Project Summary Report
Florida Department of Environmental Protection (FDEP)
Coral Protection and Restoration Program

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Assessing the contribution of groundwater to phosphorous loadings to canals and tributaries discharging to Biscayne Bay

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In 2019 and 2020 Miami-Dade County conducted an effort to characterize nutrient concentrations in north Dade using existing shallow groundwater wells at permitted industrial sites. This previous survey showed concerningly high concentrations of total phosphorus (TP) in many sites located in close proximity of small tributaries, canals and water bodies that likely contribute to direct discharges to Biscayne Bay. The 2019-2020 values of TP in groundwater ranged from ND (2.8 µg/L) to as high as 10,000 µg/L, with a median value of 56 µg/L, which is five times higher than the than the currently available thresholds for Biscayne Bay. These previous results also showed that the 85th centile of a universe of 468 sites is 290 µg/L, representing extremely elevated values for TP. Given the magnitude of these contribution a more detailed study was proposed to corroborate the TP values observed in groundwater over a specific geographical and temporal domain relevant to potential discharges to Biscayne Bay. In this initial effort, the team revisited 10 sites that had concentration threshold of more than 100 ug/L and/or were in the proximity of a relevant waterway or water body. The main goal was to determine the phosphorus levels using the traditional digestion/colorimetric TP method and also a secondary verification of the TP values using an inductively coupled plasma mass spectrometer (ICP-MS) as an alternative technique that is less prone to interferences. Additional parameters were also investigated to help differentiate between sewage pollution and non-sewage pollution, and potential industrial waste streams. The parameters include soluble nutrients (nitrite, nitrate, ammonia and soluble reactive phosphorus), total organic carbon (TOC), total nitrogen (TN) and silica, specific groundwater tracers (Mg, Ca, K, Sr, Gd), a list of 18 minor and trace metals (Be, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sn, Sb, Ba, Hg, Pb) and 2 major elements (Al and Fe).

For the 2023 revisiting survey, the 10 selected sites were sampled two times to broadly coincide with the end of the dry season to the onset of the wet season. The first sampling occurred in April 19 and 20, and the second sampling in May 18 and 22. The sample collection were conducted by MDC and Arcadis personnel following all the requirements and criteria in the DEP SOPs. The chemical analyses were performed by CAChE-Nutrient Analysis Core Facility at Florida International University (FIU). All analytical methods are recognized and approved by DEP, with the exception of the method for trace metals, inorganic tracers and Total Phosphorous based on Inductive Couple Plasma – Triple Quadrupole-Mass Spectrometry (ICP-QQQ-MS), which is described in the approved Standard Quality Assurance Plan

for this project. This method significantly lowers the MDL for most analytes and allows for the determination of TP with and MDL of 0.000060 ppm (0.060 ppb).

The TP results are very consistent between the automated colorimetric FIA and ICP-MS methods (Table 1, Figs. 1 and 2). All results obtained for TP in the current survey remain higher than the existing Numeric Nutrient Criteria (NCC) for TP for the Northern North Bay (NNB) and Southern North Bay (SNB) segments of Biscayne Bay (12 and 10 µg/L TP respectively). The higher TP values (> 500 ug/L) were found for Facilities 4693, 7917, 5390 and 6011. Exceptionally high concentrations of 2,076 and 1,968 ug/L were found in Facility 6011 for the April sampling but decreased to 459 and 784 ug/L in May. Differences between April and May samplings were observed for most sites and seems to reflect a temporal heterogeneity in the groundwater quality parameters. When compared to the 2019-2020 survey, the stations 6011 and 5372 presented higher concentrations, especially for the month of April. Stations 5909 and 4693, however, showed concentrations for the month of April 2023 that are 20 and 3 times lower than the 2019-2020 results, respectively. Sites 7971, 3189, 5978, 7917, 5390 and 6841 presented comparable TP concentrations between 2019-2020 and 2023 surveys. Other analyzed parameters that show a covariation with TP are the soluble nutrients SRP and ammonia, and also the TOC, Sr, Fe and Ba.

Table 1: Results of TP (ug/L) for the 2019-2020 and 2023 surveys.

Facility	**DERM ID**	**Latitude**	**Longitude**	**TP (ug/L) 2019-2020**	**TP (ug/L) 2023-April**	**ICP-MS P (ug/L) 2023-April**	**TP (ug/L) 2023-May**	**ICP-MS P (ug/L) 2023-May**
5909	8505684	25.9116	-80.1663	450	28	21	260	359
4693	8504895	25.9079	-80.1702	1200	383	453	388	508
7971	8839865	25.8895	-80.1668	270	44	43	281	334
3189	8504037	25.8787	-80.1674	100	87	111	55	75
5978	8505786	25.8743	-80.1706	160	168	211	175	273
7917	8838676	25.8989	-80.1942	300	122	160	511	515
5390	8505416	25.8697	-80.2072	440	411	500	425	659
5372	8505412	25.8638	-80.1933	73	224	296	76	148
6011	8505801	25.8471	-80.1967	300	2076	1968	459	784
6841	8506357	25.8413	-80.1965	270	200	259	202	408

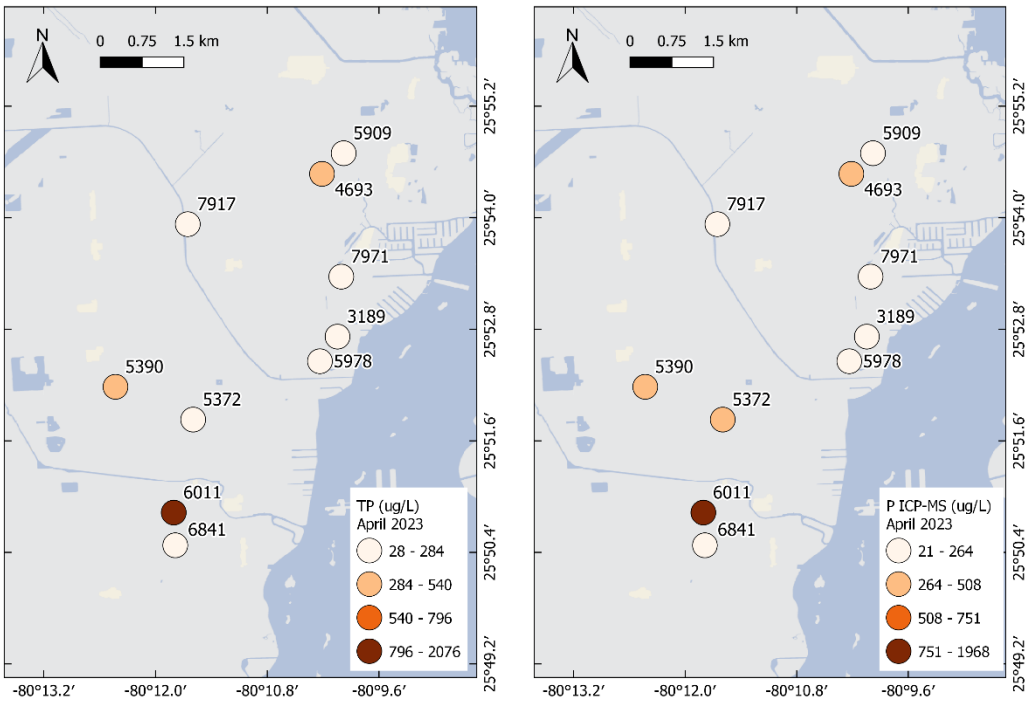

Figure 1: Total phosphorus (TP) concentrations (ug/L) for the sampling conducted in April 2023 using the colorimetric and ICP-MS methods.

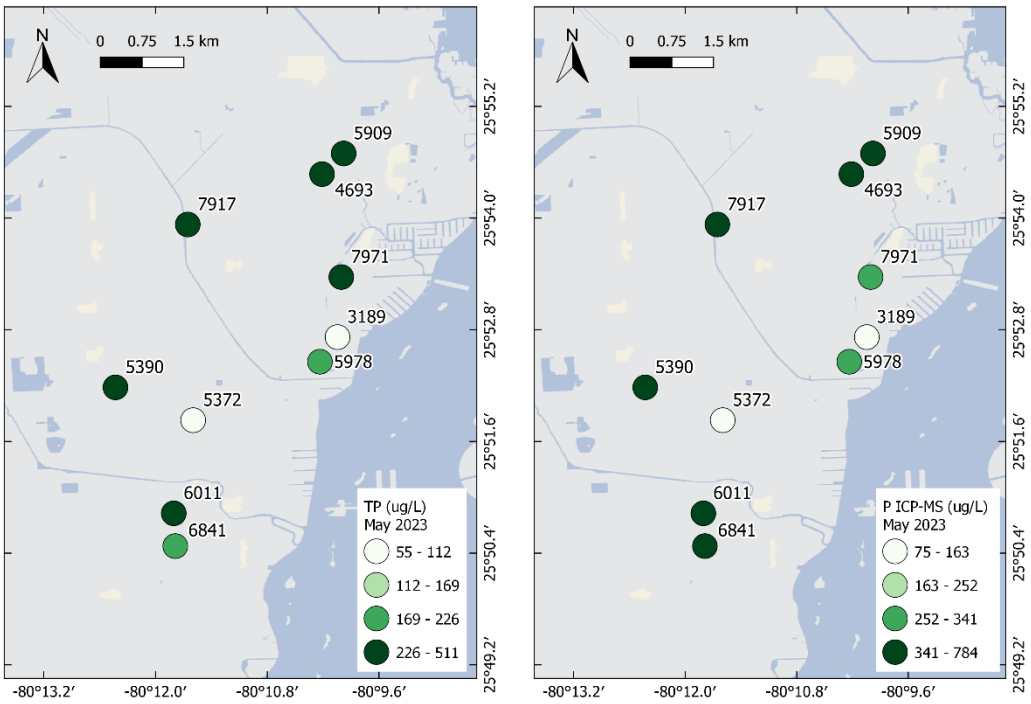

Figure 2: Total phosphorus (TP) concentrations (ug/L) for the sampling conducted in May 2023 using the colorimetric and ICP-MS methods.

Organic tracers, often linked to specific wastewater sources, were also measured in the samples. Sucralose concentrations ranged between 29.3 and 2074 ng/L, with an average of 535 ± 572 ng/L. The highest concentrations of 2,074 and 1,791 ng/L were found in April for sites 5909 and 6841 (Figure 3). During the May sampling event, site 5909 decreased to 106 ng/L, whereas site 7917 decreased to 953 ng/L, which is still one of the highest sucralose concentrations as compared to the other sites (Figure 4). Atrazine, a commonly used herbicide, was detected above the MDL in 6 samples, with the highest values of 25.1 and 16.3 ng/L found for station 4693 in April and May, respectively. These levels suggest background levels rather than a specific contamination source. A high concentration of caffeine of 1050 ng/L was found in station 5390 for the month of April (Figure 3), but decreased to 24.0 ng/L in May (Figure 4). Apart from this exceptionally high value, the caffeine concentrations varied between 14.4 and 154.0 ng/L, with an average of 48.4 ± 31.8 ng/L. It is important to consider that the field, equipment and flask blanks showed caffeine concentrations between 18.7 and 39.7 ng/L. These values were above the method detection limit of 1.32 ng/L thus the values were qualified. Carbamazepine was found above the MDL for 11 samples, with the highest concentrations of 16.3 and 12.0 ng/L found in April for stations 5978 and 7917, respectively. In May, station 5978 decrease to <MDL, while station 7917 decrease to 4.9 ng/L. Sulfamethoxazole was detected only in site 6841 in April with a concentration of 28.3 ng/L. The results from the organic tracers did not present any notable correlation among sites and varied between the two sampling events, which might be indicative of contributions of multiple and intermittent sources of pollution to the groundwater. It is worth noticing that this was a pilot study aimed mainly to confirm the elevated concentration of phosphorous in groundwater. The inorganic and organic tracers were used to explore if significant associations did exist. Due to the sampling size and the number of events the interpretation of those links is limited and a larger assessment will be needed to answer that question.

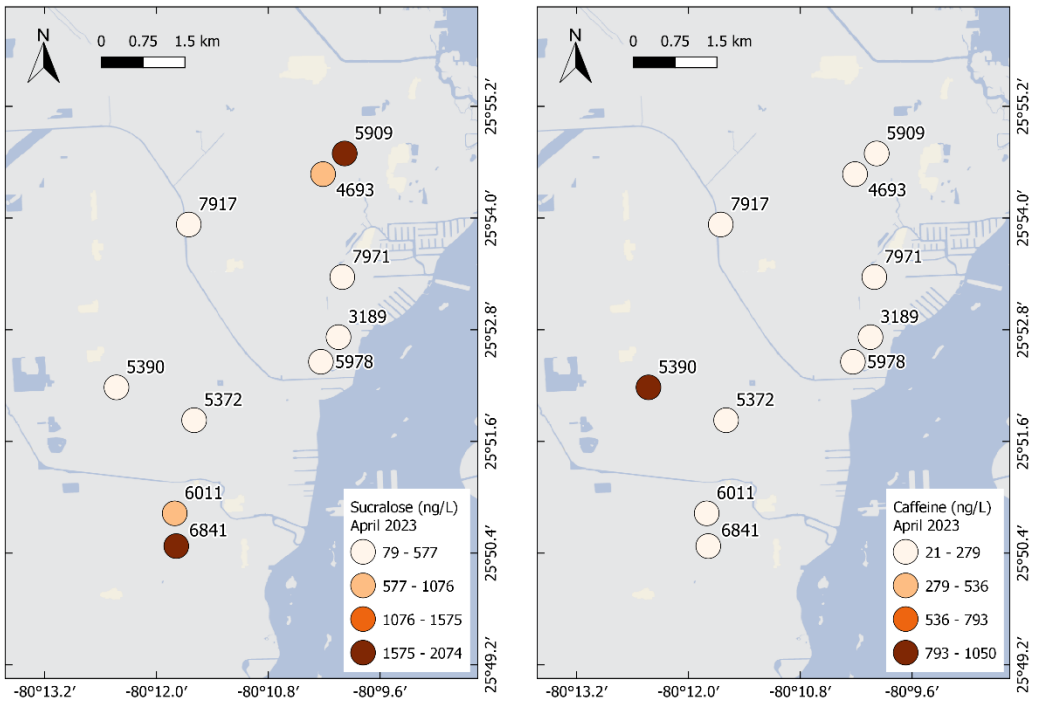

Figure 3: Sucralose and caffeine concentrations (ng/L) for the sampling conducted in April 2023.

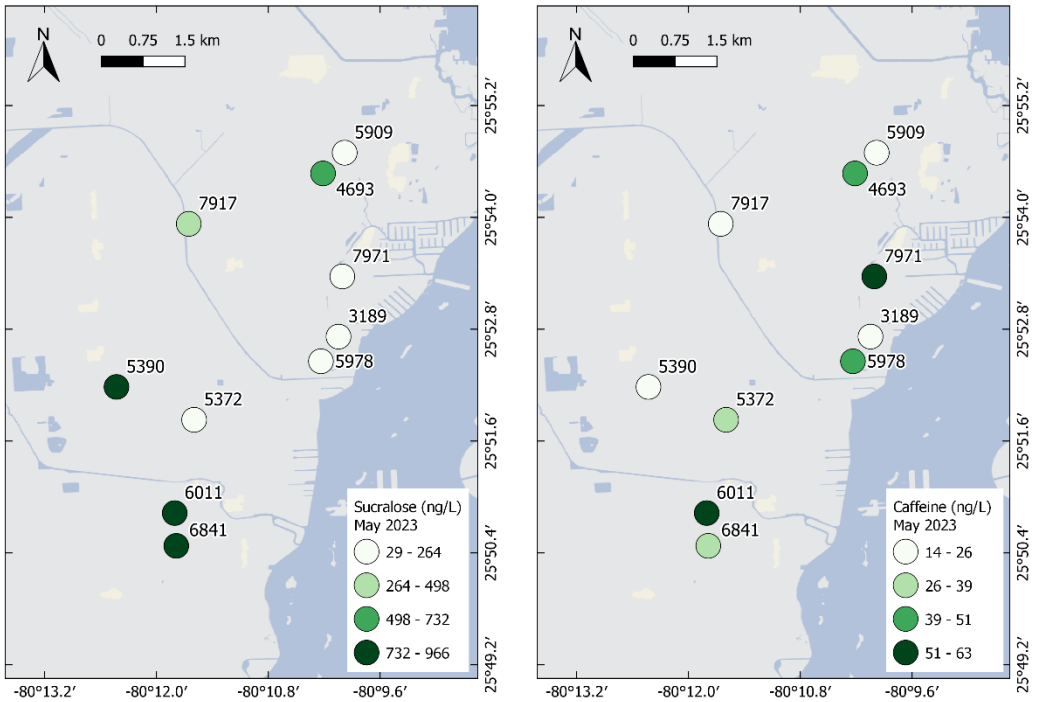

Figure 4: Sucralose and caffeine concentrations (ng/L) for the sampling conducted in May 2023.

The results of this exploratory pilot effort corroborate the high amounts of phosphorous previously observed in groundwater of specific areas in MDC during the 2019-2020 survey by two complementary but orthogonal detection techniques. Even though phosphorus is a naturally occurring element essential for algae and aquatic plant production, excessive amounts can lead to harmful algal blooms and other environmental impacts. One important example of continued degradation in the North Biscayne Bay waters are the fish kill events that happened in 2020 and 2022. Because phosphorus is known to be the limiting nutrient in Biscayne Bay, a continued, long-term monitoring effort at these 10 sites is needed. In addition, a more detailed survey including other sampling sites is crucial for understanding the magnitude and the spatial/temporal extent of the phosphorous groundwater variability, its contribution to the canals and potential discharge into the bay waters. Further studies are also required to investigate the sources and transport mechanisms of this recurrent, elevated phosphorus concentrations, which will help prioritize strategic actions informing the Biscayne Bay Reasonable Assurance Plan (RAP).