

University of Memphis

University of Memphis Digital Commons

Electronic Theses and Dissertations

6-19-2023

Natural Attenuation of Chromium and TCE on Memphis Aquifer Sand, a Bench-Scale Study

Donya Sharafoddinzadeh

Follow this and additional works at: <https://digitalcommons.memphis.edu/etd>

Recommended Citation

Sharafoddinzadeh, Donya, "Natural Attenuation of Chromium and TCE on Memphis Aquifer Sand, a Bench-Scale Study" (2023). *Electronic Theses and Dissertations*. 3062.

<https://digitalcommons.memphis.edu/etd/3062>

This Dissertation is brought to you for free and open access by University of Memphis Digital Commons. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of University of Memphis Digital Commons. For more information, please contact khhgerty@memphis.edu.

NATURAL ATTENUATION OF CHROMIUM AND TCE
ON MEMPHIS AQUIFER SAND, A BENCH-SCALE STUDY

by

Donya Sharafoddinzadeh

A Dissertation

Submitted in Partial Fulfillment of the

Requirements for the Degree of

Doctor of Philosophy

Major: Civil Engineering

The University of Memphis

May 2023

Copyright© Donya Sharafoddinzadeh

All rights reserved.

DEDICATION

I would like to dedicate this dissertation to

Mr. Mehdi Hashemi,

who introduced me to the wonders of chemistry,

and in doing so changed my life forever.

ACKNOWLEDGEMENTS

First and foremost, I extend my gratitude towards my amazing advisor, Dr. Brian Waldron, who is not only the most supportive advisor, but has also created an energetic and friendly workplace for all his students.

I would also like to thank my advising committee for their instructive comments and their availability at all odd times during the pendency of this project.

Many thanks to my friends and colleagues at CAESER, who were working alongside me, assuring me I was not alone on this journey.

I need to thank University of Memphis, Herff College of Engineering, for giving me the opportunity to come to the United States and start my PhD journey.

I am also grateful to the fund provider of my research, Memphis Light, Gas, and Water (MLGW), for their financial support, which has made this study possible.

And last but not least, a huge thank you to my best friend, who was by my side at all times during this project. My brother, who gave me constant encouragement and support, not only in these years, but rather my whole life. And my father who by example taught me how to persevere and never give up on my dreams.

PREFACE

This dissertation is comprised of two peer-reviewed journal articles. Chapter one contains the first paper, in its entirety, as it was submitted. The first one is submitted to the MethodsX Journal and is awaiting publication. This paper describes the novel method which was developed in this study, as well as the experimental procedure and the method validation techniques and results. The second paper is presented in chapter two. The second paper will be submitted to the Journal of Contaminant Hydrology after receiving the final comments from my advising committee. The second paper describes the results which were obtained when the proposed method was implemented to study the adsorption of hexavalent chromium on different sand samples collected from across Shelby County. A third paper will be published from this study, which will focus on the results obtained from Trichloroethylene experiments. But due to time constraints, that paper could not have been included in this dissertation.

ABSTRACT

Groundwater serves as a major source of drinking water for many people across the world. Aquifer properties have been studied extensively, as well as contaminant transport within aquifers and remediation of contaminated aquifers. A common component of alluvial aquifers is sediment deposition. ASTM-D2419-14 defines sand as particle of rock with size range of between 0.075 mm and 4.75 mm. Sand is mostly composed of silica and has physical and chemical attributes which cause its specific characteristics. Silica is considered chemically inert, unable to enter most chemical reactions in aqueous geochemistry field. However, would it be wise to disregard the potential effect that sand may have on the adsorption process of contaminants, or do researchers need to take a closer look at the sand characteristics specific to the research location or remediation site? The aim of this dissertation is to first determine if sand characteristics, physical and chemical, can influence the adsorption patterns of various contaminants. Secondly, to provide a standard method with high reliability and reproducibility by which others can also test the sand they have at their disposal to determine if and how the sand specific to their location interacts with their chosen contaminant. The third goal was to utilize such method on three different contaminants: Hexavalent Chromium as a heavy metal and oxyanion, Trichloroethylene (TCE) as a chlorinated volatile organic solvent, and Bromide as a conservative tracer which passes through the system with no interaction. These three contaminants are significantly different from each other, and not only do they represent a wide range of behaviors expected from contaminants, but they are also commonly found in urban or industrial superfund sites. During this study, six different sand samples were collected from three different core samples drilled. The six sand samples covered both geographical and depth variations. The method was developed, optimized, validated, and the reproducibility was calculated using %RSD values, which were recorded for <1% for bromide, indicating a high reproducibility value. Furthermore, when the three types of chemicals were

interacted with the sand samples, the results confirmed that the sand characteristics do in fact impact the adsorption behaviors. In short, it is paramount for the purposes of modeling contaminant transport as well as remediation specialists to study the effects of sand specific to their region on the contaminant they are working with. The experiments performed consist of pH studies, kinetic studies, isotherm studies, and additional experiments. These experiments differentiated the sand samples into three distinct groups behaviorally. One cluster of sand samples showed no interaction with the contaminants, one group showed minimal interaction, and the other group showed distinguishable adsorption patterns. The influential factors on the adsorption behaviors found to be the organic carbon content, the iron content, grain size, and percentage of fine material (silt and clay). Also, it is worth mentioning that a specific sand sample can exhibit different adsorption patterns when interacted with different chemicals.

TABLE OF CONTENTS

PREFACE	5
ABSTRACT.....	6
CHAPTER ONE	10
A PROCEDURE FOR STUDYING THE ADSORPTIVE BEHAVIOR OF NATURAL SAND IN A LABORATORY	
SETTING.....	11
Abstract.....	11
Graphical Abstract.....	12
Background	12
Method Details	16
Discussion.....	21
Conclusion.....	24
References	26
CHAPTER TWO	31
INVESTIGATING THE EFFECTS OF SAND CHARACTERISTICS ON THE ADSORPTION PATTERNS OF	
HEXAVALENT CHROMIUM	32
Abstract.....	32
Introduction	33
Experimental	36
Site Description	36
Materials	36
Methods.....	37
Instrumentation	38
Results and discussion	38
Oxidation reduction potential and speciation of chromium	38
Background chromium concentration	41

pH studies	42
Kinetic studies	43
Isotherm studies	45
Effects of sand characteristics	46
Conclusion.....	48
References	50

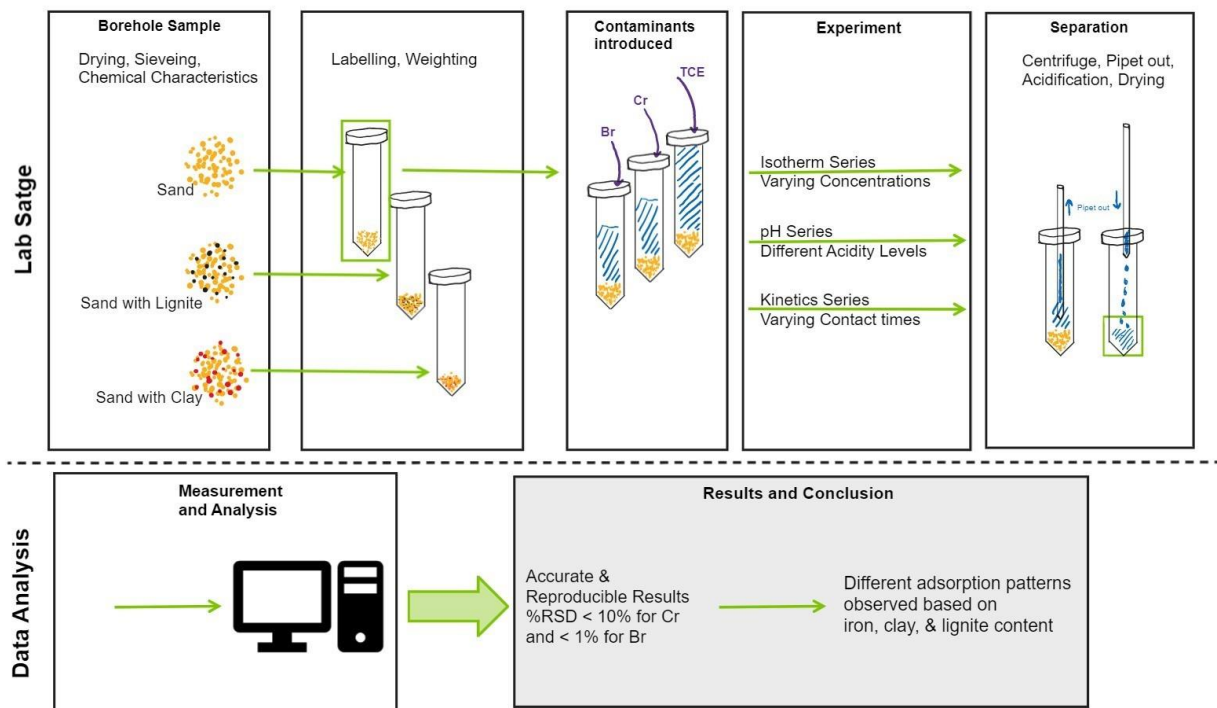
CHAPTER ONE

A PROCEDURE FOR STUDYING THE ADSORPTIVE BEHAVIOR OF NATURAL SAND IN A LABORATORY SETTING

Abstract

With numerous people across the world relying on groundwater for drinking water, many studies aim at better understanding these systems, as well as remediation and tracking of contaminants. A very important, yet commonly neglected aspect of many hydrogeologic studies of sedimentary aquifers, is the interaction of contaminants with aquifer framework grains. Many studies choose to investigate synthetic materials to limit complications due to sediment heterogeneity; however, study of sediment in its natural form is paramount for providing accurate background information to track interactions with contaminant plumes, as well as assess remediation strategies. This study provides a comprehensive and a need-based guide on preparation and experimental setup for investigating the contaminants' adsorption patterns of natural sand under varying conditions. The sand samples used in this study contained significantly different chemical and physical compositions in terms of grain size, iron content, and organic carbon content. This study shows that these characteristics significantly impact the adsorption patterns of three different contaminants (i.e., TCE, chromium and bromide) in terms of kinetic, isotherm, and pH characteristics. Results indicate that this method produces highly accurate and reproducible results, with RSD values of less than 10% for chromium and 1% for bromide.

Graphical Abstract



Background

[literature review] Aquifer properties, contaminant transport within aquifers,¹⁻³ and remediation of contaminated aquifers have been studied extensively worldwide.^{4,5} With groundwater serving as a major source of drinking water, the importance of such studies needs no emphasis.^{6,7} Studies may idealize conditions in order to limit the impact of externalities (such as back-diffusion from clay layers) and media complexity (such as fluctuations in grain size and organic carbon content) when simulating contaminant transport in porous media. This allows for more direct control over the parameter(s) of interest, without over-complication of the model which results in extensively long run time. When focusing on water movement and flow in sedimentary aquifers, researchers commonly prefer to use glass beads or artificial sand, which ensures homogeneity and control over grain size and porosity.⁸ Studies focusing on developing new remediation materials and methods,

especially those using modified-sand materials or *in-situ* remediation techniques, assume that the adsorptive effects of sand are negligible.⁹⁻¹¹ Numerical modelers attempt to match plume shape and extent by modifying hydrodynamic dispersivity similar to a control knob, and in doing so, inadvertently account for aquifer heterogeneity,¹² changes in porosity, and other parameters such as hydraulic conductivity, which are key to groundwater flow and contaminant transport.^{13,14} However, natural sand is neither uniform nor homogeneous; furthermore, it can participate in chemical and microbial reactions that may significantly effect contaminant fate and transport.^{15,16}

Even in a geographically small area (see site description section), sand can have significant variations in grain size, fine particle percentage, and chemical composition.^{17,18} This study aims to provide a comprehensive, adaptable, step-by-step guide in bench-scale studies or when natural attenuation is being experimentally assessed. By implementing this method, researchers can obtain highly reproducible and comparable results that focus solely on the adsorptive behavior of sand and highlight the effects that small changes in sand characteristics have on the adsorption patterns.

[site description and sample collection] This study was conducted in Shelby County, Tennessee, USA, where the majority of drinking water is pumped from the Memphis aquifer, a sand-dominated aquifer.⁶ Although the Memphis aquifer is mostly confined beneath a thick clay aquitard (upper Claiborne confining unit, UCCU) that protects it from contamination present in the uppermost water-table aquifer, called the shallow aquifer, recent investigations show that contaminant plumes can leak into the confined Memphis aquifer through preferential pathways within the aquitard, termed “breaches” (i.e., paleo-valleys, faults), due to downward flow of groundwater, exacerbated near wellfields in urban areas.^{19,20} Three sample locations were selected (i.e., MSA-1, 99s2, and CVL-1) in the City of Memphis and the Town of Collierville due to their

proximity to a wellfield, and based on available core samples from soil boring or well installations that used sonic drilling, which offers excellent core sample recovery.

One sand sample was collected at specific depths from MSA-1 and 99s2 cores, and four sand samples were collected from the CVL-1 core. The distribution of samples allowed for depth-related variation assessment as well as location-based variations within Shelby County. Table 1 indicates the sample depth, designated identification, and hydrostratigraphic unit. Though the Memphis aquifer ranges in thickness from 150-270 m,²⁰ the total depths of the selected locations are in the upper section of the Memphis aquifer, limiting the sample depth range throughout the unit. However, younger, lesser quality water has been found in the upper sections of the Memphis aquifer²⁰ and reflect the aquifer section most prone to contamination.

Table 1, Sampling location, depth, and ID

Sample Location	Sample Depth (m)	Sample ID	Hydrostratigraphic Unit	Organic Carbon Content (% w/w)	Iron Content (mg/kg)
CVL-1	17*	C057	Shallow (fluvial-alluvial) aquifer	0.05	4050
CVL-1	54	C177	Memphis aquifer	0.06	1120
CVL-1	66	C217	Memphis aquifer	0.11	117

CVL-1	76	C250	Memphis aquifer	0.05	167
MSA-1	72	A237	Memphis aquifer	0.30	641
99s2	76	S250	Memphis aquifer	0.06	159

*This sample is representative of the shallow aquifer overlaying the UCCU, through which contaminants must pass before entering the Memphis aquifer via an aquitard breach.

[research goals] The collection of six sand samples gathered in this study represent geographical and depth variations (Table 1). To render these qualitative characteristics to quantifiably variables, samples were analyzed for three different measurable variables pertinent to contaminant transport: iron (Fe) content as mg/kg [milligrams of iron per kilograms of sand], organic carbon (lignite) content as % w/w [percentage, weight of lignite per weight of sand], and grain-size distribution (silt and clay percentage).

A common group of subsurface contaminants present in the Memphis area are volatile organic compounds (VOCs), including chlorinated solvents (e.g., tetrachloroethylene (PCE) and trichloroethylene (TCE)), which are common subsurface contaminants in other urban environments.^{21,22} Additionally, hexavalent chromium (Cr^{6+}) is a contaminant of concern to the Memphis aquifer in the Collierville area.^{23,24}

The experimental setup designed for this study enables researchers to investigate a broad spectrum of adsorptive behaviors to aquifer sand when different chemicals (i.e., TCE, Cr^{6+} , and bromide (as a conservative tracer)) are introduced to sand samples. By designing the experimental conditions according to their specific needs, researchers can investigate the effects of adsorption, pH, kinetics, and other specific conditions (e.g., temperature and added adsorbents). The methodology

developed throughout this study presents a step-by-step guide on the preparation of samples and experimental procedures. This method uses unaltered sand, meaning samples can be used as-is from a core sample.

Method Details

For this study, the batch method was chosen as opposed to conducting a column test, since column tests are prone to scalability problems.²⁵ Batch experiments are carried out in test tubes (15 ml polypropylene centrifuge tubes with screw caps). Three chemicals from different chemical groups have been chosen to represent a variety of behaviors: (1) Cr^{6+} is an ionic compound, highly soluble and mobile, a heavy metal, and an oxyanion; (2) TCE is a volatile organic compound, a dense non-aqueous phase liquid (DNAPL), and a chlorinated solvent; and (3) bromide is a conservative tracer with no interaction during the transport phase. The preparation of a sand sample prior to the experiment consists of:

1. Drying the sand in an oven (12 hours at 40° C) to remove excess humidity and water from the core sample as they came from saturated sections of the core.
 - a. If left to dry under ambient conditions, the sand will not be completely dry at the time of weighting, unless a dehumidifier/desiccator is used, or a long waiting time is imposed.
 - b. Ovens are the preferred method of drying over desiccators as they are faster and more efficient. However, to preserve the possible microbial content of samples, it is recommended to quickly remove the humidity of the samples. When using an oven, higher temperatures should be avoided so that the microbial content is preserved as well as the chemical composition of less stable species such as Fe^{2+} cations.^{26,27}

- c. Undesirable complexation reactions might occur if the temperature is excessively high, yet a more common undesirable reactions can include oxidation of metallic species.²⁷ Drying the samples at 40°C guaranties a complete removal of relative humidity with minimal risk of altering the chemical or microbial composition of the sample.^{26,27}
- 2. Since this study is focused solely on sand, gravel was removed from the sand samples using a No. 4 sieve, following ASTM D2487-17.²⁸
- 3. Organic carbon content was measured using Walkley-Black method,^{29,30} and iron content is measured using EPA method 6010D.³¹

Before beginning the experiment:

- 4. Samples are run in duplicates.
- 5. A sterile polypropylene centrifuge tube (Fisher Scientific) is properly labelled in accordance with the experimental conditions. Table 2 shows the labelling system used with an example.

Table 2. Labeling method for marking centrifuge tube samples with an example.

Variable	Sample ID With Depth	Run number	Experiment Series	Condition Number	Contaminant
Abbreviation*	SAID.	R;	E:	N#	Ch
	SAID.R;E:N#Ch				

Example	CVL-1 core from	Second	pH	Fifth	pH
	66 m (217 ft)			condition	Bromide
	<u>C217.2;P:5#Br</u>				

*The symbols used in the abbreviation help create, automate, concatenate, and filter hundreds of labels at the same time.

- a. When labelling centrifuge tubes, two copies of each individual label must be prepared. The reaction will take place in the first centrifuge tube and the second labelled tube is saved for step 11.
6. From here on, the whole process can be conducted under anaerobic conditions (if necessary, for example, when working with TCE) inside a glovebox filled with argon gas, where the oxygen content is kept under 2% (monitored by an oxygen sensor) to avoid oxidation/degradation of the sample and to control the microbial reactions when applicable.
7. A pre-weighed amount of sand sample (3 g) is added to each labelled centrifuge tube. The weight of sand samples is up to the discretion of the researcher, with consideration of parameters such as bulk density and test tube size, and quantity needs to be representative of aquifer variability. Coarser and texturally heterogeneous sediment requires larger sample mass.

8. In this step, the prepared aqueous solution of the target chemical is added to the centrifuge tube already containing sand. The preparation of the mentioned aqueous solution is determined by the experimental requirements.

8.1) *Isotherm series*: To investigate the effect of the initial concentration on adsorption and maximum adsorption capacity, several solutions with different initial concentrations can be prepared. In this study, six different solutions were prepared: 0.1 mg/l, 0.5 mg/l, 1 mg/l, 2.5 mg/l, 5 mg/l, and 10 mg/l. The pH and shaking time were kept constant with pH of 6 and shaking time of one hour.

8.2) *pH series*: To investigate the effect of the pH on adsorption behavior and critical points of change, several solutions of progressively increasing pH were prepared at pH's of 4, 5, 6, 7, 8, and 9. Initial concentration was set to 1 mg/l and shaking time to one hour.

8.3) *Kinetic series*: To investigate the effect of shaking time, ten different solutions were prepared and shaken over the following time periods in minutes: 5, 10, 15, 30, 60, 240, 480, 1440 (24h), 2880 (48h) and 4320 (72h). Initial concentration and pH were held constant at 1 mg/l and 6, respectively. These time intervals helped determine whether the sand adsorbs the chemicals rapidly or slowly and how long it takes for the equilibrium to be reached.

The conditions for steps 8.1-8.3 are summarized in table 3.

Table 3 Experiment parameters for series 5.1-5.3.

Experiment	pH	Contact time (min OR h)	Initial concentration (mg/l)

8.1 Isotherm	6	1 h	0.1, 0.5, 1, 2.5, 5, 10
8.2 pH	4, 5, 6, 7, 8, 9	1 h	1
8.3 Kinetic	6	5, 10, 15, 30 min 1, 4, 8, 24, 48, 72 h	1

- a. Total volume of solution added to each centrifuge tube is the researcher's choice; however, when working with volatile organic compounds it is paramount that the vials be completely filled, leaving no headspace, in order to minimize evaporation during the experiment.
9. Centrifuge tubes were agitated horizontally on a shaker for the required amount of time (see table 3), to stop the reaction and precipitate the finer clay and silt particles suspended in the solution.
10. Centrifuge tubes were placed in a centrifuge (3000 rpm, 30 minutes). The centrifuge settings were determined experimentally; therefore, can highly differ depending on the characteristics of the sand. However, it was observed that under shorter time settings or lower rpm settings, the silt and clays present in the sample were not fully compacting with the larger particles.
11. The supernatant was pipetted out into an identically labelled centrifuge tube.
12. The sand sample is then dried and saved for further analysis if desorption studies are appropriate.

13. The supernatant was acidified in accordance with EPA sample preservation guidelines depending on the chemical used (EPA method 200.2 for Chromium, EPA method 8260B for TCE, and EPA method 9211 for Bromide).³²⁻³⁴
14. The concentration of the chemical that either desorbed from the dried sand or remained in the supernatant is measured using the appropriate instrument. Instrumentation can vary between Atomic Adsorptions (AAs), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) for metallic compounds, to different gas chromatography-mass spectrometry (GC-MS) setups for organic contaminants, and even Ion chromatography (IC) instruments. However, it must be noted that direct colorimetric or spectrophotometric devices are not recommended because even after centrifuging the samples, the supernatant can still have a background color or suspended particles that may interfere with such devices.

Discussion

This method was implemented for three different chemicals: hexavalent Chromium, TCE, and Bromide. With a minor change such as using a glovebox, this method was applicable to three very different chemicals using multiple quality control checks. The comparison of the first and second runs of each sample between the pairs of duplicate samples can flag potential errors. Furthermore, certain conditions are analyzed three times to assess variance. In Table 3, the condition under which the initial concentration is 1 mg/l, pH = 6, and shaking time is one hour, is repeated in all three experimental series. This was intended as a measure of reproducibility of the experiments. When Residual Standard Deviation (%RSD) values were calculated across all six times that a specific sample was being tested (Table 4), the results showed extremely low %RSD

values (<10% for hexavalent chromium and <1% for bromide) across all samples, which indicates that results were extremely reproducible.

Table 4. %RSD values for hexavalent chromium and bromide.

Sample ID	Experiment Series	Condition Number	Sample Label Refer to Table 2	%RSD	
				Chromium	Bromide
A237	Isotherm series	I:3	A237.1;I:3	8.022	0.244
			A237.2;I:3		
	pH series	P:3	A237.1;P:3		
			A237.2;P:3		
	Kinetic series	K:5	A237.1;K:5		
			A237.2;K:5		
C057	Isotherm series	I:3	C057.1;I:3	3.788	0.104
			C057.2;I:3		
	pH series	P:3	C057.1;P:3		
			C057.2;P:3		
	Kinetic series	K:5	C057.1;K:5		
			C057.2;K:5		
C177	Isotherm series	I:3	C177.1;I:3	6.391	0.064
			C177.2;I:3		
	pH series	P:3	C177.1;P:3		
			C177.2;P:3		
	Kinetic series	K:5	C177.1;K:5		

			C177.2;K:5		
C217	Isotherm series	I:3	C217.1;I:3	4.232	0.117
			C217.2;I:3		
	pH series	P:3	C217.1;P:3		
			C217.2;P:3		
	Kinetic series	K:5	C217.1;K:5		
			C217.2;K:5		
C250	Isotherm series	I:3	C250.1;I:3	3.454	0.075
			C250.2;I:3		
	pH series	P:3	C250.1;P:3		
			C250.2;P:3		
	Kinetic series	K:5	C250.1;K:5		
			C250.2;K:5		
S250	Isotherm series	I:3	S250.1;I:3	3.404	0.082
			S250.2;I:3		
	pH series	P:3	S250.1;P:3		
			S250.2;P:3		
	Kinetic series	K:5	S250.1;K:5		
			S250.2;K:5		

Results also show that even though the six sand samples were collected in a rather small geographical area, very different adsorption patterns are observed. The hypothesis of this study was that the iron content of the samples would affect the adsorptive behavior, as well as the organic

carbon content. The results show that not only does iron and organic carbon contents significantly alter the adsorptive behavior of sand samples, but the clay content and grain size are also very important. Samples with high organic carbon content showed rapid adsorption, yet the percentage of organic carbon in the sample can be considered as very small (0.11% maximum), which leads to the active spots filling quickly. Samples with high clay content and fine particles showed slow adsorption yet high capacity (8.44 mg/kg for hexavalent chromium). In summary, the chemical composition of sand can affect its adsorption of certain chemicals.¹⁸ It is always helpful to know if there are any chemical species present in the sand sample that might have an affinity towards the chemical, such as iron. Although iron potentially can reduce other chemicals, such as TCE and Cr^{6+} , for such reactions to take place the iron must be in the form of Fe^{2+} . In one of the sand samples tested in this study, iron species were present; however, since the iron was in the form of Fe^{3+} , it did not interact with the chemicals. Meanwhile some non-reactive sand samples showed no adsorption under any conditions, and for those samples one can safely state that adsorption is negligible. On the other hand, several sand samples had significant effects on adsorption and kinetics. Therefore, when deciding whether natural attenuation is an appropriate course of action, it would be important to know how the sand would react to such conditions, for which this research provides a road map on how to determine such characteristics of sand.

Conclusion

This study provides a step-by-step guide for preparation of a natural sand sample, as well as an experimental plan to study the adsorptive behavior of sand taken from different core samples in response to different experimental conditions. By implementing this method, researchers can obtain highly reproducible and comparable results that focus solely on the adsorptive behavior of sand and highlight the effects that small changes in sand characteristics have on the adsorptive

behavior. Studying sand taken directly from cores is critical in providing background information to assess contaminant fate and transport, as well as plume size and shape. This is particularly useful for those professionals selecting remediation techniques such as natural attenuation, as the in-situ sand attributes could be a decisive factor. Even in samples collected from a small geographic region, the adsorptive behavior of sand can vary significantly depending on sampling location and depth, resulting in different iron and organic carbon contents, grain size, and silt and clay content, or other sediment properties. Iron, if in the right form, can enter chemical reactions with target chemicals and have an impact on adsorption. Organic carbon acts as a strong physical adsorbent that is fast acting and can rapidly adsorb the chemical. The presence of clay and fine particles not only can act as a physical adsorbent, but also act as charged nuclei that can attract other charged species. In short, researchers cannot simply assume that all sand samples are inert and have either no adsorptive capabilities or their adsorption is negligible. This procedure is flexible enough to conform to different experimental needs and goals, yet it provides a well-needed framework for such studies to be conducted more frequently and for the results attained from such studies to be as comparable as possible. The quality control checks embedded in this procedure suggest the results attained from this study are highly reproducible and reliable.

References

1. You X, Liu S, Dai C, Guo Y, Zhong G, Duan Y. Contaminant occurrence and migration between high- and low-permeability zones in groundwater systems: A review. *Science of The Total Environment*. 2020;743:140703. doi:10.1016/J.SCITOTENV.2020.140703
2. Sen TK, Khilar KC. Review on subsurface colloids and colloid-associated contaminant transport in saturated porous media. *Adv Colloid Interface Sci*. 2006;119(2-3):71-96. doi:10.1016/J.CIS.2005.09.001
3. Mackay Paul V Roberts DM, Cherry JA. Transport of organic contaminants in groundwater Distribution and fate of chemicals in sand and gravel aquifers. Accessed November 23, 2022. <https://pubs.acs.org/sharingguidelines>
4. Fan T, Yang M, Li Q, et al. A new insight into the influencing factors of natural attenuation of chlorinated hydrocarbons contaminated groundwater: A long-term field study of a retired pesticide site. *J Hazard Mater*. 2022;439:129595. doi:10.1016/J.JHAZMAT.2022.129595
5. Liu JW, Wei KH, Xu SW, et al. Surfactant-enhanced remediation of oil-contaminated soil and groundwater: A review. *Science of The Total Environment*. 2021;756:144142. doi:10.1016/J.SCITOTENV.2020.144142
6. Sahagún-Covarrubias S, Waldron B, Larsen D, Schoefnacker S. Characterization of Hydraulic Properties of the Memphis Aquifer by Conducting Pumping Tests in Active Well Fields in Shelby County, Tennessee. *JAWRA Journal of the American Water Resources Association*. 2022;58(2):185-202. doi:10.1111/1752-1688.12991
7. Carrard N, Foster T, Willetts J. Groundwater as a Source of Drinking Water in Southeast Asia and the Pacific: A Multi-Country Review of Current Reliance and Resource Concerns. *Water* 2019, Vol 11, Page 1605. 2019;11(8):1605. doi:10.3390/W11081605

8. Bradford SA, Yates SR, Bettahar M, Simunek J. Physical factors affecting the transport and fate of colloids in saturated porous media. *Water Resour Res.* 2002;38(12):63-1-63-12.
doi:10.1029/2002WR001340
9. Kanel SR, Nepal D, Manning B, Choi H. Transport of surface-modified iron nanoparticle in porous media and application to arsenic(III) remediation. *Journal of Nanoparticle Research.* 2007;9(5):725-735. doi:10.1007/S11051-007-9225-7/TABLES/4
10. Zadaka D, Mishael YG, Polubesova T, Serban C, Nir S. Modified silicates and porous glass as adsorbents for removal of organic pollutants from water and comparison with activated carbons. *Appl Clay Sci.* 2007;36(1-3):174-181. doi:10.1016/J.CLAY.2006.04.012
11. Wang Q, Song X, Wei C, et al. In situ remediation of Cr(VI) contaminated groundwater by ZVI-PRB and the corresponding indigenous microbial community responses: a field-scale study. *Science of The Total Environment.* 2022;805:150260. doi:10.1016/J.SCITOTENV.2021.150260
12. Fakhreddine S, Lee J, Kitanidis PK, Fendorf S, Rolle M. Imaging geochemical heterogeneities using inverse reactive transport modeling: An example relevant for characterizing arsenic mobilization and distribution. *Adv Water Resour.* 2016;88:186-197.
doi:10.1016/J.ADVWATRES.2015.12.005
13. Chapman SW, Parker BL, Sale TC, Doner LA. Testing high resolution numerical models for analysis of contaminant storage and release from low permeability zones. *J Contam Hydrol.* 2012;136-137:106-116. doi:10.1016/J.JCONHYD.2012.04.006
14. Parker BL, Chapman SW, Guilbeault MA. Plume persistence caused by back diffusion from thin clay layers in a sand aquifer following TCE source-zone hydraulic isolation. *J Contam Hydrol.* 2008;102(1-2):86-104. doi:10.1016/J.JCONHYD.2008.07.003

15. Weatherill JJ, Atashgahi S, Schneidewind U, et al. Natural attenuation of chlorinated ethenes in hyporheic zones: A review of key biogeochemical processes and in-situ transformation potential. *Water Res.* 2018;128:362-382. doi:10.1016/J.WATRES.2017.10.059
16. Hyldegaard BH, Jakobsen R, Weeth EB, Overheu ND, Gent DB, Ottosen LM. Challenges in electrochemical remediation of chlorinated solvents in natural groundwater aquifer settings. *J Hazard Mater.* 2019;368:680-688. doi:10.1016/J.JHAZMAT.2018.12.064
17. (PDF) Sedimentology and petrology of the Eocene Memphis Sand and younger terrace deposits in surface exposures of western Tennessee. Accessed November 24, 2022.
https://www.researchgate.net/publication/287432324_Sedimentology_and_petrology_of_the_Eocene_Memphis_Sand_and_younger_terrace_deposits_in_surface_exposures_of_western_Tennessee
see
18. Larsen D, Gentry RW, Solomon DK. The geochemistry and mixing of leakage in a semi-confined aquifer at a municipal well field, Memphis, Tennessee, USA. *Applied Geochemistry.* 2003;18(7):1043-1063. doi:10.1016/S0883-2927(02)00204-4
19. Jazaei F, Waldron B, Schoefnacker S, Larsen D. Application of Numerical Tools to Investigate a Leaky Aquitard beneath Urban Well Fields. *Water 2019, Vol 11, Page 5.* 2018;11(1):5.
doi:10.3390/W11010005
20. Villalpando-Vizcaino R, Waldron B, Larsen D, Schoefnacker S. Development of a numerical multi-layered groundwater model to simulate inter-aquifer water exchange in shelby county, Tennessee. *Water (Switzerland).* 2021;13(18). doi:10.3390/w13182583
21. Parks WS, Mirecki JE. HYDROGEOLOGY, GROUND-WATER QUALITY, AND POTENTIAL FOR WATER-SUPPLY CONTAMINATION NEAR THE SHELBY COUNTY LANDFILL IN MEMPHIS, TENNESSEE. Published online 1992.

22. Jia C, Foran J. Air toxics concentrations, source identification, and health risks: An air pollution hot spot in southwest Memphis, TN. *Atmos Environ.* 2013;81:112-116.
doi:10.1016/J.ATMOSENV.2013.09.006
23. U.S.EPA. First Five-Year Review Report for SMALLEY-PIPER SUPERFUND SITE Shelby County, Tennessee. 2017;(July).
24. U.S.DeptHealthandHumanServices. SMALLEY-PIPER Collierville, Shelby County, Tennessee. 2006;(May).
25. Schulze-Makuch D. Longitudinal dispersivity data and implications for scaling behavior. *Groundwater.* 2005;43(3):443-456. doi:10.1111/J.1745-6584.2005.0051.X
26. Pavlovska M, Prekrasna I, Parnikoza I, Dykyi E. Soil Sample Preservation Strategy Affects the Microbial Community Structure. *Microbes Environ.* 2021;36(1):n/a.
doi:10.1264/JSME2.ME20134
27. Loeppert RH, Clarke ET. Reactions of Fe²⁺ and Fe³⁺ in calcareous soils. <https://doi.org/101080/01904168409363182>. 2008;7(1-5):149-163.
doi:10.1080/01904168409363182
28. ASTM D2487 17 Classification of Soils for Engineering Purposes Unified Soil Classification System - Studocu. Accessed January 30, 2023.
<https://www.studocu.com/ec/document/universidad-nacional-de-chimborazo/ensayo-de-materiales/astm-d2487-17-classification-of-soils-for-engineering-purposes-unified-soil-classification-system/7642846>
29. Standard operating procedure for soil organic carbon Walkley-Black method Titration and colorimetric method.

30. WALKLEY A, BLACK IA. An Examination of the Degtjareff Method for Determining Soil Organic Matter, and a Proposed Modification of the Chromic Acid Titration Method. *Soil Sci.* 1934;37(1):29-38.
31. EPA Method 6010D (SW-846): Inductively Coupled Plasma - Atomic Emission Spectrometry | US EPA. Accessed January 30, 2023. <https://www.epa.gov/esam/epa-method-6010d-sw-846-inductively-coupled-plasma-atomic-emission-spectrometry>
32. Usepa. Method 200.2, Revision 2.8: Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements. Accessed January 30, 2023. www.epa.gov
33. SW-846 Test Method 8260B: Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) | Hazardous Waste Test Methods / SW-846 | US EPA. Accessed January 30, 2023. <https://archive.epa.gov/epa/hw-sw846/sw-846-test-method-8260b-volatile-organic-compounds-gas-chromatographymass-spectrometry.html>
34. SW-846 Test Method 9211: Potentiometric Determination of Bromide in Aqueous Samples with Ion-Selective Electrode | US EPA. Accessed January 30, 2023. <https://www.epa.gov/hw-sw846/sw-846-test-method-9211-potentiometric-determination-bromide-aqueous-samples-ion-selective>

CHAPTER TWO

INVESTIGATING THE EFFECTS OF SAND CHARACTERISTICS ON THE ADSORPTION PATTERNS OF HEXAVALENT CHROMIUM

Abstract

Clastic sediment is the most important component of alluvial aquifers. Sand is the predominant grain size in these aquifers and is mostly composed of silica, mainly mineral quartz. Quartz has low chemical reactivity and high physical resistance, many research or industrial projects neglect to study the potential role of sand when they model the contaminant transport and fate or study the remediation options when a spill happens. Hexavalent chromium (Cr^{6+}) is a heavy metal species that forms the chromate oxyanion in water. Chromium can be introduced into water from anthropogenic or natural pathways. Many industries including electroplating, tanning, battery manufacturers, and textiles are amongst the common activities that release chromium in their wastewater. Hexavalent chromium is a carcinogen and mutagen; the US Environmental Protection Agency (USEPA) recommends the total chromium concentration in drinking water to be kept below 0.1 mg/l. Once Cr^{6+} contamination finds its way to a body of water, different remediation options become available. Regardless of which method is chosen for remediation, no clean up action can take place without thoughtful consideration of the effects of the sand. Although many studies assume that the effectiveness of sand and matrix materials are negligible in the adsorption process, this study intends to shine a light on the importance of studying the sand and varying sand characteristics can have on the adsorption patterns. This study is focused on investigating the adsorption of hexavalent chromium on Coastal Plain sand-rich sediments from the Memphis, Tennessee area. Multiple core samples were selected with varying grain size and clay content, and different chemical components, such as iron and organic carbon content. The core samples, having been collected from different locations and depths, were intended to cover a wide variety of

physical and chemical attributes of the Memphis aquifer in Shelby County, Tennessee. Different sets of experiments including pH studies, kinetic studies, and isotherm studies were performed to investigate the adsorption patterns of chromium on various sand samples under different conditions. In short, fine clay particles will result in an instant adsorption of hexavalent chromium, while organic carbon content yields the maximum adsorption capacity given enough time. Other chemicals present in the sand sample, such as iron, can also influence the adsorption. This study shows that not only the effect of sand in the adsorption process of hexavalent chromium is not negligible, but also the characteristics of sand can alter the way it affects the adsorption process.

Introduction

Clastic sediment is the most important component of alluvial aquifers¹. Sand is the predominant grain size in these aquifers and is mostly composed of silica, mainly mineral quartz². Quartz has low chemical reactivity and high physical resistance. ASTM-D2419-14 defines sand as particle of rock with size range of between 0.075 mm and 4.75 mm. As the proportion and grain size of sand increases in a sample of alluvium, the specific surface area decreases, thus decreasing interaction with its surroundings. Higher percentages of fine content (<75 um) in an alluvial sample increases the specific surface area and commonly includes chemically reactive clay-sized particles, which also have adsorptive capacity and lattice charge. Clay-sized particles commonly include silicate clay minerals, iron and aluminum oxides and hydroxides, organic carbon and sparingly soluble salts (e.g., calcite, dolomite, etc.)³. It is primarily the fine content of sand that dictates the overall chemical and physical interaction of sand with solutes and gases in water.

Whether the source of our drinking water is surface water or groundwater, the media in which the water flows and is stored affects the quality of water. In the case of surface water, water can be clean and pure at the source (rain), yet it may dissolve chemicals along the way and become

contaminated by the time it reaches the water treatment plant. Gotvand Dam, Iran, was constructed on a large salt deposit and as the water stagnated behind the dam, it dissolved the salt⁴. After time, the salinity of the water in Karoon River, the largest river in Iran, increased so much that more than 400,000 palm trees died and the biggest wetland in Iran turned to a wasteland⁵. Groundwater quality can also be altered while it is stored underground. Weathering of limestones can cause the dissolution calcite and dolomite, releasing calcium and magnesium species into groundwater, altering its quality and chemistry⁶. Anthropogenic contamination of groundwater can also happen via direct discharge of contaminants from the land above or next to the aquifer. Chrome-plating industries have been documented to be the source of soil and groundwater contamination across the US⁷. In Shelby County, Tennessee, Smalley-Piper facility was responsible for releasing hexavalent chromium into the aquifer, calling for a massive clean-up operation to begin to remediate the Superfund site. Whatever the cause and mechanism of contamination, investigation of how particular contaminants react, degrade or sorb on near-surface sediments is critical to remediation of surface water and groundwater pollution.

Hexavalent chromium (Cr^{6+}) is a heavy metal species that forms the chromate oxyanion in water. When heavily charged Cr^{6+} ions are released into water, they form oxygenated ions, and in that process overcompensation for charge occurs, giving this specific species a total negative charge⁸. The chromate ion is only fully protonated at very low pH ($\text{pH} \ll 1$) and as such forms a soluble oxyanion under near-surface conditions⁹. Chromium can be introduced into water from anthropogenic or natural pathways. Many industries including electroplating, tanning, battery manufacturers, and textiles are amongst the common activities that release chromium in their wastewater¹⁰⁻¹². Mining activities and weathering of rocks can also introduce chromium into water¹³. The chance for chromium contamination to occur is more likely in industrial and urban

areas. Hexavalent chromium is a carcinogen and mutagen, the US Environmental Protection Agency (USEPA) recommends the total chromium concentration in drinking water to be kept below 0.1 mg/l.

Once Cr⁶⁺ contamination finds its way to a body of water, different remediation options become available. Regardless of which method is chosen for remediation, no clean up action can take place without thoughtful consideration of the effects of the sand. One of the commonly implemented methods of remediation is using various adsorbents. Other methods can include ion exchange, chemical precipitation, and redox reactions^{8,14,15}. Natural attenuation due to biodegradation is not really an option, since chromium is not biodegradable and the bacteria digesting it are not readily available¹⁶. Since hexavalent chromium is stable and non-volatile, the only major factor contributing to its concentration loss is via sorption processes. Although many studies assume that the effectiveness of sand and matrix materials are negligible in the adsorption process, this study intends to shine a light on the importance of studying the sand and varying sand characteristics can have on the adsorption patterns.

This study is focused on investigating the adsorption of hexavalent chromium on Coastal Plain sand-rich sediments from the Memphis, Tennessee area. Multiple core samples were selected with varying grain size and clay content, and different chemical components, such as iron and organic carbon content. The core samples, having been collected from different locations and depths, were intended to cover a wide variety of physical and chemical attributes of the Memphis aquifer in Shelby County, Tennessee (Figure 1). It was the investigators' intention to show that not only the effect of sand in the adsorption process of hexavalent chromium is not negligible, but also the characteristics of sand can alter the way it affects the adsorption process.

Experimental

Site Description

Shelby County, Tennessee, is both geographically the largest county in the state of Tennessee, and houses close to a million people, making it the most populous county in the state of Tennessee¹⁷. Located at the southwestern corner of the state, it sits along the Mississippi River and neighbors the states of Arkansas and Mississippi and is located on the northern part of the Mississippi embayment (Figure 1). The focus of the study is the unconsolidated sand-dominated Pliocene and Eocene fluvial to deltaic Coastal Plain deposits. The Eocene Memphis aquifer supplies most of the drinking and industrial water in western Tennessee, and is confined to semi-confined by the overlying upper Claiborne confining unit (UCCU)¹⁸⁻²¹. The UCCU separates the unconfined shallow aquifer, which is mainly comprised of the Pliocene Upland Complex and Pleistocene to Holocene fluvial-terrace and alluvium, and the Memphis aquifer²². The mineralogy of the shallow, Memphis, and locally present Cockfield, aquifers is mostly quartz, with varying quantities of clay and iron oxyhydroxides; fine lignitic organic are present, especially in deltaic sediments²³⁻²⁵. The clay mineralogy is primarily kaolinite and illite with varying content of smectite^{23,24,26}.

Materials

Sodium Chromate was used as the main source to produce hexavalent chromium into the solutions. Nitric acid and sodium hydroxide were used to adjust the pH of the solutions. Iron(II) chloride and activated charcoal were used as reagents in additional experiments. Sodium bromide was also used as a conservative tracer. All chemicals used in this study were of analytical grade and were used without further purification. The experiments were performed in the batch method, utilizing 15 ml

polyethylene centrifuge tubes. These centrifuge tubes have been shown to not release microplastic to the system even with shaking, and not to interfere with the reaction in any other fashion⁸.

Methods

Core samples were collected using sonic drilling technique. A total of six sand samples were collected from boreholes drilled at three locations, primarily from the Memphis aquifer but also a sample representing the shallow aquifer. Figure 1 shows the approximate locations of the monitoring wells. One sand sample was collected from each of MSA-1 and 99s2 wells, and four sand samples were collected from different depths of CVL-1 well.

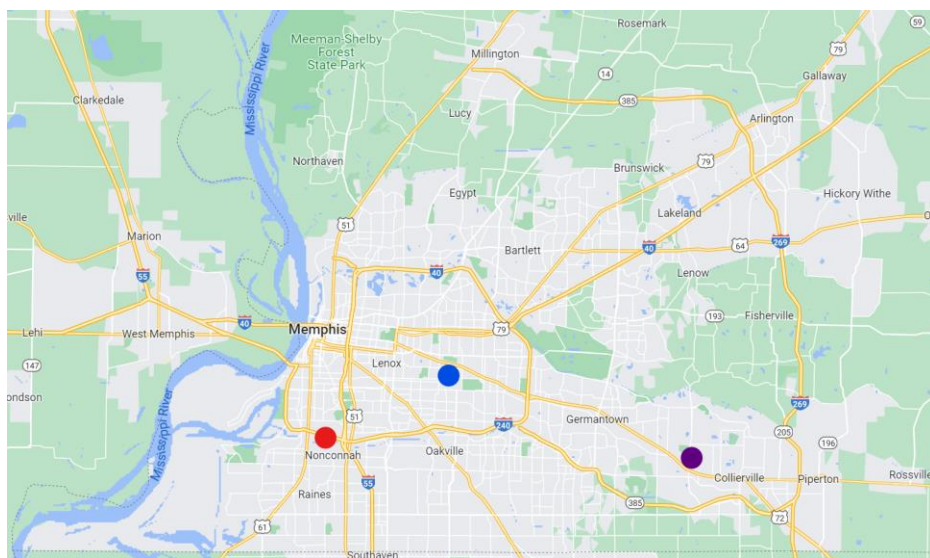


Figure 1: Borehole sample locations in Shelby County, Tennessee.

The red, blue, and purple dots respectively reflect the locations of MSA-1, 99s2, and CVL-1 monitoring wells.

The experimental methods used in this paper have been previously explained at length in Sharafoddinzadeh et al. (in review). Samples identification is explained in Table 1.

Table 1: Sand samples location, depth, and ID.

<i>Sample Location</i>	<i>Sample Depth (m)</i>	<i>Sample ID</i>	<i>Aquifer</i>
<i>CVL-1</i>	<i>17*</i>	<i>C057</i>	<i>Shallow</i>
<i>CVL-1</i>	<i>54</i>	<i>C177</i>	<i>Memphis</i>
<i>CVL-1</i>	<i>66</i>	<i>C217</i>	<i>Memphis</i>
<i>CVL-1</i>	<i>76</i>	<i>C250</i>	<i>Memphis</i>
<i>MSA-1</i>	<i>72</i>	<i>A237</i>	<i>Memphis</i>
<i>99s2</i>	<i>76</i>	<i>S250</i>	<i>Cockfield</i>

Instrumentation

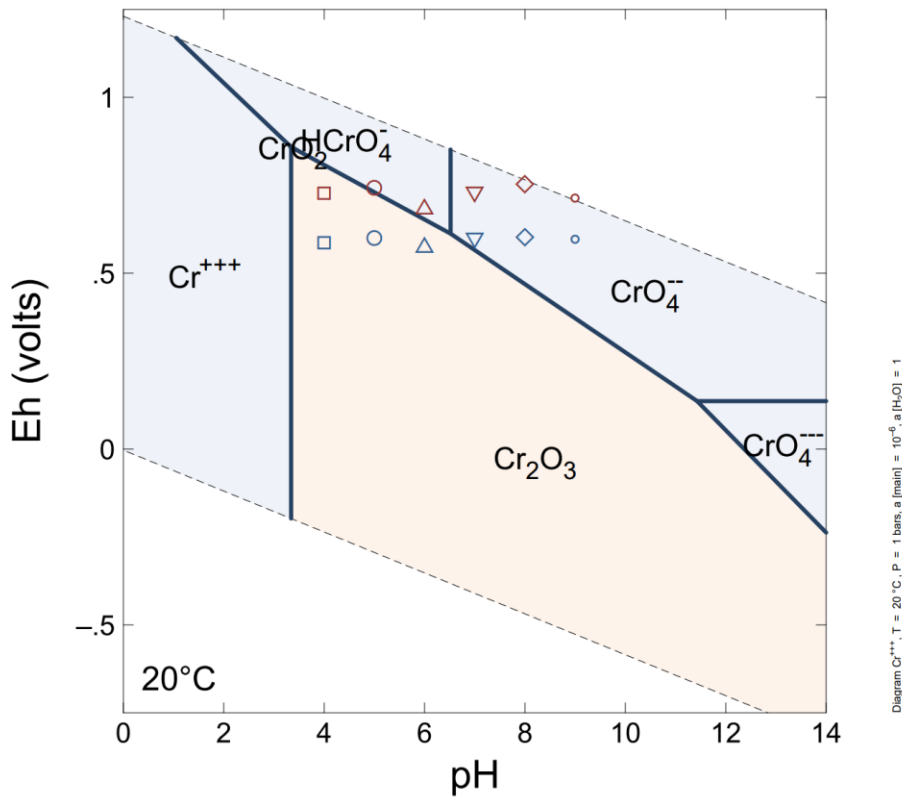
A pH meter was used to measure and set the pH of the solutions to the desired value. Oxidation Reduction Potential (ORP) meter was used to measure the oxidation-reduction potential of the prepared solutions. The concentration measurements were done using a UV-Vis spectrophotometer at first, but later was changed to using an ICP-MS (Inductively Coupled Plasma-Mass Spectroscopy) instead due to the fact that even after centrifugation some of the solutions contained suspended colloidal particles.

Results and discussion

Oxidation reduction potential and speciation of chromium

In this study, the ORP of every solution was measured to indicate the speciation of chromium species present in the solution. Chromium can be present in a solution in various different oxidation states, hexavalent chromium being the dominant state in aqueous form. The speciation of

hexavalent chromium in an aqueous solution can change depending on the concentration of chromium in the solution, the pH of the solution, temperature, pressure, and other chemicals present in the system. The ORP measurements of all solutions showed positive values, determining the solution to be in oxidizing state. The oxidizing state of the solution in addition to the type of salt used for this study, i.e. sodium chromate, points to the speciation of chromium to be hexavalent rather than trivalent chromium. Figure 2 shows the Pourbiac diagrams for chromium speciation under experimental conditions.



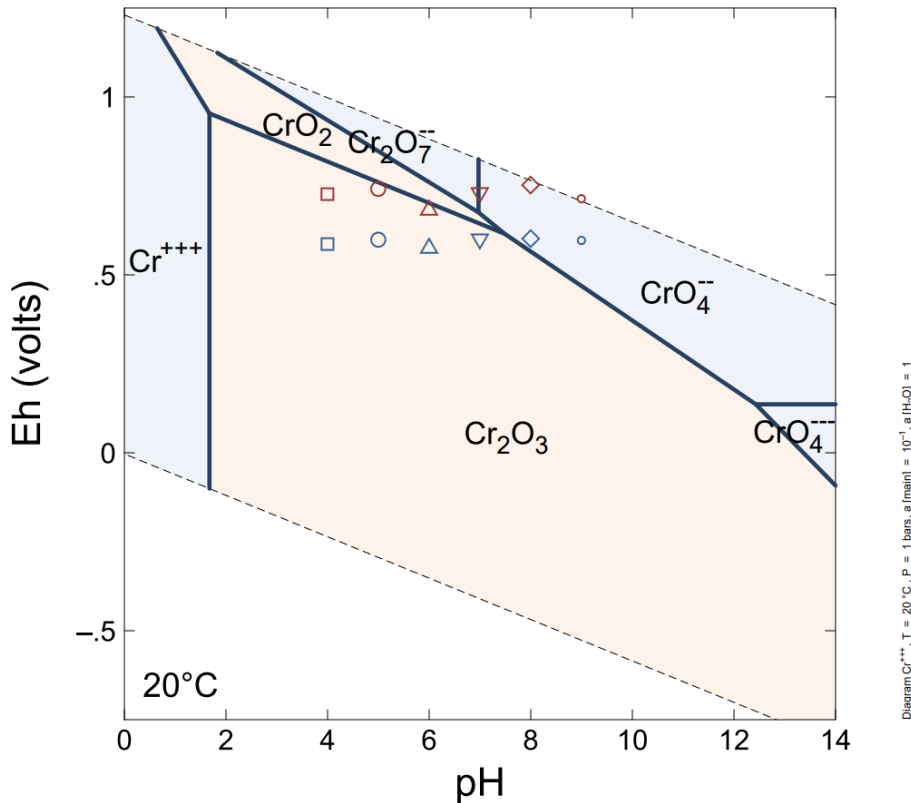


Figure 2: Pourbaix diagrams for chromium speciation under different initial concentrations.

Dark red marks A237 samples and blue marks C057 samples.

Depending on the initial Cr concentration, activity changes between 10^{-6} mol to 1 mol, Cr minerals and aqueous phases also change. Although the initial inclination was that the primarily considering speciation is hexavalent Chromium, the Eh-pH diagrams suggest a tendency for chromium speciation to partition into Cr_2O_3 as stable phases. However, the visual inspection of the solutions in the lab provided proof that all of the chromium in the solution was in the aqueous phase and no precipitate was observed in the solution. Therefore, the experimental results reflect a metastable condition that over time will result in mineral partitioning of Cr, especially for the lower Eh condition ($\sim 0.5 - 0.6\text{V}$). These diagrams were generated using computer software, and the conditions were not buffered.

Background chromium concentration

In this study, the adsorption was calculated using mass balance equation. Therefore, it is necessary to examine whether the sand samples have been exposed to chromium prior to the excavation and experiments in the lab. This factor, known as the background concentration, was measured for all sand samples prior to the other experiments via acidifying the sand samples at $\text{pH} = 2$ and $\text{pH} = 6$ to determine if the sand samples contain any chromium, and if those chromium concentrations can be released at the pH intended for the experiments to take place. The results showed below detection limit concentrations of chromium under all tested conditions. Therefore, the answer to both questions is no, and the mass balance equation could be used without considering a separate term for background concentration. Although background concentration was not detected, by using mass balance equation an unwanted instrumental error can be created in cases where the adsorbed amount is below detection limit. These numbers, if measured directly, would have come back as negligible, below the instrument's detection limit. However, since mass balance equation is being used to calculate these concentrations instead of directly measuring them, a certain number is being returned as adsorbed concentration. In order to remedy this error, it must be mentioned that for the instrument in this study, the method detection limit was anything lower than 0.040 mg/l , and any number reported which is lower than the method detection limit should be regarded as zero or below detection limit. Desorption of chromium through acid release and direct measurement of the concentration is not recommended in this study because the desorption efficiency is not 100% and at these concentrations where the adsorption capacities are very low the inefficiency of the desorption method generates big errors. Acid desorption is also cost and labor intensive, and environmental unfriendly.

pH studies

The first set of experiments performed to study the effect of different types of sand samples on adsorption behavior of chromium was pH studies. During the entirety of this project, the goal was to keep the conditions as close to the natural aquifers as possible. However, it was deemed important to cover a wide range of different pH conditions, in order to be able to observe the reactions which might occur under harsh conditions. For this set of experiments, the initial concentration of chromium in the solutions was set to 1 mg/l. The shaking time was fixed at 1 hour, and the pH ranged from 4 to 9. This experiment had six varying pH conditions, where pH was set to 4, 5, 6, 7, 8, and 9, respectively. Figure 3 shows the adsorption of chromium under varying pH conditions.

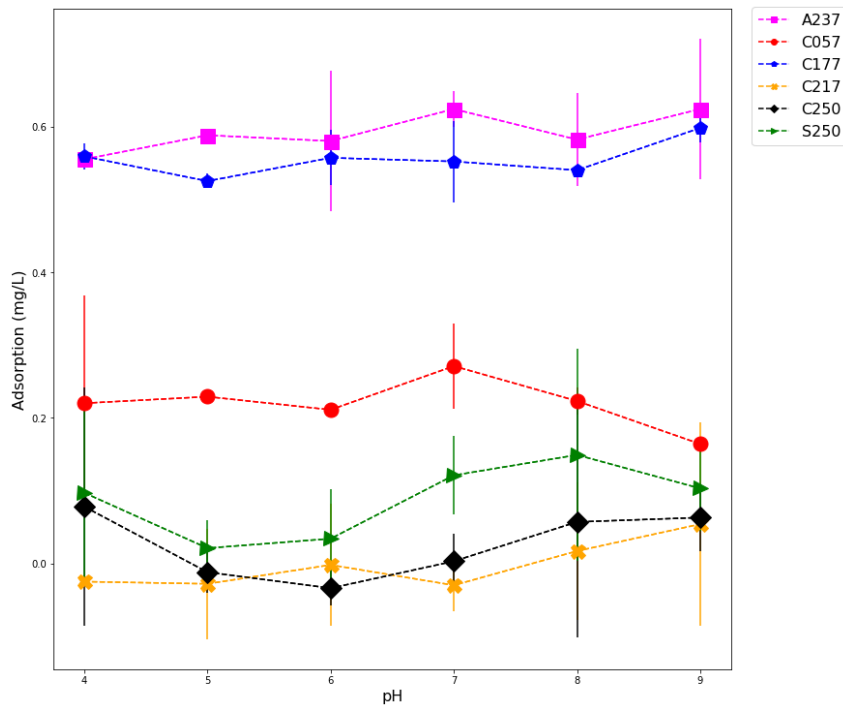


Figure 3: Adsorption of chromium under varying pH conditions.

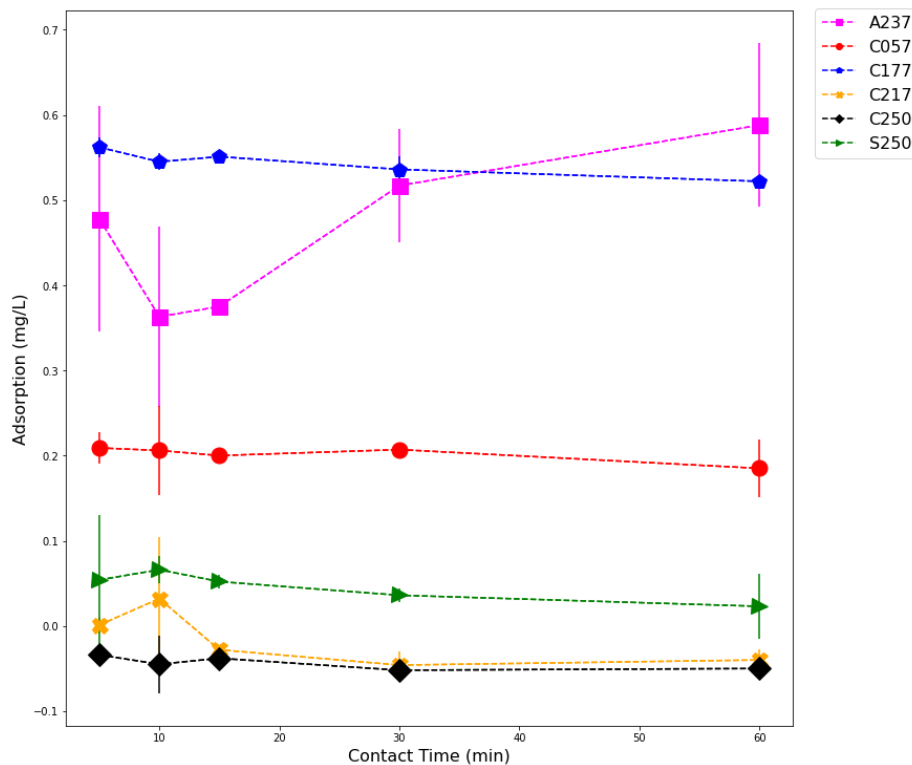
As observed in Figure 3, within the pH range of 4 to 9, pH has no significant effect on adsorption.

However, another pattern starts to emerge which separates the sand samples into two distinct

groups, one group shows adsorption while the other group shows minimal or no interaction between the sand and chromium.

Kinetic studies

Kinetic studies were the second set of experiments performed on the sand samples. Kinetic studies were performed to find the rate at which the reaction between the sand samples and chromium reaches equilibrium. For these experiments the pH was set at 6, and the initial concentration was kept constant across the experiment at the value of 1 mg/l. The shaking time of samples varied from 5 minutes to 72 hours, in non-equal discretization. In the first hour of shaking, five samples were collected at the increments of 5 minutes, 10 minutes, 15 minutes, 30 minutes, and 60 minutes. After the initial hour passed, the next five samples were collected at the increments of 4 hours, 8 hours, 24 hours, 48 hours, and 72 hours; making up the ten experimental conditions chosen for this set of experiments. Figure 4 A and B show the adsorption of chromium at different time intervals.



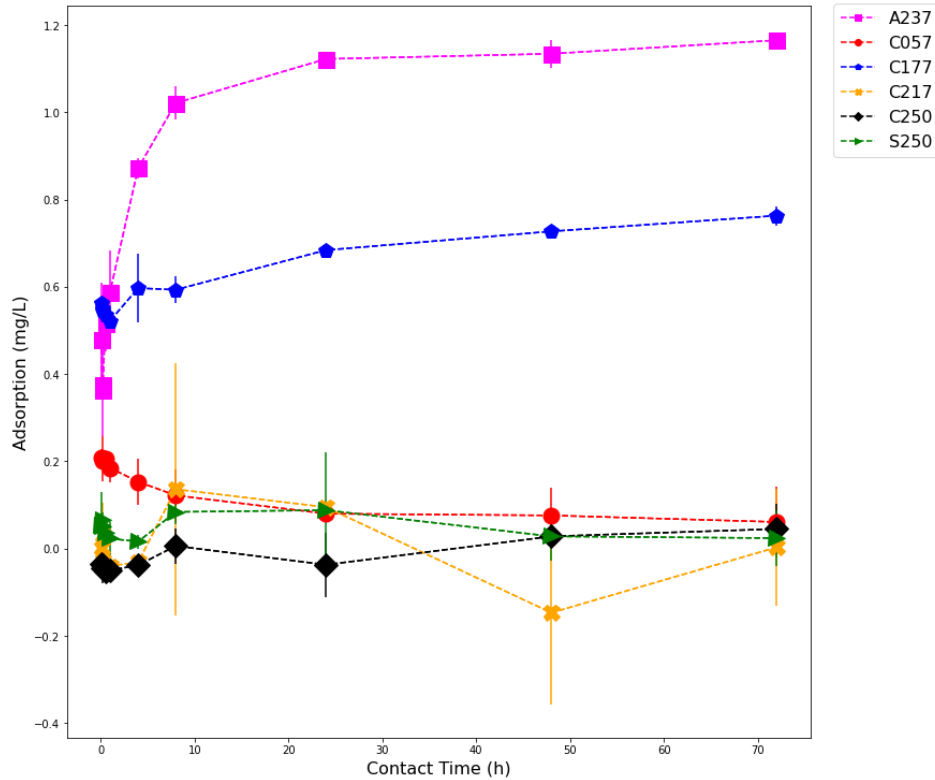


Figure 4: adsorption of chromium at different time intervals.

Figure Four A shows the adsorption within the first hour, while Figure Four B shows the whole 72 hours of the experiment. The distinct separation of the sand samples which was observed in the previous experiment is also pronounced here. The group of sand samples which showed minimal or no interaction with chromium remained the same between the first 5 minutes to the last 72 hours. The two sand samples which show adsorption towards chromium show more adsorption capacity with addition of time. Although the equilibrium seems to be reached 24 hours, it was decided to set the experimental time for other set of experiments to 1 hour due to experimental conditions and equipment deficiencies. The difference between adsorption at 1 hour mark and 24 hours mark was insignificant and keeping the temperature constant for 24 hours while shaking the samples seemed too arduous. In the group of sand samples which show adsorption towards chromium, two distinct patterns can be observed. C177 sample shows a rapid, almost instantaneous adsorption within the

first five minutes. On the other hand, A237 sample shows a slow, yet steady uptake in the adsorption capacity, until equilibrium is reached in about 24 hours.

Isotherm studies

The third set of experiments performed was conducted to investigate the effect of initial concentration of chromium on the adsorption patterns. Isotherm studies help determine the adsorption mechanisms. For this set of experiments the pH of chromium solutions was set to 6, and the shaking time was fixed at 1 hour, the amount of time necessary for chemical equilibrium to be reached. The initial concentration of the solutions varied from 0.1 mg/l to 10 mg/l, making up a total of six varying conditions. The concentration of the solutions was 0.1, 0.5, 1, 2.5, 5, and 10 mg/l, respectively. Figure 5 shows the effect of initial concentration on the adsorption capacity of different sand samples.

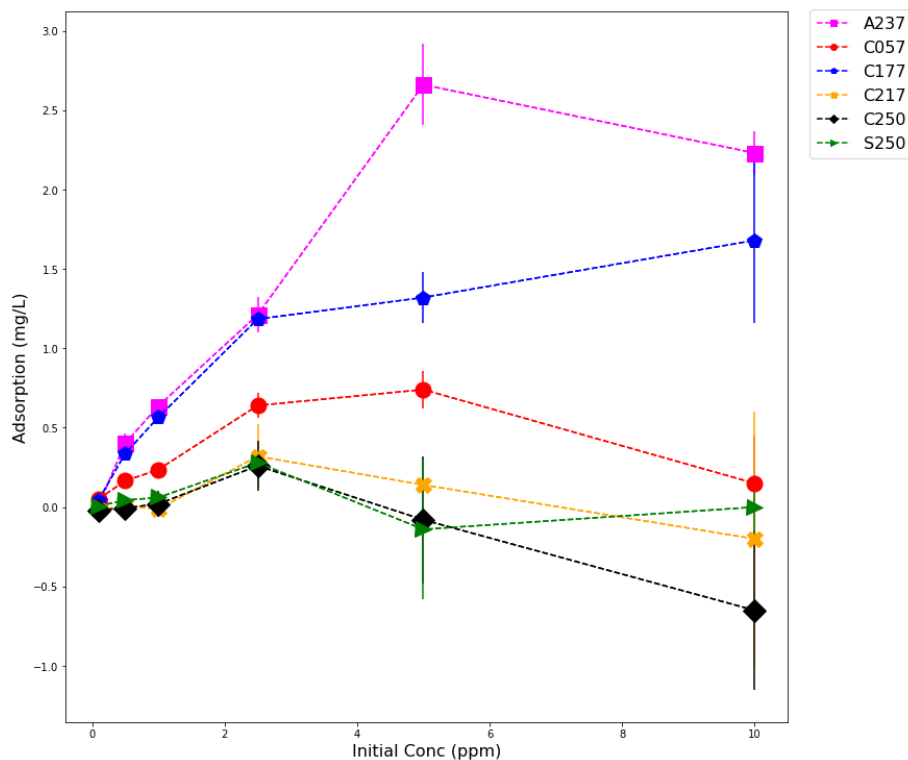


Figure 5, adsorption of chromium at varying initial concentrations.

As shown in Figure 5, the sand samples exhibit three distinct behaviors. C217, C250, and S250 samples show no chromium adsorption across the different concentrations. C057 shows minimal adsorption, and C177 and A237 show distinct interaction between sand samples and chromium. These distinct behaviors are highlighted when attempting to fit the isotherm data obtained from these experiments on peer-reviewed adsorption isotherm models such as Langmuir and Freundlich. Isotherm models could not be fitted for the samples which showed no adsorption. However, the calculated R^2 values showed that Langmuir model best describes the adsorption behavior of C057, C177 and A237 samples. This result was expected in accordance with the definition of Langmuir model, which is described as a physical, single-layer adsorption of the adsorbate on the surface of the adsorbent. Therefore, it can be stated that the process is adsorption, not absorption. Langmuir constants and R^2 values for these three samples are available in the supplemental file.

Effects of sand characteristics

Upon completion of the above-mentioned sets of experiments, the investigation shifted into finding out why the sand samples reacted differently when the chromium was introduced into the system. The three sand samples singled out by the experiments were A237, C057, and C177 which contained the highest percentage of organic carbon, highest concentration of iron, and smallest grain size with high percentage of fine (silt and clay) content, respectively. A237 has shown the highest adsorption capacity throughout the experiment with the highest of them all being 9.29 mg/kg of soil. A237 also has shown the biggest difference between the duplicate sample (error bars). This is due to the nature of the sample, which contained lignite grains. Since this study attempted not to alter the sand samples characteristics as much as possible, these irregularities in the sand samples were not homogenized. Lignite is organic carbon, and it behaves in a similar fashion to activated charcoal, which is a known adsorbent. Therefore, it is not surprising that the

sample which contains the highest amount of lignite shows the highest adsorption capacity. The adsorption of chromium on A237 over time exhibited the pattern expected of activated charcoal-based adsorbents, where the maximum adsorption capacity increases over time until it reaches equilibrium, and the trend is logarithmic. On the other hand, C057 sample which contained the highest amount of iron did not show as much adsorption as expected. Iron has the potential to reduce chromium⁶⁺ to chromium³⁺, which renders it insoluble in water resulting in precipitation of chromium³⁺. Based on the observations during the experiments, it was determined that the iron present in the sand sample collected from the shallow aquifer was in the form of iron³⁺, not iron²⁺. Iron²⁺ is the speciation which can act as the electron donor, releasing one electron and reducing chromium⁶⁺ to chromium³⁺. But the speciation present in the sand sample collected from the shallow aquifer was mostly in the form of iron³⁺, therefore it was incapable of reducing chromium⁶⁺. The highest adsorption capacity observed for C057 sample was recorded at 2.26 mg/kg of soil. The sample which was most unexpected to show adsorptive behavior was C177. This sand sample was collected from right under the UCCU, and it had the smallest grain size and highest amount of fine (silt and clay) content. This sample showed the second highest maximum adsorption capacity with 6.46 mg/kg of soil. C177 also showed instantaneous adsorption, where about 75% of adsorption happened in the 5 minutes of the experiment. This proves that even physical characteristics of sand samples can play a huge role in the transport and fate of contaminants.

In order to verify whether the patterns observed were in fact due to the presence of organic carbon and iron, the most inert sand sample was chosen (C250). C250 sand sample was dosed with 3 different concentrations of activated charcoal, and again in a separate batch doses three times with 3 different concentrations of Fe(II) chloride, to comprise a final total of six samples. These six

additional sand samples underwent the experimental procedure exactly the same as described before. The initial concentration of the chromium solution was set at 1 mg/l, pH was set at 6, and the shaking time was 1 hour. These samples showed a direct correlation between the concentration of the added adsorbents (activated charcoal and Iron(II) chloride) and the amount of chromium adsorbed, further validating the hypothesis that the chemistry of sand samples effects the adsorption of various potential contaminants.

Conclusion

This study pursued two goals, first to demonstrate the importance of studying the sand prior to conducting any contaminant transport modelling or remediation effort. This goal was achieved by highlighting the different behaviors the sand samples exhibited when chromium was introduced to the system. While some samples showed no interaction between the sand and chromium, others showed patterns of retardation or adsorption of chromium. The second goal focused on how each of the characteristics of the sand affect the contaminant transport. The contributing factors determined to be physical, as in grain size and fine (clay) content, or chemical, as in iron or organic carbon content. The experiments performed consist of pH studies, kinetic studies, isotherm studies, and additional experiments. These experiments differentiated the sand samples into three distinct groups behaviorally. One cluster of sand samples showed no interaction with the contaminants, one group showed minimal interaction, and the other group showed distinguishable adsorption patterns. The sample containing the most clay content (C177) showed instant retardation of chromium. The sample with organic carbon content (A237) showed slow, yet steady adsorption of chromium which was impacted by time and concentration of chromium. C057 contained the most amount of iron and was expected to reduce the hexavalent chromium to trivalent chromium, however the oxidation of iron prevented it from entering the reaction as expected. Knowing the

attributes of the sand, and how those attributes affect a specific contaminants' transport and fate helps the modelers to better understand and calibrate their models to what is likely to happen in the natural setting.

References

1. Ahmed KM, Bhattacharya P, Hasan MA, et al. Arsenic enrichment in groundwater of the alluvial aquifers in Bangladesh: an overview. *Applied Geochemistry*. 2004;19(2):181-200.
doi:10.1016/J.APGEOCHEM.2003.09.006
2. Négrel P, Petelet-Giraud E, Barbier J, Gautier E. Surface water–groundwater interactions in an alluvial plain: Chemical and isotopic systematics. *J Hydrol (Amst)*. 2003;277(3-4):248-267.
doi:10.1016/S0022-1694(03)00125-2
3. Nyakairu GWA, Kurzweil H, Koeberl C. Mineralogical, geochemical, and sedimentological characteristics of clay deposits from central Uganda and their applications. *Journal of African Earth Sciences*. 2002;35(1):123-134. doi:10.1016/S0899-5362(01)00077-X
4. Jalali L, Zarei M, Gutiérrez F. Salinization of reservoirs in regions with exposed evaporites. The unique case of Upper Gotvand Dam, Iran. *Water Res*. 2019;157:587-599.
doi:10.1016/J.WATRES.2019.04.015
5. Gutiérrez F, Lizaga I. Sinkholes, collapse structures and large landslides in an active salt dome submerged by a reservoir: The unique case of the Ambal ridge in the Karun River, Zagros Mountains, Iran. *Geomorphology*. 2016;254:88-103. doi:10.1016/J.GEOMORPH.2015.11.020
6. Singh AK, Mondal GC, Kumar S, Singh TB, Tewary BK, Sinha A. Major ion chemistry, weathering processes and water quality assessment in upper catchment of Damodar River basin, India. *Environmental Geology*. 2008;54(4):745-758. doi:10.1007/S00254-007-0860-1/FIGURES/13
7. Hausladen DM, Alexander-Ozinskas A, McClain C, Fendorf S. Hexavalent Chromium Sources and Distribution in California Groundwater. *Environ Sci Technol*. 2018;52(15):8242-8251.
doi:10.1021/ACS.EST.7B06627/ASSET/IMAGES/LARGE/ES-2017-06627H_0005.JPEG

8. Sharafoddinzadeh D, Salehi M, Jansone-Popova S, Herath A, Bhattacharjee L. Advance modification of polyacrylonitrile nanofibers for enhanced removal of hexavalent chromium from water. *J Appl Polym Sci.* 2022;139(20):52169. doi:10.1002/APP.52169
9. Prieto M, Heberling F, Rodríguez-Galán RM, Brandt F. Crystallization behavior of solid solutions from aqueous solutions: An environmental perspective. *Progress in Crystal Growth and Characterization of Materials.* 2016;62(3):29-68.
doi:10.1016/J.PCRYSGROW.2016.05.001
10. Laxmi V, Kaushik G. Toxicity of Hexavalent Chromium in Environment, Health Threats, and Its Bioremediation and Detoxification from Tannery Wastewater for Environmental Safety. *Bioremediation of Industrial Waste for Environmental Safety.* Published online 2020:223-243.
doi:10.1007/978-981-13-1891-7_11
11. Velusamy S, Roy A, Sundaram S, Kumar Mallick T. A Review on Heavy Metal Ions and Containing Dyes Removal Through Graphene Oxide-Based Adsorption Strategies for Textile Wastewater Treatment. *The Chemical Record.* 2021;21(7):1570-1610.
doi:10.1002/TCR.202000153
12. Kumar V, Dwivedi SK, Oh S. A review on microbial-integrated techniques as promising cleaner option for removal of chromium, cadmium and lead from industrial wastewater. *Journal of Water Process Engineering.* 2022;47:102727. doi:10.1016/J.JWPE.2022.102727
13. Bolaños-Benítez V, van Hullebusch ED, Birck JL, et al. Chromium mobility in ultramafic areas affected by mining activities in Barro Alto massif, Brazil: An isotopic study. *Chem Geol.* 2021;561:120000. doi:10.1016/J.CHEMGEO.2020.120000

14. Liu X yin, Xu L hua, Zhuang Y feng. Effect of electrolyte, potential gradient and treatment time on remediation of hexavalent chromium contaminated soil by electrokinetic remediation and adsorption. *Environ Earth Sci.* 2023;82(1):1-13. doi:10.1007/S12665-022-10673-6/TABLES/6
15. Siddika A, Islam MM, Parveen Z, Hossain MF. Remediation of Chromium (VI) from Contaminated Agricultural Soil Using Modified Biochars. *Environ Manage.* 2022;71(4):809-820. doi:10.1007/S00267-022-01731-7/FIGURES/6
16. Akram A, Tara N, Khan MA, et al. Enhanced remediation of Cr⁶⁺ in bacterial-assisted floating wetlands. *Water and Environment Journal.* 2020;34(S1):970-978. doi:10.1111/WEJ.12551
17. Tennessee Counties by Population. Accessed June 5, 2023. https://www.tennessee-demographics.com/counties_by_population
18. Carmichael JK, Kingsbury JA, Larsen D, Schoefnacker S. Preliminary evaluation of the hydrogeology and groundwater quality of the Mississippi River Valley alluvial aquifer and Memphis aquifer at the Tennessee Valley Authority Allen Power Plants, Memphis, Shelby County, Tennessee. *Open-File Report.* Published online 2018. doi:10.3133/OFR20181097
19. Sahagún-Covarrubias S, Waldron B, Larsen D, Schoefnacker S. Characterization of Hydraulic Properties of the Memphis Aquifer by Conducting Pumping Tests in Active Well Fields in Shelby County, Tennessee. *JAWRA Journal of the American Water Resources Association.* 2022;58(2):185-202. doi:10.1111/1752-1688.12991
20. Hydrogeology and Ground-water Flow in the Memphis and Fort Pillow Aquifers ... - J. V. Brahana, Robert E. Broshears - Google Books. Accessed June 5, 2023. <https://books.google.com/books?hl=en&lr=&id=onXuAAAAMAAJ&oi=fnd&pg=PP7&dq=%3B+Brahana+and+Broshears,+2001&ots=jqieGaCFNZ&sig=YWrkzLbtNEARQPprQ10zzrgOe4E#v=onepage&q=%3B%20Brahana%20and%20Broshears%2C%202001&f=false>

21. Geology and Ground-water Resources of the Memphis Sand in Western Tennessee - William Scott Parks, J. K. Carmichael - Google Books. Accessed June 5, 2023.
https://books.google.com/books?hl=en&lr=&id=nExBOc-RcAwC&oi=fnd&pg=PA1&dq=Parks+and+Carmichael,+1990&ots=1pHqsZlp5V&sig=U_jOGSsQmOHhG0ERX8mQAt1MnNM#v=onepage&q=Parks%20and%20Carmichael%2C%201990&f=false
22. Van Arsdale RB, Arellano D, Stevens KC, et al. Geology, Geotechnical Engineering, and Natural Hazards of Memphis, Tennessee, USA. *Environmental & Engineering Geoscience*. 2012;18(2):113-158. doi:10.2113/GSEEGEOSCI.18.2.113
23. Novel Techniques for Investigating Recharge to the Memphis Aquifer - Randy Gentry - Google Books. Accessed June 5, 2023. <https://books.google.com/books?hl=en&lr=&id=7Fheq-pql6YC&oi=fnd&pg=PR9&dq=memphis+aquifer+Gentry+et+al.,+2006&ots=mgWk0mk1uW&sig=vIm6f6ypBTukrWFPm7SXUPXC81E#v=onepage&q=memphis%20aquifer%20Gentry%20et%20al.%2C%202006&f=false>
24. Larsen D. Petrology of the Memphis Sand in the Northern Mississippi Embayment. Accessed June 5, 2023. <https://www.researchgate.net/publication/287432323>
25. Larsen D. Larsen.fm. Accessed June 5, 2023.
<https://www.researchgate.net/publication/287432324>
26. Larsen D, Gentry RW, Solomon DK. The geochemistry and mixing of leakage in a semi-confined aquifer at a municipal well field, Memphis, Tennessee, USA. *Applied Geochemistry*. 2003;18(7):1043-1063. doi:10.1016/S0883-2927(02)00204-4