to a height of 10 cm, and the experiments were performed under saturated conditions. The MWCNTs suspensions were pumped to the top of the columns and gravity flow was used. A constant water head of 9 cm was maintained throughout the entirety of the experiment. Table 4 shows the various properties of each soil medium used in this research study, and the percent removal of MWCNTs from each of the 14 soil mediums. The results were read off published breakthrough curves (Fang, Shan, et al., 2013).

The results of this experiment determined that the transport of the MWCNTs varies with type of soil media. As seen in Figure 11, the soil with a higher clay content tended to produce higher retention of the MWCNTs. This experiment also concluded that the average soil diameter has a strong effect on the removal of MWCNTs from the soil media. This correlation agrees with the previous conclusion because the clay particles are smaller than silt and clay particles. The removal of the MWCNTs generally decreased with an increase the average diameter of the soil media. Based on the results of this study there was no significant correlation with the removal rates of the MWCNTs and the pH or the percent organic matter of the soil media.

Table 4: Soil properties and removal results of Research Study 1 (Fang, Shan, et al., 2013)

Soil	**pH**	**SOM (%)**	**Texture (%)**			**Taxonomy**	**% Removal**
			Clay (<2µm)	**Silt (2-20µm)**	**Sand (20-100µm)**		
1	8.89	0.24	1.1	5.0	93.9	Sand	16
2	7.26	2.96	19.4	47.8	32.8	Silt-sandy-loam	27
3	8.64	0.25	5.7	14.3	80.0	Sandy-loam	42
4	7.01	2.87	23.6	23.5	53.5	Silt-sandy-loam	51
5	7.57	1.74	6.7	19.4	73.9	Sandy-loam	59
6	7.32	2.03	21	21.4	47.6	Silt-sandy-loam	83
7	7.68	0.46	9.8	23.5	66.7	Sandy-loam	82
8	7.23	2.18	9.8	16.3	73.9	Sandy-loam	25
9	6.16	6.86	13.1	30.0	56.9	Loam	86
10	8.25	3.81	13.3	23.1	63.6	Sandy-loam	75
11	7.96	0.89	23.1	29.6	47.4	Loam	93
12	8.68	1.10	17.4	40.0	42.6	Silt-sandy-loam	69
13	6.93	3.32	28.2	24.5	47.4	Loam	76
14	5.26	2.59	52.7	24.5	22.9	Clay-loam	99

Clay has a small diameter, which is why the retention of the MWCNTs has a positive correlation with a smaller soil diameter. Soil #14 produced the largest deposition of MWCNTs, which is likely due to the high clay content. The small soil diameter of clay forms smaller pores than sand, which can lead to increased physical straining of the influent. Clay soils also have a higher surface area, which increases the surface interactions, such as sorption, between the nanomaterials and the soil particle. This could be a reason for the increased retention of the MWCNTs in the soil with high clay content.

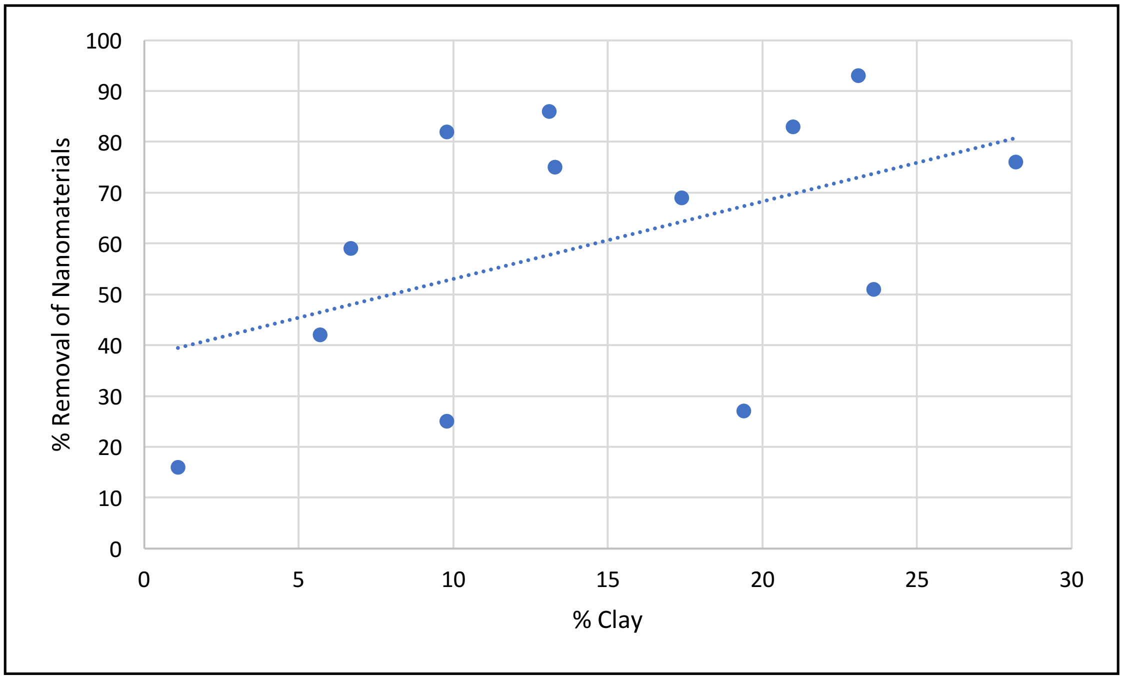


Figure 11: Relationship between total clay content and removal of nanomaterials in Research Study 1

There is also a correlation between the retention of MWCNTs and the Darcy Velocity, as seen in Figure 12. This correlation is attributed to the soil type as well. Under identical flow conditions, clay creates a much lower Darcy Velocity than sand, which means water travels much slower through the medium. The smaller velocity of the influent increases the contact time of the MWCNTs with the soil, which could promote sorption of the particles to the medium.

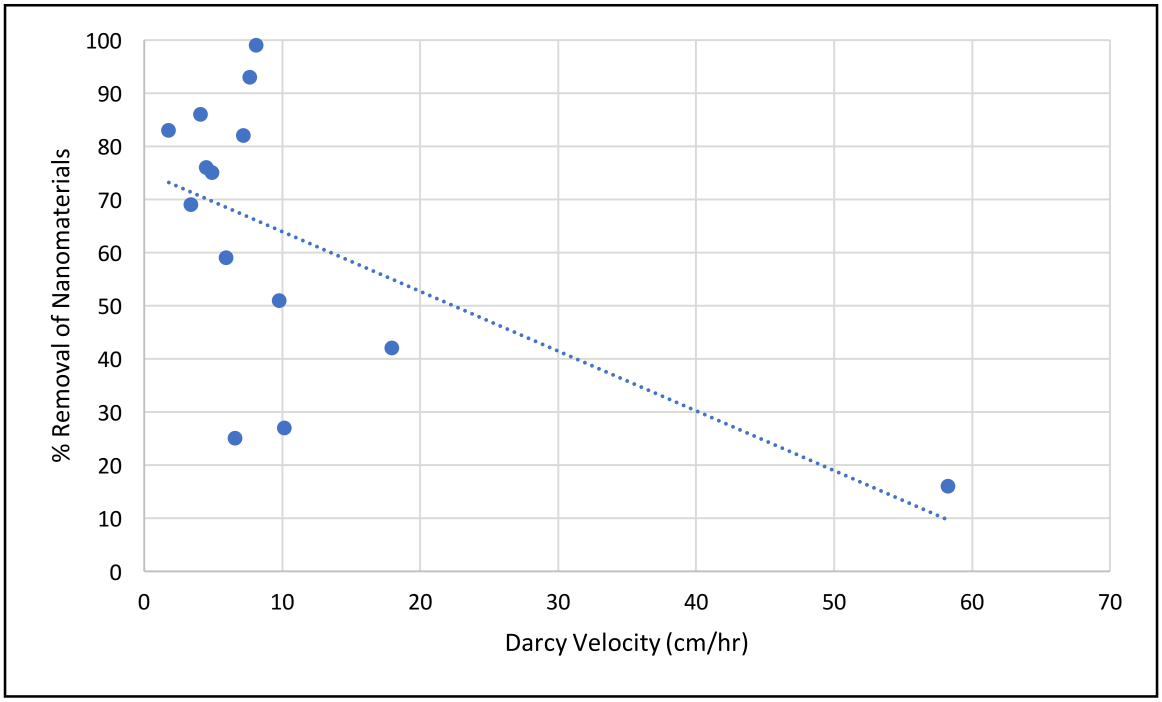


Figure 12: Relationship between Darcy Velocity and the removal of nanomaterials in Research Study 1

4.3.2.2 Research Study 2 – Transport and Deposition of Engineered Silver Nanoparticles

Research study 2 (Braun et al., 2015) investigates the transport and deposition behavior of engineered silver nanoparticles in two soil media – loamy sand and silty loam. The soils were acquired from top 30 cm of an agricultural field site in Germany, and the properties of the two soil types are displayed in Table 5. At least 99% of the silver nanoparticles were within the range of 15-20 nm.

Table 5: Soil properties of Research Study 2 (Braun et al., 2015)

	Unit	**Soil #1 (Loamy Sand)**	**Soil #2 (Silty Loam)**
Clay (<2 µm)	% mass	4.9	15.4
Silt (2-63 µm)	% mass	26.7	78.7
Sand (63-2000µm)	% mass	68.5	5.9
pH		5.9	6.2
SOM	% mass	1.1	1.3
Cation Exchange Capacity	cmol/kg	7.8	11.4

Research study 2 used glass columns with an inner diameter of 24 mm and a length of 10 cm. The influent containing silver nanoparticles was introduced into the system at the bottom of the glass columns, and a high-pressure pump was used to direct the flow in the upward direction. Various flow velocities were tested for the loamy sand, which can be seen in Table 6. The total retention of nanoparticles is also displayed in Table 6.

Table 6: Total removal of silver nanoparticles compared to soil type, Darcy Velocity, and ionic strength (Braun et al., 2015)

Sample #	**Soil Type**	**Darcy Velocity (cm/hr)**	**Ionic Strength (mM)**	**% Removal of Silver Nanoparticles**
1	Soil #1	710.64	10	14.46
2	Soil #1	11.88	10	98.23
3	Soil #1	666.36	0.1	0
4	Soil #1	673.56	50	97.5
5	Soil #2	5.04	10	100

The results of this study show that the effectiveness of SAT to remove silver nanoparticles is dependent on the type of soil, the Darcy Velocity through the soil, and the ionic strength of the effluent. The silty loam (Soil 2) completely prevented the transport of the nanomaterials through the soil. This soil had higher clay content and and lower Darcy Velocity, in concurrence with the results of Research Study 1. However, since only one sample (Sample 5) was reported for Soil 2, it is hard to draw conclusions based on a single point.

Like Research Study 1, Research Study 2 suggests that slower groundwater velocities produce higher retention rates than sandier soil, as seen in Figure 13. Figure 13 presents the Darcy Velocity of soils at the same ionic strength of solution (Samples 1, 2, and 5). The removal trend in Figure 13 can be attributed to the increased contact time of the silver nanoparticles with the soil media, which causes higher sorption rates of particles to soil.

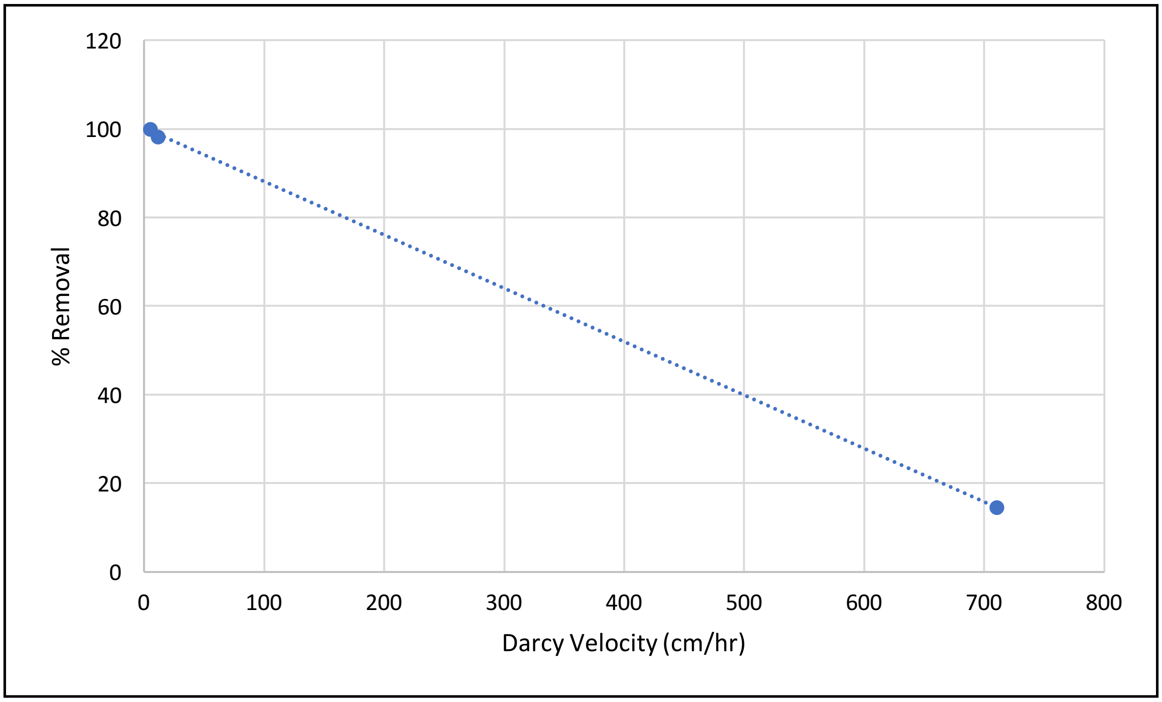


Figure 13: Relationship between Darcy Velocity and % Removal of Nanomaterials at Ionic Strength 10 mM in Research Study 2

The Darcy Velocity seems to be the dominant property affecting the transport nanomaterials in this study.

4.3.2.3 Research Study 3 –Transport of Titania Nanoparticles in Saturated Soil

Research Study 3 (Fang et al., 2009) investigated the transport of Titania nanoparticles through 12 soil types from China. The properties of the soil can be found in Table 7. Glass columns were used for the transport experiment. The columns were 20 cm in length with an inner diameter of 25 mm. They were packed with 10 cm of soil. The influent was pumped from the bottom of the columns in the upward direction and maintained a constant head of 9 cm throughout the duration of the experiment. The concentration of the effluent was monitored at specified time intervals.

Table 7: Soil properties and removal rates of Research Study 3 (Fang et al., 2009)

Soil	**pH**	**SOM (%)**	**Texture (%)**			**Taxonomy**	**% Removal of Titania**
			Clay (<2µm)	**Silt (2-20µm)**	**Sand (20-100µm)**		
1	7.26	2.96	19.4	47.8	32.8	Silt-sandy-loam	17
2	6.39	6.86	13.1	30	56.9	Loam	54
3	6.32	1.82	32.3	47.4	20.3	Silt-clay-loam	99.8
4	6.67	2.51	32.2	59.1	8.7	Silt-clay-loam	97.7
5	6.98	1.14	45.6	23.5	30.9	Clay-loam	98.7
6	7.4	4.46	19.8	48	32.2	Silt-loam	62.4
7	7.96	3.81	13.3	23.1	63.6	Sandy-loam	81.2
8	8.14	1.1	7.8	34.5	57.7	Sandy-loam	41.6
9	7.99	1.1	27.7	41.5	30.8	Clay-loam	100
10	8.05	1.28	10.7	72.3	17	Silt-loam	100
11	7.5	1.97	22.4	55.6	22	Silt-loam	100
12	7.97	0.96	20.5	56.7	22.8	Silt-sandy-loam	100

The results of this study, shown in Table 8, indicate that a higher silt and clay content in soil promotes higher removal rates in SAT for Titania nanoparticles.

Table 8: Soil conditions for Research Study 3 (Fang et al., 2009)

Soil	Avg. Diameter (µm)	Darcy Velocity (cm/hr)	Pore Volume V_0 (mL)	% Removal of Titania
1	76	5.06	22.6	17
2	120	1.75	27.8	54
3	51	0.34	24.2	99.8
4	30	0.41	27.8	97.7
5	67	0.67	24	98.7
6	74	1.38	28.6	62.4
7	132	2.71	24.2	81.2
8	122	4.4	24.1	41.6
9	70	0.11	27.5	100
10	49	1.06	27.6	100
11	56	0.8	23.9	100
12	57	0.91	23.2	100

The relationship between clay content and removal of Titania nanoparticles can be seen in Figure 14. With one exception, the soils that resulted in 97% and higher removal rates all had clay content above 20%. Additionally, Figure 15 shows that the soils with higher Darcy Velocities promoted greater retention of the nanoparticles.

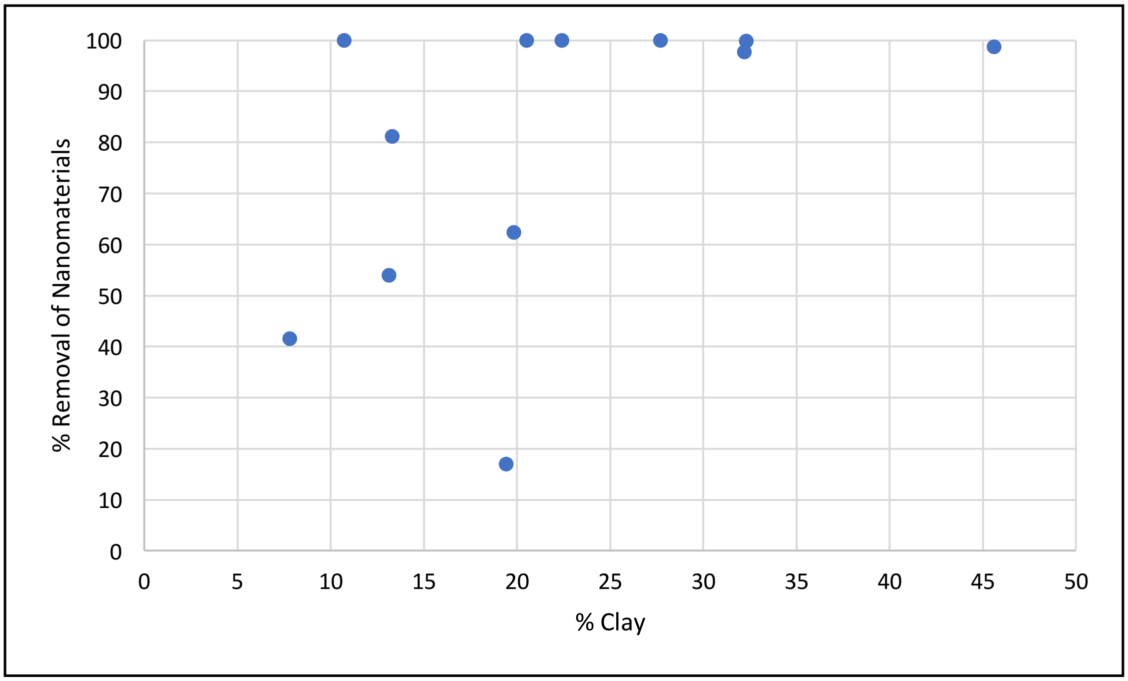


Figure 14: Relationship between total clay content and the removal of nanomaterials in Research Study 3

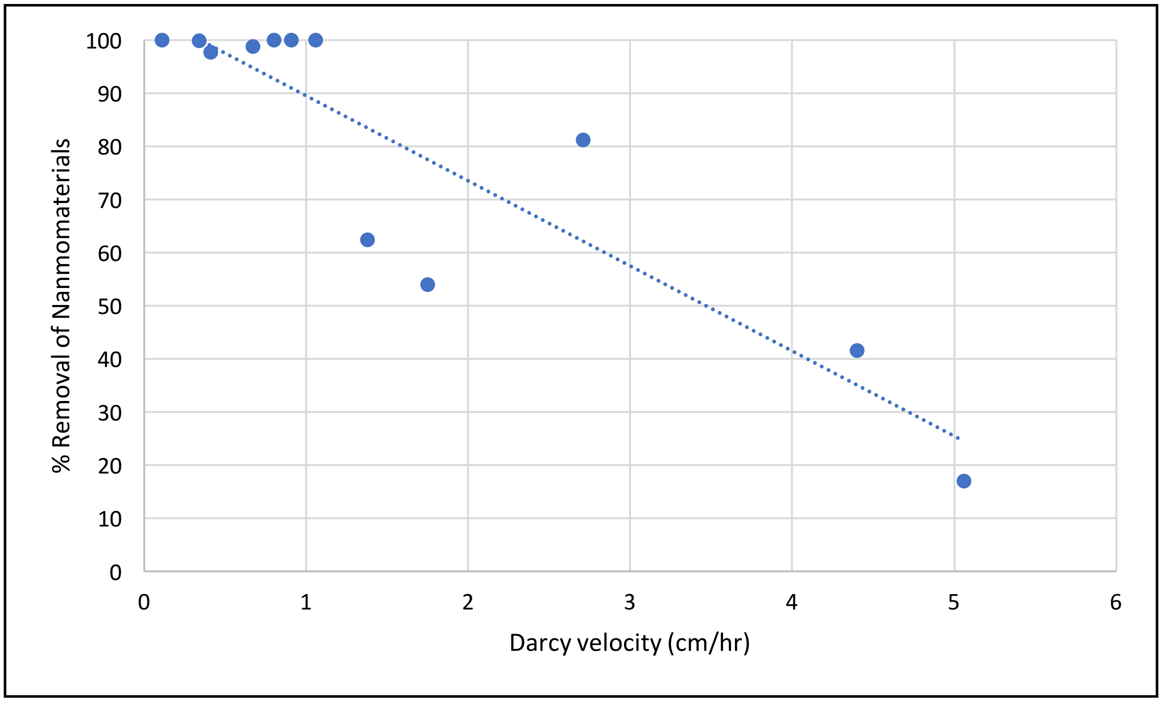


Figure 15: Relationship between Darcy Velocity and the removal of nanomaterials in Research Study 3

These findings concur with the two previously-shown Research Studies, suggesting that clay content and velocity are significant factors in SAT efficacy, regardless of type of nanomaterial.

4.3.2.4 Summary of Research Studies 1-3

Research Studies 1-3 analyzed the transport of various nanomaterials through soil media. Based off the data from these studies, it can be concluded that the transport of nanomaterials is largely dependent on the total clay content of the soil media and the Darcy Velocity of the solution through the soil. A high clay content tended to retain a larger percentage of nanomaterials in the soil media, as seen in Figure 16. This is likely due to the smaller diameter of clay which increases pore straining mechanisms, and the large available surface area which promotes high sorption rates. Figure 16 yielded a R-squared value of 0.28 when using a logarithmic trend line. R-squared is a statistical measure of how close the data points are to to the regression line. There was a wide amount of variability in the study, so a lower R-squared value is the expected. But in general, higher clay contents tend to promote higher removal of nanomaterials.

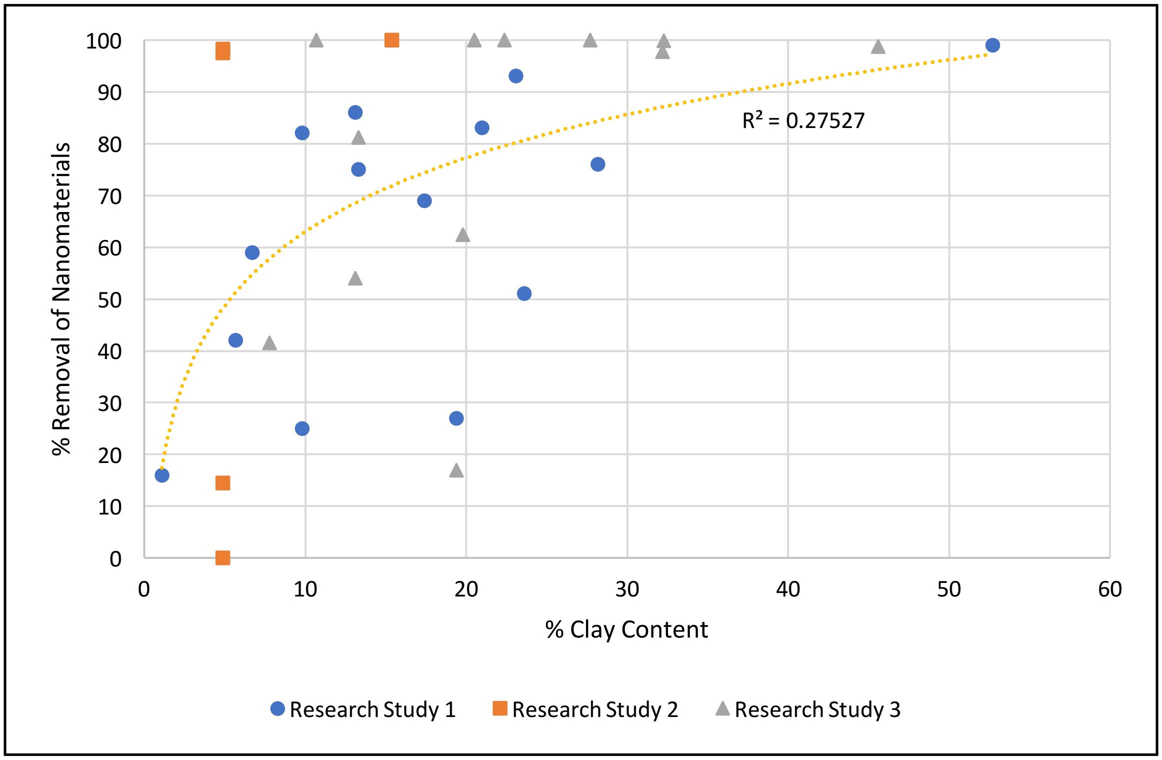


Figure 16: Relationship between total clay content and removal of nanomaterials from Research Study 1-3

There was also an inverse correlation with the Darcy Velocity and the removal of nanomaterials, as seen in Figure 17. Note that that the high Darcy Velocity from Research Study 1 was not included in Figure 17 to make the trend more discernible. Figure 17 produced a R-squared value of 0.26. This shows there is a correlation between the data points, but this correlation is not high due to the variability in this study. A lower Darcy Velocity correlates generally with higher ENM removal. Overall, a Darcy Velocity of about 4 cm/hr or less produced the most consistent high removal rates for Research Studies 1-3. Furthermore, as the Darcy Velocity decreases to quantities below 4 cm/hr, the average removal of the ECs increases to higher levels.

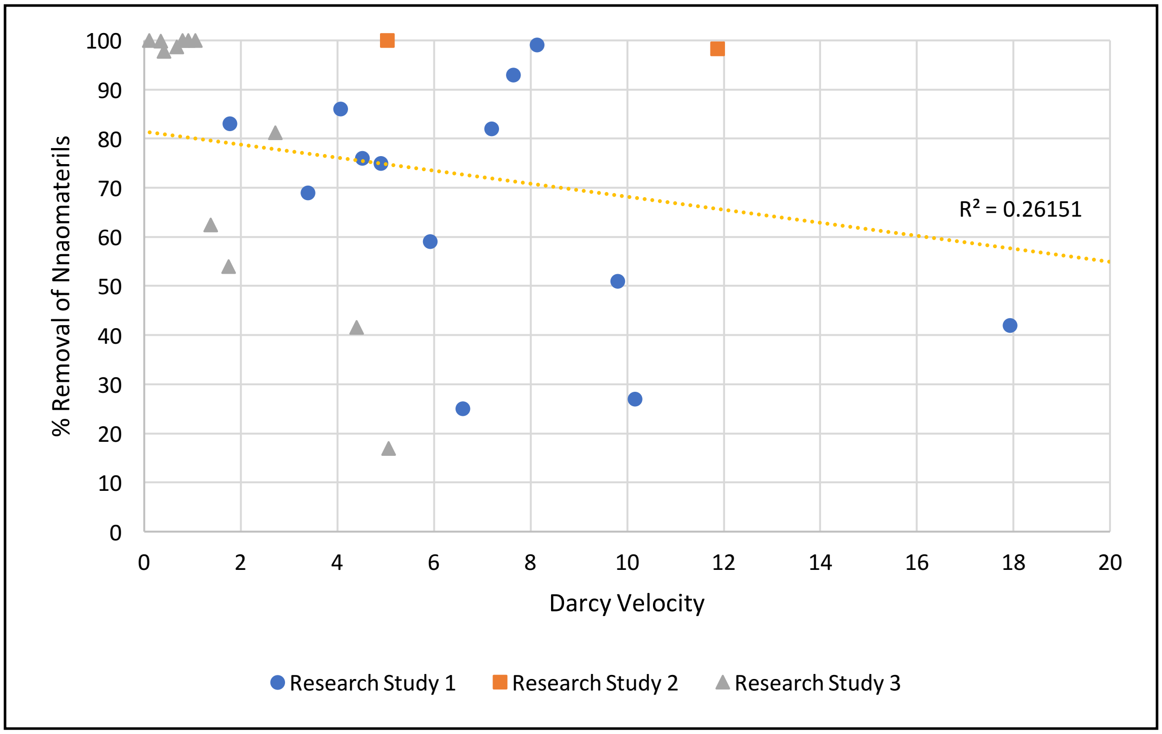


Figure 17: Relationship between Darcy Velocity and removal of nanomaterials from Research Study 1-3

These two findings are in agreement, since clay slows the flow of groundwater through soil because of the smaller pores, which increase the the contact time between the nanomaterials in the groundwater and the soil particles. The increases contact promotes sorption of the nanomaterial to the soil. Clay contents above about 10% proved to produce high removal rates of all nanomaterials, which is displayed in Figure 16. The removal rates varied from about 80%-100%, with an average of over 96% removal.

There was also an inverse relationship observed between the total sand content and the total removal of nanomaterials in Research Studies 1-3. This relationship can be seen in Figure 18, which produced a R-squared value of 0.3 using a linear trend line. An apparent trend is present where the total removal of nanomaterials increases with decreasing sand content, but there are some data points that skew the R-squared value.

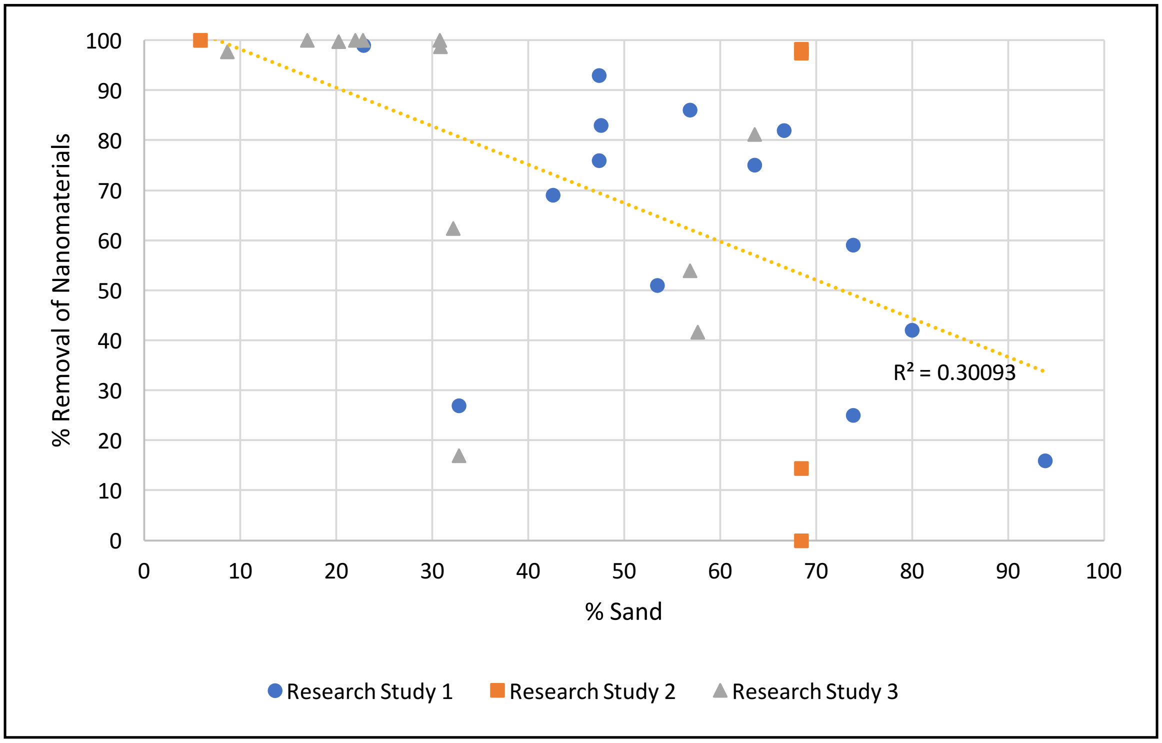


Figure 18: Relationship between between total sand content and removal of nanomaterials from Research Study 1-3

The information provided in Figure 18 could be useful when selecting a SAT site. While there is no data to suggest a relationship between nanomaterial retention and silt content, sites with lower sand content, not just high clay content, may also show increased removal of nanomaterials from the effluent.

Additionally, it can be concluded from Research Studies 1-3 that there is not a correlation between the total soil organic matter and the removal rates of the nanomaterials analyzed. As shown in Figure 19, no clear trend can be found between SOM % and total nanomaterial removal. Figure 19 yielded a R-squared value of 0.01, which confirms there is no relationship between the two variables.

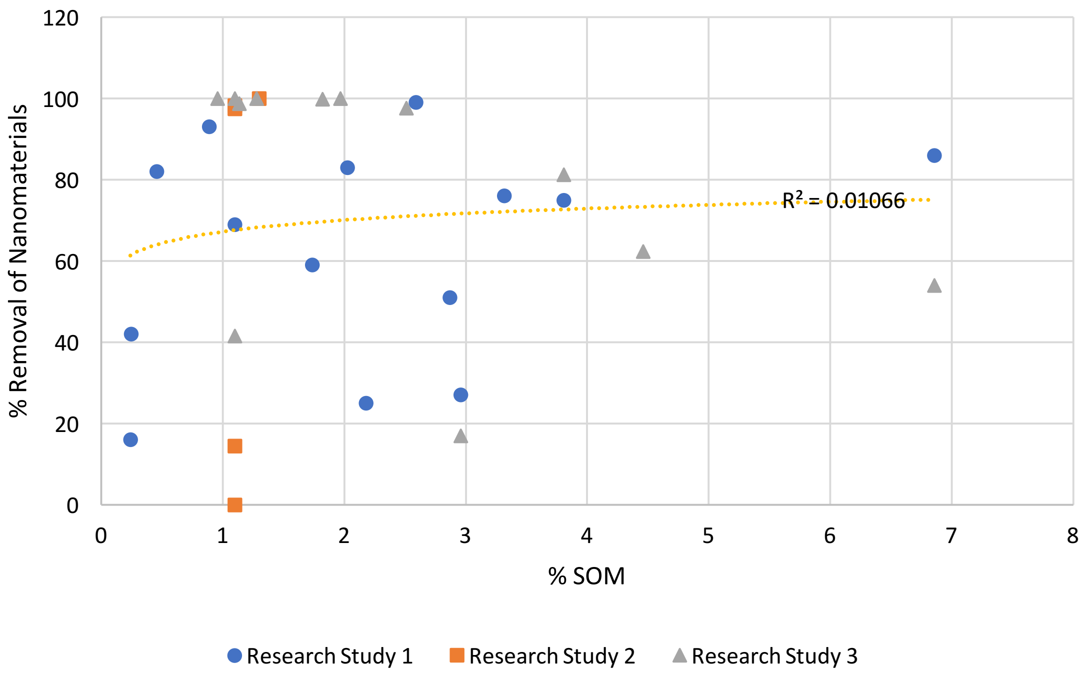


Figure 19: Relationship between total soil organic matter and removal of nanomaterials from Research Study 1-3

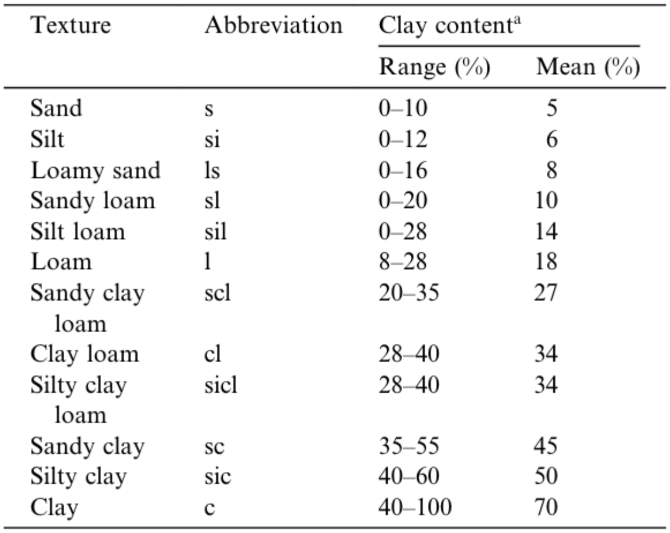
4.3.3 Pharmaceuticals and Personal Care Products- Properties of Soil Media

This section discusses the various properties of soil media that affect the fate and transport of PPCPs in soil media. This data will help to assess the effectiveness of a specific aquifer as a polishing treatment step for effluent containing ECs.

4.3.3.1 Soil Media – Impact on Removal of Pharmaceuticals and Personal Care Products

Many studies have confirmed that soil media with a higher clay and/or organic matter content produce greater retention rates of common PPCPs, such as ibuprofen (Xu et al., 2010; Kreuzig et al., 2003). Clay and organic matter are considered colloids, which are categorized as fine sized soil media. Colloids have both a large specific surface area and a high density of reactive sites, which typically causes them to have a strong absorption capacity (Xing et al., 2016). To determine the effectiveness of the removal of PPCPs from groundwater, it is important to analyze the total clay content of the soil media. Table 9 shows the estimated clay contents of different soil media.

Table 9: Clay content of characterized soil media (Soil Taxonomy, 1975)



Texture	Abbreviation	Clay content[a]	
		Range (%)	Mean (%)
Sand	s	0–10	5
Silt	si	0–12	6
Loamy sand	ls	0–16	8
Sandy loam	sl	0–20	10
Silt loam	sil	0–28	14
Loam	l	8–28	18
Sandy clay loam	scl	20–35	27
Clay loam	cl	28–40	34
Silty clay loam	sicl	28–40	34
Sandy clay	sc	35–55	45
Silty clay	sic	40–60	50
Clay	c	40–100	70

The effect of colloid content on the fate and transport of PPCPs depends on the sorption characteristics of the contaminant. The sorption affinity of a PPCP largely relies on the K_d factor. The USEPA defines the K_d value of a contaminant as "the ratio of the contaminant concentration associated with the solid to the contaminant concentration in the surrounding aqueous solution when the system is at equilibrium" (EPA 1998). While K_d is considered a contaminant property, it is typically highly related to the organic matter in the soil as well. K_d reflects the affinity of the contaminant for organic matter (K_{ow} or K_{oc}) times the fraction of organic matter in the soil (f_{oc}) (EPA 1998). A higher K_d value indicates stronger sorption of a given PPCP to soil media (Weber et al., 2004). For example, the transport of PPCPs with a high affinity to sorb to colloids, such as ciprofloxacin (K_d ~10^{4-5} L/kg), are strongly controlled by total clay and organic matter content (X. Chen et al., 2017). The transport of PPCPs with intermediate attraction to colloids, such as tetracycline (K_d ~10^{3-4} L/kg), is variable with chemistry of the solution (e.g. ionic strength and pH) (X. Chen et al., 2017). The transport of PPCPs with a low affinity to sorb to colloids, such as ibuprofen (K_d ~10^{2-3} L/kg), is more controlled by other factors, such filtration mechanisms and moisture content (X. Chen et al., 2017).

A research study completed by Qin, et. al. investigated the effect of soil organic matter on the retention of the three PPCPs: ibuprofen (dissociated), carbamazepine (non-dissociated), and bisphenol A (non-dissociated). PPCPs can exist in either a dissociated or non-dissociated state in groundwater. When a PPCP is dissociated, it is broken down into smaller molecules. Non-dissociated PPCP's remain in their original state. This dissociation process can happen in the human body, at the wastewater treatment plant, or even in the environment. The study determined that both surface-coating and pore-filling of soil media with soil organic matter affects the transport of PPCPs. Adding organic matter to the surface of the soil media decreased the sorption of dissociated PPPCs due to electrostatic repulsion to the negatively charged organic matter, as seen in Figure 20.

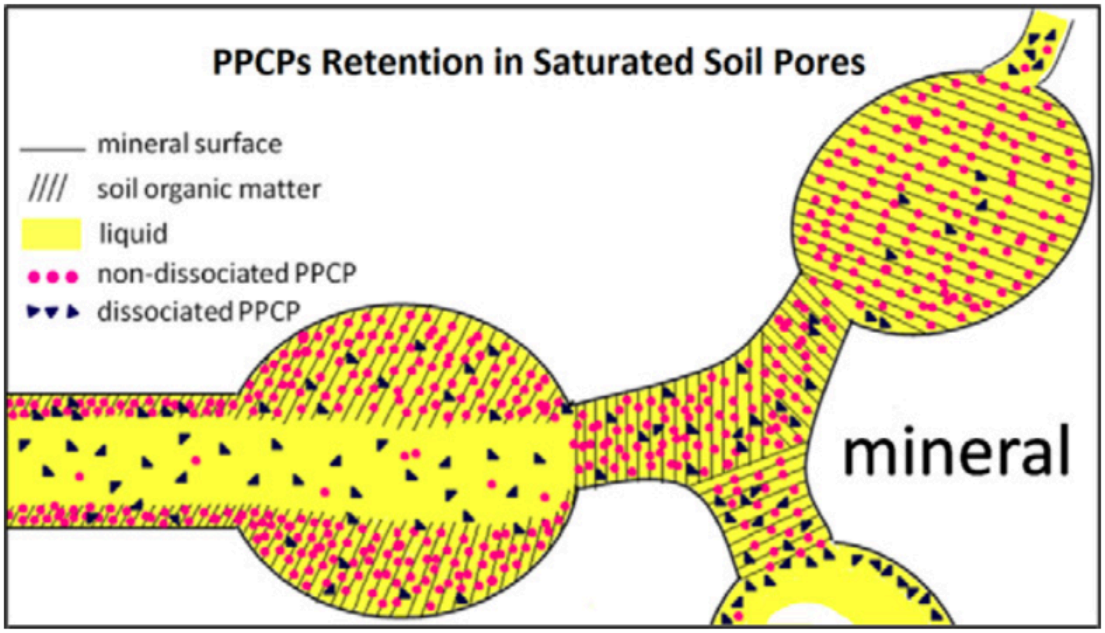


Figure 20: Effect of organic matter surface-coating and pore-filling on the retention of PPCPs in soil media (Qin et al., 2017)

Conversely, adding organic matter increased the sorption of non-dissociated PPCPs because they were attracted to the soil organic matter from hydrophobic interactions. On the other hand, pore-filling with organic matter increased the retention of all the PPCPs under investigation. This is due to the nano/micro – pores which limit diffusion of PPCPs in the groundwater solution. (Qin et al., 2017)

4.3.3.2 Surface Properties – Impact on Removal of Pharmaceuticals and Personal Care Products

Surface characteristics of soil media, such as specific surface areas of soil particles, can impact the removal of PPCPs from effluent in groundwater (He et al., 2016). The specific surface area of a soil sample refers to the total surface area of soil particles contained in a specified unit mass of soil (ICT International., 2006). A high specific surface area suggests higher water holding capacities, and therefore higher adsorption of contaminants (ICT International., 2006). Higher adsorption will occur with PPCPs that are hydrophobic, as outlined in the "Particle Surface Properties – Impact on Mobility of Pharmaceuticals and Personal Care Products" section. The retention of PPCPs is enhanced with increasing specific surface area of soil media (He et al., 2016).

In addition to available surface area, the physiochemical nature the soil media also influences the transport of PPCPs through the soil (Chefetz et al., 2008). For example, studies have determined that nonpolar soil organic matter has stronger sorption capabilities for the PPCP carbamazepine than polar soil organic matter (Chefetz et al., 2008; Qin et al., 2017).

4.3.3.3 Moisture Content – Impact on Removal of Pharmaceuticals and Personal Care Products

Frequently, the majority of the removal process of the PPCPs occurs in the vadose zone of the aquifer. This is due to the aerobic condition that exists in the unsaturated portion of the aquifer (He et al., 2016). A study done by K. Lin & Gan, researched the sorption and degradation of five PPCPs, including ibuprofen and diclofenac, in aerobic versus anaerobic conditions. The researchers determined these drug species showed poor absorption in the soil samples with higher anaerobic conditions (K. Lin & Gan, 2011; Liu & Wong, 2013). This confirms that more PPCPs will be removed in the vadose zone via sorption or physical straining than the saturated zone of the aquifer during SAT.

A recent study by Silver, Matthew, et. al. used column experiments to investigate the attenuation of PPCPs using different soil conditions: continuous infiltration versus wetting and drying cycles. This study concluded that wetting and drying are useful in promoting retention of certain PPCPs. This could be because during the drying cycle, oxygen enters the soil pores and fosters oxidizing conditions which encourages PPCP breakdown, compared to continuous infiltration. (Silver et al., 2018)

4.3.4 Research Studies for Pharmaceuticals and Personal Care Products

As outlined above, many factors control the fate and transport of PPCPs in the environment. All of these factors are important to consider in determining the effectiveness of SAT as a polishing step for effluent. The following research studies (4 – 6) analyze the fate and transport of PPCPs through soil media with various characteristics. These studies all utilize soil columns under saturated flow conditions to investigate a variety of soil types and PPCPs.

4.3.4.1 Research Study 4 – Transport of Bisphenol A and S in Saturated Soils

The fate and transport of the PPCPs bisphenol A (BPA) and bisphenol S (BPS) were analyzed through various soil column experiments in Research Study 4 (Shi et al., 2019).

BPA/BPS are used in epoxy resins, polycarbonates, and other plastics. They are considered endocrine disruptors, and can cause poor reproductive function, diabetes, and obesity. Due to their widespread use, the transport of these PPCPs through soil is an important topic of concern.

In Research Study 4, the transport of BPA and BPS was evaluated using seven different soils with various properties, which are displayed in Table 10. Polytetrafluoroethylene columns (a non-reactive material) 12 cm in length and 2.5 cm in diameter, were used for this experiment. A high-precision syringe pump was placed at the bottom of the columns and the influent was pumped in the upward flow direction at a flow rate of 50 L/min. The soil columns were completely saturated for the duration of the experiment. Effluent samples were collected at the top of the columns, and the total concentration of the PPCPs were determined, as seen in Table 10. (Shi et al., 2019)

Table 10: Soil properties and removal rates of Research Study 4 (Shi et al., 2019)

Soil	**pH**	**SOM (%)**	**Texture (%)**			**% Removal of BPA**	**% Removal of BPS**
			Clay (<2µm)	**Silt (2-20µm)**	**Sand (20-100µm)**		
1	9.75	0.16	3.56	10.37	86.07	11.74	0.44
2	7.75	0.89	9.87	83.47	6.66	31.46	13.27
3	7.51	0.46	8.60	77.76	13.64	19.53	7.24
4	7.62	0.29	8.65	76.87	14.48	14.87	3.86
5	6.51	2.57	11.90	75.00	13.10	100	100
6	6.17	1.02	7.26	64.62	28.12	59.91	44.23
7	6.12	0.53	8.65	63.65	27.70	26.71	25.67

The results of this study concluded that the transport of BPA and BPS decreases both when the total clay content and when the soil organic matter content are higher, as seen in

Figure 21 and Figure 22 respectively. The removal rates of the PPCPs most likely tended to increase with higher clay levels because the the sorption affinity of PPCPs to clay soil.

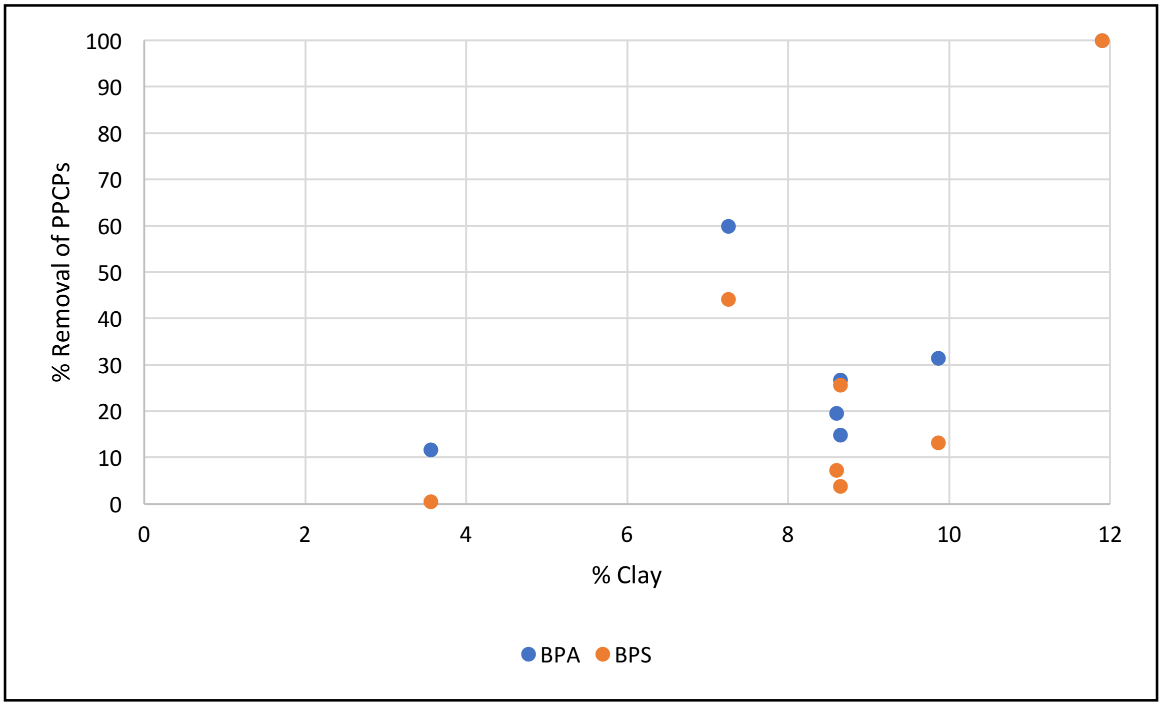


Figure 21: Relationship between total clay content and removal of PPCPs for Research Study 4

The soil organic matter is related to the total colloids in the soil media, so higher clay contents typically produce higher soil organic matter. Figure 22 shows that small increase of the total soil organic matter (e.g. 0.5% to 1%) has a large effect on the retention of BPA and BPS.

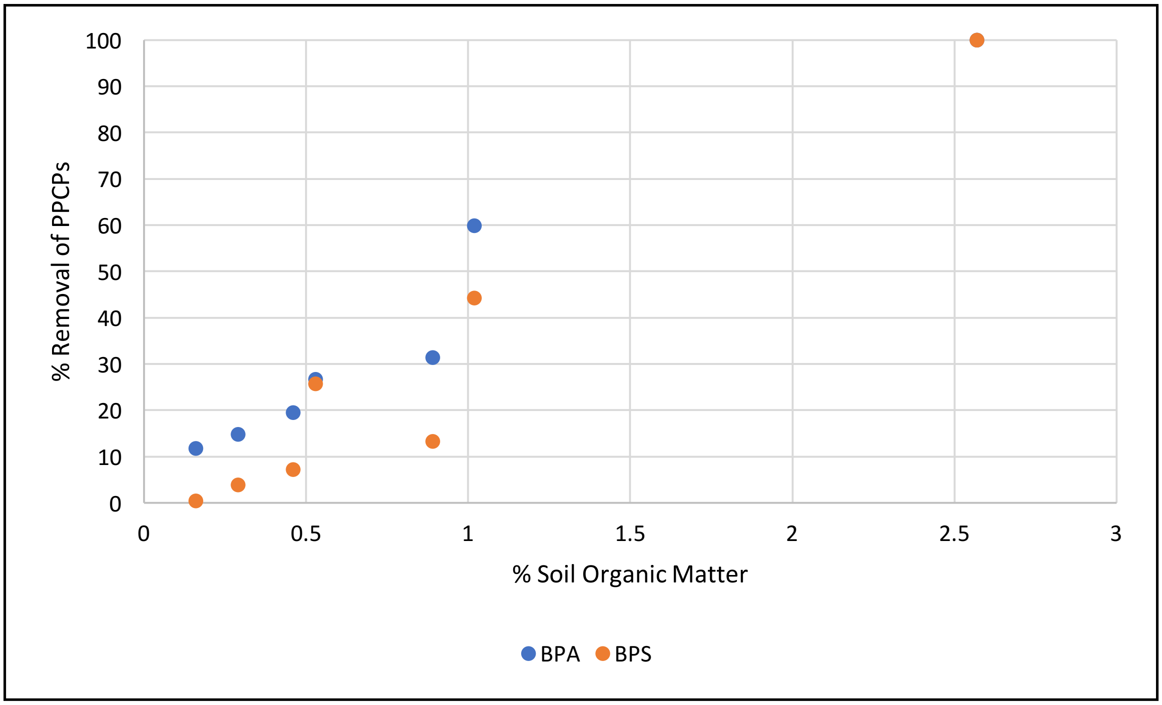


Figure 22: Relationship between total soil organic matter content and removal of PPCPs for Research Study 4

4.3.4.2 Research Study 5 – Transport of Antibiotics in Agricultural Soils

The fate and transport of sulfonamide antibiotics, a common PPCPs used in the veterinary industry, was evaluated for Research Study 5 (Park & Huwe, 2016). Sulfonamides can be excreted from animals or can enter the environment via manufacturing or disposal. Since these antibiotics are so common, SAT may be a viable polishing treatment step for their removal.

In Research Study 5, soils samples were taken from a large farming region in South Korea. The properties of the soil can be found in Table 11. The transport of three different sulfonamide antibiotics was analyzed – sulfamethoxazole (SZO), sulfadimethoxine (SXI), and sulfamethazine (SZI), with varying pH levels. Note that this research analyzed transport of these PPCPs through disturbed vs undisturbed soil at various solution pH values. For the purposes of this thesis, only the disturbed soil and solution pH of 6.0 was considered, as these conditions were most consistent with other studies reviewed.

Soil was packed into stainless steel cylinders to conduct soil column transport experiments. The cylinders were 30 cm in length with a 15 cm inner diameter. A peristaltic pump was placed on the top of the columns to maintain a steady flow rate of 3.6 mL/min. The influent containing the initial concentration of PPCPs was allowed to percolate through the soil, and the effluent concentration was recorded. (Park & Huwe, 2016)

Table 11: Soil Properties and removal rates of Research Study 5 (Park & Huwe, 2016)

Soil	**pH**	**SOC (%)**	**Texture (%)**			**% Removal**		
			Clay (<2µm)	**Silt (2-20µm)**	**Sand (20-100µm)**	**SZO**	**SXI**	**SZI**
1	5.7	2.21	5.50	20.00	74.50	78	68	75
2	5.5	3.97	8.10	26.70	65.20	81	81	82

The total clay content in this study did not vary significantly, although there was a slight increase in the total removal of the antibiotics with increasing clay content. This relationship can be seen in Figure 23. The soil containing 8.10% clay consistently removed over 80% of the total PPCPs in the influent, whereas the soil with 5.50% clay had an average removal rate of 73.7%.

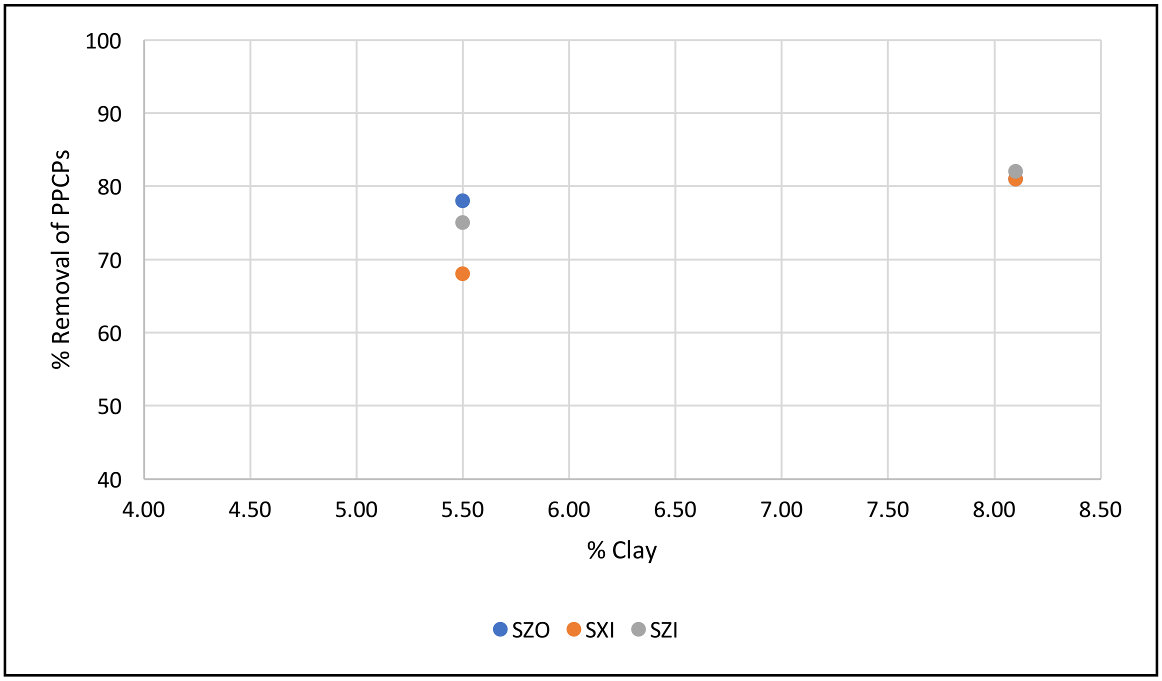


Figure 23: Relationship between total clay content and removal of PPCPs for research Study 5

An increase in soil organic carbon content also produced an increase in the removal of the antibiotics from the influent. This relationship can be seen in Figure 24, and produces the same general trend in Figure 23. There was a slight increase in the retention of the antibiotics when the organic carbon content was increased from 2.2% to 4%. All other research studies analyzed the soil organic matter instead of the soil organic carbon. The total soil organic matter of a medium represents the fraction of all elements present in the soil that are constituents of the organic matter. The soil organic carbon only incorporates the total carbon fraction in the soil.

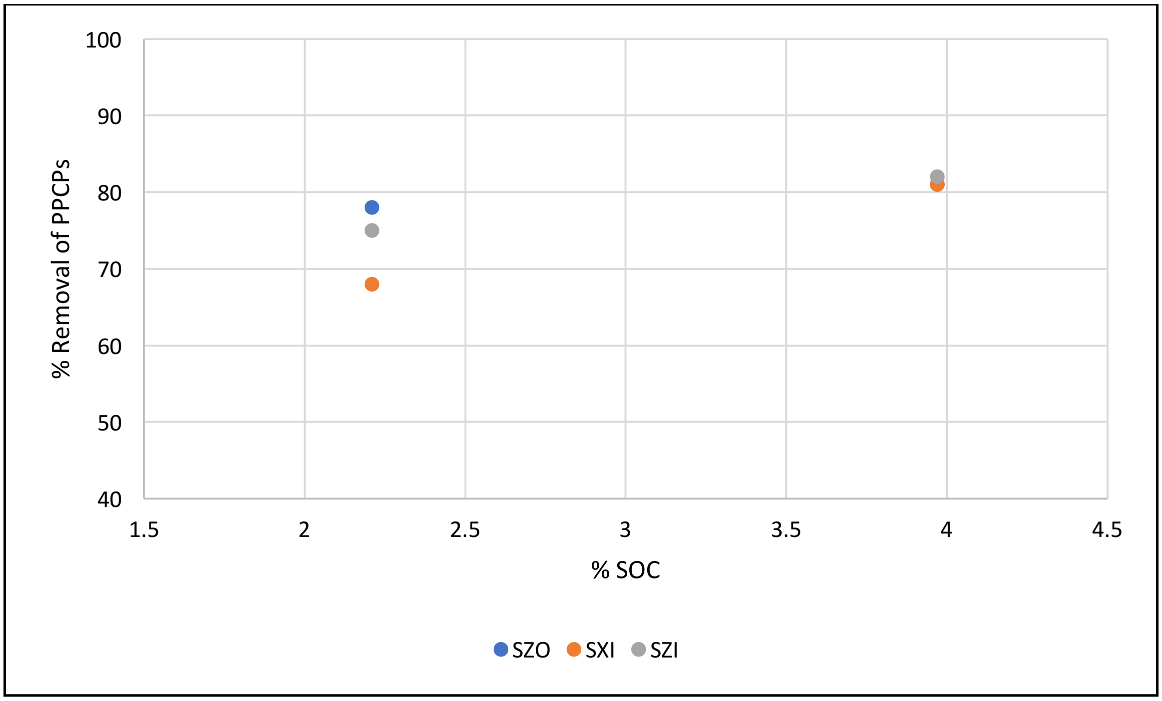


Figure 24: Relationship between total soil organic carbon content and removal of PPCPs for Research Study 5

4.3.4.3 Research Study 6 – Transport of Anti-Inflammatory Drugs in Soils

Research study 6 (Xu et al., 2010), analyzed the fate and transport of the following four anti-inflammatory drugs through three different soils: ibuprofen (IBF), naproxen (NAX), ketoprofen (KPF), and diclofenac sodium (DLF). The properties of the soils can be found in Table 12. Stainless steel columns 122 mm in length with a diameter of 15 mm were used to analyze the transport of the contaminants. 22 grams of soil were packed into each column until a bulk density of 1.33 g/cm3 was reached. The solution was introduced to the system through a tube at the top, and percolated through the soil via gravity draining. The soil column was saturated and maintained a head of 1 cm. The concentration of each contaminant was collected after the solution drained through the soil media.

Table 12: Soil properties and removal rates of Research Study 6 (Xu et al., 2010)

Soil	**pH**	**SOM (%)**	**Texture (%)**			**% Removal**			
			Clay (<2µm)	**Silt (2-20µm)**	**Sand (20-100µm)**	**IBF**	**NAX**	**KPF**	**DLF**
1	7.1	1.9	13	17	71	54.4	70.9	69	54.4
2	7.5	2.5	43	47	11	64.2	78.7	82.9	56.3
3	5.9	5.5	18	50	32	67.6	83	74.3	64.3

The results of Research Study 6 show that there is a slight correlation with retention of anti-inflammatory drugs and the total clay, which can be seen in Figure 25. The soil with the lowest clay/silt content, Soil 1, allowed the largest transport of the PPCPs. Soils 2 and 3 had higher clay content, which could be the reason for their higher removal rates. There was a similar trend with the total soil organic matter, as seen in Figure 26.

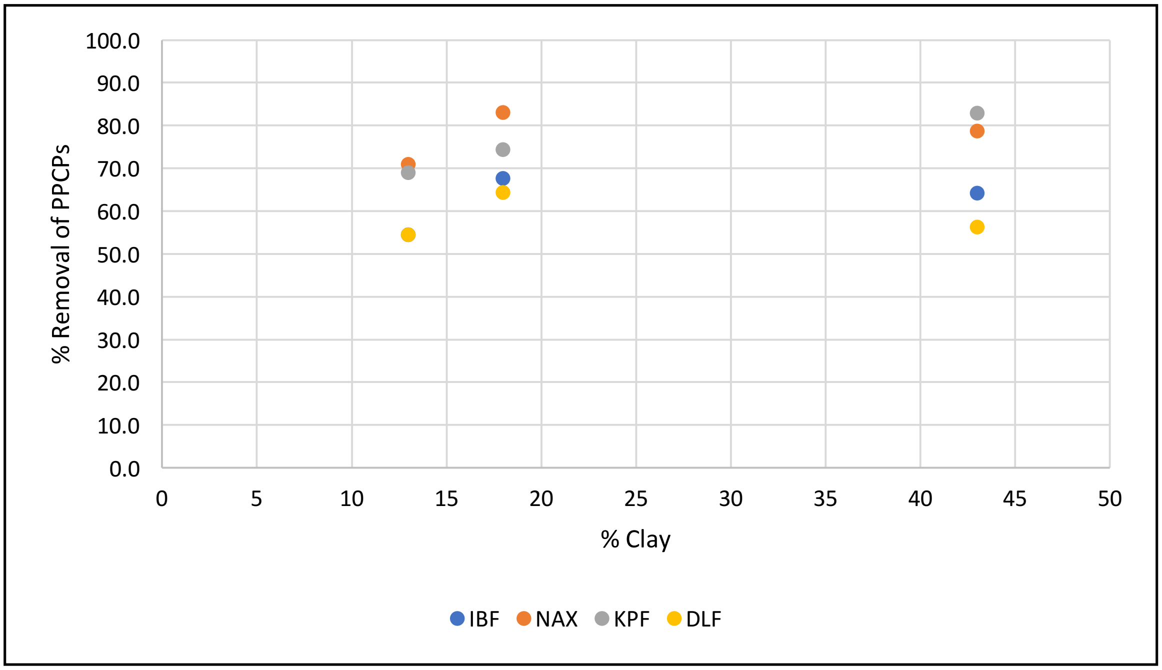


Figure 25: Relationship between total clay content and removal rates of PPCPs for Research Study 6

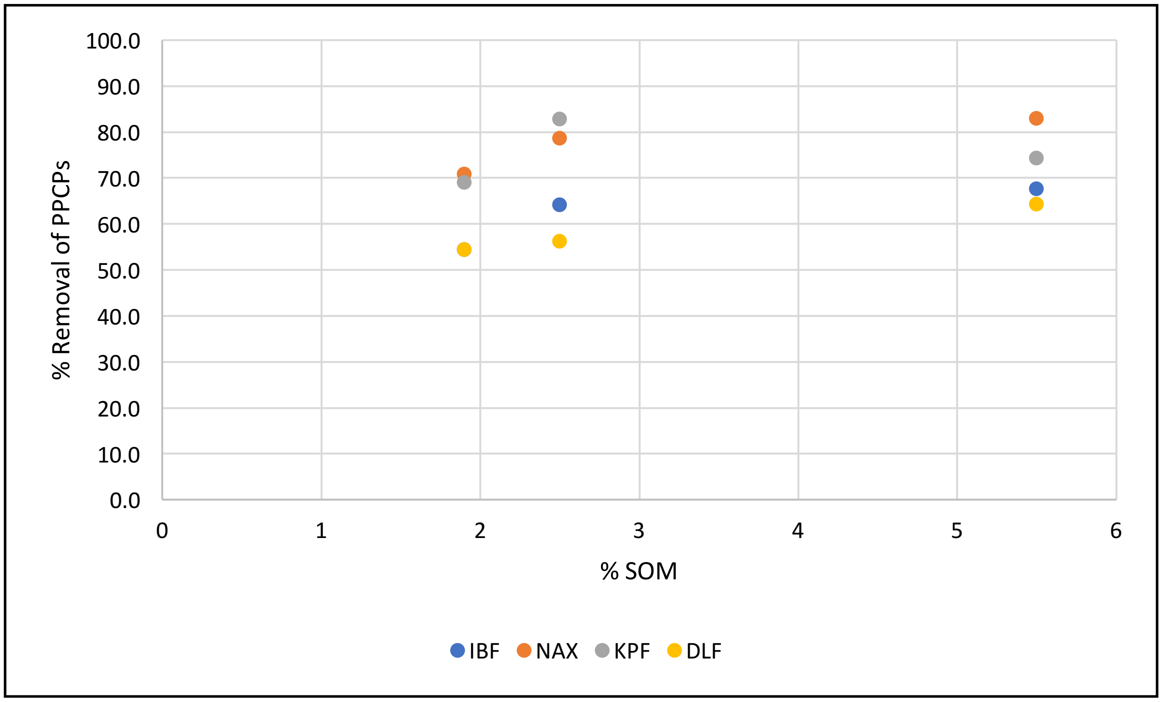


Figure 26: Relationship between total soil organic matter content and removal rates of PPCPs for Research Study 6

4.3.4.4 Summary of Research Studies 4-6

Research Studies 4-6 analyzed the effects of the type of soil on the efficiency of SAT for removal of various PPCPs. Based on the results, the general conclusion of the studies shows that clay content and the soil organic matter/carbon content have the greatest effect on the removal of PPCP in soil. Higher clay contents tend to cause higher removal rates of PPCPs, as seen in Figure 27, for several reasons. The diameter of clay is much smaller when compared to sand. Small soil particle diameter generally relates to higher specific surface area, which can promote the retention of ECs through increased opportunity for sorption. As seen in Figure 27, clay contents above around 10% caused the highest removal of PPCPs from the influent. The R-squared value seen in Figure 27 is 0.44 using a logarithmic trend line, which is high given the wide amount of variability in this study, suggesting a relatively strong correlation between clay content and PPCP removal.

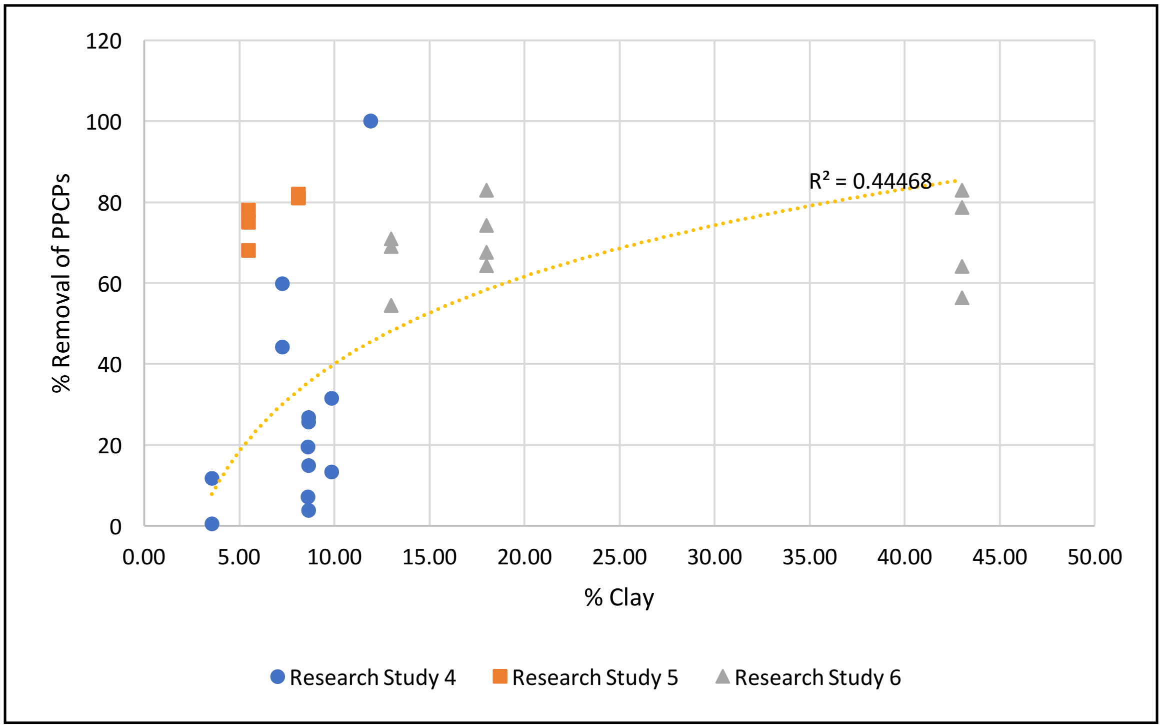


Figure 27: Relationship between clay content and removal of PPCPs for Research Studies 4-6

Soil organic matter and soil organic carbon level also played a role in the removal of the PPCPs, as seen in Figure 28. Generally, an increase in the soil organic matter/carbon content lead to an increase in the removal of PPCPs. Figure 28 produced a R-squared value of the 0.78; this is the highest value seen in this study. The data points fit very closely to the logarithmic regression line. The PPCP molecules were most likely attracted to the surface of the organic soil, which increased the retention of the PPCP through the mechanisms of sorption.

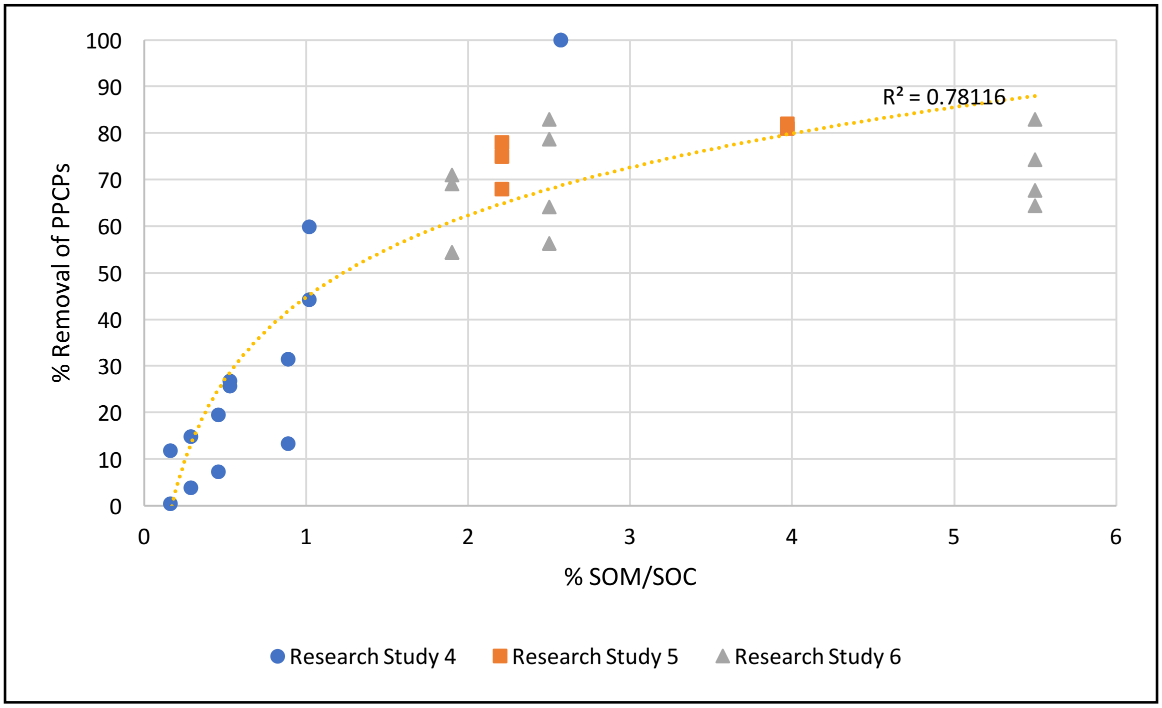


Figure 28: Relationship between SOM or SOC content and removal of PPCPs for Research Studies 4-6

Unlike nanomaterials, there was not an inverse relationship seen between the total sand content and the removal of PPCPs investigated in Research Studies 4-6. As shown in Figure 29, there is no clear trend between sand content and removal of PPCPs. This is confirmed with the low R-squared value of 0.01. Based on Research Studies 4-6, the total sand content of the soil does not have an impact on the total removal of ECs from effluent. Soil organic matter and clay seem to be the properties that dominate the fate and transport of the PPCPs in soil media, based on the data from Research Studies 4-6.

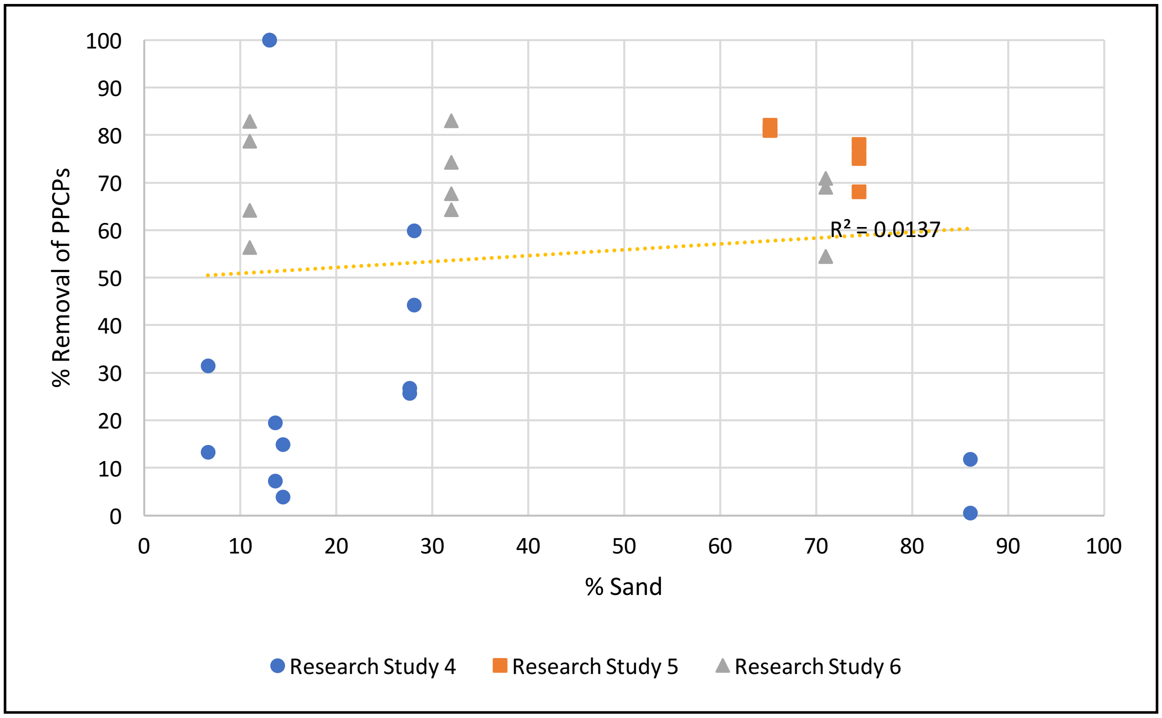


Figure 29: Relationship between sand content and removal of PPCPs for Research Studies 4-6

CHAPTER 5

CONCLUSIONS

The transport of ECs in soil media has received much more attention in recent years due to their increased presence in the environment and the potential health concerns that they pose to humans and ecosystems. This study suggests that the use of SAT as a polishing step to remove ECs from effluent may be a viable treatment alternative to advanced treatment at a wastewater treatment plant, if soil conditions are suitable. Advanced treatment is extremely expensive to implement and maintain, and expends high energy levels. A more sustainable alternative is the use of SAT. SAT uses physical, chemical, and biological properties to remove contaminants from the groundwater within an aquifer.

This study reviewed published research that analyzed the fate and transport of both nanomaterials and PPCPs. The removal capabilities of SAT rely on three factors: *(1) the properties of the ECs, (2) and the properties/nature of the groundwater flow, (3) the properties of the soil media.* The main focus of this study was on the properties of the soil media.

The properties of the ECs can effect the efficiency of a SAT system. Some of these properties include the shape/size of the particle, the surface properties of the particle, and the chemical makeup. The surface properties of an EC may play the most important role. The hydrophobicity, polarity, and surface charge of an EC can dictate the attraction of the contaminant to a soil particle. These characteristics can have a larger effect on SAT effectiveness in the saturated zone of the aquifer. It is important to consider the properties of the ECs in the effluent being treated by SAT, although this may be hard given ECs have such a large range of possible surface properties, and that typical wastewater effluent may include an extensive mixture of ECs. If the goal of the SAT is to remove a large variety of ECs, then the properties of the soil media provide a constant amid the many variables determining the transport of ECs. On the other hand, if the goal of the SAT is to remove a large quantity of a few specific ECs, then both the soil media and EC properties should be considered.

The nature and properties of the groundwater flow must also be considered when determining the effectiveness of SAT for ECs. The properties include the velocity of the groundwater flow, the direction of the flow, the pH of the solution, and the ionic strength of the solution. The velocity of the flow is a very important parameter. This is largely affected by the soil media; clay has smaller pores due to the particle's small diameter, which impedes the flow of the groundwater. Slower velocity results in longer contact times between the contaminant and the soil media. This promotes sorption of the EC to the soil particle, resulting in more effective SAT.

It is very important to consider the soil media to find an effective aquifer for SAT. Soil properties are the most consistent and predictable of the three factors that affect SAT efficacy. Properties of the soil media that affect the removal capabilities of SAT include the type of media, surface properties, moisture content, and chemical characteristics. All these properties point to high clay contents as an important quality of an effective SAT system. Both physical and chemical properties of clay generally inhibit the transport of ECs. Research Studies 1-6 all demonstrate the importance of clay content in SAT systems. Based on soil column studies, there is a correlation with high clay contents and removal rates of ECs, as shown in Figure 30. The open circles represent nanomaterials and closed circles represent the PPCPs investigated in Research Studies 1-6. The R-squared values for nanomaterials and PPCPs are roughly the same, as displayed in Figure 30. This suggests that, given the same conditions tested in this study, clay has similar removal capabilities for both ECs investigated.

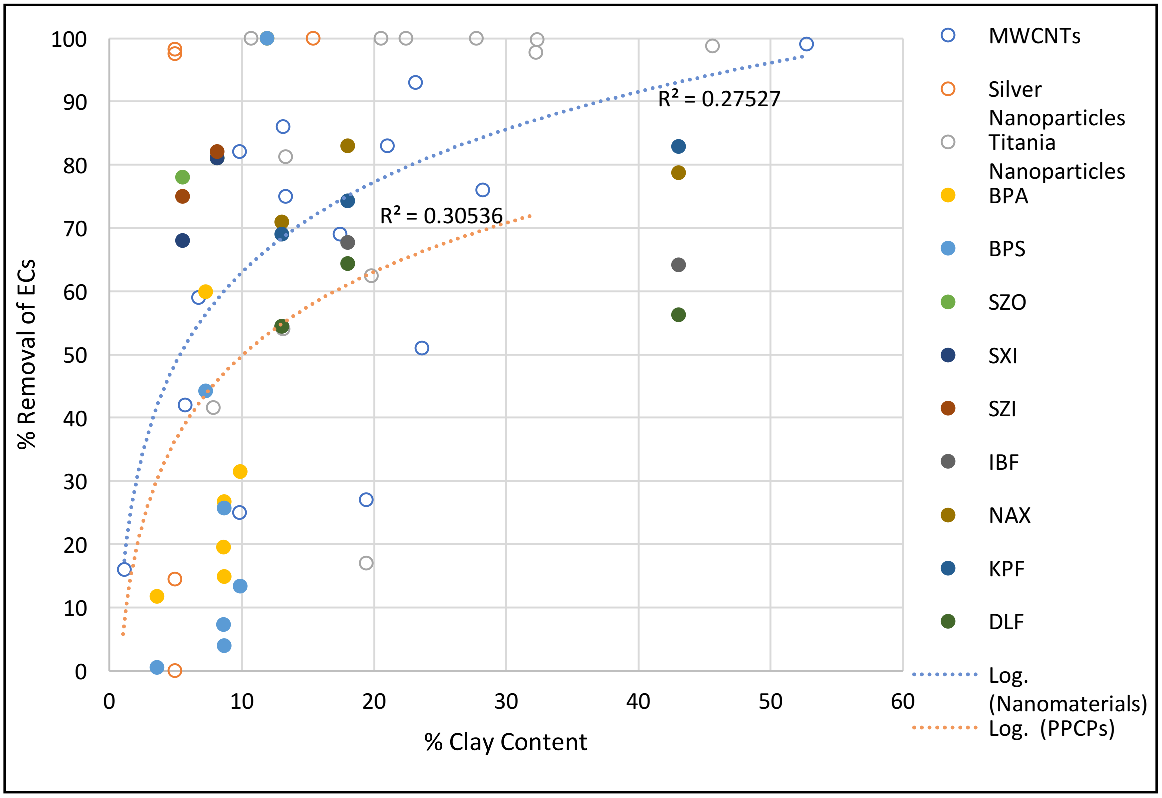


Figure 30: Relationship between total clay content and the removal of ECs from Research Studies 1-6

Figure 30 shows that as low as a 10% clay soil content produces typical removal rates above 60%. As the clay content increases, the average total removal rate increases as well This finding is important to note because clay content impacts infiltration rate in soil. The lower the clay content that allows for a SAT system to be an efficient polishing step for a wastewater treatment plant, the better for infiltration considerations.

Research Studies 1-3 determined that the removal of the nanomaterials did not have a strong correlation with the total the soil organic matter content. This is confirmed in Figure 31 given an R-squared value of 0.01. On the other hand, the Research Studies 4-6, which analyzed PPCPs, had a much stronger relationship between the removal of the contaminant and the total soil organic matter content. A much higher R-squared value of 0.78 is presented for PPCPs. The results of these studies are displayed in Figure 31. The open circles represent nanomaterials, and the closes circles represent PPCPs. Wastewater effluent will be a combination of nanomaterials and PPCPs, so it is important analyze the transport of both ECs. The high removal rates of the PPCPs is most likely due to an organic affinity (represented by K_{OW} of the contaminant) where organic compounds tend to sorb to organic materials. Organic matter/carbon contents above 2% produced the highest removal of ECs.

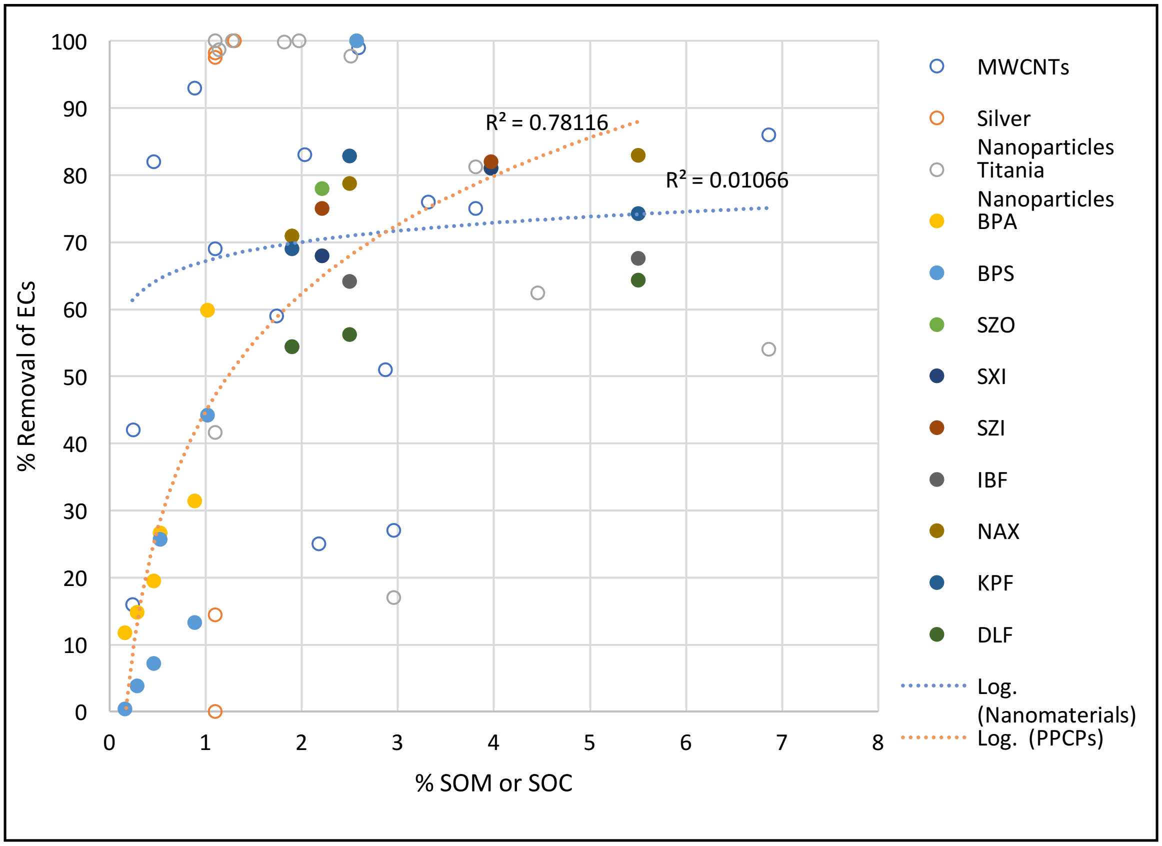


Figure 31: The relationship between soil organic matter/carbon and the removal of ECs from Research Studies 1-6

Research Studies 1-3 determined there is an inverse relationship with the total sand content in the soil and the removal of nanomaterials from the effluent. This is most likely due decreased pore straining mechanisms as a result in the increase in sand content (decrease in clay). Conversely, there was no significant correlation with the total sand content and the removal of PPCPs from Research Study 4-6, which yielded an R-squared value of 0.01. The results of the relationship between total sand content and removal of ECs for Research Studies 1-6 are displayed in Figure 32. The open circles represent nanomaterials, and the closes circles represent PPCPs.

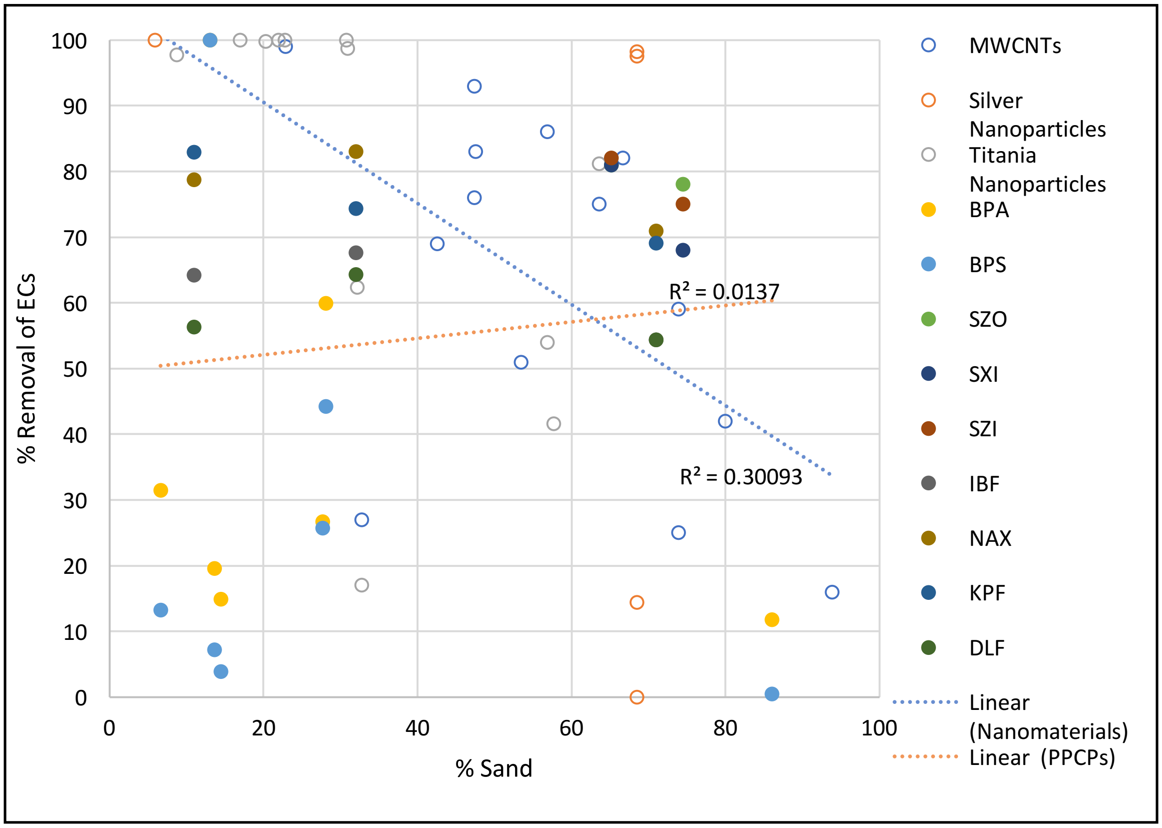


Figure 32: Relationship between total sand content and removal of ECs from Research Studies 1-6

Comparing the results from Figure 31 and 32, it can be concluded that the removal of nanomaterials versus PPCPs is likely dominated by different mechanisms. Given the conditions tested, the following conclusions can be drawn from Figures 30, 31, and 32: *(1) nanomaterials are removed by high clay contents or low sand contents, but the total soil organic matter content does not matter; (2) PPCPs are removed by high clay or high soil organic matter contents, but the total sand content does not matter.* The removal of nanomaterials is primarily governed by physical removal mechanisms. The the total clay and sand contents had an impact on the removal, which demonstrates that that soil particle size, velocity of flow, and soil type are most likely the driving mechanisms for removal. On the other hand, chemical removal mechanisms, such as sorption, play a larger role in the removal of PPCPs. The highest removal of PPCPs was seen when clay contents and soil organic matter contents were high. The PPCPs most likely had a high affinity to sorb to the to the outside of the colloids. High clay contents facilitate the removal of both nanomaterials and PPCPs. It is important to note the transport of ECs in the environment is very complex, so the results are only valid under the same conditions. The fate and transport under changed circumstances could yield different results.

SAT is a cost effective and sustainable treatment method for numerous applications, including wastewater effluent. Overall, soils with clay contents as low as 10% can produce high removal rates of ECs from effluent. Soil with high clay contents cause higher pore straining mechanisms, decrease the velocity of the groundwater, and increase the sorption of ECs to soil particles. A combination of clay and soil organic matter could produce a very efficient SAT site to be used as a polishing step for wastewater effluent, effectively removing the majority of both nanomaterials and PPCPs.

However, SAT will only be effective if the aquifer contains the properties required for a successful treatment operation. High clay content soils have low infiltration rates, which can cause ponding areas to arise (Ascuntar-Rios, 2014). Finding a balance between high clay and organic matter content and sufficiently high infiltration rates for effective SAT operation may be a challenge. One way to mitigate this could be to provide a large infiltration footprint to allow for slower infiltration rates, or to employ injection wells.

There are many important factors that need to be considered for SAT to be used effectively in practice. The infiltration basin used for recharge needs to be close to the wastewater treatment plant. The soil used for SAT should to be evaluated to determine if the soil composition is appropriate for the contaminants of concern. For example, the data presented in this thesis suggests clay contents between 10% - 20% produce high removal of ECs. It is also important to control the infiltration rate to the soil based on the capacity of the SAT system. The treatment capacity of the soil could limit the SAT system below the effluent levels discharged from the wastewater treatment plant.

5.1 Future Research

Future research may reveal additional solutions to effectively remove ECs without sacrificing SAT efficacy or operational capabilities. For example, another possible technique to increase the infiltration rate of the clay soil media is with the use of nanoclays. The addition of nanoclay content to the existing soil of an infiltration basin could potentially allow for increased hydraulic conductivities, while maintaining the important removal properties of the clay (Siddiqi, 2017). Additional research on the feasibility and effectiveness of this technique is needed.

Another disadvantage to SAT as a polishing step for effluent, is that the contaminants will remain in the soil if they sorb to the particle or are removed by physical straining. The location of recharge must ensure the groundwater will not leach into other water bodies to prevent contamination of animals and the environment. One possible mitigation technique is through plant-based remediation removal or phytoremediation. Plants are known to extract a variety of natural and harmful compounds from both groundwater and soil media through their root systems (Gupta, & Gupta, 2013). Plants exhibit adaptability, versatility, and diversity in the existing environment, so they can be excellent system of remediation for most contaminants (Gupta, & Gupta, 2013). Further research needs to be completed to examine effective plant species to uptake ECs in the environment to remediate the site.

Another potential mitigation approach is the application of bioremediation, which introduces microorganisms to the soil or relies on existing microorganism populations. Bioremediation may only be effective for PPCPs. A successful bioremediation project would ensure the retention of ECs via sorption to the soil particle, and therefore make them available to the microorganisms (Delgado-Moreno et al., 2019). The microorganisms will eventually break down the ECs to produce a less dangerous resultant. Bioremediation is credited with much of the removal of traditional wastewater contaminants in vadose-zone SAT (Essandoh et al., 2011; Fox, P., & Makam, R. 2011). Other studies have shown that bioremediation is effective at removing certain PPCPs (diclofenac, ibuprofen and triclosan), but further research should be completed to determine the effectiveness of bioremediation for other PPCPs and nanomaterials (Delgado-Moreno et al., 2019).

The use of an effective SAT system to remove ECs from effluent will require land for infiltration basins, the possible addition of engineered soil, and remediation techniques to remove the contaminants from the soil. For instance, if the clay content is below the necessary levels, the existing site may need to be reengineered to meet requirements. An economic evaluation which compares an engineered SAT system versus the addition of advanced treatment to the wastewater treatment plant should be completed to determine if the SAT system is truly cost effective.

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