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THE PLACEMENT OF REMEDIATION AMENDMENTS INTO CONTAMINATED SEDIMENTS VIA WATERJET TECHNOLOGIES

by

GAVIN H. R. RISLEY

A THESIS

Presented to the Faculty of the Graduate School of the

MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY

In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE IN ENVIRONMENTAL ENGINEERING

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Approved by

Dr. Andrew Curtis Elmore, Advisor Dr. Joel G. Burken, Advisor Dr. Grzegorz Galecki

PUBLICATION THESIS OPTION

The purpose of Sections 1-3 is to provide background information exceeding that displayed within the journal manuscript which is found on pages 12-35. The paper in this thesis was submitted as a journal article to Journal of Environmental Engineering on February 1, 2010 and is currently under review. The final section, Section 4, has been added for supplemental information.

ABSTRACT

The use of amendments to perform in situ remediation of contaminated sediments is a technique that is relatively mature. The need exists to develop a method of amendment delivery that will efficiently place the amendments into the contaminated zone at depth with minimal impacts to the benthic communities and contaminant resuspension. Waterjets have been used for hundreds of years as an excavation, cutting, and cleaning tool, but they can also be used to inject remediation amendments into contaminated sediments if setup properly. In order to test this concept, a waterjet amendment injection system and nozzle have been developed and tested. The system functionality was tested by the characterization of the concentration distributions of the injected amendments into a surrogate sediment. The powdered activated carbon characterization was performed through the use of a novel spectroradiometry technique developed in this work, while granular iron characterization was done using visual comparison and a digestion/Inductive Coupled Plasma mass spectrometry analysis. The distribution patterns exhibited by both of the injected amendments were very similar, while the injection depths varied between the two types of amendment. Analysis of these patterns and depths provides insight as to what occurs during an injection and can lead to the more efficient placement of these waterjet injected remediation amendments.

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SECTION

1. INTRODUCTION

1.1 CONTAMINATED SEDIMENTS

Beginning in the early 1970s, concerns began to develop over the quality of our surface waters. As the contamination of these waters was studied more closely, and the contaminants infecting these waters were better understood, the sediments that underlie these contaminated water bodies also gained interest. Many of the contaminants typically found in these polluted water bodies exhibit hydrophobic tendencies, and therefore tend to adsorb very strongly to sediment particles. This means that many times, it is the sediment that will be more contaminated than the water column lying directing above. Therefore, more research towards the understanding of sediment/contaminant relationships has been undertaken as a means towards the remediation and cleanup of these areas.

When examining contaminated sediment it is important to understand what exactly constitutes contaminated sediment, to recognize the impacts of contaminated sediments, and to comprehend the quantity of sediments that are considered to be contaminated. The United States Environmental Protection Agency (US-EPA) (1993) defines contaminated sediment as soils, sand, organic matter, or minerals that accumulate on the bottom of a water body and contain toxic or hazardous materials that may adversely affect human health or the environment. This contaminated sediment may wash from land, be deposited from the air, erode from aquatic banks or beds, or form from underwater breakdown or buildup of minerals. This is a broad definition that encompasses a large quantity of the United States' sediment. The US-EPA (1998) estimated that approximately 10 percent of the sediment underlying our Nation's surface water is sufficiently contaminated with toxic pollutants that pose potential risks to fish, humans, and wildlife that eat fish. This means that approximately 1.2 billion cubic yards out of approximately 12 billion cubic yards of total surface sediments are contaminated, which is where many organisms reside and where exchange processes between the sediment and overlying surface water occur.

The US-EPA's (1993) contaminated sediment definition is obscure when describing the types of contaminants affecting sediments. The definition states contaminant sediments are toxic or hazardous materials that may adversely affect human health or the environment. This could be any number of compounds, but perhaps the most common and researched are those known as hydrophobic organic compounds (HOCs). These compounds bioaccumulate and even biomagnify in many aquatic organisms, which can lead to many possible adverse effects. Research performed by Helm et al. (2008) exhibited this by showing that for certain polychlorinated biphenyl (PCB), which are HOC's, congeners there was an increasing mean concentration exhibited from plankton to forage fish. Helm at al. (2008) also states that the benthic dwelling *Diporeia* and slimy sculpin used in testing displayed greater relative PCB congener concentrations to other invertebrates and forage fish. Once the contaminants affect these organisms and enter the food chain, they have the potential to affect human health, which was illustrated in work performed by Juan et al. (2002). Juan et al. (2002) performed a mass balance and found that food consumed containing PCB congeners led to PCB absorption within the human body. These absorbed contaminants may potentially cause harm to human health depending on the level of exposure. Rahuman et al. (2000) denotes that PCBs have the

aptitude to cause a variety of conditions including liver damage, skin irritation, reproductive dysfunction, and even cancer. It is due to these prospects of exposure to both aquatic organisms and the human population that enforces the importance of this effort to remediate contaminated sediments.

1.2 CONTAMINATED SEDIMENT REMEDIATION ALTERNATIVES

The US-EPA created a guide for selecting contaminated sediment remediation techniques in 1993. This guide indicates that there are two foremost remediation options, which are dredging of the contaminated sediments from the area or in situ treatment of the contaminated area. While dredging is quite often considered to be the best possible option at many contaminated sites, there has been research performed that suggests that this method has several potential drawbacks. Sanchez et al. (2002) made reference to a dredging study performed by the General Electric Company (GEC). Sanchez et al. (2002) summarized GEC's review of 54 dredged sites by stating the five reoccurring faults GEC discovered in their research. These five reoccurring faults were 1) many times the environmental dredging process will not effectively reduce the surface sediment concentrations to acceptable levels; 2) dredging has yet to be linked to reductions in fish contaminant levels; 3) dredging projects are expensive and timely; 4) dredging causes resuspension of contaminants into the water; and 5) dredging technologies and expertise in large rivers is limited. Other researchers have found similar faults in this remediation technique, especially when studying the issue of contaminant resuspension during the dredging process (Gustavson et al., 2008 and Sanchez et al., 2002). Therefore, because of the issues associated with dredging, the use of an effective in situ treatment would be much more preferable.

The US-EPA (1993) stated several different in situ treatment possibilities, which include biological treatment, chemical treatment, solidification/stabilization treatment, and subaqueous capping methods. Biological treatment is a proven technology for a wide range of organic contaminants, but it fails to effectively remediate inorganics (US-EPA, 1993). The remediation of organics, however, like PCBs, has been extensively researched. A recent research performed by May et al. (2008) and Bedard (2008) both illustrate the possible effectiveness that this type of treatment can obtain through the use of bacterial cultures from contaminated sites. Bedard (2008) reviews several published works on the use of bacteria for PCB remediation. The author's review of her own 1995 research indicated that through the use of bacteria a 62% reduction of the PCB molar percentage (mol%) in the sediment could be achieved within 93 days of bacteria delivery. While there have been several published sets of data with similar results, this method does rely on specific bacteria, and if these organisms are not previously present in the contaminated area or if the conditions in an area are unsuitable for these organisms, success is unlikely. Even if the conditions are appropriate, the use of the specific inoccula is not a proven technology.

When considering chemical treatment, possibly the most researched and proven option is the employment of amendments in order to dechlorinate contaminants. Reductive dechlorination is a remediation technology that is implemented to degrade chlorinated contaminants by chemical reduction with the release of inorganic chloride ions. This practice was discovered during research by Reynold et al. (1990), and since that time vast amounts of research has been performed by O'Hannesin et al. (1998), Blowes et al. (1995), and others to demonstrate the effectiveness of this method as a groundwater remediation technique. The work performed by O'Hannesin et al. (1998) on the use of zero-valent iron (ZVI) for the reduction of chlorinated solvents resulted in reported reductions of 90% and 86% of trichloroethene (TCE) and tetrachloroethene (PCE), respectively, over a span of several years. It is due to this type of demonstrated success that has led granular iron to be a predominate choice for groundwater remediation and possibly contaminated sediment remediation in some instances.

Solidification/stabilization treatment is defined by the US-EPA (1993) as treatment to immobilize sediment and contaminants by treating them with reagents to solidify or fix them. While stabilization here refers to solidifying sediment, it can also refer to the chemical stabilization of contaminants, which is more common and more practical than the solidification/stabilization of areas of sediment. Chemical stabilization sequesters chemical in-situ and lowers the chemical activity and bioavailability. Contaminant stabilization exploits activated carbon's large adsorption capacity to hold contaminants in place, so that natural degradation can still occur and contaminants will not reenter the water column. The process is time inclusive, yet it has been proven effective at both reducing contaminant concentrations in the sediment pore water and in the biouptake by organisms in both Zimmerman et al. (2004) and Werner et al. (2005) research. The use of this method in the field is also well documented by Cho et al. (2009) and Cho et al. (2007), and up to approximately 90% reductions in aqueous PCB concentrations have been reported.

When attempting to perform biological treatment, chemical treatment, or contaminant stabilization, it is important that the organisms or amendments delivered come into intimate contact with the contaminants. Many of these contaminants are known

to be HOCs, which means that these contaminants do not reside in water at high concentrations and therefore are typically found adsorbed to the sediments. While the bonding between the contaminant and the sediment will reduce bioavailability and concentrations in the water column, the availability of the contaminant for contact with the added organisms or amendments will also be decreased. This phenomenon has been researched in more depth by Xing et al. (1996) and Ghosh et al. (2000) in an attempt to better understand and characterize the relationship between contaminants and sediments. Xing et al. (1996) performed an extensive literature review on this topic and concluded that the adsorption and desorption of organic compounds on natural particles are typically very slow processes. Xing et al. (1996) states that in order to increase the rate of desorption of contaminants from the sediment particles several different approaches may be taken: 1) addition of biological agents capable of reaching remote molecules; 2) application of heat; 3) addition of chemical additives that displace the contaminant or alter the soil structure; and/or 4) physical methods that alter the soil structure. Ghosh et al. (2000) established analytical techniques for spatial characterization of polycyclic aromatic hydrocarbons (PAHs) found with natural sediments, which allows for a better understanding of the contaminant/sediment interactions and locations. It is important to recognize these contaminant/sediment relationships when selecting a remedial action, which could potentially result in increased remediation performance.

Subaqueous capping is another well-researched contaminated sediment treatment method that had been used full scale. This process acts through the implementation of a strategically placed layer of material (sand or other geosorbent) over top of the contaminated area. This cap is applied as a means to reduce flux of contaminants into the water column as well as contaminant availability to benthic organisms. These caps can be composed of a variety of different materials that should be chosen based upon their physical and chemical compatibility with the area where they are to be placed (Danny Reible, unpublished EPA Sediment Remedies Internet Seminar). Once implemented, these caps have exhibited great reductions in the flux of contaminants from the sediment to the water column. Wang et al. (1991) displayed flux reductions from 18.4 milligramcentimeter per second (mg·cm· $^{-2}$ s⁻¹) to 0-3.3 mg·cm· $^{-2}$ s⁻¹ when capped with clean sediment during the first day of leaching. In a laboratory study, Himmelheber et al. (2007) used a cap supplemented with electron donors as a means to reduce PCE within contaminated sediment samples. These are two examples of the versatility of subaqueous capping, yet there are still some shortcomings to this approach. Researchers have shown that while subaqueous capping is cost effective and quickly reduces risks, it allows the contaminated sediment to remain in the aquatic environment, it is difficult to place accurately and uniformly, it requires long term monitoring/maintenance, it reduces the water depth, and it can broken down due to storms or other weather events (Danny Reible, unpublished EPA Sediment Remedies Internet Seminar).

1.3 ZERO-VALENT IRON REDUCTIVE DECHLORINATION AND ACTIVATED CARBON ADSORPTION MECHANISM

The mechanisms that allow zero-valent iron (ZVI) and activated carbon to function as remediation amendments have been highly researched. It is best to understand these basic mechanisms when selecting which alternative will be most effective for a certain area. As previously mentioned zero-valent iron performs by ultimately dechlorinating chlorinated contaminants or reducing other compounds. The process is an oxidation/reduction reaction that is explained by Agrawal and Tratnyek (1996), who state that there are three main pathways contributing to this process. Agrawal and Tratnyek (1996) illustrate these pathways by using three stoichiometric equations using alkyl halide (RX) reduction as an example.

$$Fe^{\circ} + RX + H^{+} \rightarrow Fe^{2+} + RH + X^{-}$$
(1)

$$2Fe^{2+} + RX + H^+ \rightarrow 2Fe^{3+} + RH + X^-$$
(2)

$$H_2 + RX \rightarrow RH + H^+ + X^-$$
(3)

Equation (1) illustrates the pathway that involves the metal directly and implies that the reduction occurs by electron transfer from the Fe° (reductant) ion surface to the adsorbed RX, while equation (2) displays the pathway involving the Fe²⁺ ion that is an immediate product of corrosion in aqueous systems. In equation (2) the Fe²⁺ ion takes over as the reductant, which will cause the reaction to proceed at a slower rate than that of equation (1). Equation (3) involves the hydrogen produced as a product of corrosion with water. In order for equation (3) to take place and for H₂ to become a reductant, the proper catalyst must be present. Excessive amounts of H₂ present at the metal surface can even lead to corrosion inhibition and an overall reduction in reactions, so a balance of the proper elements must be present for equation (3) to perform effectively. Agrawal and Tratnyek (1996) state that the understanding of these pathways will be essential to predicting field performance of iron-based remediation technologies.

Activated carbon uses an entirely different type of process for remedial action. As stated above, activated carbon works by allowing contaminants to adsorb to its surface and then by holding those adsorbed contaminants in place. The surface of an activated carbon molecule is composed of graphitic planes and fissures, which result in the molecules having extremely large surface areas (Bandosz, 2006). This expansive surface area allows activated carbon to contain many sites for physical/chemical interactions between other molecules to occur, resulting in an adsorbed molecule. This adsorptivity possessed by activated carbon is extremely well documented and has been used in water treatment beginning in the early 1900s. More recent research by Jonker and Koelmans (2002), Zimmerman et al. (2004), Millward et al. (2005), Werner et al. (2005), McLeod et al. (2007), among others have demonstrated the ability of activated carbon to adsorb contaminants, resulting in reductions in their pore water concentrations and biouptake.

2. DETERMINATION OF DELIVERED AMENDMENT CONCENTRATIONS

The ability to determine the amount of amendment delivered to the contaminated area can be vital to a remedial action's success. Zimmermann et al. (2005) illustrated that the amount of activated carbon delivered to the sediment will directly influence the aqueous concentration of contaminants. Zimmermann et al. (2005) found that aqueous concentrations of PCBs were reduced by 44% to 87% for activated carbon doses of 0.34% weight (wt.) and 3.4% wt., respectively. This illustrates that significant differences in contaminant concentrations can occur based upon the dose of activated carbon introduced to the contaminated area. Therefore, methods to determine the amount of amendments delivered are extremely important. Grossman et al. (2009) developed a chemical oxidation method to oxidize natural organic matter in a sample, while preserving the activated carbon that was previously delivered. Through this effort, Grossman et al. (2009) was able to more accurately determine the amount of delivered activated carbon than the previous thermal oxidation methods. In this process, approximately 98% of the natural organic matter was able to be removed, while preserving 95% of the activated carbon. These results were better than the previous method of thermal oxidation, because thermal oxidation tends to result in significant losses of activated carbon in the sample (Grossman et al., 2009). This developed method displayed significant improvements in activated carbon measurements and accuracy, however this process requires the use of several different chemicals and instruments, and is very time inclusive. If this process is being used to monitor a field location that has already been amended with activated carbon then it is quite possibly the best alternative,

but if the purpose of quantifying the delivered amendments is to calibrate the delivery equipment then a different alternative should be considered.

A spectroradiometer is a viable alternative for delivered amendment quantification, as a means to calibrate the delivery implement. A spectroradiometer collects reflected light through a fiber optic bundle and projects this light onto a holographic diffraction grating. The wavelength components of the reflected light are then separated and reflected for independent measurement by the instruments internal detectors. These detectors convert the incident photons into electrons, which can either be stored or integrated until the detector takes a read out. When the read out occurs, the photoelectric current for each of the detectors is converted to a voltage that is then digitized by a 16-bit analog to digital converter. This digital data is then sent to the computer's main memory to be processed by the controlling software. Through this process, the reflectance of delivered carbon in a white media can be measured and compared to standards previously collected. This results in the ability to quickly and conveniently quantify the amount of carbon that was delivered, which then allows for the adjustment of the delivery mechanism so that the proper concentrations maybe attained. The spectroradiometer method works well for the quantification of delivered activated carbon into light colored surrogate sediment due the immense contrast between the light media and the black activated carbon. These contrasts allow the spectroradiometer to make accurate determinations of the delivered amounts of activated carbon.

The ability to quantify the amounts of delivered zero-valent iron must be approached by a different methodology. The Fe^o ion does not have the highly contrasting color to the light colored injection media that the activated carbon exhibits; therefore it is extremely difficult for the spectroradiometer to differentiate between different concentrations of the injected Fe° ion. The alternative that is possibly most proven and accurate for Fe° ion quantification in sediment is the through digestion followed by Inductive Coupled Plasma (ICP) analysis mass spectrometry. Visual comparison analysis could also be used for these quantifications, as well.

3. OBJECTIVES AND GOALS

The objective of this research is to develop a method of remediation amendment delivery that effectively and efficiently places both zero-valent iron and activated carbon into contaminated sediment. The developed method should be able to attain previously proven delivered amendment concentrations as well as delivery depths. Once delivered a characterization of the distribution of the delivered amendments should be performed to better understand what takes place during an injection, so that improvements to system can be made.

This research will establish a framework for further research on this innovative remediation delivery system and its ability to efficiently place amendments while reducing risks to benthic organisms typically associated with said placement. Through this research a better understanding of what occurs during and following a remediation amendment injection should be better recognized, in order to aid in the further development of this technology.

PAPER

PLACEMENT OF WATERJET-INJECTED AMENDMENTS TO REMEDIATE CONTAMINATED SEDIMENTS

CE Database Subject Headings: environmental engineering, remediation, pollution, sediment

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ABSTRACT

The effective delivery of remediation amendments into contaminated sediments, while minimizing impacts to benthic organisms and their environments has proven to be a challenging endeavor. Waterjets are a viable alternative for placement of remediation amendments at depth. An amendment injection system and waterjet nozzle has been developed to test the merit of this concept. Characterization of the waterjet delivered amendment concentration distributions throughout a surrogate sediment was performed to test the developed injection system's performance. These characterizations were performed through the use of a novel spectrometry technique for powdered activated carbon and two different methods, visual comparison and Inductive Coupled Plasma analysis, for granular iron. The distribution of the delivered amendments followed a

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similar pattern for a range of injection times and amendment types. The depth of injection, however, was dependent upon the type of amendment being injected. Analysis of these findings have lead to increased knowledge on what takes place during an amendment injection, which will allow for a more controlled placement of remediation amendments and aid in further development of this remediation delivery mechanism.

INTRODUCTION

Contaminated sediments are a widespread issue, and the United States Environmental Protection Agency (USEPA-1998) estimates that approximately 10 percent of the sediment underlying our surface waters is sufficiently contaminated to cause health issues for benthic communities, their food chains, and human health. A significant amount of research has been performed and is ongoing in order to determine the possible methods for mitigating the risks that contaminated sediments pose to human health and the environment.

Sediment remediation technology is relatively mature. Several different treatment technologies have been studied and are typically considered for remediation of contaminated sediments. The main three alternatives are capping, dredging, and chemical/physical treatment. Wang et al. (1991), Murphy et al. (2006), and Reible et al. (2003) demonstrated *in-situ* capping with various materials such as sand and reactive core mats can reduce the flux of contaminants from the sediment to the water column. While this capping technique effectively reduces the flux of contaminants, contaminants could be released back into the environment if the cap is disturbed (Reible et al. 2003). Capping could also potentially change the topography of the bottom of a water body, which could be an issue for navigable waterways. Dredging removes of the contaminated

sediment from the ecosystem. Sanchez et al. (2002) cited results of an extensive General Electric Company (GEC) study on dredged sites. GEC's study results indicated that many times dredging did not effectively reduce surface sediment contaminant concentrations and in many instances led to resuspension of contaminants into the water (Sanchez et al. 2002). An *in-situ* approach to remediating contaminated sediments is through the use of chemical or physical methods. A chemical technique known as reductive dechlorination uses zero-valent iron (ZVI) to reduce chlorinated compounds to less harmful products. The ZVI reductive dechlorination process has been well documented and established in groundwater remediation research by Reynolds et al. (1990), Blowes et al. (1995), Gillham and O'Hannesin (1994), and others. It is important to note that many times reductive dechlorination takes place through the use of what is known as granular iron rather than ZVI. Granular iron is essentially a ZVI core that is covered by oxide layers. These layers form due to exposure of the ZVI to oxygen and water which causes rapid oxidation to occur at the surface. This phenomenon is discussed in research performed by Scherer et al. (1997) where the authors studied the dechlorination rates of both ZVI and oxide covered ZVI. The authors indicated that both the oxide-free ZVI and the oxide-covered granular iron both displayed kinetic behaviors typical for reaction-controlled processes. For this paper granular iron will be used, as the iron used in this study was exposed to both oxygen and water.

A common physical means of contaminated sediment remediation is the use of activated carbon (AC) to adsorb the contaminants, thereby reducing the aqueous contaminant concentration and in turn its bioavailability. The attraction between contaminants and carbon particles is also very well documented by Jonker and Koelmans

(2002), Zimmerman et al. (2004), Ghosh et al. (2001), among others. This process has been proven to reduce the negative impacts of contaminants on benthic organisms by reducing their contaminant uptake. Zimmerman et al. (2004) displayed the effectiveness of this type of treatment by achieving 87 percent reductions in the aqueous equilibrium PCB concentrations treated with 3.4 weight percent AC and McLeod et al. (2007) observed reductions in the uptake of PCBs by 84 percent in the *Macoma balthica*, clam. These chemical/physical techniques are effective at remediating the contaminants, but the problem with these treatment amendments lies in their placement techniques. Currently, amendments are typically delivered through mixing. Cho et al. (2007) and Cho et al. (2009) both illustrate that the mixing method can lead to reductions in the bioaccumulation of contaminants in benthic organisms and aqueous contaminant concentrations. However, there are still some complications with this method. For example, the mixing technique is typically used in tidal mudflats at low tide conditions; this prevents the treatment of areas that are continuously submerged. Mixing implements, such as the commonly used rotovator, are certain to cause a high mortality rate to the benthic organisms dwelling in the treatment area and cause the resuspension of sediment in the water column.

The amount of amendment that can be successfully added to the contaminated sediment by any delivery method is a variable that should be considered when selecting a treatment delivery system. Cho et al. (2009) successfully achieved 2.0 to 3.2 percent by weight concentrations of activated carbon in sediment through the use of a mixing implement delivery method, which was sufficient for approximately 90 percent reductions in the aqueous equilibrium PCB concentrations 18 months after amendment

delivery. The authors attempted to mix the AC through the uppermost 30 cm of sediment, as they considered this to be the biologically active layer. Laboratory research by Rysavy et al. (2005) illustrated that at the proper dosage ZVI can reduce the lag time for the dechlorination of some PCB congers by up to 100 days in contaminated sediments. The amount of these amendments delivered to the contaminated sediment is important as the interaction between amendment and contaminant will control the remedial effectiveness (Zimmerman et al. 2004).

Remediation of contaminated sediments can be accomplished through several different methods. Research on the use of amendments for contaminated sediment remediation has displayed exemplary results. However, the delivery of these amendments remains to be the significant drawback of this technique as common delivery methods cause drastic impacts to the benthic environment and only excel during low tide conditions. Waterjets have demonstrated the potential to place remediation amendments in both tidal mudflats and subaqueous environments, while minimizing the effects to benthic organisms. Once placed it is necessary to understand the distribution and concentration of the delivered amendments. Therefore, colorimetric techniques have been developed to quantify the amount and pattern the distribution of these waterjet placed remediation amendments.

TRADITIONAL WATERJET USE

Waterjets have been used in a variety of applications for hundreds of years. Initially used in mining and excavation practices, the benefits of using waterjets were quickly recognized. Waterjets today are used in a variety of mining, cleaning, and machining applications. Possibly one of the most innovative developments to waterjet

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usage is the addition of abrasives to the waterjet stream. The addition of these abrasives allows for a wider range of products to be cut with the jet as well as enhanced waterjet cleaning. These abrasive waterjet cutting/cleaning systems function by combining the force of a high pressure water stream with the bombardment of the abrasive on a material to be cleaned or cut. These operations are typically performed at pressures from 140 to 4,000 bar (Summers 1995).

MATERIALS

AMENDMENTS

The type of granular iron used throughout the testing process was obtained from Quebec Metal Powders (QMP), Ltd. out of Quebec, Canada. The type of iron selected was QMP's ATOMET 86 which was fine enough that 73 percent of the powder would pass through a 325 mesh sieve. This relatively small grain size oxidizes relatively rapidly and is readily accommodated by the waterjet system.

Calgon Carbon Corporation's (Calgon) powdered activated carbon (PAC) known as WPH was also used as an experimental amendment. The WPH PAC is an extremely fine carbon powder and approximately 90 percent of the powder would pass through a 325 mesh sieve.

SURROGATE SEDIMENT

Surrogate sediment was used in many of the injection system performance tests. The surrogate chosen was kaolin clay acquired from Unimin Corporation. Kaolin was chosen for is cohesive nature, that is thought to be exhibited by many sediments, and for its extremely white color. The white color allowed for both visual inspection of amendment delivery and aided in the spectroradiometer measurements. The surrogate sediment was mixed using a concrete mixer and was created using the same recipe for each test. The surrogate was created by mixing 45.4 kg of the kaolin powder with 31.2 liters of water.

EXPERIMENTAL SECTION

NOZZLE DEVELOPMENT

The idea of injecting remediation amendments into contaminated sediment has been previously researched by Cantrell et al. (1997) and by Cable et al. (2005). Both of these research groups attempted to develop a delivery method that would inject amendment slurry into the sediment. These slurries were composed of a type of polymer (for example, guar gum), water, and the amendment. The slurry's purpose was to hold the amendments in suspension, allowing them to be pumped into the exiting high pressure water stream. It was discovered during this research process that the ability to retain dense particles like granular iron in suspension was difficult. Continuous mixing of the slurry was required and even then pump clogging and pulsating flow was witnessed during testing. It was due to this inability to provide uniform discharge that led to the development of a new delivery system that would avoid these issues.

An amendment delivery system that used a pressurized air and water stream was then considered. The system would function through the development of a specialized nozzle. The type of nozzle being considered has been previously used in abrasive waterjet cleaning and cutting (Summers 1995), and the design of these nozzles was used as a departure point for this design process. The nozzle was machined from a solid piece of aluminum. The nozzle also incorporated a fully adjustable mixing chamber, to reduce amendment plugging problems within the chamber. The nozzle included a point of attachment for the waterjet lance as well as an interchangeable collimating nozzle. The interchangeable collimating nozzle used in the initial testing worked well for fine grained amendments, but the nozzle exhibited plugging when using coarser grained particles. Therefore, different collimating nozzles could be created and used for injecting a wide range of particle sizes. By changing the diameter and/or shape of the collimating nozzle's exiting orifice, the flow's velocity and dispersion would also change. Figure 1 illustrates the configuration of the nozzle's different components. There were two different types of water injection nozzles fabricated for testing. A concave, cone shaped nozzle and a cylindrical shaped nozzle were both tested. The concave, cone shaped nozzle resulted in amendment buildup in the void space around the nozzle and eventually led to plugging. Therefore this was not considered to be the optimum configuration and the cylindrical nozzle was used for the remainder of the experiments.



Figure 1. Injection nozzle components.

INJECTION SYSTEM

Figure 2, shows the four main components of the experimental waterjet system. First, commercially-available pressure washers were used as the waterjet platform because these units were capable of injections at lower pressures and flowrates. A gasoline-powered unit (Troy-bilt Model# 020344) was used for tests at pressures from 48 to 103 bar, while an electric unit (Task Force Model# TF1600) was used for pressures below 35 bar. Traditional abrasive waterjet cleaning and cutting methods are typically performed at higher pressures ranging from 140 to 4,000 bar, while minimizing the solids used. For this research, the low pressures and flow rates are targeted to prevent unnecessary water input, while maximizing the amendment delivery. A commercial pneumatic sandblasting tank was used to deliver amendment to the mixing chamber.

Third, a standard pressure washer lance and trigger assembly were used, with the addition of a pressure gauge. Finally, the fourth component of the system was the nozzle itself.



Figure 2. Injection system configuration.

PERFORMANCE TESTING

Concentration tests were run to characterize the water and air pressure settings that would allow the highest percentage of amendment to be mixed into the collimating stream of amendment/air/water. This would prevent the injection of excess water and air into the contaminated environment and the length of injection time to reach the target amendment concentrations would be shortened. The test nozzle was calibrated so that the maximum amount of amendment flow in the discharge could be achieved. The chamber volume was set with 8.89 cm of setback distance from the collimating nozzle exit; allowing for the maximum flow to be achieved by the incoming amendment feed line. The incoming pneumatic amendment pressure was set to approximately 4.1bar, and once set this pressure was maintained for the duration of the tests. The pressure of the water jet entering the mixing chamber was chosen to be the variable in these tests, as this parameter was thought to be the controlling factor for the depth of injection, the concentration of amendment found in the exiting stream, and for the effects to the benthic communities.

Once the injection system was setup, the testing was commenced. The testing apparatus was created from a ten foot long, four inch diameter PVC pipe that was capped on one end. The uncapped end of the PVC pipe was then fitted with a 15 cm diameter, one micron bag filter (Midstates high strength, one micron, polyester, double chain stitched bag filter)so that the bag filter was held open and in place at the open end of the pipe. The pressurized amendment/air/water stream was then injected through the bag filter and down into the PVC pipe. The amendment was captured in the filter and the water was collected within the PVC pipe. The mass of both amendment and water leaving the collimating nozzle could then be determined. The process was timed so that a flow rates could be calculated. These tests provided a departure point for the next series of surrogate media bed injection tests.

SURROGATE SEDIMENT INJECTIONS

The injection system was tested on a surrogate sediment to determine its ability to deliver amendments to a target depth and concentration. Targets were set for both the depth and concentration reached during each injection. The targets were based off of results published by Zimmerman et al. (2004) and Cho et al. (2007 and 2009). The depth target was 30 cm, and the concentration target was 3.4 dry weight percent of activated carbon within the sediment. (Zimmerman et al. 2004 and Cho et al. 2007).

Granular iron is typically used and has been proven effective in permeable reactive barriers for groundwater remediation. The depth and thickness of the barrier and the amount of iron used in the barrier is dependent upon the contaminant concentration and the groundwater characteristics. The use of granular iron for the remediation of contaminated sediments has not been researched as greatly therefore the same targets were used for the granular iron injections.

The surrogate test beds were 30.5 cm diameter PVC tubes 864 cm long which were filled with the sediment surrogate and capped with a vented 30.5 cm PVC cap. Once filled and capped, the PVC tube was then submerged in a 246 liter water vessel, to simulate working in a subaqueous environment. The depth from the water surface to the surrogate surface was measured both before and following each injection to determine if the escape of surrogate had occurred. Once the system was calibrated a stream of amendment was injected into the surrogate column. The injection was performed with the discharging nozzle at the surrogate surface and each injection was timed. Following the injection, the PVC tube containing the surrogate column was removed from the water filled vessel and the surrogate was dried using electro osmosis. Once dried the surrogate column was removed from the PVC tube and then sliced horizontally at 2.54 cm intervals down the column. Samples were taken from each of these slices, so that each sample could be analyzed for the concentration of amendment delivered to each. The samples were taken from each slice with the assumption that the concentration would be uniformly distributed around the point of injection. Therefore samples were taken from the point of injection along the radius to the outer edge of each slice. The symmetrical distribution assumption was checked periodically by taking samples on the radius directly opposite. A blank sample was collected from each surrogate filled tube. Pictures were also taken of each slice immediately before removal of the samples.

ACTIVATED CARBON CONCENTRATION DISTRIBUTION ANALYSIS

The sample analysis for activated carbon injected surrogate columns was performed using a FieldSpec Pro model spectroradiometer from Analytical Spectral Devices, Inc (ASDI). The spectroradiometer measures the reflectance of light off a sample. The reflectance is output by the spectroradiometer in terms of a reflectance factor and is given versus the wavelength emitted from the light source. The spectroradiometer was calibrated and setup according to the ASDI user's instructions manual. The outputted reflectance factor versus wavelength plots were compared to standards consisting of a known dry percent by weight of activated carbon. The spectroradiometer was able to differentiate between PAC concentrations differences as small as 0.1 percent by dry weight.

GRANULAR IRON CONCENTRATION DISTRIBUTION ANALYSIS

The granular iron used in the testing exhibited a light gray color that did not contrast enough with the white surrogate sediment to allow the spectroradiometer to
accurately characterize the concentration of granular iron in the surrogate. Therefore, the iron-containing samples were analyzed using two different methods. First, each slice was photographed immediately after being removed from the surrogate column. These photographs were visually compared to a color chart to characterize the relative difference in iron concentrations as shown in Figure 3.



Figure 3. Visual comparison analysis using color chart to predict delivered granular iron distributions.

Samples were also collected from the slices at various intervals and sent to ACME Analytical Laboratories (ACME Labs) in Vancouver, Canada, where the samples were dried, digested, and run through ICP emission spectrometry to determine the percent weight of iron delivered to each surrogate column sample. The laboratory data were used to quantify the relative values used for the colorimetric analysis.

RESULTS

DISCHARGE CONCENTRATION TESTING

The injection system was initially tested to determine the maximum concentration of amendment that could be mixed into stream exiting the nozzle. These tests were performed for both PAC as well as granular iron, and the results are given in Table 1.

Type of	Waterjet	Percent Weight	Amendment Volume
Amendment	Pressure	of Amendment	in Discharge
	(bar)	in Discharge	(mL)
PAC	1	0.500	48.1
	3.8		
PAC	2	0.200	12.5
	0.7		
PAC	4	0.200	15.9
	8.3		
PAC	6	0.100	8.9
	8.9		
Granular Iron	4	33.0	162
	8.3		
Granular Iron	6	54.8	397
	8.9		
Granular Iron	1	46.8	290
	03.2		
Granular Iron	1	46.5	311
	03.2		

 Table 1. Discharge concentration testing results illustrating percent and volume of amendment in discharge.

*Tests performed with pressure vessel pressure between 4.1 to 4.9 bar.

Extreme differences existed between the data collected for the two different amendments, as a significantly higher volume of granular iron was able to be mixed into the exiting stream. The difference appeared to be a function of the pressure vessel. The vessel was designed to pressurize larger, denser particles like the granular iron rather than the light, less dense PAC particles. The data gathered during this experiment did illustrate the effectiveness of the system to mix the granular iron into the discharge stream, as nearly 54 weight percent of granular iron in the discharge was able to be achieved. This data also provided a departure point for the surrogate injection tests as the time required to achieve the target amendment concentration within the surrogate could be determine based off the flowrate of amendment exiting the nozzle.

PAC SURROGATE INJECTIONS

The duration of PAC injections to attain the target concentration were calculated based off the flowrates found in the discharge concentration testing and the volume of the surrogate within each column. The durations were long, on the order of hours, as was expected of the light PAC particles. As a departure point, PAC injections were carried out at both 5 and 10 minute durations. The results from the 5 minute injection are illustrated below in Figure 4. It was predicted that these longer duration injections would increase the amount of PAC in the surrogate, but in fact resulted in the liquification and excavation of approximately 7.6 cm and 15.2 cm of clay for the five and ten minute injections, respectively. During the long duration injections the waterjet injection reached a point at which it began to excavate the sediment rather than inject into it. The results of spectroradiometry analysis for these long duration injections illustrated the effect that this excavation had on the system's ability to place amendments. The 5 minute injected surrogate column contained a vein of PAC ranging in concentration from approximately 0.5 to 3.0 dry weight percent down through the first 20 cm of surrogate, Figure 4. Below 20 cm there did not appear to be a significant amount of PAC. The 10 minute injected surrogate column only contained two sample locations with PAC concentrations exceeding 0.1 percent throughout its depth. The 10 minute injection appeared to behave similar to other injections, but following approximately 6 minutes of injection time liquification and subsequent excavation of the uppermost 15 cm of sediment occurred. The removal of this uppermost 15 cm of sediment would most likely have been the removal of the amendment delivery zone. The PAC surrogate injections were initiated with a goal to attain previously proven concentrations at proven depths. It

was discovered that the experimental injection system could not deliver the target PAC concentrations to the target depth. The injection system was able to place amendments to the target depth during the 5 minute PAC injection; however the target concentration was only achieved at 5.1 cm below the surface.



Figure 4.Distribution of PAC following a 5 minute injection. The color scale indicates the percent by weight of PAC in the surrogate.

GRANULAR IRON SURROGATE INJECTIONS

The distribution patterns for the three granular iron injections are depicted in Figure 5.1, 5.2, and 5.3. The time of injection to reach the targets was calculated using the discharge concentration testing results given in Table 1 to be 0.5 to 1 minute. Therefore, tests were performed at 0.5 minutes, 1 minute, and 3 minutes. The visual comparison distribution is presented by the different shading with the color scale presenting the different concentrations present in each column. The circles indicate the sample locations that were analyzed by ICP analysis and the results for each of these locations are provided within each circle. There are similarities between the semiquantitative and visual comparison analysis, which allows for a comparison between the two as a means to estimate the granular iron concentrations throughout the surrogate column. The depth of amendment placement for these injections was 2.5 times deeper than those experienced during the PAC injections. The granular iron was able to reach depths of approximately 51 cm in each of the injections taken. The concentration of delivered granular iron exceeded the target of 3.4 percent by dry weight. Concentrations were as high as 60-70 percent by weight in some samples taken along the path of injection in the surrogate columns. However, the distribution was not evenly distributed through the length of the column as the vein of injected iron took on more of an hour glass shape. The symmetrical assumption samples that were analyzed indicated that in many instances the distribution was not uniform about the line of injection. However, this observation may have been affected due to the line of injection being slightly skewed within the surrogate column.



Figure 5.1. Distribution of granular iron for 0.5 minute injection.



Figure 5.2. Distribution of granular iron for one minute injection.



Figure 5.3. Distribution of granular iron for three minute injection.

DATA MODELING

Groundwater model calibration equations were used to compare the ICP data to the visual comparison data. The coefficient of residual mass (CRM) equation is given by Spitz and Moreno (1996) as:

$$CRM = \frac{\sum_{i=1}^{n} o_i - \sum_{i=1}^{n} p_i}{\sum_{i=1}^{n} o_i}$$

Where O is the observed value (ICP data), P is the predicted value (visual comparison data), and n is the number of data sets compared. Spitz and Moreno (1996) state that the closer the CRM value is to zero, the more accurate the prediction. The CRM was 0.44 using the visual comparison concentration range shown in the figures. DISCUSSION AND CONCLUSIONS

Through experimentation and analysis of the gathered data several key observations were made on the application of a waterjet injection system for the delivery of remediation amendments to contaminated sediments. First, it was shown that both granular iron and PAC could be injected into sediment. Target depths and amendment concentrations could be achieved with the granular iron, but the experimental system did not deliver a sufficient volume of PAC necessary to achieve the corresponding target concentrations.

Secondly, and possibly the most significant finding from this study, the distribution of the injections seemed to follow a distinctive pattern. The pattern could be characterized as being larger diameter, high concentration amendment pockets connected by smaller diameter, lower concentration veins of amendment. This distribution pattern was characterized for both the granular iron and PAC injections. This pattern indicates the repetition of a cycle of energy build-up and dissipation. The jet of amendment/water/air initially contains a significant amount of energy in the form of momentum, but as it travels down into the surrogate bed the energy begins to dissipate until it reaches a point where downward motion ceases. At this point lateral motion begins and a pocket of amendment begins to form. As the pocket grows so does the pressure, which eventually leads to enough energy build up and downward motion

resumes. The process appears to occur downward through the surrogate column until eventually either there is no longer a sufficient amount of energy for propagating the injection or the time for energy build up was not attained.

Thirdly, it was discovered that the granular iron was capable of reaching greater depths within the sediment. This could be associated with the fact that much smaller volumes of PAC were being injected into the surrogate, but more likely this occurred because of the difference in mass and resulting momentum between the two types of amendment. Momentum is described as the product of the mass and the velocity, and the system was setup so that the velocity during each of the injections would be nearly equal. Therefore, differences in amendment momentum would be solely dependent upon the mass of the amendment being injected. As a significantly higher volume of the higher density granular iron was placed in the injection stream, it can be inferred that these injections would have a much higher momentum than that created by a PAC injection. This would account for the deeper penetration of the granular iron injections.

Finally, there were some less positive observations made during the course of the project. Limitations were discovered for the volume of PAC that could be injected from the system. A significant volume of granular iron could be mixed into the stream exiting the injection nozzle (up to 54 weight percent), but only very small volumes of PAC could be achieved (0.5 weight percent). This is due to extreme differences in the density of these amendments, as the granular iron was found to be nearly eight times denser than the PAC. The next important finding was a direct result from this PAC injection limitation. It was hypothesized that by increasing the injection duration for PAC injections that the concentration goal might be achieved. These long duration injections eventually led to

the injection system turning into an excavation implement causing large amount of both surrogate and amendment to be removed from the testing apparatus. The loss of surrogate caused the testing apparatus to transition from a confined to a semi-confined system, as a significantly larger head space developed above the surrogate surface as more surrogate was excavated. This resulted in the loss of the amendment delivery zone and created a much further distance for the stream to travel before contacting the remaining surrogate.

These findings provide information needed to characterize and improve upon the injection of remediation amendments into contaminated sediment, which will allow for the future development of the injection system for a more controlled and efficient placement.

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SECTION

4. RECOMMENDATIONS FOR FUTURE WORK

This research has only laid the framework for future exploration into the use of waterjets for remediation amendment delivery. Throughout the experimentation process it was observed that the use of a cap above the injection area prevented the blow back of amendment and/or surrogate. Further investigation on this phenomenon could possibly be researched, through the development of a capping apparatus that attaches itself to the injection nozzle and can be moved along with the nozzle during an injection. Another possibility for further technology development would be the testing of different collimating nozzle configurations to determine the delivered amendment distribution pattern associated with each. By using nozzles with different orifice diameters/shapes the properties of the amendment/water/air stream will change, which should affect the concentration pattern observed. During the experimentation and analysis stages of this project it was evident that the injection system had a problem injecting high concentrations of PAC. The factor causing this limitation was the pressure vessel being used, as it was design to pressurize much coarser, denser particles. Therefore, future research and development on the introduction of high PAC volumes into the nozzle should be undertaken. Finally several preliminary tests were run and not included within this thesis, in which a PAC cap was placed on the surface of the surrogate and then blasted with a high pressure water stream. This test was performed to determine if a waterjet could push PAC into the surrogate rather than inject it. Further analysis on this type of delivery could prove to be beneficial.

APPENDIX A.

FILTER BAG TEST DATA AND TEST PARAMETERS

Waterje	Dry	Wet	Dry	Time	Volume	Mass	Mas	%	Volum
t	Mass	Mass	Mass	(s)	Of Water	of	s of	PA	e of
Pressure	of bag	bag +	Bag +		Collecte	Water	PAC	С	PAC
(psi)	(g)	PAC	PAC		d	(g)	(g)		(mL)
		(g)	(g)		(mL)				
200	265.8	1180.1	284.1	44.5	2950	3846	18.3	0.47	48.1
	0	2	2	5					
300	253.4	864.77	258.2	40.1	2420	3026.	4.8	0.16	12.5
	9		5	5		5			
700	260.8	975.56	266.8	30.3	3150	3858.	6.1	0.16	15.9
	1		7	0		7			
1000	254.2	884.25	257.6	24.6	2900	3526.	3.4	0.10	8.9
	2		0	1		7			

PAC Filter Bag Testing

*Tests were run between 60-70 psi on the amendment pressure vessel.

Granular Iron Filter Bag Testing

		U	U						
Waterje	Dry	Wet	Dry	Time	Volume	Mass	Mass	%	Volum
t	Mass	Mass	Mass	(s)	Of	of	of Fe	Fe	e of Fe
Pressur	of bag	bag +	Bag +		Water	Water	(g)		(mL)
e (psi)	(g)	Fe (g)	Fe (g)		Collecte	(g)	_		
_	_	_	_		d	_			
					(mL)				
700	254.3	1257.2	743.37	10.7	480	993.9	489.0	33.	162.3
	5	6		7				0	
1000	249.8	1954.7	1445.8	9.17	480	988.9	1196.	54.	397.0
	2	2	5				0	7	
1500	250.5	1710.6	1124.8	7.60	410	995.8	874.4	46.	290.2
	1	2	6					8	
1500	251.0	1784.0	1186.7	7.83	480	1077.	935.7	46.	310.6
	9	3	8			3		5	

*Tests were run between 60-70 psi on the amendment pressure vessel.

APPENDIX B.

SPECTRORADIOMETER DATA FOR FIVE MINUTE PAC INJECTION

The following plots were generated from data gathered through the use of a spectroradiometer. The heavier weighted line indicated the samples analyzed, while the light weight lines indicated the standards analyzed by the spectroradiometer. The standards are set with zero percent by weight PAC at the top of the plot and the concentrations increase as you move down the y-axis. The plots are each assigned a letter of the alphabet, which corresponds to a slice from the column of surrogate. The slice labeled A is the uppermost slice and then slices are then labeled down through each inch of surrogate.





















APPENDIX C.

SPECTRORADIOMETER DATA FOR TEN MINUTE PAC INJECTION

The following plots were generated from data gathered through the use of a spectroradiometer. The heavier weighted line indicated the samples analyzed, while the light weight lines indicated the standards analyzed by the spectroradiometer. The standards are set with zero percent by weight PAC at the top of the plot and the concentrations increase as you move down the y-axis. The plots are each assigned a letter of the alphabet, which corresponds to a slice from the column of surrogate. The slice labeled A is the uppermost slice and then slices are then labeled down through each inch of surrogate.












APPENDIX D.

PHOTOGRAPHS USED FOR GRANULAR IRON VISUAL COMPARISION DATA ACQUISITION

Included with this thesis is a CD-ROM that contains the photographs and colorimeter used in the granular iron injection visual comparison analysis study. The files found on this CD-ROM were created using Microsoft Publisher. APPENDIX E.

INJECTED PAC DISTRIBUTION PLOTS

This plot was generated using Golden Software, Inc. Surfer 9 software package. This plot data was gathered using the spectroradiometer readings. The scale found on the plot indicates the percent dry weight of PAC found in the surrogate sediment.



APPENDIX F.

INJECTED GRANULAR IRON DISTRIBUTION PLOTS SHOWING BOTH VISUAL INSPECTION AND SEMI-QUANTITATIVE DATA ACQUISITION

The following plots were generated using Golden Software, Inc. Surfer 9 software package. The plot data was gathered through visual comparison analysis or through the use of a digestion/ICP analysis. The plots on the left were generated using visual comparison analysis and a colorimeter was used in this analysis. The values associated with these plots are in relation to the colorimeter used in the analysis. The plots on the right were created from data analyzed by digestion/ICP analysis by ACME Analytical Laboratories for various slices taken from each column.

0.5 minute Granular Iron Injection



One minute Granular Iron Injection



Three minute Granular Iron Injection



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VITA

Gavin Hunter Ray Risley was born in Springfield, Illinois to Brian and Roxann Risley. Gavin grew up on the family farm located west of Perry, Illinois and attended Griggsville-Perry High School. In high school, Gavin participated in varsity baseball and basketball and was a member of several academic organizations. Gavin spent the majority of his time, however, working on the family farm, hunting, and fishing. Gavin enrolled in what was then known as the University of Missouri – Rolla in the fall of 2004 as a Civil Engineering major. In the fall of 2006 Gavin switched to the Environmental Engineering program and graduated with Summa Cum Laude honors with Bachelor of Science in Environmental Engineering degree from what was then known as the Missouri University of Science and Technology. During his time at the university Gavin was a member of Sigma Pi Fraternity, Chancellor's Leadership Academy, Tau Beta Pi, Chi Epsilon, and Phi Kappa Phi. Gavin worked as an Undergraduate Research Assistant for Dr. Richard Elgin's surveying laboratory for six semesters. Gavin also worked for two summers as an intern at Benton and Associates, Inc. in Jacksonville, Illinois. Gavin's final summer internship was with Chesapeake Energy Corporation in Oklahoma City, Oklahoma as an Environmental, Health, and Safety Intern. Gavin became registered as an Engineering Intern with the State of Missouri in the Summer of 2009 and completed his Master's degree in Environmental Engineering in May 2010. Upon completion of his Graduate Degree, Gavin plans to move to Palmyra, Missouri with his wife Mallory and work in the Hydrology Department at Klingner and Associates, P.C. in Quincy, Illinois.






















































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