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# ASSESSING THE IMPACT OF RADIONUCLIDES RELEASED INTO THE FLORIDAN AQUIFER BY A MASSIVE SINKHOLE ON LOCAL MUNICIPAL WATER SUPPLIES

by

### MARIA I. ARENAS, E.I. B.S. Env.E. University of Central Florida, 2016

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the Department of Civil, Environmental, and Construction Engineering in the College of Engineering and Computer Science at the University of Central Florida Orlando, Florida

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Major Professor: Steven J. Duranceau

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### ABSTRACT

In late August 2016, a sinkhole spanning 45 feet (13.7 meters) in diameter opened at a phosphate fertilizer facility (Mosaic Company) near Mulberry, Florida, leaking an estimated 215 million gallons (813,000 cubic meters) of radionuclide-contaminated water 300 feet into the Floridan aquifer. An investigation to determine possible impacts to the environment and local community drinking water supplies was implemented that focused on two 1.5 million gallon per day (MGD) Tampa Bay Water (TBW) production wells and two Polk County Utilities (PCU) water treatment facilities. Water samples collected between June 2017 and January 2018 at the TBW and PCU sites were found to contain radionuclides below regulated levels. To evaluate the effectiveness of membrane treatment should the TBW and PCU drinking water wells be affected by the spill in the future, bench-scale, flat-sheet reverse osmosis (RO) and nanofiltration (NF) membrane process testing was performed using TBW and PCU wellfield sample aliquots. NF and RO were shown to be capable of removing at minimum of 86 and 92 percent, respectively, of the barium content that had been spiked into groundwater testing aliquots. Based on testing results, a conceptual opinion of probable capital cost for a membrane process ranged from \$1.7 and \$3.5 million for a 0.25 MGD and 2.0 MGD design capacity, respectively. Process operation and maintenance costs ranged between \$0.99/Kgal and \$0.26/Kgal for a 0.25 MGD and 2.0 MGD design capacity, respectively. The amortized total cost based on a 20-year period and 8 percent interest rate ranged between \$1.88/Kgal for a 0.25 MGD and \$0.49/Kgal for a 2.0 MGD design capacity plant. An estimate of unavailable water value due to a long-term well shut-down was approximated as \$0.64/Kgal.

To my family. Your support made all of this possible.

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# LIST OF ACRONYMS AND ABBREVIATIONS

1-D	One-dimensional
ACS	American Chemical Society
BAT	Best available technology
DBP	Disinfection by-product
DOC	Dissolved organic carbon
ENR	Engineering News Record
EPA	Environmental Protection Agency
GPD	Gallons per day
IC	Ion chromotography
ICP	Inductively coupled plasma spectrometer
I-stat	Industrial statistic
LCL	Lower control limit
LWL	Lower warning limit
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
MDL	Minimum Detectable Limit
MF	Microfiltration
MGD	Million gallons per day
NF	Nanofiltration
NOM	Natural organic matter

NSF	National Science Foundation
O & M	Operation and maintenance
PCU	Polk County Utilities
PHREEQC	pH Redox Equilibrium (in C language)
POE	Point of entry
POTW	Publicly owned treatment works
PPM	Parts per million
QA	Quality assurance
QC	Quality control
RAPID	Rapid response research
RO	Reverse osmosis
RPD	Relative percent difference
SAC	Strong acid cation
SBA	Strong base anion
SCHM 5D	South Central Hillsborough Monitoring well 5 Deep
SCHM 5IA	South Central Hillsborough Monitoring well 5 Intermediate Aquifer
SDWA	Safe Drinking Water Act
SSCT	Small system compliance technology
TBW	Tampa Bay Water
TDS	Total dissolved solids
UCF	University of Central Florida

UCL	Upper control limit
UF	Ultrafiltration
UWL	Upper warning limit
WTP	Water treatment plant

### **CHAPTER 1. INTRODUCTION**

Sinkhole formation is a naturally occurring geological feature common in Florida. Central Florida is subject to sinkhole occurrences as it is underlain by carbonate deposits that are susceptible to dissolution by flowing groundwater; Polk and Hillsborough Counties are among the top ten sinkhole-prone counties in Florida (Insurance Journal, 2011). The accelerated development of land and groundwater resources in west-central Florida has occasioned the development of many new sinkholes.

A large phosphate mining and processing industry is located in west-central Florida. In late August, 2016, a massive sinkhole collapsed at a phosphate-based fertilizer production facility (Mosaic Co.) near Mulberry, Florida. The monitoring system at Mosaic's New Wales facility showed a decline in water levels in the retention pond that contained a 120-foot gypsum stack. Approximately 215 million gallons of contaminated water spilled into the Floridan Aquifer due to a sinkhole formation under the stack; limestone beneath the stack likely had a preexisting dissolution cavity that collapsed into a sinkhole, providing a direct pathway for contaminated (phosphogypsum) water to enter the aquifer.

Phosphogypsum is a radioactive byproduct resulting from the production of phosphate-based fertilizers. It is believed that the Minnesota-based company immediately reported the incident to state and federal environmental authorities; however, Mosaic did not otherwise report the incident publicly until almost three weeks had passed. The sinkhole, located about 30 miles from Tampa, damaged the liner system at the base of the stack, causing the pond on top to drain. Seepage continued and the sinkhole reached Florida's aquifer; the leaked water is enough to fill more than

300 Olympic swimming pools. The released water caused concern should it be transmitted through the subsurface geologic strata and possibly impact neighboring water purveyor's drinking water supplies. The closest drinking water utilities to the sinkhole zone include Polk County Utilities (PCU) and Tampa Bay Water (TBW), located in southwest Polk County and western Hillsborough County, respectively.

Mosaic claimed that the contaminated water is being successfully contained on site (Mosaic Co., 2017); however, public concern remained regarding the possible impacts of this sinkhole formation on the surrounding environment, with emphasis on the local drinking water supplies as most of central Florida's water supply relies on groundwater sources. For this reason, the National Science Foundation (NSF) awarded the University of Central Florida (UCF) a rapid response research grant (RAPID) in the spring of 2017. UCF collaborated with PCU and TBW to conduct research to analyze water quality in the water purveyor's closest groundwater production wells. An assessment of potential impacts on nearby water purveyors and their ability to treat contaminants was hence conducted. Water quality parameters that were considered indicative of the type of water released by the sinkhole included pH, conductivity, turbidity, sodium, sulfate, fluoride, total dissolved solids, gross alpha, combined radium, and uranium.

The rate and direction of water migration in this region of the Floridan aquifer were considered important parameters that could be used to evaluate the impacts of the sinkhole event on the adjacent community water supplies. Should the released water be transported into regional water supplies through limestone conduits in the underlying subsurface, neighboring water purveyors' groundwater quality would be degraded and treatment would be required to maintain usefulness of the water supply. The implementation of advanced treatment techniques required to provide treatment would result in additional infrastructure construction, operation and maintenance activities, therefore, affecting overall regional water supply costs.

The goals of this project therefore are as follows:

- Monitor water quality in the aquifer knowledge of pre-spill contaminant levels is prerequisite to observe deviations during monitoring practices.
- 2. Characterize the impact to the environment and local drinking water supplies.
- 3. Present a mitigation plan for the drinking water facilities located in proximity to the radioactive water spill accompanied by a cost analysis for the implementation of such plan. The cost estimates provided in this study are not exact and should be used only for comparative purposes.

### **CHAPTER 2. LITERATURE REVIEW**

In drinking water treatment, radionuclides are elements of concern due to their emission of radiation during radioactive decay. Over time, radionuclides decay to result in greater atomic stability by emitting radiation via alpha particles ( $\alpha$ ), beta particles ( $\beta$ ), or gamma rays ( $\gamma$ ). Nearly every radionuclide found in drinking water supplies occurs naturally and their concentrations vary according to the source. Radionuclides in drinking water are formed from three natural radioactive series: the uranium series, the thorium series, and the actinium series. The radioactive elements of concern in drinking water are uranium (U), radium (Ra), and radon (Rn) (Cothern & Rebers, 1990). Congress enacted the Safe Drinking Water Act (SDWA) in 1974 to protect public health. Contaminants can be naturally-occurring or man-made and the EPA is authorized by the SDWA to set national standards for drinking water. EPA's Radionuclides Final Rule published on December 7, 2000 regulates the maximum contaminant levels (MCL) of radionuclides in drinking water; Table 2-1 presents the regulations of radionuclides. An MCL is the threshold limit on the concentration of constituents that can be found in drinking water to protect public health from potential health effects that may result from chronic exposure above the MCL.

Radionuclide	MCL	Potential health effects
Uranium	30 µg/L	Increased risk of cancer Kidney toxicity
Combined radium (Ra 226+228)	5 pCi/L	Increased risk of cancer
Gross alpha*	15 pCi/L	Increased risk of cancer

Table 2-1: Regulations of radionuclides (USEPA, 2009)

\* Gross alpha includes all alphas except radon and uranium

#### Radionuclides in the Environment

Uranium occurs naturally in the environment. Uranium can be found in rocks, soils, and water, and it decays into other elements, such as radium, releasing energy in the form of alpha particle and gamma radiation. The most predominant isotope is U-238, which can be found in phosphate-bearing rocks due to the redeposition of uranium that was in a dissolved form in the waters of ancient oceans (Watson, Etnier, & McDowell-Boyer, 1983).

Radium is a radioactive metal that forms naturally from the decay of uranium and thorium, which are found in trace amounts in rocks and soils. Ra-226 (formed from the decay of uranium) and Ra-228 (formed from the decay of thorium) are the most commonly found radium isotopes in the environment. This radioactive metal emits energy as alpha particles and gamma rays, and its decay leads to the formation of radon gas. Radium is a known carcinogen and chronic exposure to this radioactive element causes adverse health effects (Sidhu & Breihart, 1998). Radium behaves similarly than calcium, an element found in bones, and when radium is ingested it concentrates in the bone (Cothern & Rebers, 1990).

Alpha radiation exists in water, in soil, and in air; the amount of radioactivity in groundwater depends on the concentration of radioactive elements contained in bedrock. Gross alpha is a test that measures the overall radioactivity of radionuclides that emit alpha particles in drinking water (Aieta et al., 1987). The gross alpha activity of a drinking water sample is intended to approximate the activity of alpha emitters including Ra-226, U-234, and U-238.

The elements of concern in drinking water therefore are uranium and the radium isotopes Ra-226 and Ra-228; the characteristics of these radionuclides are summarized in Table 2-2. The time

required for the decay of the radioactive atom, or half-life, varies for each radionuclide. Depending on the radionuclide, the decay can be fast or take a long time; half-lives can range from milliseconds to millions of years. Also, different radionuclides emit different types of radiation. Uranium and its daughter, Ra-226, emit alpha particles and gamma rays. Ra-228, a decay product of thorium, emits beta particles.

Radionuclide	Radiation	Half-life
Ra-226	α-activity, γ-activity	1,622 years
Ra-228	β-activity	6.7 years
U-238	$\alpha$ -activity, $\gamma$ -activity	4.5 x 10 <sup>9</sup> years

Table 2-2: Characteristics of radionuclides (Froehlich, 2009)

#### **Sinkholes**

#### Sinkhole Formation

Limestones (CaCO<sub>3</sub>) and dolomites (CaMg(CO<sub>3</sub>)<sub>2</sub>) constitute the carbonate rocks that are sculpted through the dissolution and weathering processes and erode into what is known as karst terranes. Limestone is slightly soluble in groundwater that contains carbon dioxide; therefore, limestone dissolution and groundwater flow can lead to the formation of sinkholes. As water percolates through the upper soil, it interacts with carbon dioxide (CO<sub>2</sub>), forming carbonic acid (H<sub>2</sub>CO<sub>3</sub>) and thus a slightly acidic solution that reaches the underlying carbonate rocks. These rocks may have dissolution cavities that are enlarged as water passes through. If the voids become large enough,

they will not be able to support the overlying sediment and will collapse as a sinkhole (Spechler & Kroening, 2007).

#### Sinkholes in Central Florida

Sinkholes are naturally occurring and widely distributed in central Florida karst terrains. Due to a rapid increase in the discovery and reporting of sinkhole occurrence since the 1950s, sinkholes have been recognized as a primary geologic hazard in central Florida (Tihansky, 1999; Rupert and Spencer, 2004). Sinkholes are catastrophic for populated cities and residential communities, causing substantial property damage and structural problems of buildings, roads, bridges, power transmission lines, pipelines and croplands (Sinclair, 1982; Bengtsson, 1987). Central Florida karst terrains are prone to sinkhole occurrences, and sinkholes that occurred in previous decades have caused financial loss to the region (Jammal, 1982; Wilson et al., 1987; Whitman et al., 1999; Brinkmann et al., 2008; Gray, 2014). The Florida Office of Insurance Regulation reported that insurers had received a total of 24,671 claims for sinkhole damage in Florida between 2006 and 2010 totaled \$1.4 billion (Floir, 2010). Polk and Hillsborough Counties are two of the top ten sinkhole-prone counties in Florida. Figure 2-1 shows the reported sinkholes will continue to occur in the future.

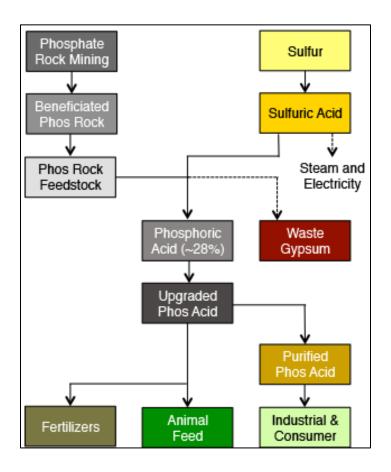


Figure 2-1: Reported sinkholes from 1950-2013 in Polk and Hillsborough Counties (pink dots) obtained from Florida Subsidence Incident Reports (FDEP, 2016)

The Floridan aquifer is Florida's principal source of fresh water. Development of this groundwater resource for water supply creates a decline of the groundwater level that plays a role in the formation of sinkholes; therefore, making the Floridan aquifer more susceptible to contamination from surface water drainage (Tihansky, 1999). The Mosaic sinkhole is located in Polk County, bordering Hillsborough County.

#### Wet Processing of Phosphate Rocks

Sedimentary phosphate rocks contain phosphate minerals and may carry considerable amounts of radioactive materials such as uranium, thorium, and their decay products. The production of phosphate-based fertilizers can be completed using the *wet acid method* where phosphate rocks are treated with sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) to produce phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) based on Equation (2-1) (Sahu et al., 2014). Figure 2-2 presents the steps involved in the process of fertilizer production where phosphoric acid and waste phosphogypsum are products of the wet acid method.



 $\rightarrow 6 H_3 PO_4 + 10 CaSO_4 \bullet 2H_2O + 2 HF$ 

Figure 2-2: Wet processing of phosphate rocks (JDC Phosphate, 2014)

Phosphogypsum ( $CaSO_4 \cdot 2H_2O$ ) is a waste by-product generated in large amounts by the processing of phosphorites through the wet process; for every ton of phosphate produced, 5 tons of phosphogypsum are generated (Sahu et al., 2014). This by-product is partly recycled, but most of it is disposed without any treatment into large stockpiles, covered with water to forestall emanation of radon, and is left exposed to weathering processes. The water stored on top of the

stack is acidic (pH is between 1.5 and 2.0) and contains high concentrations of inorganic constituents including fluoride, sodium, phosphate, and sulfate (Fuleihan et al., 1997).

Phosphorites treatment by the wet process causes selective separation of naturally occurring radionuclides. The most important source of radioactivity in gypsum is Ra-226 as there is accumulation of this radionuclide; about 80-90 percent of radium is concentrated in phosphogypsum. While nearly 86 percent of uranium is accumulated in the phosphoric acid, gypsum carries appreciable amounts of radioactive uranium; 9.5 mg of uranium are contained in 1 kg of gypsum (Erdem et al., 1996).

Gypsum discharged in stockpiles is a potential source of enhanced natural radiation and heavy metals that can cause negative atmospheric impacts. The erosion of gypsum piles, the release of polluting substances, and the leaching of hazardous elements are matters of concern as atmospheric agents can transport the contamination to surrounding areas (Sahu et al., 2014).

#### Treatment Methods

Florida's primary drinking water source, the Floridan Aquifer, typically has low levels of radioactivity that are not usually considered a public health concern. However, the release of concentrated radionuclides from atop a gypsum stack into the aquifer may result in the degradation of groundwater quality and the radionuclide concentrations may exceed present drinking water standards. Radionuclides present in drinking water supplies pose a risk to public health due to their hazardous characteristics. Several regulatory approaches can be implemented to protect public health, but the feasibility and cost of compliance must be considered (Milvy & Cothern,

1990). There are numerous alternative technologies that can be used for the removal of radium and uranium from drinking water and their performance data is summarized in Table 2-3.

Method	Removal Efficiency, %		
	Radium	Uranium	
Activated alumina	N/A*	90	
Coagulation-filtration	N/A	80-98	
Electrodialysis	90	N/A	
Green sand	25-50	N/A	
Hydrous manganese oxide filter	90	N/A	
Ion exchange	81-99	90-100	
Lime softening	80-92	85-99	
Membrane technology	80-95+	90-99	

 Table 2-3: Technology and performance of processes for removing radionuclides from drinking water (adapted from Crittenden et al., 2012)

N/A = not applicable

Ion exchange, lime softening, and reverse osmosis are capable of removing radium and uranium simultaneously. These technologies are identified by the US EPA as a "best available technology" (BAT) and "small system compliance technology" (SSCT) for radium, uranium, and gross alpha. Since lime softening can be costly if softening is not a treatment goal, only ion exchange and reverse osmosis will be further studied for the removal of radionuclides.

#### Ion Exchange

The use of ion exchange (IX) in water treatment has increased due to the increased concern for the health effects of contaminant ions such as fluoride, barium, radium, and uranium. During IX

treatment, water passes through a resin that contains exchangeable ions; an ion in an aqueous state is exchanged for an ion in a solid state. In this way, dissolved ionic constituents that can cause aesthetic or health issues are removed (Crittenden et al., 2012). Weaker binding ions are removed from the water as they are displaced by stronger binding ions. IX columns can be divided in two categories:

- Cation exchange, which involves the exchange of positively charged ions such as sodium (Na<sup>+</sup>) and calcium (Ca<sup>2+</sup>)
- Anion exchange, which consists on the exchange of negatively charged ions such as sulfate
   (SO<sub>4</sub><sup>2-</sup>) and chloride (Cl<sup>-</sup>).

A sodium cation exchange resin can be used for radium removal as it is simple and economic. The removal of this radium is accomplished by passing contaminated water through a bed of strong acid cation (SAC) resin in the sodium form (Clifford & Zhang, 1994). Uranium can be removed by anion exchange resins, predominantly strong base anion (SBA) resins. Weak base resins can be used as well; however, their use is more limited (Gindler, 1962).

A fixed bed resin of two layers, 10 percent SBA and 90 percent SAC resins, can be used for radium and uranium removal. Clifford and Zhang (1994) conducted a study of the resins mixture using a water that contained 25 pCi/L radium and 120  $\mu$ g/L uranium; the fixed bed was able to treat the water to less than 1 pCi/L radium and 20  $\mu$ g/L uranium. The best resin regenerant was determined to be potassium chloride.

#### Membrane Technology

Membrane treatment uses differences in permeability as a separation technique between water and its constituents. This technology utilizes pressure to pass water against the surface of a semipermeable membrane to generate a product stream and retain impermeable components that are concentrated in the waste stream. The four main membrane processes used in drinking water treatment are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). The classification of membrane processes is summarized in Table 2-4.

In water treatment applications, the four types of membranes can be grouped in two distinct physicochemical processes: (1) membrane filtration and (2) reverse osmosis. Membrane filtration encompasses MF and UF, where suspended particles that are in the solid phase are separated from a liquid phase as water passes through the membrane. The resulting product stream is free of the targeted solids. Reverse osmosis includes NF and RO. NF is typically used to soften water by removing calcium and magnesium from water and RO is predominantly used as a desalination technology or to remove specific dissolved contaminants (Howe et al, 2012).

Membrane Technology	<b>Operating</b> <b>Pressure</b>	Minimum Approximate Particle Size Removed	Targeted Contaminants for Removal
MF	4-70 psi	0.1 µm	Particles, turbidity, bacteria & protozoa, coagulated organic matter, inorganic precipitates.
UF	4-70 psi	0.01 µm	Includes the above plus, viruses, organic macromolecules, colloids.
NF	70-140 psi	0.001 µm	Includes the above plus, hardness, color, DBP, precursors, larger monovalent ions, pesticides.
RO	140-700 psi	0.0001 µm	Includes the above plus, monovalent ions

Table 2-4: Membrane processes characteristics (adapted from Yonge, 2016)

#### Nanofiltration

Often referred as low pressure RO, NF membranes are used to reduce hardness in water by removing calcium and magnesium, freshening brackish waters, and reducing the concentration of dissolved organic carbon (DOC) that may serve as a disinfection by-product (DBP) precursor (Crittenden et al., 2012). NF membranes typically consist of a thin, semipermeable polymer material comprised in a spiral wound configuration where contaminants are separated from water by pressure. Feed water flows through the membrane following a spiral path and falls into a center collection tube producing clean water known as permeate, while constituents that do not pass through the membrane are rejected in a concentrate stream as seen in Figure 2-3 (Howe et al., 2012; Baker, 2004).

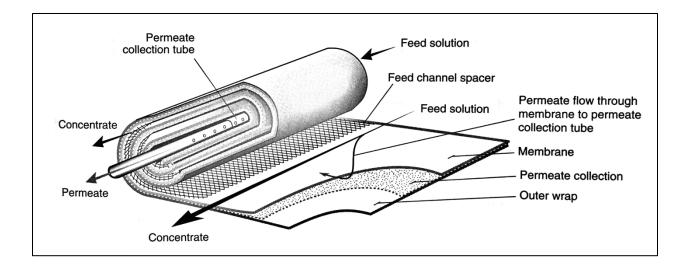


Figure 2-3: Construction of spiral-wound membrane element (Howe et al., 2012)

#### Reverse Osmosis

RO is a membrane treatment process that consists on the passage of a solvent through a semipermeable membrane to remove dissolved solutes from water. RO technology is typically used for desalination as it is effective in treating salinity from brackish and seawater sources. A high pressure stream is directed through a semipermeable membrane that rejects monovalent ions, increasing the osmotic pressure differential. RO requires additional pressure to overcome the osmotic pressure of the water required to achieve a solvent-solids separation. Osmosis is the passage of a solvent through a membrane from a more dilute to a more concentrated solution until concentrations equal on each side of the membrane. Reverse osmosis, on the other hand, is based on the diffusion of a solvent from a region of high salt concentration to a region of low salt concentration producing water known as permeate (Crittenden et al., 2012). Along with desalination, RO membranes can be used for other treatment purposes as it is capable of removing

specific dissolved contaminants. Removal efficiencies for the removal of radium and uranium are up to 95 and 99 percent, respectively.

Salt rejection using membrane technology can be accomplished due to the difference in mass transfer between water and salts. The percentage of salt rejected can be used as a performance parameter to determine if a membrane is suitable for various applications. Salt passage and salt rejection can be calculated as follows

$$SP = \left(\frac{C_p}{C_f}\right) \ \mathbf{100\%}$$

$$SR = 100\% - SP \tag{2-3}$$

Where,

#### SP is the salt passage

C<sub>p</sub> is the salt concentration in the permeate

C<sub>f</sub> is the salt concentration in the feed water

#### SR is the salt rejection

Permeate flux is the water flow rate that is diffused through a specified area of the membrane surface. High flux rates decrease permeate salinity but increase feed pressure and, depending on the water source, could result in fouling (Wilf, 2011). Low flux rates may not remove sufficient contaminants from feed water and therefore the permeate stream may not be sufficiently clean. Permeate flux is calculated by Equation (2-4). Membrane productivity indicates the percentage of permeate produced from the feed stream. Following a mass balance, the remaining amount of feed

water is concentrated in the waste or concentrate stream. The percent of feed water recovered as permeate, percent recovery, is calculated by Equation (2-5).

$$J_w = \frac{Q_p}{A} \tag{2-4}$$

$$\% recovery = \frac{Q_p}{Q_c} \ \mathbf{100\%}$$

Where,

A is the membrane surface area, m<sup>2</sup>

- $Q_p$  is the permeate flow rate, m<sup>3</sup>/day
- $Q_c$  is the concentrate flow rate, m<sup>3</sup>/day

The salt that limits the productivity of the membrane due to scaling is known as the "limiting salt." Calcium carbonate (CaCO<sub>3</sub>), calcium fluoride (CaF<sub>2</sub>), calcium sulfate (CaSO<sub>4</sub>), and barium sulfate (BaSO<sub>4</sub>) are common salts that can limit membrane's productivity. A general reaction of salts can be written following Equation (2-6); the percent recovery is determined by the solubility product as shown in Equation (2-7). Solubility product is a fundamental concept that indicates that all solids are soluble to some degree, even if they are considered insoluble (Sawyer, McCarty, & Parkin, 2003). Temperature correction of the solubility product constant is calculated by Equation (2-8). Determination of the limiting salt is important as it limits the productivity of water and, thus, the overall recovery of the water treatment plant.

$$A_n B_m(s) \leftrightarrow nA + mB \tag{2-6}$$

$$K_{sp} = \left[\frac{A}{x}\right]^n \left[\frac{B}{x}\right]^m \tag{2-7}$$

$$ln\left(\frac{K_{T_2}}{K_{T_1}}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$
(2-8)

Where,

K<sub>sp</sub> is the solubility product constant

n, m are the reaction order constants

Ea is the activation energy, J/mol

R is the universal gas constant, J/mol-K

T is temperature, K

Table 2-5 presents a summary of IX and RO processes for radionuclides removal. Radium and uranium can be simultaneously removed by RO membranes. IX technology requires a mixture of SBA and SAC for combined radium and uranium removal. The summarized processes are capable of lowering target contaminants' concentration to levels that meet the MCL limit. However, concentrate produced in the process is considered a radioactive waste that needs to be appropriately disposed. Concentrate can be disposed via underground injection. Class I injection wells are used for disposal of radioactive, hazardous, or other wastes; a waste is considered radioactive when radium concentration is higher than 60 pCi/L and uranium concentration is higher than 300 pCi/L (USEPA, 2001).

	Effects of treatment					
Water Treatment	Pote		ntial problems			
Process	Additional benefits	Radioactive-waste byproduct requiring proper disposal	Other			
Radium						
Cation exchange	<ul> <li>Removes hardness.</li> <li>Removes radium until hardness- removal capacity is exhausted.</li> <li>Inexpensive and widely used.</li> </ul>	Brine.	<ul> <li>Adds sodium.</li> <li>Softened water is corrosive.</li> </ul>			
	Radium an	d Uranium				
Reverse osmosis	- Decreases total dissolved solids.	Liquid.				
	Ura	nium				
Anion exchange		Brine.	<ul> <li>Sensitive to water pH.</li> <li>Suitable for treating large volumes of water.</li> </ul>			

Table 2-5: Summary of IX and RO processes (adapted from Zapecza and Szabo, 1986)

### United States Geological Survey Geochemical "PHREEQC" Model

The United States Geological Survey (USGS) has developed and released "PHREEQC", which stands for pH Redox Equilibrium (in C language). This available software to the public is a general purpose geochemical model for reactions in water and between water and rocks and sediments.

PHREEQC provides a one-dimensional (1-D) transport simulation for multiple environments including regional aquifer studies (US Geological Survey, 2016). The program is capable of (1) calculating speciation and saturation indices; (2) predicting one-dimensional transport with reversible and irreversible reactions; and (3) modeling inverse geochemistry (Parkhurst & Appelo, 2016). Results of PHREEQC modeling in similar studies have been relied on to study the transport of radionuclides through a 1-D column by the simulation of advection, diffusion, adsorption, and chemical reactions to estimate contaminant travel times which are of interest to the research presented herein (Sandhu, Manuscript in Progress).

# **CHAPTER 3. EXISTING CONDITIONS**

In late August 2016, a sinkhole spanning 45 feet (13.7 meters) in diameter opened at a Mosaic Company's (Mosaic) phosphate fertilizer facility near Mulberry, Florida, leaking an estimated 215 million gallons (813,000 cubic meters) of contaminated water into the Floridan aquifer. Mosaic reported on August 27, 2016 that the monitoring system at its New Wales facility at Mulberry, Florida, showed a decline in water levels from the retention pond of a phosphogypsum stack, a hill of hazardous waste. Phosphogypsum is a radioactive byproduct resulting from the production of phosphate. It is believed that the Minnesota-based company immediately reported the incident to state and federal environmental authorities; however, Mosaic did not otherwise report the incident publicly until almost three weeks had passed. The sinkhole, located about 30 miles from Tampa, damaged the liner system at the base of the stack, causing the pond on top to drain. Seepage continued and the sinkhole reached Florida's aquifer.

Since the water released into the aquifer through the sinkhole may degrade groundwater quality, an effort was made to characterize the impacts on water quality on the surrounding communities. To this end, PCU and TBW allowed UCF to access their water purveyor's closest groundwater production wells in Hillsborough and Polk County. PCU's closest municipal water well is located approximately 6 miles from the Mosaic sinkhole and two of TBW production wells are located in the vicinity of the sinkhole. These wells that are located within the dispersed wellfield in Hillsborough and Polk County are shown in Figure 3-1.

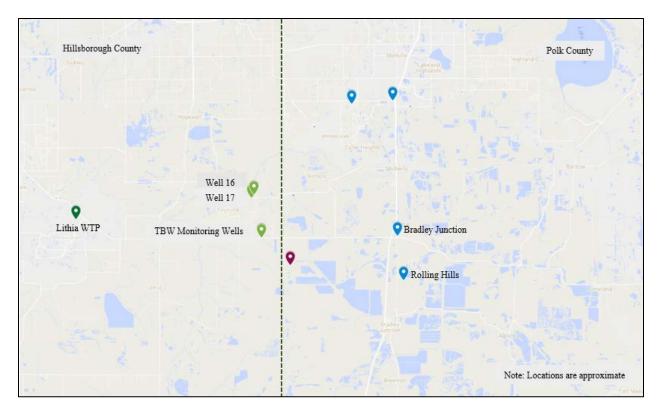


Figure 3-1: PCU and TBW's monitoring locations used in this study

# Polk County Utilities

PCU has several small water treatment plants (WTP) that provide water to its customers; the ones of interest are Bradley Junction and Rolling Hills due to their closeness to Mosaic's New Wales facility. The characteristics associated with the groundwater production wells are summarized in Table 3-1; flow rate is expressed as gallons per day (gpd). The groundwater is of high quality, therefore, only disinfection is required before distribution. The water pumped from the well is treated with free chlorine as hypochlorous acid for disinfection prior to entering the storage tank. Figure 3-2 illustrates the schematic of the treatment process of Bradley Junction and Rolling Hills WTPs.

Table 3-1: PCU's groundwater production wells characteristics

Well	Depth, ft	Capacity, gpd
Bradley Junction	551	410,000
Rolling Hills	812	588,000

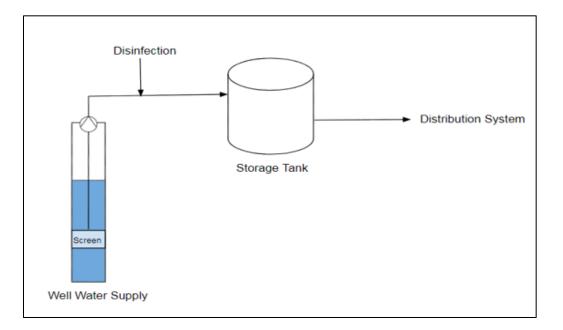


Figure 3-2: Schematic of PCU's WTP Process flow

### Tampa Bay Water

TBW's Lithia WTP is located in Hillsborough County, west of the Mosaic sinkhole. Lithia WTP is supplied with groundwater from the Floridan Aquifer by several production wells; UCF was allowed to access two production wells and two monitoring wells by TBW for sampling and monitoring of groundwater quality:

- Production Well 16

- Production Well 17
- South Central Hillsborough Monitoring Well 5 Intermediate Aquifer (SCHM 5IA)
- South Central Hillsborough Monitoring Well 5 Deep (SCHM 5D)

The use of Well 16 and Well 17 was stopped as a protective measure to minimize the potential of the contaminated plume to be transmitted into the water purveyor's drinking water system. This action prevents the compromise of water quality.

The characteristics of the wells are presented in Table 3-2; flow rate is expressed as million gallons per day (mgd). Treatment of water consists on addition of ozone ( $O_3$ ) for hydrogen sulfide ( $H_2S$ ) removal, addition of free chlorine as hypochlorous acid followed by the addition of ammonia for chloramines production as shown in Figure 3-3. The finished product water from the south central wellfield is then blended with treated surface water and sent to the distribution system.

Well	Depth, ft	Capacity, mgd
Well 16	910	1.5
Well 17	903	1.5
SCHM 5IA	98	N/A
SCHM 5D	255	N/A

Table 3-2: TBW's groundwater production wells characteristics

N/A = not applicable

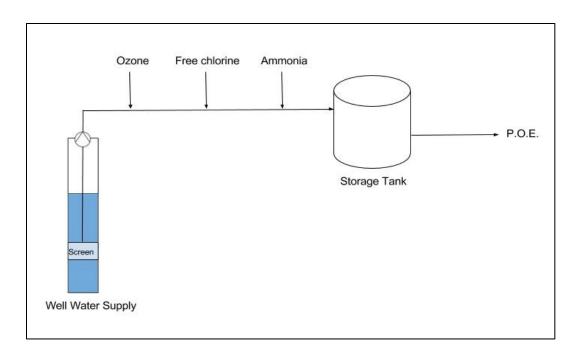


Figure 3-3: Schematic of Lithia WTP process flow

Table 3-3 depicts average raw water quality for each well prior to the sinkhole event; the historical data was provided by PCU and TBW. These values represent typical background levels of the Floridan wells in this region of the state. It was noted that gross alpha levels are less than 3.0 pCi/L, and that radium-226 and radium-228 are both less than 1.0 pCi/L each; these numbers serve as a baseline condition for radionuclides concentration in this region of Florida. A deviation of typical levels would be noticed during sampling events; small anomalies in radionuclides or inorganic constituents content will be observed should the plume disperse into the regional water supplies. During water quality monitoring, groundwater samples will be analyzed for constituents that are indicative of the type of water that was released by the sinkhole into the Floridan Aquifer including pH, conductivity, turbidity, sodium, sulfate, fluoride, total dissolved solids (TDS), gross alpha, combined radium, and uranium.

Parameter	Bradley Junction	Rolling Hills	Well 16	Well 17	SCHM 5IA	SCHM 5D
рН	7.80	7.80	7.60	7.60	11.1	7.50
Temperature, °C	25.6	26.5	25.9	26.6	24.4	24.8
Conductivity, µS/cm	375	443	462	459	533	512
Turbidity, NTU	0.340	0.080	0.240	0.330	5.87	0.070
Sodium, mg/L	6.15	6.86	8.51	16.6	4.77	7.07
Calcium, mg/L	43.9	53.4	42.9	48.2	34.1	55.4
Magnesium, mg/L	13.1	14.0	13.8	7.70	13.8	17.0
Fluoride, mg/L	0.250	0.220	0.320	0.360	0.450	0.240
Sulfate, mg/L	44.8	56.7	19.5	67.8	3.90	70.6
TDS, mg/L	205	243	206	260	77	194

Table 3-3: Regional water quality parameters pre-spill

### The Mosaic Company

Mosaic is a phosphate-based fertilizer production company located in Polk County, FL. A sinkhole collapsed underneath one of the gypsum stacks in Mosaic's New Wales facility, leaking approximately 215 million gallons of water into the Floridan Aquifer. Phosphogypusm, a fertilizer production byproduct, was contained in the active stack. Accumulation of phosphogypsum is accomplished by separating the byproduct from the produced phosphoric acid by a filter system and then washed from the filters with process water. Phosphogypsum is then pumped as a slurry from the filters into the stack system. Average characteristics of the untreated process water used to pump the phosphogypsum into the stack are presented in Table 3-4. The process water is radioactive (gross alpha levels are 3,891 pCi/L) and fluoridated (fluoride levels account for 28 percent of the total dissolved solids in the product waste). Combined radium concentration (79

pCi/L) is well higher than the drinking water regulatory limit (5pCi/L) and so are the other water characteristics presented, including inorganic constituents. Background concentrations of water contaminants found atop the stack are important to determine the impact of the sinkhole event on the quality of water in the surrounding environment.

Parameter	<b>Untreated Process Water</b>
рН	1.31
Calcium, mg/L	1,962
Magnesium, mg/L	616
Sodium, mg/L	2,109
Potassium, mg/L	295
Aluminum, mg/L	241
Iron, mg/L	233
Manganese, mg/L	11.1
Chloride, mg/L	190
Fluoride, mg/L	13,207
Silica, mg/L	6,543
Sulfate, mg/L	8,024
Total Phosphorus as P, mg/L	9,207
Ammonia Nitrogen as N, mg/L	872
Combined Radium, pCi/L	79
Gross alpha, pCi/L	3,891
TDS, mg/L	46,584

Table 3-4: New Wales Process Water Characteristics (FDEP, 2017)

Following the opening of the sinkhole, Mosaic started diverting the process water from the gypsum stack to minimize the amount of water spilled into the aquifer. It was determined that in the

particular site underneath the New Wales facility the aquifer moves in a westward direction at a rate of 130 feet per month (Ardaman & Associates, Inc., 2017). This means that it would take more than 2 years for the released water to move past Mosaic's property boundaries. Mosaic is interceding by drawing water from the aquifer back to the surface using a recovery well located immediately west of the sinkhole. Mosaic has also been monitoring groundwater quality utilizing several monitor wells that tap into the Floridan Aquifer within the property's boundaries to secure the integrity of drinking water. The company confirms that the lost water has not moved past the recovery well, as expected by simulation models (Mosaic Co., 2017).

Mosaic hired a geotechnical engineering consultancy to evaluate and implement the necessary steps to repair the sinkhole. Remediation incorporates the use of a cement-grout mixture to fill the cavity from bottom to top. Grouting activities consists of an initial stabilization phase where concrete mix is injected in the base of the sinkhole cavity through deep angled holes. Deep injection grouting is also used for the stabilization of the confining layer; the grout mixture is injected into the confining layer around the base of the sinkhole through angled drilled holes as seen in Figure 3-4 (Mosaic Co., 2017; Fuleihan et al., 1997).

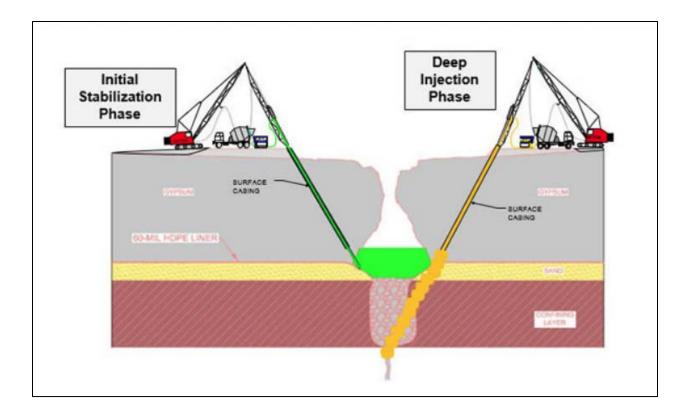


Figure 3-4: Sinkhole repair process (Mosaic Co., 2017)

The 2016-sinkhole is the second sinkhole that opens at the New Wales site. In 1994 a sinkhole collapsed under a gypsum stack at the New Wales's facility, the company was then known as IMC-Agrico Co. The opening of the first sinkhole resulted in the implementation of lining systems underneath new gypsum stacks to obstruct the infiltration of process water (Tihansky, 1999). Mosaic used the mitigation plan for the 1994-sinkhole as a base for remediating the latest sinkhole. Given the case that the same engineering consultancy was hired to remediate the sinkhole, the procedures to contain the contaminated groundwater and to fill the cavity were already known. Pumping of process water by recovery wells to prevent its movement off-site and angled drilling processes to fill the sinkhole cavity were measures taken on both occasions to repair the damage.

# **CHAPTER 4. MATERIALS AND METHODS**

This chapter presents the procedure and materials used in this study. Laboratory quality assurance and quality control (QA; QC) procedures were followed in accordance with Standard Methods for the Examination of Water and Wastewater (2017) for this study. However, basing laboratory experiments on standards methods does not indicate that accurate and reliable results will be obtained. Method specific containers are a requisite to maximize the quality of data, which depends on the integrity of the samples and materials utilized to perform analyses.

### Water Quality Monitoring

Monitoring of the water quality was performed at specific well-sites at each of the two counties that were deemed having the highest chance of being impacted by the radioactive spill into the aquifer. Limited sampling was completed post-spill to determine the concentration of radionuclides and inorganic constituents in groundwater. Temperature, pH, conductivity and turbidity were determined on-site. Bulk water samples were collected and transported to UCF for analysis of sodium, magnesium, calcium, barium, fluoride, sulfate, TDS, and alkalinity. Additional bulk water samples were collected and sent to Florida Radiochemistry Services Inc. (5456 Hoffner Ave. #201, Orlando, FL 32812) for analysis of radium-226, radium-228, uranium, and gross alpha; and to Advanced Environmental Laboratories Inc. (380 Northlake Blvd., Altamonte Springs, FL 32701) for analysis of total phosphorus (total-P).

### Flat Sheet Performance Testing

Literature indicates that nanofiltration and reverse osmosis are capable of treating radionuclides in drinking water. Consequently, reverse osmosis membrane technology was evaluated to confirm that the process could efficiently remove radionuclides from TBW and PCU's well water supplies. A bench-scale, flat-sheet membrane testing unit was used to evaluate the performance of the technology, confirm the assumptions described in literature, and document the performance experienced in the field.

Groundwater was collected from Tampa Bay Water's production Well 17, which was not in service at the time the research was conducted. To collect water samples at the production well, TBW would run the well at full capacity for 20 minutes prior to sampling by UCF; the water was discharged to irrigation ditches as if a distribution system flushing event was executed. TBW would shut down the well after sampling. Bulk water samples were taken to UCF, where reverse osmosis and nanofiltration flat sheets were tested at a bench scale using a CF042 cross flow flat sheet membrane filtration unit (CF042, Sterlitech, Kent, WA). The flat sheet testing apparatus allows for an evaluation of an active surface area of 42 square centimeters (cm<sup>2</sup>) of the membrane film.

A solution was prepared to measure the removal efficiency of the membranes based on different initial concentrations of barium and fluoride, which were used as surrogates for radium and uranium since UCF was unable to secure a permit by the U.S. Nuclear Regulatory Commission that allows testing using radioactive elements. Barium is utilized as a conservative surrogate as it follows radium chemistry. Fluoride was selected as a surrogate as it is a pollutant contained in phosphate fertilizer manufacturing waste; fluoride is about 19 percent of the total product waste (Glasser, 1998). A reduction of barium and fluoride concentrations from the feed stream supposes a reduction of radium and uranium. The removal efficiency of the surrogates is determined by

$$\% removal = 100\% - \left(\frac{C_p}{C_f}\right)$$
(4-1)

Where,

C<sub>p</sub> is the salt concentration in the permeate

### C<sub>f</sub> the salt concentration in the feed water

Several studies were conducted utilizing different concentrations of the surrogates. Fluoride and barium were spiked into groundwater from TBW's production Well 17, creating the solution to be tested. Feed water samples were taken for each solution prior to its loading into the flat sheet testing unit. Dow FilmTec flat sheet membranes were used to test the performance of reverse osmosis technology; membrane NF270 was used to test NF and membrane BW30LE was used to test RO.

The pre-cut membranes were placed in a beaker with distilled water for 24 hours prior to the test. To start the experiment, the membranes were loaded into the cell and the system was run for 20 minutes with distilled water under recommended pressure (55 psi for NF; 200 psi for RO) to remove any residual chemicals from manufacturing. Distilled water was then drained and the prepared solutions using TBW groundwater were loaded into the system for testing.

Figure 4-1 shows the flat sheet testing unit. The unit consists of a 1.5 gallon reservoir that pushes feed water by a high-pressure pump to the membrane cell. Two valves are located on the bypass and concentrate flow lines and are used to adjust flow rate and pressure. A schematic flow diagram of the flat sheet testing unit is illustrated in Figure 4-2. Permeate and concentrate streams are recycled back into the reservoir for a period of 8 hours to allow the system to equilibrate. Once the system has equilibrated, a permeate sample can be collected followed by appropriate cleaning of the unit using distilled water.



Figure 4-1: CF042 flat sheet testing unit

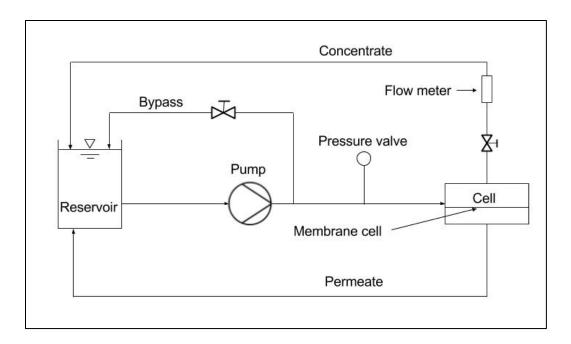


Figure 4-2: Flat sheet apparatus flow diagram

#### Analytical Methods

Sampling and collection procedures were followed in accordance with Standard Methods (2017). The methods and equipment used for the evaluation of water quality parameters by UCF is presented in Table 4-1; the equipment used for cation and anion analyses in the UCF drinking water laboratories is presented in Table 4-2.

During laboratory testing, duplicates and spikes were prepared every five samples for TDS, metal, and anion analyses for quality analysis and quality control purposes. Duplicates are used to assess precision determined by relative percent difference (RPD). Spikes help determine the accuracy of the samples based on the average percent recovery, warning limits, and control limits.

Test	<b>Testing Location</b>	<b>Method/Equipment Description</b>	
pH, Temperature,		PCU: YSI Professional Plus	
Conductivity	On-site	TBW: In-Situ Smartroll Multiparameter Probe	
Tuchidity	On site	PCU: Hach 2100 Q Portable Turbidimeter	
Turbidity	On-site	TBW: In-Situ Smartroll Multiparameter Probe	
Alkalinity	UCF Laboratory	SM 2320 B. Titration Method	
TDS	UCF Laboratory	SM 2540 C. Total dissolved solids dried at 180 °C	
Total phosphorus	AEL Inc.	EPA 265.4 Copper sulfate digestion	
Gross alpha	EDS Inc	EPA 900.0 Gross alpha and gross beta	
Gross alpha FRS Inc.		radioactivity	
Ra-226; Ra-228	FRS Inc.	EPA 903.1 Radium-226; EPA Ra-05 Radium-228	
Uranium	FRS Inc.	EPA 908.0 Uranium	

Table 4-1: List of methods and equipment for water quality analysis (adapted from Myers, 2016)

Table 4-2: Equipment used for anion and cation analyses at UCF laboratory (adapted from Myers, 2016)

Analysis	Parameter	Equipment
Ion chromatography (IC)	Anions (F <sup>-</sup> , SO4 <sup>2-</sup> )	Dionex ICS-110 with AS40 automated sampler
Inductively coupled plasma (ICP) spectrometer	Cations (Na <sup>+</sup> , Ca <sup>2+</sup> , Mg <sup>2+</sup> , Ba <sup>2+</sup> )	Perking Elmer Optima 2100 DV

### Laboratory Quality Control

Laboratory quality control measures were applied to produce reliable data in accordance with Method 1020 B. Quality Control from Standard Methods (2017). Glassware and sample containers used in this study were washed with laboratory grade detergent, acid-washed using a 1:1 HCl solution, and rinsed with distilled water prior to use. Reagents used for analyses were American Chemical Society (ACS) grade chemicals. A Barnstead-Thermolyne distillation unit was utilized for distilled water production; a Thermo Scientific Barnstead Water Purification System was used for deionized water production.

# Precision

Duplicates are used to assess the precision of a sample set. Duplicates are a separate aliquot of a sample, resulting in the analysis of two independent samples. Precision can be determined by RPD or the industrial statistic (I-stat) as shown in Equation (4-2) and Equation (4-3), respectively. Deviations in sample preparation procedure can be detected in precision control charts that are developed based on RPD or I-stat.

$$RPD = \frac{X_1 - X_2}{\frac{X_1 + X_2}{2}} \ 100\%$$
(4-2)

$$I - stat = \left| \frac{X_1 - X_2}{X_1 + X_2} \right|$$
(4-3)

Where,

 $X_1$  is the sample concentration, mg/L.

X<sub>2</sub> is the duplicate sample concentration, mg/L.

### Accuracy

Spiked samples are used to assess the accuracy of a sample. A known concentration of an ACS grade analyte is added to a sample to determine the accuracy and consistency of the analytical instrumentation (IC; ICP). Percent recovery of the spiked samples is calculated using Equation (4-4). Recoveries considered acceptable are within the range of 80 and 120 percent.

$$\% Recovery = \frac{C_{sample+spike} - C_{sample}}{C_{spike}} 100\%$$
(4-4)

### Where,

C<sub>sample</sub> is the concentration of the sample, mg/L.

C<sub>spike</sub> is the concentration of the known spike added, mg/L.

C<sub>sample+spike</sub> is the concentration of the spiked sample, mg/L.

# **CHAPTER 5. RESULTS AND DISCUSSION**

During water quality monitoring, a comparison between pre and post spill raw water quality data helped analyze if the plume dispersed into regional water supplies. Pre spill data served as a baseline condition and post spill data was used to determine any increase in contamination levels. Any irregularities in typical values could indicate the plume was transmitted to local drinking water supplies. In the case contaminant levels surpassed EPA's regulation limits, a mitigation plan would be necessary to meet drinking water standards.

#### Post-Spill Conditions

PCU and TBW collaborated with UCF in the sampling and monitoring practices to characterize the quality of water in the Floridan Aquifer subsequent to the spill. Sampling from four production wells (two in Polk County and two in Hillsborough County) and two monitoring wells (Hillsborough County) was completed to determine raw water quality post-spill. Samples were collected between June 2017 and January 2018. Table 5-1 displays present raw water quality for every well.

Water quality data to-date indicates that there is no evidence of an increasing trend in contaminants concentrations. Concentrations at neighboring wells are stable and do not show a changing trend, increasing or decreasing. The water quality parameters evaluated were found to fall well within the primary and secondary limits for every well sampled. Combined radium levels are well below the MCL, 5 pCi/L. Gross alpha levels are close to the baseline concentration determined pre-spill as 3 pCi/L for this region of the aquifer. Uranium levels are below detection limits. Fluoride concentrations are within the range of values of pre-spill data. The remaining water quality

parameters possess no change in concentrations when comparing pre and post-spill results. This evidence indicates that the contaminated plume has not been transmitted to this region of Florida and therefore the nearby communities have not been affected in their drinking water supplies at this point in time. Although the data suggests that the wells are not impacted by the spill, this is not to say that the wells would not be impacted in the future.

Parameter	Bradley Junction	Rolling Hills	Well 16	Well 17	SCHM 5IA	SCHM 5D
рН	7.80	7.80	7.60	7.70	11.1	7.50
Temperature, °C	25.3	26.0	25.8	26.8	24.2	24.2
Conductivity, µS/cm	373	434	442	476	421	512
Turbidity, NTU	0.340	0.080	0.520	0.390	6.40	0.090
Sodium, mg/L	6.09	6.84	8.46	14.6	4.81	7.16
Calcium, mg/L	43.8	50.1	42.9	49.6	30.1	55.7
Magnesium, mg/L	13.0	14.0	13.8	12.3	7.60	17.1
Barium, mg/L	0.0069	0.0055	0.015	0.024	0.062	0.010
Fluoride, mg/L	0.380	0.390	0.440	0.470	0.650	0.600
Sulfate, mg/L	44.7	56.6	19.8	67.2	4.09	71.2
TDS, mg/L	202	241	201	257	65	215
Gross alpha, pCi/L	2.55	2.07	2.53	3.29	2.40	1.87
Radium-226, pCi/L	0.590	0.720	0.700	0.810	1.08	0.770
Radium-228, pCi/L	0.860U	0.880U	0.830U	0.860U	0.950U	0.870U
Uranium, pCi/L	0.490U	0.400U	0.470U	0.530U	0.450U	0.400U
Total P, mg/L	0.049U	0.054U	0.068U	0.050U	0.048U	0.047U
Alkalinity, mg/L as CaCO <sub>3</sub>	176	139	155	117	61	153

Table 5-1: Regional water quality parameters post-spill

#### Impact

An assessment of potential impacts on nearby water purveyors and their ability to treat contaminants should the plume migrate into the regional water supplies is presented in this report. An adequate characterization of the impacts of the sinkhole collapse on the regional environment involves the analysis of water quality. If the plume disperses into the wellfield located in the vicinity of the sinkhole, Hillsborough and Polk County's water communities may be economically affected. The aquifer's groundwater generally flows in a westward direction and it is expected that the plume migrates following the projected direction of flow. Due to this fact, TBW's wellfield can be compromised in regards to water quality as it is located west of the sinkhole as shown in Figure 5-1. Two of TBW's production wells (each well has a capacity of 1.5 mgd) were taken offline after the sinkhole collapse as a protective measure to minimize the potential of the contaminated plume to flow into their drinking water system. However, had the wells continued to be used, drawdown could pull contaminated water to the wells and affect drinking water quality.

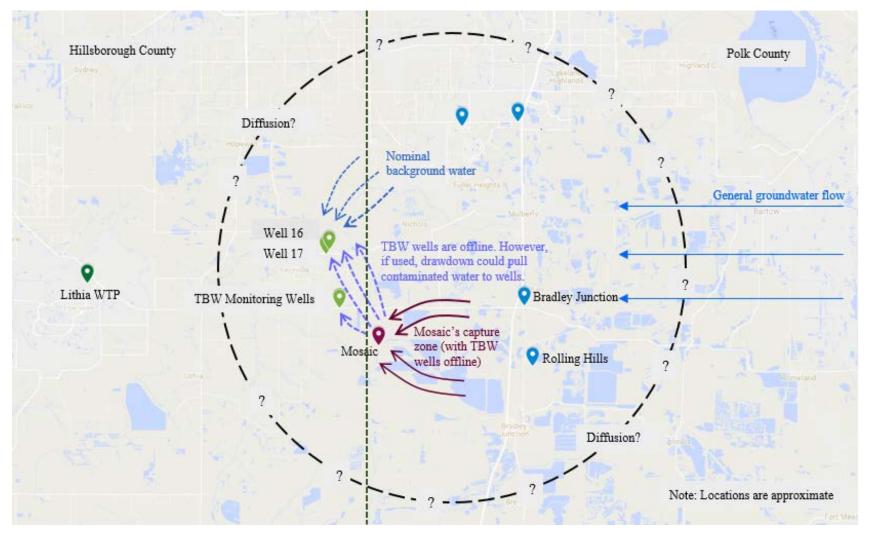


Figure 5-1: TBW and PCU's monitoring locations used in this study and general groundwater flow direction

Since that time of the breach in the pond liner, Mosaic has recovered water on-site by pumping it at a rate of 3 mgd through a well that taps into the Floridan aquifer and is located west of the sinkhole as displayed in Figure 5-2. Exact timelines are not available but continued during the timeline of this study reported upon herein. Capturing of the spilled water on Mosaic's site, along with the interrupted use of two of TBW's production wells, seems to be a good remediation technique as it appears that the contamination is successfully being contained. Drawdown at Mosaic's well seems to impede the movement of the contaminated water along the Floridan aquifer, preventing the transmission of a contaminated plume into regional water supplies.

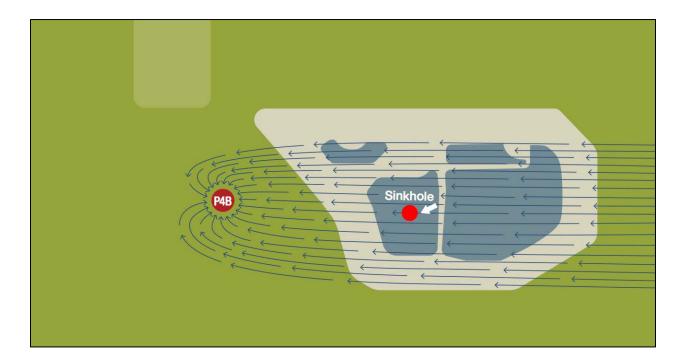


Figure 5-2: Recovery well in zone of capture (Mosaic Co., 2017)

Due to the elevated levels of the contaminants in the released process water, it is assumed that a deviation of the Floridan Aquifer typical water characteristics would be easily noticed if affected by the spill. Groundwater samples were analyzed for constituents that indicate if the water supply

would be impacted by the released water. Raw water quality pre-spill was used as a baseline condition to compare against raw water quality post-spill; any anomalies would be observed. However, water quality data to-date indicates that there is no evidence of an increasing trend in contaminants concentrations. Concentrations at neighboring wells are stable and do not show a changing trend, increasing or decreasing.

The impact of the sinkhole event on the water purveyors is a function of their ability to treat water contaminated with radioactive waste and other pollutants. Although water quality and production data appear to indicate that there are no impacts on the neighboring water purveyors, there is still the need to guide water communities for dealing with a contaminated plume in case they are ever affected. Meeting drinking water standards is the ultimate requirement and therefore a plan for optimizing groundwater remediation measures is presented herein. From the existing conditions in PCU and TBW's water treatment plants, additional treatment is required for the removal of the released contaminants from water. To this end, nanofiltration is recommended as the treatment technology for the removal of radionuclides and other pollutants.

### Flat Sheet Performance Testing

A bench-scale, flat-sheet membrane testing unit was used to evaluate the performance of nanofiltration and reverse osmosis technologies regarding radionuclides removal. Several studies were conducted utilizing TBW's groundwater spiked with different concentrations of fluoride and barium that were used as surrogates for radium and uranium. The removal efficacy of both technologies is determined by the surrogates' concentrations in the feed and permeate streams.

Testing was completed by running the system at a recommended pressure of 55 and 200 psi for nanofiltration and reverse osmosis, respectively, for an 8-hour period. Membrane productivity, determined by permeate and concentrate flow rates, is presented in Table 5-2 for NF and RO. Permeate flux rate is also shown in Table 5-2 for a membrane surface area of 42 cm<sup>2</sup>, as specified in Chapter 4. Flux rate is a relevant design parameter as if it is high, fouling can occur and pressure costs increase whereas if it is low, treatment may result in insufficient removal of contaminants. The system was allowed to run at different percent recoveries for NF and RO treatment.

Membrane technology	Q <sub>p</sub> , mL/min	Qc, mL/min	% Recovery	J <sub>w</sub> , mL/min-m <sup>2</sup>
NF Treatment	4.99	19.9	25.0	1,190
RO Treatment	1.52	14.3	10.6	362

Table 5-2: Percent recovery and permeate flux

Barium's initial concentrations range from 0.060 mg/L to 0.090 mg/L. Results are provided in Table 5-3 with Dow FilmTec NF and RO membranes for the barium test. NF and RO were shown to be capable of removing 86 and 92 percent, respectively, of the barium content that had been spiked into TBW and PCU well water testing aliquots as performed under these simulated conditions. These specific results indicate that RO provides only a 6 percent advantage over NF for barium removal effectiveness; hence either technology could be applied for treatment. Permeate barium content was found to be less than the equipment's detection limit; it is reasoned that removal efficiency of NF and RO may in fact be greater than the calculated value, based on the minimum detection limit (MDL) of 0.005 mg/L for Ba.

NF Treatment			RO Treatment		
Feed, mg/L	Permeate, mg/L	Removal, %	Feed, mg/L	Permeate, mg/L	Removal, %
0.061	< 0.005	91.8*	0.063	< 0.005	92.1*
0.071	< 0.005	93.0*	0.073	< 0.005	93.2*
0.080	0.008	90.0	0.083	< 0.005	94.0*
0.090	0.013	85.6	0.093	< 0.005	94.6*

Table 5-3: Flat sheet testing results for barium test

\* Assuming permeate concentration is at MDL

Removal of fluoride was also tested as New Wales untreated process water contains high levels of fluoride. NF and RO membranes were analyzed at a bench scale level using a flat-sheet membrane testing unit. Fluoride treatment was equal to barium treatment in this study; feed water was circulated for an 8-hour period at a recommended pressure of 55 and 200 psi for NF and RO, respectively. An initial fluoride concentration of 0.74 mg/L was used to determine the removal efficiency of both treatment methods. Permeate concentrations were 0.11 and 0.07 mg/L and thus NF and RO were shown to remove a minimum of 85 and 91 percent, respectively, of fluoride from water.

Control on the percent recovery was not accomplished in this study. However, literature supports the removal efficiencies tested using a flat-sheet unit, confirming that membrane technology can be used to treat radionuclides in this region of the aquifer. Laboratory results show that membrane processes are capable of removing at least 85 and 92 percent of surrogates fluoride and barium, respectively, from the groundwater supply. This data agrees with minimum removal efficiencies specified in literature as 80 and 90 percent for radium and uranium, respectively (Crittenden,

Trussell, Hand, Howe, & Tchobanoglous, 2012). Therefore, removal of the selected surrogates could correlate to the removal of radium and uranium, attributed to the comparable efficiencies of contaminants removal.

Results indicate that both treatment technologies would be effective in removing radionuclides from groundwater based on the barium and fluoride tests. NF technology is sufficient to treat radionuclides in drinking water premised on a tested minimum removal efficiency of 85 and 91 of fluoride and barium, respectively. Since NF is able to remove the studied surrogates at the observed high efficiency rates, RO is not further considered as a treatment method because of its high operational costs.

### Limiting Salts

The salt that limits the productivity of the membrane, known as limiting salt, was determined in order to identify the maximum percent recovery of raw water from Well 17. The studied salts were CaCO<sub>3</sub>, CaF<sub>2</sub>, CaSO<sub>4</sub>, BaSO<sub>4</sub>. Water quality information, including ions concentration and water temperature, was obtained from Table 5-1 as it indicates typical groundwater characteristics in the studied section of the aquifer. The effect of ionic strength was not considered in this research. The calculated percent recovery is presented in Table 5-4. Barium sulfate was determined to be the limiting salt as it had a negative recovery of 36 percent. Addition of sulfuric acid and antiscalant should be implement as pretreatment techniques to improve the recovery of the membrane plant.

Salt	% Recovery
CaCO <sub>3</sub>	- 13.0
CaF <sub>2</sub>	63.6
CaSO <sub>4</sub>	72.0
BaSO <sub>4</sub>	- 36.0

Table 5-4: Percent recovery of salts

### Quality Control Results

This section presents the quality control measures that were conducted in accordance with Standard Methods as described in Chapter 4. The laboratory analysis conducted throughout this study include barium and fluoride. Data sets were analyzed for accuracy and precision. Duplicates are used to assess the precision of a sample set by RPD or I-stat. Spiked samples are used to assess the accuracy of a sample by analyzing the percent recovery. Precision and accuracy were controlled based on Table 5-5.

Control	RPD	Percent Recovery
Good	Below 5%	90% - 110%
Pass	5% - 10%	80% - 120%
Fail	Above 10%	Above 120% or Below 80%

Table 5-5: Quality control guidelines

Shewhart control charts show statistical data for precision and accuracy. However, due to limited sampling, there were not sufficient samples to generate control charts in this research. Typically, a minimum of thirty duplicates and spikes are used to create Shewhart control charts; twenty points

are used to generate the chart and ten points are plotted for testing. For this reason, quality control parameters are instead presented in Table 5-6 and Table 5-7 for barium, and Table 5-8 and Table 5-9 for fluoride. There was one percent recovery fluoride value violation. The violation corresponded to a sample set taken on July 18<sup>th</sup>, 2017. The values of the original sample and spiked sample are 0.33 and 0.45 mg/L, respectively. The spiked concentration was intended to be 0.2 mg/L; however, the samples values show only a 0.12 mg/L difference. The insufficient spiked amount is likely due to human error.

Sample #	% Rec	% Rec Control	RPD	<b>RPD</b> Control
1	89	Pass	1.00	Good
2	90	Good	0.20	Good
3	102	Good	1.00	Good
4	98	Good	1.20	Good
5	100	Good	5.50	Pass
6	101	Good	4.10	Good
7	107	Good	7.80	Pass
8	107	Good	1.18	Good
9	111	Pass	2.78	Good
10	104	Good	0.52	Good
11			0.73	Pass

Table 5-6: Percent recovery and RPD of barium

Sample #	Duplicate A	Duplicate B	I statistic
1	0.02	0.02	0.106
2	0.08	0.08	0.001
3	0.01	0.01	0.154
4	0.092	0.091	0.006
5	0.004	0.005	0.027
6	0.001	0.001	0.020
7	0.006	0.005	0.039
8	0.021	0.021	0.006
9	0.003	0.003	0.014
10	-0.004	-0.004	0.003
11	0.063	0.063	0.004

Table 5-7: Precision assessment for barium quality control

Table 5-8: Percent recovery and RPD of fluoride

Sample #	% Rec	% Rec Control	RPD	<b>RPD</b> Control
1	91	Pass	0.16	Good
2	91	Pass	0.09	Good
3	55	Fail	1.79	Good
4	86	Pass	3.39	Good
5	110	Good	4.98	Good
6			1.27	Good

Sample #	Duplicate A	Duplicate B	I statistic
1	0.38	0.38	0.001
2	0.57	0.57	0.000
3	0.24	0.24	0.009
4	0.33	0.34	0.017
5	0.02	0.03	0.025
6	0.24	0.24	0.006

Table 5-9: Precision assessment for fluoride quality control

#### Application of PHREEQC Results to Estimate Radionuclide Zones of Influence

The soil in southwest Florida is primarily made up of carbonate minerals, such as calcite and dolomite. For this reason, results of PHREEQC modeling studies that simulate the transport of radium contaminated groundwater assuming carbonate-rich soils were relied on to estimate radium levels at the distance between the sinkhole and each well monitored in this research (Sandhu, Manuscript in Progress).

An initial radium concentration of 79 pCi/L was used based on levels found in the process water stored atop the New Wales gypsum stack (FDEP, 2017). In the software, contaminants concentrations are naturally lowered as groundwater flows by advection and diffusion. Adsorption by the carbonate soil further reduces radium levels in groundwater; the reaction for radium sorption by carbonate surfaces is defined in Equation (5-1) (Reese & Langmuir, 1985).

$$Ra^{2+} + CO_3^{2-} \rightarrow RaCO_3$$
  $log K = 2.5$  (5-1)

Results indicate that radium concentrations in groundwater are lowered to levels below regulatory limits (5 pCi/L) at an approximate distance of 3.1 miles (5.0 km) from the New Wales facility.

Table 5-10 shows the predicted impact time and radium concentration for the distance between each well and the sinkhole, based on the simulation results. The impact time was determined by the estimated 130 feet per month rate of groundwater movement and the distance between each well and the New Wales site (Ardaman & Associates, Inc., 2017).

Well	Distance from	Time to reach	Radium conc., pCi/L	
vv en	sinkhole, miles (km)	well, years		
Bradley Junction	4.9 (7.9)	16.6	4.15	
Rolling Hills	5.1 (8.2)	17.2	4.09	
Well 16	3.4 (5.5)	11.6	4.80	
Well 17	3.2 (5.1)	10.7	4.94	
SCHM 5IA; SCHM 5D	1.8 (2.8)	5.89	6.31	

Table 5-10: Predicted impact time and radium levels at specified distance

The closest PCU and TBW drinking water wells are located approximately 4.9 and 3.2 miles, respectively, from Mosaic's site. The predicted concentrations at these distances are below regulatory limits. Therefore, every production well monitored in this study appears to be safe from the contaminated plume. TBW's monitoring wells are located approximately 1.8 miles from the sinkhole and exhibit a radium concentration higher than the MCL. It is expected that the plume reaches the monitoring wells approximately 6 years subsequent to the sinkhole event. Groundwater quality monitoring should be continued for at least the time TBW is predicted to be impacted (6 years for the monitoring wells; 11 years for the closest water production well) to review if there are any changes in groundwater quality.

# **CHAPTER 6. COST EVALUATION**

### Conceptual Membrane Process Cost

Degradation of the source water quality indicates that the implementation of a treatment method would be necessary for radionuclides removal from the drinking water facilities located in the proximity to the radioactive water spill. As described in the literature and as confirmed by flat sheet performance testing, it appears that nanofiltration would provide treatment of TBW's or PCU's wells if impacted by the Mosaic sinkhole event. Consequently, a cost analysis is presented for the construction, operation and maintenance of a membrane technology process for a groundwater source in west-central Florida. The opinions of probable costs presented herein should be only used for comparative purposes to other water treatment processes as they are not based on formal design plans and drawings and hence are conceptual in nature. A much more detailed cost estimate should be performed during the design phase to adequately develop more accurate opinions of probable costs for estimating purposes. The capital costs of NF treatment would be similar to RO due to the comparable design characteristics. Costs of the two treatment processes would mainly differ in power costs as RO requires more pressure and, therefore, has higher operational costs.

The opinions of probable costs have been estimated for 0.25, 0.5, 1.0, 1.5, and 2.0 mgd flow rates for a groundwater nanofiltration system with conventional pretreatment of acid feed and filtration at 85 percent recovery and an operating pressure of 55 psi. The flow rates were chosen to satisfy three conceptual situations: (1) PCU's Bradley Junction and Rolling Hills water plants typically operate at a flow rate of 0.25 mgd; (2) the capacity of both of TBW's production wells studied in this project (Well 16 and Well 17) is 1.5 mgd; and (3) smaller scale process equipment would be required if blending is viable to comply with drinking water standards for a lower range of radionuclides. The conceptual capital and operation and maintenance (O&M) costs are shown in Table 6-1. The costs were estimated from various sources (UCF ESEI 1997; Taylor 1989; USEPA 1979) and updated using the Engineering News Record (ENR) construction cost index to 2017.

The estimated capital costs include process buildings, process equipment, and costs associated with the construction of deep well injection. The costs for land and finished water storage tanks have been excluded from the conceptual cost estimations and should be separate from the costs used for comparison purposes. The estimated capital cost was determined for the process buildings, including pretreatment, membrane process, bulk chemical storage, cleaning system, clearwell and pumps, administration and laboratory, and power vault. Capital costs of process equipment include cartridge filters, membrane process, process pumps, chemical feed, cleaning system, aerator, process piping, instrumentation and control, and electrical systems. The deep well injection structure costs include the well and the transport pipeline.

The conceptual capital costs for buildings, process equipment, and deep well system range between \$147,500 and \$503,500, \$313,000 and \$675,000, and \$1,225,000 and 2,325,000, respectively, for a process flow range of 0.25 and 2.0 mgd. Total capital costs are then estimated to range between \$1,685,000 for a 0.25 mgd and \$3,503,500 for a 2.0 mgd process flow. The capital cost per thousand gallons of water produced amortized over 20 years at 8 percent is \$1.88 and \$0.49 for the 0.25 and 2.0 mgd plants, respectively. The installed process cost per gallon per day is displayed in Figure 6-1 for the treatment plants designed.

Catagory	Plant Capacity, mgd				
Category	0.25	0.5	1.0	1.5	2.0
<u>Capital</u>					
Buildings	\$147,500	\$229,000	\$316,000	\$420,000	\$503,500
Pretreatment					
Membrane Process					
Bulk Chemical Storage					
Cleaning System					
Clearwell and Pumps					
Administration and Lab					
Power Vault					
Process Equipment	\$313,000	\$360,000	\$430,000	\$525,000	\$675,000
Cartridge Filters					
Membrane Process					
Process Pumps					
Chemical Feed					
Cleaning System					
Aerator					
Process Piping					
Instrument. & Control					
Electrical Systems					
\$/gpd installed	\$1.25	\$0.72	\$0.43	\$0.35	\$0.34
Deep Well	\$1,225,000	\$1,400,000	\$1,775,000	\$2,050,000	\$2,325,000
Injection Well					
Transport Pipeline					
Total Capital Cost	\$1,685,000	\$1,989,000	\$2,521,000	\$2,995,000	\$3,503,500
\$/Kgal (20yrs at 8%)	\$1.88	\$1.11	\$0.70	\$0.56	\$0.49
$O \approx M (non year)$	\$246 400	\$204 200	¢270.000	¢156 500	\$500 500
<u>O &amp; M (per year)</u>	\$246,400	\$304,300	\$379,000	\$456,500	\$529,500
Wages					
Power Chamical Supplies					
Chemical Supplies					
Maintenance					
Deep Well					
Other	¢0.00	<u> </u>	¢0.20	<u>ቀስ 20</u>	ф <u>о</u> ос
\$/Kgal	\$0.99	\$0.61	\$0.38	\$0.30	\$0.26
Total Cost	<b>\$3.97</b>	ф1 <b>7</b> 0	¢1 Δ0	ቀሳ ዕረ	<u>ቀ</u> ር <i>ግር</i>
\$/Kgal	\$2.87	\$1.72	\$1.08	\$0.86	\$0.75

Table 6-1: Cost estimate for nanofiltration plant

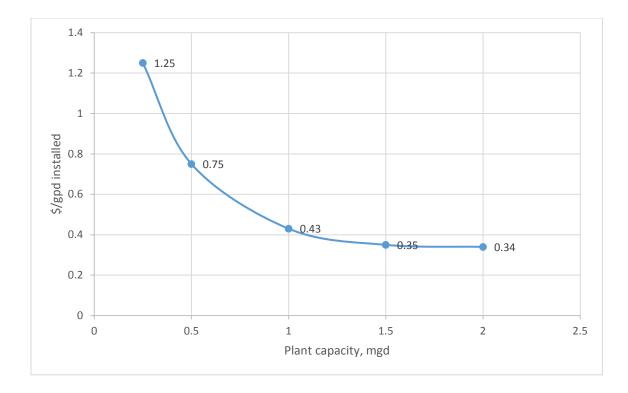


Figure 6-1: Installed process cost per gallon per day

Operation and maintenance of the groundwater nanofiltration system costs were estimated considering wages, power, chemical supplies, maintenance, and O&M costs related to the deep well system. Maintenance costs include cartridge filters replacement, membrane replacement, pump maintenance, and professional controls and electrical maintenance contracts. The total O&M costs were estimated to range between \$246,000 and \$530,000 per year or \$0.99 and \$0.26 per thousand gallons of water produced for a process flow range between 0.25 and 2.0 mgd.

The chosen method of concentrate disposal is deep well injection. The cost for deep well injection was estimated assuming only one deep well is required per plant due to their small process flows. Disposal at 85 percent recovery indicates that 15 percent of the feed flow is wasted as concentrate; for conservative purposes, the deep well is designed to hold 20 percent of the feed flow to account

for discrepancies. A 10-inch diameter ductile iron pipe was used to transport the concentrate to a distance of 5 miles from the membrane plant. Per Florida regulations, the cost of the deep well was estimated as a Class I injection well for hazardous and radioactive waste.

#### Water Quality Monitoring Extension

TBW production wells may be affected by the contaminated plume in approximately 11 years from the event, based on the estimated 130-foot per month rate of groundwater movement and the distance of 3.2 miles between the New Wales site and TBW's production wells. Groundwater quality monitoring should be continued for at least the time at which TBW is predicted to be impacted (11 years). Costs of radionuclides testing are presented in Table 6-2. It is recommended that monitoring events are conducted every 60 days for a period of 2 decades, at a minimum, to verify that radionuclide concentrations are close to typical values. Continuing quality monitoring of two production wells and two monitoring wells supposes an \$840 cost per sampling event and an annual cost of \$5,040. If any deviations in water quality are observed, further treatment would be necessary.

Table 6-2: Radionuclides testing costs

Parameter	Cost	
Gross alpha	\$ 30	
Combined radium	\$ 120	
Uranium	\$ 60	

## Unavailable Water Considerations on Cost

TBW ceased production of two 1.5 mgd capacity groundwater production wells closest to the spill as a protective measure to prevent contaminated water to flow into the water purveyor's system. Since the wells are useful but not being used, halting their use represents an opportunity loss that would impact TBW as the amount of costs of the wells exceed their revenue produced. Restraining from the use of the production wells affects TBW because (1) the cost of maintenance of the wells continues to accumulate even though they are not being used and (2) TBW is obliged to obtain raw water from a different source.

The sinkhole collapse at Mosaic's New Wales facility represents a consequence to the unrelated drinking water facility TBW. The release of contaminated water into the Floridan Aquifer lead to externalities to TBW as they had to take action to protect the integrity of drinking water. Had the sinkhole not happened, TBW would continue normal operations of both production wells. However, two production wells were shut down and are not longer being operated. This represents a cost for equipment and water that is not yielding public benefit as designed. Additionally, having the wells on continuous standby may in the future cause wear on the equipment due to non-use.

TBW is required to flush the wells every 180 days for 20 minutes to avoid a bacteriological clearance event. Treatment of biofouling, or biological clogging, consists on disinfection of the wells by adding a dose of 50 parts per million (ppm) of free chlorine and agitating the well water. The chlorine is allowed to stay within the well for a 24-hour period to kill the bacteria or other microorganisms. Once the 24 hours have elapsed, the well system is flushed to remove the microorganisms and the chlorinated water. The extensive bacteriological clearance event is

avoided by periodical flushing of the wells conducted by TBW operators, which represents a cost to TBW that had the sinkhole not occurred, TBW would not be paying.

The efforts of TBW in maintaining the two out-of-service production wells incurs a cost to the utility, and would include maintenance, labor, and groundwater quality monitoring for radionuclides. Based on TBW's base water cost of \$2.56/Kgal, and assuming that the daily well use approximates 25 percent, then an annual "unavailable" water cost can be approximated to be \$350,400 per year (per well), or \$0.64 per thousand gallons. This number represents the value that the water holds when not in use, as it is considered unavailable. Additional costs will continue to be incurred in the future as well maintenance continues in addition to recommended periodic radionuclide and frequent surrogate monitoring occur at both TBW and PCU wellfields that are located closest to the Mosaic sinkhole for the next two decades, at a minimum.

## **CHAPTER 7. CONCLUSIONS AND RECOMMENDATIONS**

The release of contaminated water by the sinkhole collapse under Mosaic's New Wales facility lead to public concerns regarding the possible impacts to the surrounding environment and the local drinking water supplies. For this reason, monitoring of groundwater quality was conducted from June 2017 to January 2018 where water quality parameters that were considered indicative of the type of water released by the sinkhole were analyzed. Water quality parameters included pH, sulfate, fluoride, TDS, combined radium, uranium, and gross alpha. Water samples collected by UCF at the TBW and PCU sites were found to contain radionuclides below regulated levels. This indicates that Mosaic's claims of water containment on their site appear to be true and regional water supplies have not been affected. It is concluded that TBW's preventative measure to discontinue the use of two of their production wells allowed for the containment of the released water by Mosaic. This conclusion is based on the fact that TBW's drawdown could pull contaminated water to their wells given the groundwater is projected to flow in a westward direction.

The information collected in the water quality evaluation component of the work conducted herein was used to model the transport of groundwater using the computer program PHREEQC. Results indicate that advection and diffusion processes lower radium concentrations in groundwater to levels below regulatory limits at an approximate distance of 3.3 miles (5.3 km) from the New Wales facility. The closest PCU well is located approximately 4.9 miles (7.9 km) from the sinkhole and most likely will not be impacted by the plume should one exist. TBW drinking water wells and monitoring wells are located approximately 3.2 miles (5.1 km) and 1.8 miles (2.8 km)

from Mosaic's site. Based on PHREEQC results, the time it will take the plume to reach TBW wells was predicted to be approximately 6 and 11 years for the monitoring wells and the closest water production well, respectively. For this reason, groundwater quality monitoring should be continued for at least the time TBW is predicted to be impacted to review if there are any changes in groundwater quality.

To evaluate the effectiveness of membrane treatment should the TBW and PCU drinking water wells be affected by the spill in the future, bench-scale, flat-sheet RO and NF membrane process testing was performed using wellfield sample aliquots from this region of the aquifer. Barium and fluoride were used as surrogates of radionuclides in this study. NF and RO were shown to be capable of removing a minimum of 85 and 92 percent, respectively, of the barium content that had been spiked into the testing aliquots. Removal efficiencies of fluoride were a minimum of 86 and 91 percent for NF and RO, respectively. Results indicate that both treatment technologies would be effective in removing radionuclides; however, NF technology is sufficient to treat radionuclides based on the observed high efficiency rates and therefore RO is not further considered as a treatment method because of its high operational costs.

Although the data suggests that the wells have not been impacted by the spill, this is not to say that the wells would not be impacted in the future. For this reason, a nanofiltration system was designed at different flow capacities, ranging from 0.25 to 2.0 mgd, to be implemented in drinking water utilities should they be affected by the contaminated plume. A conceptual opinion of probable process capital cost that includes a building and deep well for concentrate disposal as well as the process operation and maintenance was presented for the different NF flow rates. The implementation of a nanofiltration system costs were completed for the drinking water utilities in the vicinity of the sinkhole should they have to implement further treatment methods to remove radionuclides from groundwater. The opinions of probable costs have been estimated for 0.25, 0.5, 1.0, 1.5, and 2.0 mgd flow rates. The conceptual capital costs range between \$1,685,000 and \$3,503,500 for a process flow range of 0.25 and 2.0 mgd, respectively. The total O&M costs were estimated to range between \$246,000 and \$530,000 per year or \$0.99 and \$0.26 per thousand gallons of water produced for a water flow range between 0.25 and 2.0 mgd. An estimate of unavailable water value due to a long-term well shut-down was approximated as \$0.64/Kgal.

## APPENDIX. WATER QUALITY MONITORING COMPLETED DURING STUDY

June	6,	2017
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Parameter	Bradley Junction	Rolling Hills	Well 16	Well 17	SCHM 5IA	SCHM 5D
pН	7.62	7.67	7.59	7.59	11.1	-
Temperature, °C	25.2	27.0	25.9	25.9	24.2	-
Conductivity, µS/cm	391	453	411	411	427	-
Turbidity, NTU	-	-	0.410	0.400	4.59	-
Sodium, mg/L	6.40	7.01	8.67	9.04	5.20	-
Calcium, mg/L	42.9	50.6	40.3	53.7	25.9	-
Magnesium, mg/L	-	-	-	-	-	-
Barium, mg/L	0.01	0.007	0.022	0.030	0.081	-
Fluoride, mg/L	0.420	0.900	0.440	0.480	0.630	-
Sulfate, mg/L	47.5	56.1	11.9	69.1	-	-
TDS, mg/L	199	231	176	260	70	-
Gross alpha, pCi/L	2.05	1.90U	3.60	2.75	2.30	-
Radium-226, pCi/L	0.40	0.20U	0.70	0.85	1.00	-
Radium-228, pCi/L	0.80U	1.0	0.80U	0.95	1.1	-
Uranium, pCi/L	0.55U	0.40U	0.60U	0.40U	0.4U	-
Total P, mg/L	0.048U	0.092	0.048U	0.048U	0.048U	-
Alkalinity, mg/L as CaCO3	-	-	-	-	-	-

	Jul	у 1	8,	20	17
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Parameter	Bradley Junction	Rolling Hills	Well 16	Well 17	SCHM 5IA	SCHM 5D
рН	7.66	7.69	7.66	7.69	11.1	7.53
Temperature, °C	26	25.9	25.8	27.3	24.4	24.8
Conductivity, µS/cm	403	469	512	506	533	512
Turbidity, NTU	0.340	0.080	0.070	0.250	5.87	0.07
Sodium, mg/L	5.46	6.21	7.40	7.71	4.50	6.88
Calcium, mg/L	43.7	54.1	39.3	54.5	34.7	54.5
Magnesium, mg/L	-	-	-	-	-	-
Barium, mg/L	0.007	0.005	0.017	0.023	0.092	0.012
Fluoride, mg/L	0.470	0.380	0.520	0.550	0.730	0.640
Sulfate, mg/L	45.0	58.2	13.6	66.2	3.88	70.6
TDS, mg/L	193	228	181	260	95	95
Gross alpha, pCi/L	1.70U	1.80U	2.20	5.70	2.70	1.60U
Radium-226, pCi/L	0.40	0.60	0.50	1.0	1.0	0.60
Radium-228, pCi/L	0.80U	0.80U	0.80U	0.80U	0.80U	0.80U
Uranium, pCi/L	0.40U	0.40U	0.40U	0.60U	0.40U	0.40U
Total P, mg/L	0.048U	0.048U	0.048U	0.048U	0.048U	0.048U
Alkalinity, mg/L as CaCO3	-	-	-	-	-	-

November	1,	20	17
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Parameter	Bradley Junction	Rolling Hills	Well 16	Well 17	SCHM 5IA	SCHM 5D
pН	7.73	7.65	7.70	7.59	11.1	7.52
Temperature, °C	24.9	25.7	25.7	27.1	24.3	23.7
Conductivity, µS/cm	389	460	394	502	328	498
Turbidity, NTU	-	-	1.12	0.61	3.31	0.1
Sodium, mg/L	5.5	6.35	7.73	55.4	4.61	7.26
Calcium, mg/L	45.2	55.6	41.6	17	41.6	56.32
Magnesium, mg/L	13.1	14	13.8	7.74	13.8	17
Barium, mg/L	0.0055	0.0050	0.0180	0.0220	0.0184	0.0094
Fluoride, mg/L	0.480	0.400	0.540	0.580	0.730	0.620
Sulfate, mg/L	45.5	56.8	14.6	64.6	4.30	71.7
TDS, mg/L	214	247	210	273	66	292
Gross alpha, pCi/L	2.60	1.60U	-	2.40U	1.80	1.70U
Radium-226, pCi/L	0.40	0.60	-	0.40	0.70	0.30
Radium-228, pCi/L	0.70U	0.80U	-	0.90U	0.90U	0.90
Uranium, pCi/L	0.60U	0.40U	-	0.60U	0.50U	0.40U
Total P, mg/L	0.048U	0.048U	0.048U	0.048U	0.048U	0.048U
Alkalinity, mg/L as CaCO3	130	139	153	120	62	157

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Parameter	Bradley Junction	Rolling Hills	Well 16	Well 17	SCHM 5IA	SCHM 5D
рН	7.42	7.69	7.61	7.75	11.0	7.45
Temperature, °C	25.2	25.2	25.7	27.1	23.9	23.5
Conductivity, µS/cm	390	390	402	510	309	512
Turbidity, NTU	-	-	1.09	0.52	6.92	0.10
Sodium, mg/L	5.51	6.42	7.54	7.89	4.92	7.33
Calcium, mg/L	43.3	40.1	40.1	53.6	18.1	56.2
Magnesium, mg/L	12.8	13.9	13.7	16.8	1.37	17.1
Barium, mg/L	0.0050	0.0050	0.0018	0.0210	0.0570	0.0090
Fluoride, mg/L	0.380	0.330	0.430	0.460	0.50	0.530
Sulfate, mg/L	44.6	54.8	19.2	62.7	4.40	72.1
TDS, mg/L	182	224	149	246	30	257
Gross alpha, pCi/L	2.10U	1.70U	1.80U	2.30U	2.80	2.30U
Radium-226, pCi/L	0.90	1.10	0.900	1.00	1.60	1.40
Radium-228, pCi/L	1.3	0.90U	0.90U	0.80	1.0	0.90
Uranium, pCi/L	0.40U	0.40U	0.40U	0.50U	0.50U	0.40U
Total P, mg/L	0.046U	0.046U	0.046U	0.046U	0.046U	0.046U
Alkalinity, mg/L as CaCO <sub>3</sub>	222	139	157	113	60	148

## REFERENCES

- Aieta, E. M., Singley, J. E., Trussell, A. R., Thorbjarnarson, K. W., & McGuire, M. J. (1987). Radionuclides in Drinking Water: An Overview. *American Water Works Association*, 144-152.
- Ardaman & Associates, Inc. (2017). Zone of Capture Evaluation, New Wales Phosphogypsum Stack System, Mosaic Fertilizer.
- Baird, R. B., Eaton, A. D., & Rice, E. W. (2017). Standard Methods for Examination of Water and Wastewater 2017. Washington, DC: American Public Health Assn.
- Baker, R. W. (2004). *Membrane Technology and Applications*. West Sussex, England: John Wiley & Sons Ltd.
- Benefield, L. D., Judkins, J. F., & Weand, B. L. (1982). Process Chemistry for Water and Wastewater Treatment. Englewoods Cliffs, NJ: Prentice-Hall, Inc.
- Bengtsson, T. O. (1987). The hydrologic effects from intense ground-water pumpage in eastcentral Hillsborough County, Florida. In proceedings 2nd Multidisciplinary Conference on Sinkholes and the Environmental Impacts of Karst. Balkema, Rotterdam (pp. 109-114).
- Brinkmann, R., Parise, M., & Dye, D. (2008). Sinkhole distribution in a rapidly developing urban environment: Hillsborough County, Tampa Bay area, Florida. *Engineering Geology*, 99(3-4), 169-184.

- Burnett, W. C., & Elzerman, A. W. (2001). Nuclide migration and the environmental radiochemistry of Florida phosphogypsum. *Jorunal of Environmental Radioactivity*, 54(1), 27-51.
- Clifford, D., & Zhang, Z. (1994). Modifying Ion Exchange for Combined Removal of Uranium and Radium. *American Water Works Association*, 86 (4): 214-227.
- Cothern, C. R., & Rebers, P. A. (1990). Radon, radium, and uranium in drinking water. CRC Press.
- Crittenden, J. C., Trussell, R. R., Hand, D. W., Howe, K. J., & Tchobanoglous, G. (2012). Water Treatment: Principles and Design (3rd Ed.). Hoboken, New Jersey: John Wiley & Sons, Inc.
- Erdem, E., Tinkilic, N., Yilmaz, V. T., Uyanik, A., & Olmez, H. (1996). Distribution of uranium in the production of triple superphosphate (TSP) fertilizer and phosphoric aid. *Fertilizer Research*, 44: 129-131.
- Falck, W. E., & Wymer, D. (2006). Uranium in phosphate ferlitizer production. *Uranium in the environment*, 857-866.

Floir. (2010). Review of the 2010 Sinkhole Data Call. Florida Office of Insurance Regulation.

- Florida Department of Environmental Protection. (2017). New Wales Process Water Characteristics.
- Froehlich, K. (2009). Environmental radionuclides: tracers and timers of terrestrial processes (Vol. 16). Elsevier.

- Fuleihan, N. F., Cameron, J. E., & Henry, J. F. (1997). The hole story: How a sinkhole in a phosphogypsum pile was explored and remediated. In B. F. Beck, & B. J. Stephenson, *The Engineering Geology and Hydrogeology of Karst Terranes* (pp. 363-370).
- Gindler, J. E. (1962, March). *The Radiochemistry of Uranium*. Illionis: Argonne National Laboratory.
- Glasser, G. C. (1998). Fluoride and the Phosphate Connection. *Earth Island Journal*, 13(3), 14-15.
- Gray, K. M. (2014). *Central Florida sinkhole evaluation*. Technical Publication, Florida Department of Transportation, District, 5.
- Helfferich, F. (1995). Ion Exchange. New York: Dover Publications, Inc.
- Howe, K. J., Hand, D. W., Crittenden, J. C., Trussell, R. R., & Tchobanoglous, G. (2012). *Principles of Water Treatment*. John Wiley & Sons.

Insurance Journal. (2011). Florida's Top 10 Sinkhole-Prone Counties.

Jammal, S. E. (1982). The Winter Park Sinkhole and Central Florida Sinkhole Type Subsidence. Winter Park, Florida: Jammal and Associates.

JDC Phosphate. (2014). The Wet Acid Process.

Johnson, B. (2010, June). Measuring Radionuclides in the Environment.

L'Annunziata, M. F. (2007). Radioactivity: introduction and history. Elsevier.

Milvy, P., & Cothern, R. (1990). Scientific background for the development of regulations for radionuclides in drinking water. In *Radon, radium and uranium in drinking water*.

Mosaic Co. (2017). New Wales Water Loss Incidet - Resources.

- Munter, R. (2011). Technology for the Removal of Radionuclides form Natural Water and Waste Management: State of the Art. *Proceedings of the Estonian Academy of Sciences*, 62 (2): 122-132.
- Myers, S. (2016). Control of Metal-Release and Tuberculation in a Silica-Laden Groundwater Distribution System on the Volcanic Island of Lana'i. (Masters Thesis), University of Central Florida, Orlando, Florida.

National Aeronautics and Space Administration. (2013). The Electromagnetic Spectrum.

- Parkhurst, D. L., & Appelo, C. (2016). Description of Input and Examples for PHREEQC Version
  3: A Computer Program for Speciation, Batch-Reaction, One-Diomensional Transport, and Inverse Geochemical Calculations. US Geological Survey.
- Reese, A. C., & Langmuir, D. (1985). The thermodynamic properties of radium. *Geochim. Cosmochim. Ac.*, 49, 1593-1601.

Rupert, F., & Spencer, S. (2004). Florida's sinkholes. Florida Geological Survey, Poster, 11.

Sahu, S. K., Ajmal, P. Y., Bhangare, R. C., Tiwari, M., & Pandit, G. G. (2014). Natural radioactivity assessment of a phosphate fertilizer plant area. *Journal of Radiation Research and Applied Sciences*, 7(1): 123-128.

- Sajih, M., Bryan, N. D., Livens, F. R., Vaughan, D. J., Descostes, M., Phrommavanh, V., . . . Morris, K. (2014). Adsorption of radium and barium on goethite and ferrihydrite: A kinetic and surface complexation modelling study. *Geochimica et Cosmochimica Acta*, 146, 150-163.
- Sandhu, D. (Manuscript in progress). Sinkhole collapse: Fate and transport of contaminated radioactive water in Floridan aquifer with implications to drinking water supply. (PhD Dissertation), University of Central Florida, Orlando, Florida.
- Sawyer, C. N., McCarty, P. L., & Parkin, G. F. (2003). *Chemistry for Environmental Engineering* and Science (5th Ed.). New York: McGraw Hill.
- Shen, J., & Schafer, A. (2014). Removal of fluoride and uranium by nanofiltration and reverse osmosis: A review. *Chemosphere*, 117, 679-691.
- Sidhu, K. S., & Breihart, M. S. (1998). Naturally occurring radium-226 and radium-228 in water supplies of Michigan. *Bulletin of environmental contamination and toxicology*, 61(6), 722-729.
- Sinclair, W. C. (1982). Sinkhole development resulting from ground-water withdrawal in the Tampa area, Florida. (No. 81-50, pp i-19). US Geological Survey.
- Spechler, R. M., & Kroening, S. E. (2007). *Hydrology of Polk County, Florida*. US Department of the Interior, US Geological Survey.
- Taylor, J. S., Duranceau, S. J., Goigel, J., & Barrett, W. (1989). Assessment of Potable Water Membrane Application and Research Needs. *The Water Research Foundation, Denver.*

Thyne, G. D. (2007). PHREEQC Modeling Short Course.

Tihansky, A. B. (1999). Sinkholes, West-Central Florida. US Geological Survey, 121-140.

University of Central Florida Environmental Systems Engineering Institute. (1997). Evaluation of membrane technology using the pilot-scale test for compliance of the information collection rules. Orlando, Florida.

US Geological Survey. (2016). PHREEQC.

USEPA. (1979). Estimating Water Treatment Costs, Vol. II (EPA-600/2-79-162n).

USEPA. (2001). Class I Underground Injection Control Program: Study of the Risks Associated with Class I Underground Injection Wells (EPA 816-R-01-007).

USEPA. (2009). National Primary Drinking Water Regulations (EPA 816-F-09-004).

- Watson, A. P., Etnier, E. L., & McDowell-Boyer, L. M. (1983). Radium-226 in Drinking Water and Terrestrial Food Chains: a Review of Parameters and an Estimate of Potential Exposure and Dose. Oak Ridge, TN: Oak Ridge National Laboratory.
- Whitman, D., Gubbels, T., & Powell, L. (1999). Spatial interrelationships between lake elevations, water tables, and sinkhole occurrences in central Florida: A GIS approach. *Photogrammetric Engineering and Remote Sensing*, 65(10), 1169-1178.
- Wilf, M. (2011). *The Guidebook to Membrane Desalination Technology*. Hopkinton: Balaban Desalination Publications.

- Wilson, W. L., McDonald, K. M., Barfus, B. L., & Beck, B. F. (1987). Hydrogeologic Factors Associated with Recent Sinkhole Development in the Orlando Area, Florida. Florida Research Institute, University of Central Florida (No. 87-88, p. 4).
- Yonge, D. (2016). Modeling mass transfer and assessing cost and performance of a hollow fiber nanofiltration membrane process. (PhD. Dissertation), University of Central Florida, Orlando, Florida.
- Zapecza, O. S., & Szabo, Z. (1986). Natural radioactivity in ground water A review. US Geological Survey National Water Summary, 50-57.