“Impact of shallow wastewater injection on the Florida Keys National Marine Sanctuary”

Semi-Annual Progress Report
EPA Grant Number 02D02621
October 2021

PI: Dr. Miquela Ingalls
Co-I: Dr. Lee Kump
Graduate Research Assistants: Kate Meyers and Megan Martin
Undergraduate Researcher: Cameron Brown

I. Work Status

In our original proposal, we predicted we would begin work in early Spring 2021. However, due to delays in funding from the EPA, we were only able to start spending in May 2021. At that time, two new graduate students at Penn State were onboarded and are now the primary actors on the project: Kate Meyers and Megan Martin. In May and June, Meyers and Martin worked on development of sampling protocols and procuring equipment and supplies for the first sampling trip. In early June, PIs Kump and Ingalls oversaw drilling of 12 monitoring wells (20’, 50’, and 90’ deep) by JC Drilling (Miami, FL) surrounding the City of Marathon Area 3 Wastewater Treatment Facility (Fig. 1). The entire Penn State team returned to Marathon in July 2021 to collect the first water sample timepoint. During this visit we gathered real-time environmental data from each well depth (temperature, salinity/conductivity, dissolved sulfide concentration, and pH; see Table 1). Within 24 hours of sample collection, we measured total orthophosphate concentrations (Table 1) using a Hach method and a spectrophotometer at Keys Marine Lab (KML). Alkalinity was determined by titration within 24 hours at KML. Additional samples were transported back to Penn State for dissolved cation and anion analyses in the PSU Laboratory for Isotopes and Metals in the Environment (LIME), and nutrient analyses by spectrophotometry. Martin and Meyers have been working on methods development for in-house nutrient analyses due to an unforeseen issue with our contracted lab (see section II).

In addition to the geochemical work we originally proposed, we have added a geophysical component to the project scope. A Penn State undergraduate, Cameron Brown, joined us on the July field trip to conduct resistivity surveys of several transects near to Area 3 WTF and our monitoring wells. The goal of the resistivity surveys is to detect the “fresh” wastewater plume via contrast with the saline, more conductive groundwater that saturates the porosity of the Key Largo Limestone.

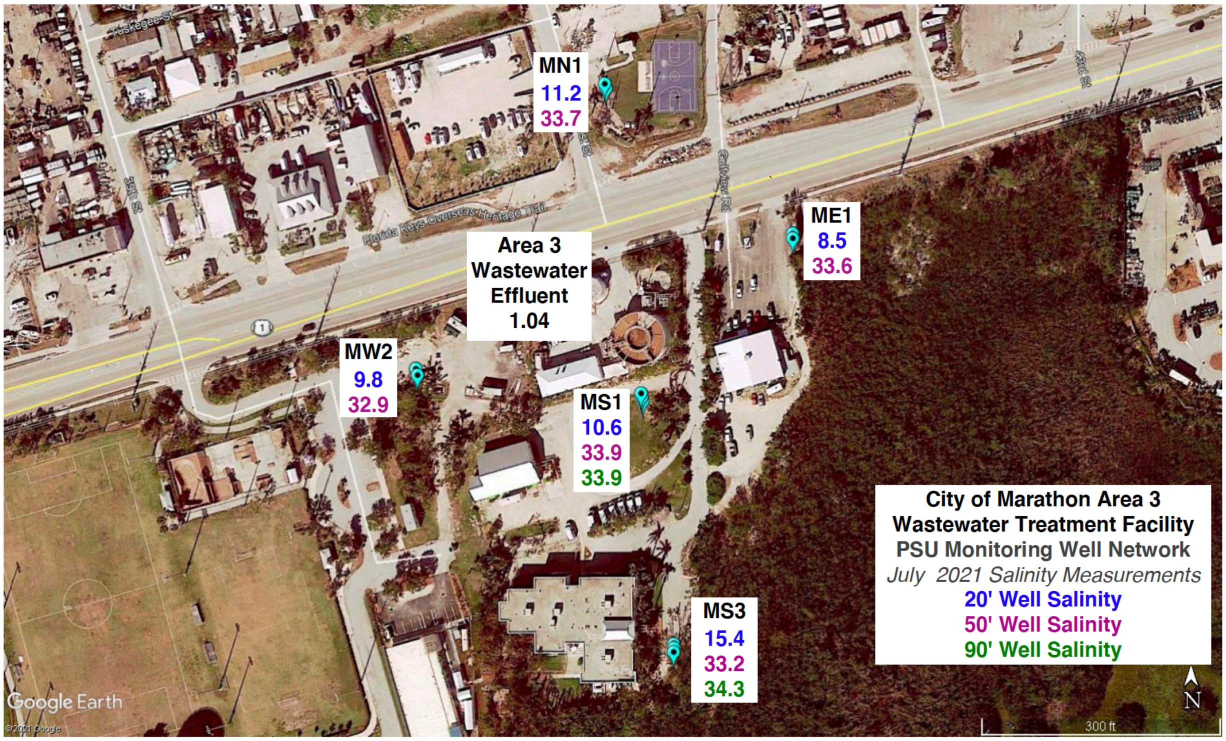

Figure 1. Area 3 Wastewater Treatment Facility site map. 5 monitoring well clusters with 2-3 depths sampled at each well cluster are mapped. At each well cluster, salinities are reported for each depth.The lower salinities reflect a greater wastewater influence.

II. Difficulties encountered

We are slightly behind our proposed schedule due to the delay in receiving funding. In addition, we originally planned to send samples to a lab at Florida International University for nutrient analyses (N, P), but encountered issues to do with incompatibility with the Penn State billing system. As an interim approach, we are now performing N and P nutrient analyses via established methods using our in-house spectrophotometer. We are exploring other options for the nutrient analyses associated with future sampling trips.

III. Preliminary results

a. Field data

Based on low salinity measurements in the field, we are confident that our shallowest wells (20’) intersect the wastewater plume, whereas the 50’ and 90’ wells were more saline, indicating that they are sampling saline groundwater. If we consider end member values of S~34 for the saline groundwater and S~1 for the Area 3 Wastewater effluent , all of the 50’ and 90’ wells are nearly pure saline groundwater, ranging in salinity from 32.9 to 34.3. The 20’ wells yielded salinities of 8.5 to 15.4 , reflecting wastewater-groundwater mixtures approximately 25-50% wastewater. Dissolved sulfide, in general, was highest at 90’ depth, and sometimes detectable at 1-2 ppm at 50’ depth. Aqueous orthophosphate (soluble reactive phosphorus) concentration of the pure effluent was 1.435 ppm-P, and ranged from 0.024 to 0.611 ppm-P in the well samples.

Table 1. Observations and measurements made in the field and at Keys Marine Lab during the July 2021 sampling trip.

Well ID	Date Sampled	Observations	Initial Depth to Water (ft)	pH	Salinity (‰)	Conductivity (mS/cm)	Sulfide (ppm)	SRP (ppm-P) 880nm	Alkalinity (meq/L)
ME1-20	7/20/21	- well cap submerged; brown water pooled inside well covering - slight oily sheen pooled water - sulfur smell present during beginning purge of well - duplicate collected at 1148	2' 2.6"	7.26	8.53	NA (was not collected)	0	0.145	6.05
ME1-20 DUP					8.53				4.66
ME1-50	7/20/21	- sulfur smell present during beginning purge of well	2' 2.2"	7.21	33.6	NA (was not collected)	0	0.236	2.74
MS1-20	7/20/21	- white to tannish white opaquness to purge water in beginning; very opaque - white, solid precipitate present inside well during purging	3' 0.5"	7.00	10.6	19.21	0	0.049	6.00
MS1-50	7/20/21	- white, solid precipitate present inside well during purging - somewhat opaque; milky color to purge water	2' 7.9"	7.26	33.9	57.5	1	0.114	2.73
MS1-90	7/20/21	- distinct, strong sulfur smell; translucent black tint color to purge water - sampled water has slight sheen	1' 8.4"	7.25	33.9	57.1	3	0.024	2.60
MW3-20	7/20/21	- fairly clear purge water - slight gray tint color to purge water	3' 0.5"	7.20	15.4	26.5	0	0.033	3.80
MW3-50	7/20/21	- purge water: dilute milky color, some gray tint - duplicate collected at 1554	2' 4.6"	7.27	33.2	55.5	2	0.027	2.71
MW3-50 DUP					33.2				2.63
MW3-90	7/20/21	- none	1' 4.2"	7.20	34.3	55.3	3	0.049	2.88

MW2-20	7/21/21	- slight milkyness at start of purging to water - sulfur smell present - water went from milky to silty tan, translucent color after ~3 minutes of purging	2' 1.6"	7.23	9.78	17.32	0	0.043	4.36
MW2-50	7/21/21	- milky color at start of purge - strong, non-sulfur smell to purge water	4' 6.5"	7.17	32.9	53.8	2	0.068	2.82
MN1-20	7/21/21	- slight grayish translucent color to water - odd smell to purge water similar to strong rubber	1' 9.8"	7.19	11.2	20.0	1	0.611	4.20
MN1-50	7/21/21	- none	1' 6.4"	7.22	33.7	55.1	3	0.053	2.61
EWW (Effluent Wastewater)	7/22/21	- none	NA	7.50	1.04	2.16	0	1.435	2.26

b. Chemical data (see next page)

Table 2. Dissolved cation data from the July 2021 well samples.

Sample #	Al (ug/mL)	Ba (ug/mL)	Ca (ug/mL)	Fe (ug/mL)	K (ug/mL)	Mg (ug/mL)	Mn (ug/mL)	Na (ug/mL)	P (ug/mL)	Si (ug/mL)	Sr (ug/mL)	Ti (ug/mL)
Detection Limit	0.01	0.005	0.01	0.005	0.01	0.01	0.005	0.01	0.01	0.01	0.005	0.005
0721-ME1-20	<0.01	<0.005	156	<0.005	116	268	<0.005	2,199	0.21	2.85	2.16	<0.005
0721-ME1-20-i-F	<0.01	<0.005	152	<0.005	122	263	<0.005	2,285	0.3	2.76	2.13	<0.005
0721-ME1-50-F	<0.01	<0.005	394	<0.005	537	1,200	<0.005	10,060	0.45	2.3	6.9	<0.005
0721-MS1-20-F	<0.01	<0.005	197	0.25	171	350	0.04	3,093	0.11	3.97	3.44	<0.005
0721-MS1-50-F	<0.01	<0.005	390	<0.005	545	1,195	<0.005	10,266	0.34	2.1	6.85	<0.005
0721-MS1-90-F	<0.01	<0.005	415	<0.005	552	1,275	<0.005	10,387	0.11	2.17	7.34	<0.005
0721-MW3-20-F	0.04	<0.005	219	<0.005	257	520	<0.005	4,603	0.15	2.85	3.61	<0.005
0721-MW3-50-F	<0.01	<0.005	400	<0.005	531	1,228	<0.005	10,237	0.28	1.99	6.98	<0.005
0721-MW3-50-i-F	<0.01	<0.005	393	<0.005	540	1,204	<0.005	10,240	0.13	1.99	6.89	<0.005
0721-MW3-90-F	<0.01	<0.005	416	<0.005	559	1,272	<0.005	10,484	<0.01	2.06	7.32	<0.005
0721-MW2-20-F	<0.01	<0.005	169	0.13	151	323	0.05	2,719	<0.01	3.48	2.62	<0.005
0721-MW2-50-F	0.04	<0.005	402	<0.005	536	1,224	<0.005	10,192	<0.01	2.04	7.02	<0.005
0721-MN1-20-F	<0.01	<0.005	164	0.04	144	314	<0.005	2,626	1.09	2.88	2.35	<0.005
0721-MN1-50-F	<0.01	<0.005	405	0.09	539	1,244	<0.005	10,240	<0.01	2.18	7.11	<0.005
0721-EWW-F	0.05	<0.005	47.4	<0.005	39	31.1	<0.005	321	3.69	2.42	0.56	<0.005
EPA standard suite												
EPA 200.7 QC standard	20	20	20	20	100	20	20	20	100	100	20	ND
EPA 200.7 diluted 1/100	0.2	0.19	0.19	0.2	0.96	0.21	0.2	0.2	1.05	1	0.2	ND
EPA 200.7 diluted 1/20	1.02	1	1	1.01	5.17	1.01	0.99	1.01	5.07	5.02	1.01	ND
EPA 200.7 diluted 1/10	2.01	2.01	1.99	2	10.2	2.01	2.01	1.99	10.1	10	2.04	ND
EPA 200.7 diluted 1/4	5.04	5.01	5	4.98	25	4.99	4.98	4.97	25.3	25.5	4.86	ND

Table 3. Dissolved anion data from the July 2021 well samples.

Sample #	F^- (ug/mL)	Cl^- (ug/mL)	SO_4^{2-} (ug/mL)	Br^- (ug/mL)
0721-ME1-20	0.01	0.02	0.05	0.01
0721-ME1-20-i-F	<0.01	3,887	493	6.66
0721-ME1-50-F	<0.01	3,602	434	3.15
0721-MS1-20-F	<0.01	16,074	2,500	72.8
0721-MS1-50-F	<0.01	5,405	851	27.8
0721-MS1-90-F	<0.01	16,266	2,500	73.8
0721-MW3-20-F	<0.01	18,579	2,796	84.6
0721-MW3-50-F	<0.01	7,431	974	24.2
0721-MW3-50-i-F	<0.01	18,291	2,825	83.8
0721-MW3-90-F	<0.01	18,303	2,854	83.4
0721-MW2-20-F	<0.01	16,666	2,553	74.2
0721-MW2-50-F	<0.01	4,177	539	6.1
0721-MN1-20-F	<0.01	18,154	2,674	85.8
0721-MN1-50-F	<0.01	4,660	606	17
0721-EWW-F	<0.01	16,977	2,473	76.7
	<0.01	505	<0.05	2.03
QC 1 ppm	1.1	1.01	0.7	0.91
QC 10 ppm	10.5	9.42	10.7	11.9

c. Resistivity results

During the July sampling trip we conducted a series of electrical resistivity surveys using a 48-channel SYSCAL Pro Earth Resistivity Meter. Inverse models are being created using RES2DINV following standard procedures. The result is a 2-D cross-section of the resistivity (inverse of conductivity) structure of the subsurface that is primarily dependent on the salinity of the fluid filling the voids in the permeable Key Largo Limestone subsurface. High resistivity zones are low salinity regions or, near the surface, above the local water table. Low resistivity zones reflect the natural, saline groundwater. We are now refining our inversions and testing sensitivity to key parameters. We expect to be able to provide key resistivity cross-sections in our next report.

IV. Expenditures during the reporting period

Thus far, we have spent \$3,642 on salary and fringe benefits, \$1,922 on graduate tuition, \$3,855 on supplies, \$3,799 on field travel, and \$6,713 on University overhead.

V. Comparison of the percentage of project completed to project schedule

We will be caught up with our proposed sampling schedule by the third sampling trip. As described in Section II, our initial well drilling and water sampling were both delayed due to a delay in funding.

VI. Explanation of significant discrepancies

VII. Statement of activity anticipated during the subsequent reporting period

In early November, Ingalls will present initial findings and a progress summary to the Florida Keys National Marine Sanctuary Water Quality Protection Program (FKNMS WQPP) meeting. These results and the presentation slides will be made publicly available to meeting attendants and stakeholders.

In late November 2021 and March 2022, Martin and Meyers will return to the field site to collect additional samples to track movement and evolution of the wastewater plume geometry and chemistry. We also received supplemental funding from the EPA to contract JC Drilling to drill additional shallow wells in early 2022. We will choose the placement of those wells based on the findings of the resistivity surveys and July 2021 water chemistry. We have chosen to primarily drill in the shallow subsurface because no wastewater was detected at our deepest (90') wells, and the resistivity surveys suggest that the plume returns to the upper few meters of the subsurface within 100 lateral meters of the injection well at Area 3.

We are also working to resolve our nutrient analysis issue.