MARCH 11, 2020

BREVARD COUNTY SAMPLING REPORT FOR THE LAND APPLICATION OF BIOSOLIDS ON DEER PARK RANCH AND OTHER POTENTIAL IMPACTS TO LAKE WASHINGTON WATER QUALITY

TASK ORDER # 215260-20-001-01

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Executive Summary

Lake Washington is an important source of drinking water to numerous cities and towns in the Melbourne region. Between July and August of 2019, Lake Washington experienced an algal bloom of the toxin producing cyanobacteria *Dolichospermum circinale*. Links between biosolid applications and harmful algal blooms have been investigated elsewhere in Florida. On October 8th, 2019, the Brevard County Commission voted to place a six-month moratorium on the expanded application of biosolids. In support of Brevard County's Biosolid Moratorium, Brevard County Natural Resources Management (BCNRM) contracted with Applied Ecology, Inc. to conduct a limited survey to determine levels of nutrients, metals, and emerging contaminants in water and vegetation in and around Lake Washington, including the Deer Park Ranch. Results from this present study will be used by the Commission to guide further regulatory action.

In total eleven locations were sampled for surface water between December 18-19, 2019, including five residential sampling locations east of Lake Washington, one location in Lake Washington, one location in the St. Johns River between Sawgrass Lake and Lake Washington and two locations southwest (upstream) of Lake Washington near where Class B biosolid applications have occurred and two locations in Jane Green swamp upstream of where biosolids have not been applied. In addition, three sites in the Deer Park Ranch were selected to sample plant tissue for pharmaceuticals.

For metals, none of the samples exceeded the drinking water standards. Arsenic, copper, molybdenum, nickel and zinc results ranged between < 0.5 to 2.4 parts per billion (ppb), <0.93 to 4.2 ppb, <0.5 to 3.1 ppb, <0.62 to 0.71 ppb, and <4.3 to 10.8 ppb, respectively. The highest copper values were observed near the ranch, while the highest arsenic and molybdenum values were observed in drainage canals east of Lake Washington.

For nutrients, ammonia, total kjeldhal nitrogen, nitrate-nitrite, total nitrogen, orthophosphate, and total phosphorous concentrations ranged between < 0.035 to 0.18 parts per million (ppm), 0.64 to 1.7 ppm, <0.33 to 0.15 ppm, 0.64 to 1.8 ppm, 0.0043 to 1.9 ppm and 0.028 to 2.2 ppm, respectively. The highest total nitrogen (TN) values were observed within Lake Washington; however, none of the discrete samples exceeded the numeric nutrient criteria (NNC) applicable to this segment of the St. Johns River. The highest total phosphorus (TP) values were observed in waters flowing off the ranch. Additionally, individual TP samples above the annual geometric means of the NNC (0.12 ppm) were observed at two ranch sites and one canal site east of Lake Washington. Low TN to TP ratio, which may favor nitrogen-fixing cyanobacteria over other algae, were observed at the two Deer Park Ranch sites (ratios of 0.6 and 0.9). These ratios were markedly lower than all other sites (ratio ranges of 4.5 to 16.9).

In addition to nutrients and metals, three sites east of Lake Washington, one site in Lake Washington, one location in the St. Johns River between Sawgrass Lake and Lake Washington, and two ranch sites were tested for a full suite of perfluoroalkyl substances (PFAS). PFAS make up a large group of persistent anthropogenic chemicals used in industrial processes and commercial products over the past 60 years. Two of the PFAS compounds tested under this study (PFOS and PFOA) have been identified as having potential human health and/or environmental impacts. Although all sites had detectable levels of PFAS, only one site located east of Lake Washington had quantifiable levels of PFOS. The PFOS concentration at this site (40 parts per trillion or ppt) exceeded the provisional Perfluorooctanesulfonic acid (PFOS) FDEP Human Health Surface Water Screening Levels (4 ppt). However, no samples exceeded the EPA Lifetime Drinking Water Health Advisory nor the FDEP Ecological Surface Water Screening Levels for Perfluorooctanoic acid (PFOA) or PFOS.

Concentrations of 58 pharmaceuticals and personal care products (PPCPs) were also analyzed in two water samples and three plant tissue samples from the ranch. No PPCPs were detected in any of the water samples. In plant tissues, one of the samples had no PPCPs detected, while two samples had quantifiable concentrations

of the anti-inflammatory drug Naproxen (0.322 and 0.713 ppb) and the antibiotic Ciproloxacin (9.84 and 35.6 ppb). Additionally, one of the plant tissue samples had quantifiable levels of Triclocarban (an anti-microbial) and quantifiable levels of Norfloxacin (an antibiotic).

Project Background

Lake Washington is an important source of drinking water to numerous cities and towns in the Melbourne region including Melbourne, Melbourne Beach, West Melbourne, Indialantic, Indian Harbour Beach, Satellite Beach, Palm Shores, Melbourne Village, and other parts of unincorporated Brevard County. Between July and August of 2019, Lake Washington experienced an algal bloom of the cyanobacteria *Dolichospermum circinale*. During this bloom event, water samples from the lake had Saxitoxin/Paralytic Shellfish Toxins between 0.06 - 0.11 ppb, below the drinking water guidelines of 3 ppb. Associations between biosolid application and harmful algal blooms (HAB) have been made in other areas along the St. Johns River (SJR).

Blue Cypress Lake, located in Indian River County, experienced a prolonged HAB during 2018. The lake, like other areas in the SJR Basin, saw an increase in Class B biosolid application after 2013 when such applications were banned from Lake Okeechobee, St. Lucie River and Caloosahatchee River basins. Blue Cypress Lake also experienced an increase in phosphorus levels in the surface water.

The land application of biosolids as a fertilizer for agricultural land provides Total Nitrogen (TN) and Total Phosphorus (TP) at a different ratio than most crops require. This can lead to the overapplication and accumulation of phosphorus and increased leaching into surrounding waterbodies. This is partially mitigated by a nutrient management plan as required in Chapter 62-640, F.A.C. An imbalance in the TN:TP ratio in surface waters can lead to the proliferation of nitrogen-fixing, and potential HAB forming, cyanobacteria (Downing and McCauley, 1992; Dolman *et al.,* 2012).

In addition to nutrients, biosolids can be a potential source of metals (Wuana and Okieimen, 2011). For this reason, Chapter 62-640.700(5)(a), F.A.C. regulates biosolids for maximum concentrations of Arsenic (75 mg/kg), Copper (4,300 mg/kg), Molybdenum (75 mg/kg), Nickel (420 mg/kg) and Zinc (7,500 mg/kg) as well as 4 other metals that commonly occur in Class B biosolids.

PFAS make up a large group of persistent anthropogenic chemicals used in industrial processes and commercial products over the past 60 years. As a result of concerns for these emergent compounds, recommended health advisory levels and provisional screening values for perfluorooctanesulfonic acid (PFOS) and/or perfluorooctanoic acid (PFOA) have been developed by the EPA and FDEP. PFAS have been found in biosolids worldwide (Bossi *et al.*, 2008; Chen et al., 2012). Despite ceases in production of many PFAS-containing products, their concentrations in biosolids do not appear to have decreased (Vankatesan and Halden, 2013).

Like PFAS, pharmaceuticals and personal care products (PPCPs) are persistent chemicals which can bioaccumulate and cause deleterious effects on human and ecosystem health (Xia *et al.*, 2005; Richmond *et al.*, 2017). PPCPs have also been found in biosolids across the world, and special focus has been given to the potential for these compounds to bioaccumulate (Wu *et al.*, 2015). Unlike PFAS, there are currently no guidelines or health advisory levels for PPCPs.

Deer Park Ranch is a major (3,270 acres) permitted site which has been accepting land application of biosolids for 25 years, having accepted about 7,484 tons of biosolids in 2018. Part of the ranch's runoff enters into the

St. Johns River, which flows north into Lake Washington. On October 8th, 2019, the Brevard County Commission voted to place a six-month moratorium on the expanded application of biosolids. In support of Brevard County's Biosolid Moratorium, Brevard County Natural Resources Management (BCNRM) contracted with Applied Ecology, Inc. to conduct a limited survey to determine levels of nutrients, metals, and emerging contaminants in water and vegetation in and around Lake Washington, including the Deer Park Ranch. In addition to the study by Applied Ecology, Inc., BCNRM collaborated with the University of Florida's Institute of Food and Agricultural Sciences (hereafter called UF), St. Johns River Water Management District, Brevard Soil & Water Conservation District, United States Department of Agriculture's Natural Resources Conservation Service, and Florida Department of Environmental Protection to conduct a study of phosphorus concentrations in soils on the Deer Park Ranch property. This soil study included the sampling and analysis of 50 soil samples within 11 pastures receiving different levels of biosolids application within the ranch, including two control samples. Results from this soil study will also be used by the Commission to guide further regulatory action.

Methods

In early December 2019, Applied Ecology, Inc. worked closely with County staff to determine sampling locations to analyze potential nutrient and pollutant contributions to Lake Washington from biosolid applications along Deer Park Ranch as well as residential areas east of Lake Washington (Figures 1 and 2).

In total eleven locations were sampled for surface water between December 18-19, 2019, including five residential sampling locations east of Lake Washington, one location in Lake Washington, one location in the St. Johns River between Sawgrass Lake and Lake Washington and two locations southwest (upstream) of Lake Washington near where Class B biosolid applications have occurred and two locations in Jane Green swamp upstream of where biosolids have not been applied. In addition, three sites in the Deer Park Ranch were selected to sample plant tissue for pharmaceuticals. It should be noted that there was a significant (>1 inch) rainfall event the day prior to the sampling event.

In addition to common water quality parameters (pH, temperature, specific conductance and dissolved oxygen), additional analytes tested included metals (arsenic, copper, molybdenum, nickel, and zinc), nutrients (ammonia, total kjeldhal nitrogen, nitrate-nitrite, total nitrogen, orthophosphate and total phosphorous), 24 different perfluoroalkyl substances (PFAS), and 58 different pharmaceuticals and personal care products (PPCPs).

On or near the Deer Park Ranch (Figure 1), two of the locations (Site 1 and 2) were receiving water from natural land use areas. These sites were sampled from the same creek and were analyzed for nutrients and metals. Another two locations (Sites 3 and 4) were located in separate drainage canals near fields used for cattle pasture and sod farming, which received high biosolid loadings and flow out of the ranch during high rainfall conditions. These sites were analyzed for nutrients, metals, PFAS, and PPCPs. Also, within the Deer Park Ranch, three locations in fields (Plant Tissue 1, 2, and 3) had vegetative tissues sampled for PPCPs. Downstream of the Deer Park Ranch, on the St. Johns River (SJR), one site (Site 12) downstream of Highway 192 was sampled for nutrients, metals, and PFAS. Due to flooded roads and lack of accessibility, Site 10 was not able to be sampled and thus dropped from the analysis.

East of Lake Washington (Figure 2), all samples were taken from unnamed canals, including one site located upstream (Site 6) and another downstream (Site 5) of treatment ponds (and firefighting training facility). Site 5 was analyzed for nutrients, metals, and PFAS, while Site 6 was analyzed for nutrients and metals. Three sites

(Sites 7, 8, and 9) were also located on canals draining residential areas. Sites 7 and 8 were analyzed for nutrients, metals, and PFAS, while Site 9 was analyzed for nutrients and metals. One site (Site 11) was taken in Lake Washington, south of the Melbourne Water Treatment Plant uptake near where the canal from Site 8 empties. This site was sampled for nutrients, metals, and PFAS.

All water quality sampling followed Florida Department of Environmental Protection (FDEP) Standard Operating Procedures (SOPs) FS 1000 and FS 2100. Water quality parameters measure *in situ* for Sites 1-4 were taken with a calibrated YSI, and Sites 5-12 were taken with a calibrated Ultrameter. All grab samples were collected using a peristaltic pump except for Site 2, which required a Van Dorn Sampler. For all sampling, precautions for cross-contamination were used, including for PFAS the use of new High-Density Polyethylene (HDPE) tubing to purge and collect surface water samples at each site as well as (for PFAS and PPCPs) a field blank.

Ammonia, Total Kjeldahl Nitrogen, Nitrate/Nitrite, and Total Phosphorus were collected in a 250 mL laboratory-provided container with sulfuric acid as preservative. Orthophosphate was collected in a 250 mL laboratory-provided container without preservative. Metals were collected in a 250 mL laboratory-provided container with nitric acid as preservative. Nutrient and metal samples were sent to Pace Analytical Services laboratory (Ormond Beach, FL) to process the following analytic measurements:

Nutrients

- EPA 350.1 - Ammonia
- EPA 351.2 - Total Kjeldahl Nitrogen (TKN)
- EPA 353.2 - Nitrate/Nitrite
- EPA 365.3 - Total Phosphorus (TP)
- EPA 365.1 - Orthophosphate

Metals

- EPA 200.8 – Arsenic (As), Copper (Cu), Molybdenum (Mo), Nickel (Ni) and Zinc (Zn)

To sample for PFAS, two 125-mL aliquots were collected in a laboratory-provided container with no preservative, sealed, labeled, packed in ice, and shipped under chain-of-custody protocol to SGS Laboratories (Orlando, FL) for analysis of PFAS, including PFOA, PFOS, and 22 additional compounds using a modified EPA Method 537Mod.

To sample for PPCPs in water, two 500 mL aliquots were collected in a laboratory-provided container. For plant tissues, 40 to 50 g of vegetative tissue (Bahia grass at Site 1 and 3 and *Hemarthria* grass at Site 2) was collected in a laboratory-provided container. The samples were with no preservative, sealed, labeled, packed in ice, and shipped under chain-of-custody protocol to SGS Laboratories (Sidney, Canada) for analysis of 58 pharmaceuticals and personal care products using AXYS Method MLA-075 (modified EPA Method 1694).

See Appendix A for additional information regarding the sampling sites.

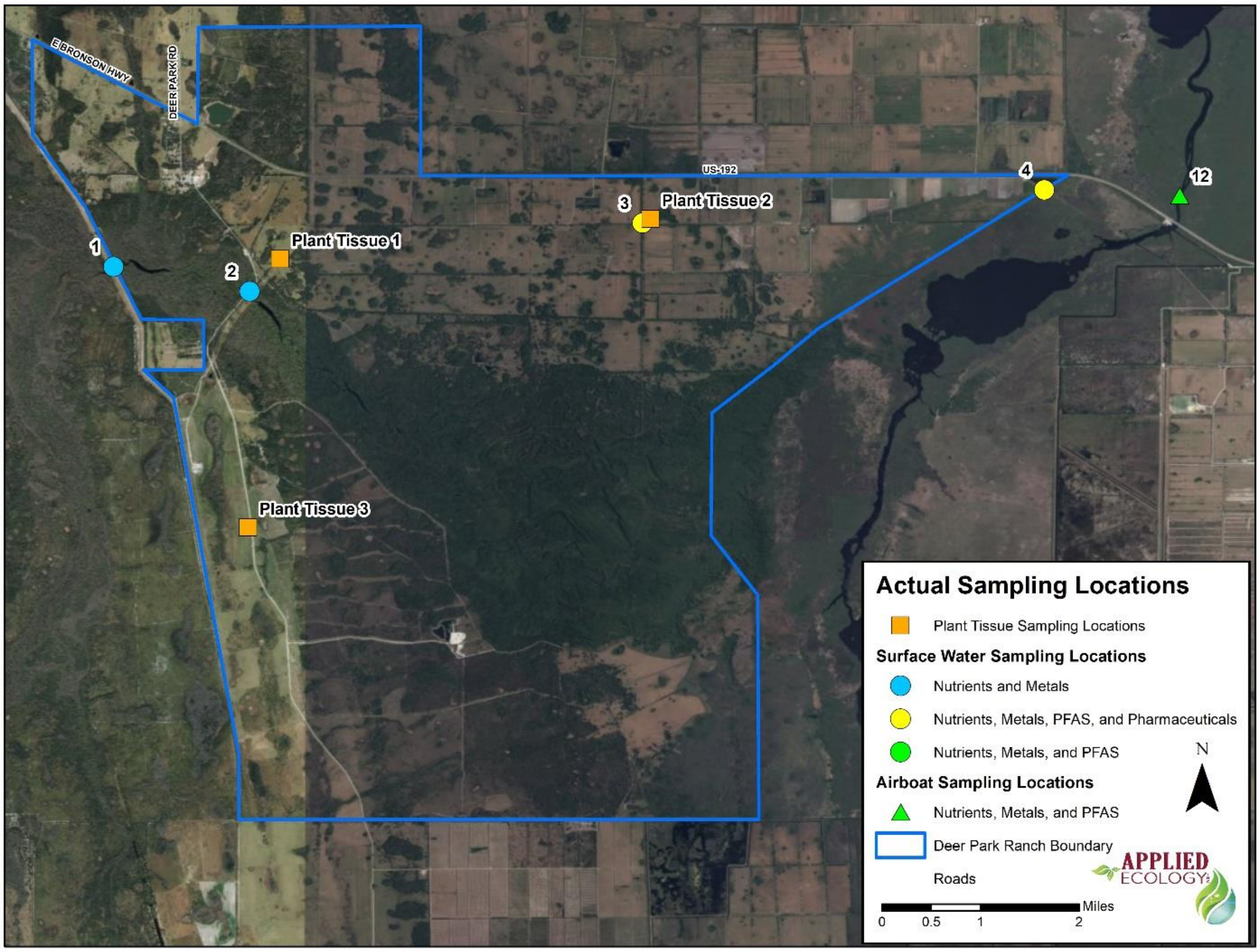

Figure 1. Site locations and parameters analyzed at 5 water quality and 3 plant tissue sites near the Deer Park Ranch where biosolids have been used for the last 25 years.

Figure 2. Sample locations and parameters analyzed at 5 water quality sites draining residential areas near Lake Washington and one site within Lake Washington.

Results

Surface Water Grabs

Applied Ecology, Inc. (AEI) went to 11 sites for surface water sampling. Field parameters collected *in situ* include the depth the sample/readings were taken in meters, air and water temperature (˚C), the pH (SU), the dissolved oxygen percentage (DO), the specific conductance (µS/cm), total dissolved solids and oxidation-reduction potential, which are provided in Table 1. Complete corresponding field and calibration logs are included in Appendix B. The water was circumneutral with temperatures ranging between 17 and 20.2 ˚C. Specific conductance and total dissolved solids (TDS) ranged between 0.175-1.089 µS/cm and 371.7-765.3, respectively. The highest specific conductance and TDS were observed at Site 9 and may have been elevated at all spots due to precipitation preceding the sampling event.

Table 1. Field parameters for the surface water sampling for Brevard County.

Site ID	Sample Date	Total Depth of Water (m)	Air Temp (˚C)	Water Temp (˚C)	pH (SU)	DO (%)	Specific Conductance (µS/cm)	Total Dissolved Solids (ppm)	Oxidation Reduction Potential (mV)	Sample Depth (m)
1	12/18/2019	> 2	17.6	20	7.76	22.3	0.1757	NA	NA	0.5
2	12/18/2019	> 2	16.6	20.2	7.07	37.1	0.1784	NA	NA	0.5
3	12/18/2019	0.3	14.5	19.9	7.24	56.5	0.3670	NA	NA	0.15
4	12/18/2019	NA	13.5	19.9	7.31	33.4	0.8460	NA	NA	0.5
5	12/19/2019	1.5	13.5	16.5	7.99	NA	0.9208	642.3	67	0.5
6	12/19/2019	1	19.5	19.5	7.48	NA	0.6889	471.1	102	0.5
7	12/19/2019	NA	18.8	19.4	7.77	NA	0.6605	451.4	112	0.5
8	12/19/2019	1	18.8	19	7.42	NA	0.9272	643.5	61	0.5
9	12/19/2019	0.25	18	17.1	7.47	NA	1.089	765.3	54	0.15
11	12/19/2019	>2	16.3	17	7.69	NA	0.7202	496.3	73	0.5
12	12/19/2019	>2	17.8	18.1	7.80	NA	0.5463	371.7	160	0.5

Metals

Applied Ecology, Inc. sampled 11 sites for metals (As, Cu, Mo, Ni, and Zn) and compared the applicable surface water criteria 62.302, F.A.C. Hardness was not measured concurrently with metals, so low and high hardness values of 25 and 400 mg/L $CaCO_3$ (as outlined in 62.302-530[1]) were presented in Table 2 for illustrative purposes. For quality assurance, a field reagent blank was also collected, which exhibited concentrations below laboratory MDL values for all five metals. Complete laboratory analytical results from the one-time sampling for metals can be found in Appendix C.

No metals were detected at Site 1. Site 2 only had detectable levels of Zn, but it had the highest observed Zn concentrations (24.0 µg/L), more than twice as much as the next highest levels observed at Site 3 and Site 9 (10.8 µg/L). Site 3 had detectable values of all analytes except for Ni, with quantifiable levels of Mo (1.8 µg/L) Zn and the highest value of Cu (4.2 µg/L). Although this Cu value is above the low hardness criteria of 2.85 µg/L, it is unlikely to be an exceedance due to the historically high hardness values observed in other waterbodies in the area. All residential sites (Sites 5-9) had quantifiable values of Mo, which does not have applicable water quality standards. Additionally, residential sites 7-11 had quantifiable levels of As (1.3 to 2.4 µg/L) well below the drinking water quality standard of 10 µg/L. In fact, all samples had metal concentration values below the drinking water quality standards in Chapter 62-550, F.A.C. assuming high water hardness values.

Table 2. Metal results for the eleven sites sampled for the Brevard County Biosolids Moratorium Monitoring. Concentration values > MDL but < PQL are italicized, values > the PQL are bolded, and values > applicable criteria or cleanup target levels are highlighted in grey.

Metals	Site Lab Results (µg/L)											Applicable FDEP Criteria (µg/L)[3]			
	1	2	3	4	5	6	7	8	9	11[4]	12[4]	FDEP Class I Criteria (Low)	FDEP Class I Criteria (High)	FDEP Class III FW Criteria (Low)	FDEP Class III FW Criteria (High)
Arsenic	0.50 U[1]	0.50 U[1]	*0.64 I[2]*	*0.54 I[2]*	*0.76 I[2]*	*0.67 I[2]*	**1.80**	**2.00**	**2.40**	**1.30**	*0.52 I[2]*	10	10	50	50
Copper	0.93 U[1]	0.93 U[1]	**4.20** [5]	0.93 U[1]	0.93 U[1]	**1.00**	0.93 U[1]	**1.80**	0.93 U[1]	**1.40**	0.93 U[1]	2.85	30.5	2.85	30.5
Molyb-denum	0.50 U[1]	0.50 U[1]	**1.80**	0.50 U[1]	**2.50**	**2.30**	**3.10**	**1.30**	**1.80**	**1.60**	*0.98 I[2]*	NA	NA	NA	NA
Nickel	0.62 U[1]	0.62 U[1]	0.62 U[1]	0.62 U[1]	0.62 U[1]	0.62 U[1]	0.62 U[1]	0.62 U[1]	0.62 U[1]	*0.71 I[2]*	0.62 U[1]	16.1	168.5	16.1	168.5
Zinc	4.30 U[1]	**24.0**	**10.8**	4.30 U[1]	4.30 U[1]	**5.30**	4.30 U[1]	**9.10**	**10.80**	**5.20**	4.30 U[1]	37.0	387.8	37.0	387.8

[1] "U" qualified values indicate the analytical concentration is below laboratory minimum detection limits (MDLs); vary depending on parameter and sample

[2] "I" qualified values indicate the analytical concentration is greater than or equal to the method detection limit but less than the practical quantitation limit.

[3] Values from Chapter 62-304.530 F.A.C. Cu, Ni and Zn are hardness based with "Low" being set to a hardness of 25 mg/L of $CaCO_3$ and "High" set to 400 mg/L of $CaCO_3$.

[4] Class I waters

[5] Value could be above Class I most stringent criteria if hardness is considered low onsite (<25 mg/L of $CaCO_3$)

Nutrients

Applied Ecology, Inc. sampled 11 sites for the following nutrients: ammonia, total kjeldhal nitrogen, nitrate-nitrite, total nitrogen, orthophosphate, and total phosphorous. Results are summarized in Table 3. Complete laboratory analytical results from the one-time sampling for nutrients can be found in Appendix C.

The highest orthophosphate (1.9 mg/L and 0.86 mg/L) and total phosphorus (2.2 mg/L and 0.95 mg/L) values were observed at Site 3 and 4 respectively. The highest ammonia (0.18 mg/L) values were observed at Site 9, while Site 11 (within Lake Washington) had the highest values of total nitrogen (1.8 mg/L), total kjeldahl nitrogen (1.7 mg/L) and nitrate-nitrite (0.15 mg/L). Based on only two data points (Sites 6 and 5), the stormwater treatment ponds may be decreasing, total nitrogen, ammonia, total kjeldhal nitrogen, nitrate-nitrite, orthophosphate and total phosphorous by as much as 26.4%, 49.3%, 16.9%, 67.0%, 53.8%, and 26.3%, respectively.

Table 3. Nutrient results for the eleven sites sampled for the Brevard County Biosolids Moratorium Monitoring. Concentration values > applicable criteria or cleanup target levels are highlighted in grey.

Nutrient Analysis	Lab Results (mg/L)											Applicable FDEP Criteria (mg/L)	
	1	2	3	4	5	6	7	8	9	11	12	FDEP NNC for Lake Washington	FDEP NNC for Streams
TN	0.980	1.000	1.300	0.820	0.640	0.870	0.860	0.970	1.200	1.800	1.300	1.91	1.54
NH_3	0.035 U[1]	0.035 U[1]	0.060	0.035 U[1]	0.035 U[1]	0.069	0.035 U[1]	0.068	0.180	0.081	0.035 U[1]	NA	NA
TKN	0.980	1.000	1.300	0.800	0.640	0.770	0.860	0.830	1.200	1.700	1.300	NA	NA
NO_X	0.033 U[1]	0.033 U[1]	0.058	0.033 U[1]	0.033 U[1]	0.100	0.033 U[1]	0.140	0.060	0.150	0.033 U[1]	NA	NA
PO_4^{3-}	0.035	0.028	1.900	0.860	0.004	0.009	0.007	0.086	0.055	0.050	0.077	NA	NA
TP	0.063	0.059	2.200	0.950	0.028	0.038	0.053	0.130	0.100	0.110	0.120	0.16	0.12
TN:TP	15.6	16.9	0.6	0.9	22.9	22.9	16.2	7.5	12.0	16.4	10.8	NA	NA

[1] "U" qualified values indicate the analytical concentration is below laboratory minimum detection limits (MDLs); vary depending on parameter and sample

PFAS

Applied Ecology, Inc. (AEI) sampled seven sites for PFAS and compared the surface water PFOA and PFAS laboratory measured results to the 0.070 µg/L EPA lifetime drinking water health-advisory (LDWHA) for PFOA and PFOS (Table 4). Additionally, AEI compared the results to FDEP provisional screening values for Human Health in Surface Water (HHSW) and Ecological Health in Surface Water (EHSW). For quality assurance, a field reagent blank was also collected, which exhibited concentrations below laboratory MDL values for all 24 PFAS compounds. Complete laboratory analytical results from the one-time sampling for PFAS can be found in Appendix D.

All sites had detectable levels of PFAS, with Perfluorobutanesulfonic acid (PFBS) and Perfluorobutanoic acid (PFBA) detected at all seven sites analyzed for PFAS. However, only four sites had quantifiable levels of PFAS. Sites 3 and 4, which are on Deer Park Ranch in canals that receive runoff from high biosolid loading areas, had quantifiable levels of PFBA (0.0164 and 0.0210 µg/L, respectively), Perfluoropentanoic acid (0.0230 and 0.0130 µg/L, respectively), Perfluorohexanoic acid (0.0121 and 0.0081 µg/L, respectively) and PFBS (0.0520 and 0.0360 µg/L, respectively). Even though many of the PFAS do not have current recommended health advisories or screening health advisories, there are recent toxicological studies that do indicate potential of other PFAS besides PFOA and PFOS , such as PFBS having development, thyroid, and kidney effects in adult and developing rats (Feng *et al.*, 2017). Site 8, which was in a canal that receives runoff from residential areas, had quantifiable levels of Perfluoropentanoic acid (0.0084 µg/L). Site 5, located downstream of the treatment ponds that also receives runoff from the Brevard County Fire Rescue Drill Yard and potentially other commercial and industrial land uses, had quantifiable levels of four PFAS: PFBA (0.0183 µg/L), Perfluorohexanoic acid (0.0095 µg/L), Perfluorohexanesulfonic acid (0.0377) and PFOS (0.0398 µg/L). This site was the only site to have quantifiable values of Perfluorohexanesulfonic acid and PFOS and was also the only site to exceed the provisional FDEP HHSW for PFOS (0.004 µg/L).

Site 7, which was located in a canal that receives runoff from residential areas, appears to have the lowest number of detections, only PFBS and PFBA were detected, but not in sufficient concentration to quantify. Sites 11 (Lake Washington) and 12 (St. Johns River) had 5 PFAS above detection limits, but not in sufficient concentration to quantify.

The following 14 PFAS were analyzed but not detected in any of the sample sites: Perfluorononanoic acid, Perfluorodecanoic acid, Perfluoroundecanoic acid, Perfluorododecanoic acid, Perfluorotridecanoic acid, Perfluorotetradecanoic acid, Perfluoropentanesulfonic acid, Perfluorononanesulfonic acid, Perfluorodecanesulfonic acid, Perfluorooctane sulfonamide, MeFOSAA, EtFOSAA, 4:2 Fluorotelomer sulfonate, 6:2 Fluorotelomer sulfonate and 8:2 Fluorotelomer sulfonate.

Table 4. Surface water PFAS analytical results for Brevard County Biosolids Moratorium Monitoring. Samples with concentration values that were <PQL but >MDL are italicized, values that were > PQL are in bold. Values that exceeded the provisional FDEP Surface Water Screening Levels for Human Health or the US EPA Lifetime Drinking Water Health Advisory are bolded and highlighted in grey.

PFAS Compound	Surface Water Lab Results (µg/L)							Target Cleanup Levels (µg/L)		
	3	4	5	7	8	11	12	EPA LDWHA[3]	FDEP HHSW[4]	FDEP EHSW[5]
Perfluorobutanoic acid (PFBA)	**0.016**	**0.021**	**0.018**	*0.006 I[2]*	*0.011 I[2]*	*0.011 I[2]*	*0.010 I[2]*	NA	NA	NA
Perfluoropentanoic acid (PFPeA)	**0.023**	**0.013**	*0.008 I[2]*	0.0023 U[1]	**0.008**	*0.005 I[2]*	*0.005 I[2]*	NA	NA	NA
Perfluorohexanoic acid (PFHxA)	**0.012**	**0.008**	**0.010**	0.002 U[1]	*0.006 I[2]*	*0.003 I[2]*	*0.002 I[2]*	NA	NA	NA
Perfluoroheptanoic acid (PFHpA)	*0.006 I[2]*	*0.004 I[2]*	*0.004 I[2]*	0.002 U[1]	*0.003 I[2]*	0.002 U[1]	0.002 U[1]	NA	NA	NA
Perfluorooctanoic acid (PFOA)	*0.008 I[2]*	*0.006 I[2]*	*0.006 I[2]*	0.002 U[1]	*0.004 I[2]*	*0.003 I[2]*	*0.003 I[2]*	0.07	0.15	1,300
Perfluorobutanesulfonic acid (PFBS)	**0.052**	**0.036**	*0.008 I[2]*	*0.002 I[2]*	*0.006 I[2]*	*0.005 I[2]*	*0.006 I[2]*	NA	NA	NA
Perfluorohexanesulfonic acid (PFHxS)	0.002 U[1]	0.002 U[1]	**0.038**	0.002 U[1]	*0.002 I[2]*	0.002 U[1]	0.002 U[1]	NA	NA	NA
Perfluoroheptanesulfonic acid	0.002 U[1]	0.002 U[1]	*0.002 I[2]*	0.002 U[1]	0.002 U[1]	0.002 U[1]	0.002 U[1]	NA	NA	NA
Perfluorooctanesulfonic acid (PFOS)	*0.003 I[2]*	0.003 U[1]	**0.040**	0.003 U[1]	*0.008 I[2]*	0.003 U[1]	0.003 U[1]	0.07	0.004	37
PFOA + PFOS (ug/L)	*0.011 I[2]*	*0.009 I[2],U[1]*	**0.046**	0.005 U[1]	*0.012 I[2]*	*0.006 I[2], U[1]*	*0.006 I[2], U[1]*	0.07	NA	NA

[1] "U" qualified value indicates that analytical concentration is below laboratory minimum detection limits (MDLs); vary depending on parameter and sample

[2] "I" qualified value indicated the analytical concentration is greater than or equal to the method detection limit but less than the practical quantification limit.

[3] US EPA Lifetime Drinking Water Health Advisories

[4] Provisional Florida DEP Surface Water Screening Levels for Human Health

[5] Provisional Florida DEP Surface Water Screening Levels for Ecological Health

Pharmaceuticals and Personal Care Products (PPCPs)

Surface Water

Applied Ecology, Inc. sampled two sites for 58 PPCPs (Sites 3 and 4, located on the Deer Park Ranch). For quality assurance, a field reagent blank was also collected, which exhibited concentrations below laboratory MDL values for all 58 compounds. None of the surface water samples had detectable PPCPs. Complete laboratory analytical results from the one-time sampling for PPCPs in surface water can be found in Appendix E.

Vegetation Tissue

Applied Ecology, Inc. sampled three sites with high biosolid loadings for 58 PPCPs (Plant Tissue 1-3). Complete laboratory analytical results from the one-time sampling for PPCPs in plant tissue can be found in Appendix F.

Plant Tissue 1 and 3 were Bahiagrass (*Paspalum notatum*) and actively or recently used for cattle grazing while Plant Tissue 2 was *Hemarthria sp.* collected in a field that was fallowed at time of sampling. Additionally, Plant Tissue 3 is located near the designated biosolids storage area. No pharmaceuticals were detected in Plant Tissue 2 (Table 5). Plant Tissue 1 and 3 both had quantifiable concentrations of the anti-inflammatory drug Naproxen (0.322 and 0.713 ppb, respectively) and the antibiotic Ciprofloxacin (9.84 and 35.6 ppb, respectively). Additionally, Plant Tissue 3 had 0.324 ppb of Triclocarban (an anti-microbial) and the other had 55.3 ppb of Norfloxacin (an antibiotic).

The following PPCPs were not detected in any of the tissue samples: Bisphenol A, Furosemide, Gemfibrozil, Glipizide, Glyburide, Hydrochlorothiazide, 2-hydroxy-ibuprofen, Ibuprofen, Triclosan, Warfarin, Acetaminophen, Azithromycin, Caffeine, Carbadox, Carbamazepine, Cefotaxime, Clarithromycin, Clinafloxacin, Cloxacillin, Dehydronifedipine, Diphenhydramine, Diltiazem, Digoxin, Digoxigenin, Enrofloxacin, Erythromycin-H2O, Flumequine, Fluoxetine, Lincomycin, Lomefloxacin, Miconazole, Norgestimate, Ofloxacin, Ormetoprim, Oxacillin, Oxolinic acid, Penicillin G, Penicillin V, Roxithromycin, Sarafloxacin, Sulfachloropyridazine, Sulfadiazine, Sulfadimethoxine, Sulfamerazine, Sulfamethazine, Sulfamethizole, Sulfamethoxazole, Sulfanilamide, Sulfathiazole, Thiabendazole, Trimethoprim, Tylosin, Virginiamycin M1 and 1,7-Dimethylxanthine.

Table 5. Plant tissue analytical results for Pharmaceuticals and Personal Care Products as part of the Brevard County Biosolids Moratorium Monitoring. No detectable results were found for Plant Tissue 2.

Site ID	Lab Results (ng/g) List 3					
	Plant Tissue 1	Flag	Plant Tissue 2	Flag	Plant Tissue 3	Flag
Naproxen	0.322		0.313	ND	0.713	
Triclocarban	0.313	ND	0.313	ND	0.324	
Ciprofloxacin	9.84		2.54	ND	35.6	
Norfloxacin	27.1	ND	5.86	ND	55.3	
ND - Non detect						

Conclusion

A total of eleven water quality stations and three plant tissue sites were sampled between December 18 and 19, 2019. None of the eleven sites sampled exceeded the drinking water standards for the metals arsenic, copper, molybdenum, nickel, and zinc. The two ranch sites of the eleven sites sampled were above the numeric nutrient criteria (which is an annual geometric mean) for total phosphorus. PFAS were detected in all seven sites sampled, with one non-ranch site exceeding the provisional FDEP Human Health Surface Water Screening Levels for PFOS. PPCPs were not detected in the two water quality samples tested. However, of the three plant tissues sampled, two had high enough concentrations of four PPCPs to be quantifiable. Currently, there are no governmental guidelines for PPCPs in plant tissue.

An objective of the present study was to analyze presence, quantities, and contributions of nutrients and pollutants (metals, PPCPs, and PFAS) to the St. Johns River (Site 12) and Lake Washington (Site 11) from areas of biosolid application (Sites 3 and 4 and Plant Tissues 1-3) and residential areas (Sites 5-9). It should be emphasized that this was a small-scale study, with only one sample taken from each site over a two-day period, therefore conclusions are limited. Furthermore, flows were not measured so loads from these two different land use types cannot be calculated. However, the present study has produced some notable results.

For metals, the highest copper value was observed at a site near biosolid application, while the other site near biosolid application did not have detectable copper. Copper is frequently found in biosolids as it readily associates with organic matter and according to Chapter 62-640.700(5)(a), F.A.C. copper in Class B biosolids can have a maximum single sample concentration of 4,300 mg/kg. However, considering the two sites both receive runoff from high biosolid loading areas, the results are inconclusive. The highest zinc value was found downstream of a bridge in a natural land use area. This higher concentration than other sites could be related to the use of galvanized steel in the bridge's construction.

For nutrients, Site 5 generally had the lowest nutrient concentrations and is downstream of a treatment pond. The highest nitrogen species concentrations were observed in Lake Washington, with generally higher values observed in the residential areas compared to natural land use areas. Nitrogen loading is typically associated with higher density residential and commercial land uses, typical of the basin draining from the east of Lake Washington. The highest TP, orthophosphate, and TN:TP values were observed at the two sites draining biosolid application areas. Generally, biosolid TN:TP is below the preferable ratio needed for plant growth (*i.e.*, crops) and when biosolids are applied on a need for nitrogen basis, it leads to excessive phosphorus build-up. The lower TN:TP has been observed in other lakes receiving runoff from biosolids application areas and has resulted in the banning of Class B biosolid applications in Lake Okeechobee, St. Lucie River and Caloosahatchee River watersheds. It is generally accepted that it is this low TN to TP ratio that leads to the proliferation of nitrogen-fixing cyanobacteria.

Although PFAS were detected in all samples, the only sample exceeding the provisional FDEP Human Health Surface Water Screening Levels was at Site 5, which is downstream of a firefighting training facility and a mix of high density residential and industrial and commercial land uses. In addition, a few months preceding the sampling date, a brush fire occurred closely near the sampling location (*i.e.*, NE of the Eau Gallie/I-95 interchange), where different firefighting products might have been used. PFOS have historically been added to aqueous film forming foam (AFFF) used to fight fires. AFFF was phased out of production in 2003 but has been used in Florida training facilities as recently as 2017. Currently, Class B firefighting foam used in Brevard

County for flammable liquids such as gasoline, oils, etc., typically still contain C6 Fluorosurfactants, which have better toxicological profiles than PFOS (a C8 fluorosurfactant) but do persist in the environment.

Site 5 had quantifiable levels of PFOS, PFHxA (C6 fluorosurfactant primary breakdown product), and PFHxS. Rotander *et al.* (2015) found that both PFOS and PFHxS levels were shown to be elevated in firefighters exposed to AFFF. Sites 3 and 4, both receiving runoff from high biosolid application areas, had quantifiable concentrations of PFBA, PFPeA, PFHxA, and PFBS. These four PFAS are commonly (60-100% of the time) found in biosolids and, despite many being phased out, continue to be observed in similar concentrations in biosolids (Venkatesan and Halden 2013).

While PPCPs were detected in two tissue samples extracted from areas where high intensity of biosolids were applied, no PPCPs were detected in the water samples leaving the ranch at Sites 3 and 4. The lack of detectable PPCPs in the surface water samples could be due to the dilution effect of a very high rainfall event immediately preceding the sampling effort. Additionally, the PPCPs were only detected in areas of recent or active grazing (Plant Tissue 1 and 3) and not on land amended with biosolids, but currently fallow (Plant Tissue 2). While both ciprofloxacin and norfloxacin are antibiotics commonly used on cattle, the landowner of the Deer Park Ranch confirmed that neither antibiotic had been used recently on his cattle. Naproxen is a nonsteroidal anti-inflammatory drug found in common pain-relieving medications (Topp *et al*., 2008), also confirmed to not have been used onsite by the landowner. Furthermore, no evidence could be found that naproxen is ever used on bovines. Topp *et al.* (2008) showed that naproxen is rapidly mineralized in soils amended with biosolids while Lin and Reinhard (2005) found naproxen rapidly photodegrades after release into the environment. Therefore, recently applied biosolids is the likely source for this particular compound. Triclocarban, originally developed for the medical field, is an antimicrobial and antifungal compound that was formerly used in personal care products such as soaps and lotions. The product began being used in the 1960s but was phased out by the FDA in 2017. Several studies have found that triclocarban from biosolid-amended fields can bioaccumulate in plants (Wu *et al.* 2010; Sabourin *et al.*, 2012; Wu *et al.*, 2014) and the concentrations observed in Site 3 were on the lower end of the range published in these studies. However, studies show the biosolid amendment inhibit the bioavailability and plant uptake of triclocarban (Fu *et al.*, 2016), which means concentrations in soils are likely much higher. In general, the highest concentrations of PPCPs and the sample that had the most PPCPs was Plant Tissue 3. A potential confounding factor is differential bioaccumulation in vegetative tissues since Plant Tissue 1 and 3 were Bahiagrass while Plant Tissue 2 was *Hemarthria sp*.

The results from this limited study, in conjunction with a soil study by an interagency team, will be used by the Brevard County Commission to guide further regulatory action regarding biosolid applications in Brevard County.

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