Proof of concept study to evaluate wastewater tracers in assessing impact of septic effluent in Benedict, Charles County, MD

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Project Goals and Design

With Charles County's interested in both tracing and documenting the impact of septic system effluent on receiving waters, we designed a pilot study to assess whether we could detect wastewater from septic systems in ground and surface water in and around the community of Benedict, Maryland. We have developed a series of wastewater tracers unique to human wastewater that might help separate sources of nutrients to the Patuxent River. This pilot study reports on the findings of this pilot study.

Wells made of 1.3" OD diameter PVC pipes and screened were installed to a depth of approximately 8 ft at 7 locations within the Benedict township. Samples were collected from 4 "*upland*" well sites and 2 "*waters edge*" edge properties. A fifth upland site never yielded water. The sites are shown on the map in Figure 1. Site 1 was located in a moderately dense area of housing, Site 2 was located on a lot across from the Benedict fire station but the coarse sediment never yielded water. Site 3 was located central to the island in an area among houses. Sites 4 and 5 were installed to create a two point transect on the east side of the peninsula wand and was close to old businesses such as the rooming house. Site 4 was located just east of Mill Creek Rd and Site 5 was located between Benedict Avenue and the Patuxent River. Site 6 and 7 formed a second transect further south and located on a property undergoing renovations. The inland Site 6 was located just east of Mill Creek Road and Site 7 was located adjacent to the Patuxent River. The idea behind these transects was to provide a gradient between the land and the receiving water of the Patuxent River. One limitation is that we do not know which direction the groundwater actually flows however and the gradient was suspected to be minimal. Surface water samples were also taken from approximately 50 meters offshore within the Patuxent River, above (Site 10) and below Benedict (Site 11) and at three locations behind the town, one at the mouth of the bay (Site 12), one adjacent to the "mainland" where agricultural runoff might be found (Site 13), and one as far up the creek we could get (Site 14). The upper portion of the creek is very shallow (water <20 cm deep) with soft organic sediment. The PVC wells were pumped 4 times after installation before use. Samples were collected on 2 occasions in 2021, on June 24 and August 4, with wells pumped prior to the second collection.

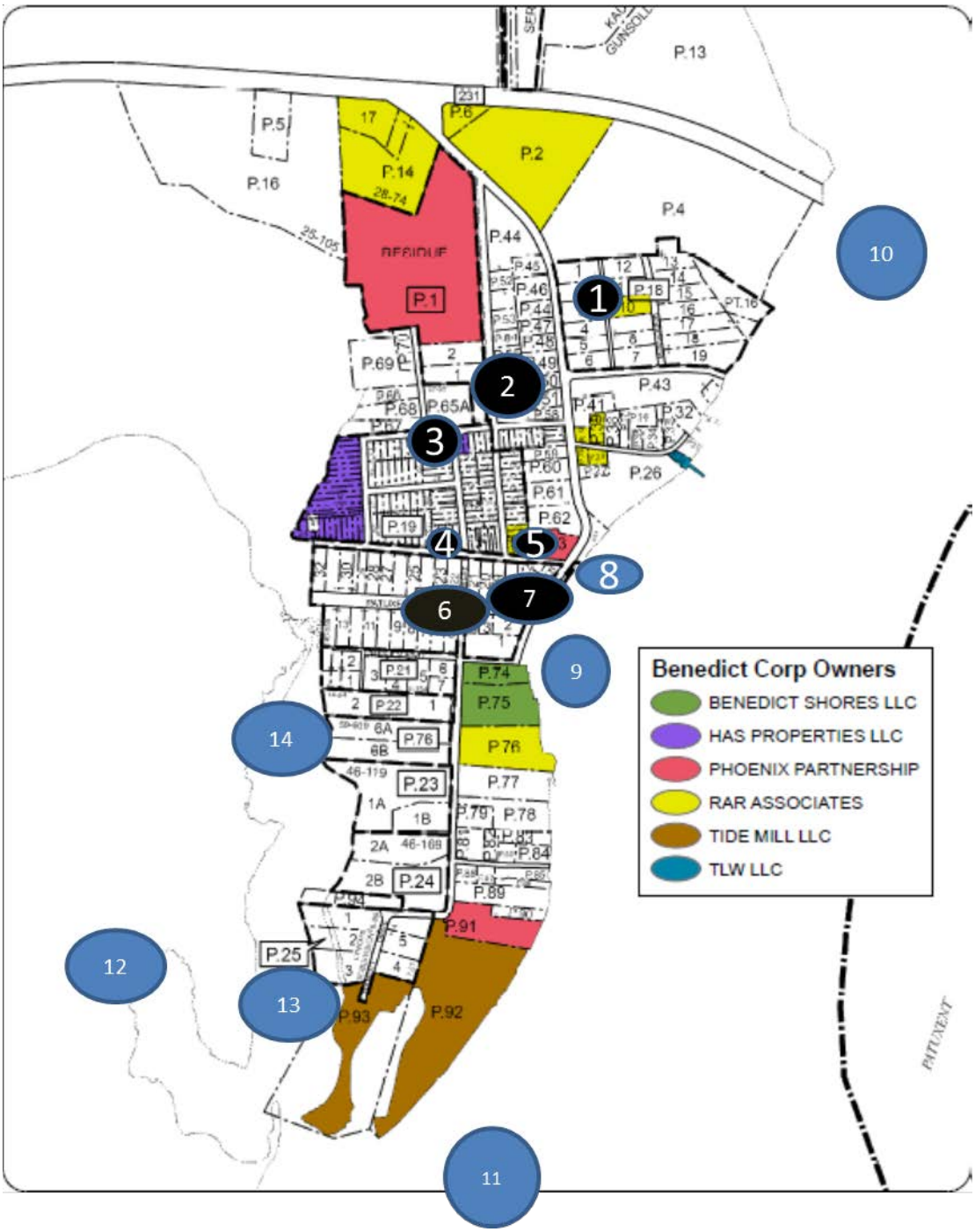

Figure 1. Sampling Locations in Benedict Maryland. Black dots indicate wells and Blue dots are Surface water samples.

Sample Collection and Observations

The goal was to sample during a wet and dry period, but to be completed in the spring/summer of 2021. The first set of samples was collected on June 24th and the second set on August 4th. The first set followed a period of small rain events prior to sampling, but after the high river flows of April (Figure 2a). The second set of samples was collected after a dry period (Figure 2b). The tidal cycle was higher during the first collection than the second collection (Figure 2). Observations of the soil and sediment made while coring to install the wells indicate the sediments underlying Benedict are generally sandy to gravel, with some pockets of more organic rich soils especially at site 7. Rain water will drain rapidly from these soils, with the release probably controlled by the River height, at least at the lower elevation sites. The town slopes from west to east, from a significant bluff (approx. 10 m high) along the western side bordering Back Creek, to a soft entry into the Patuxent River. Water levels in the wells were low during every visit, near the bottom of the wells, and suggested a heavy contribution from human activities is needed to maintain the levels with little rain occurring during the sampling period.

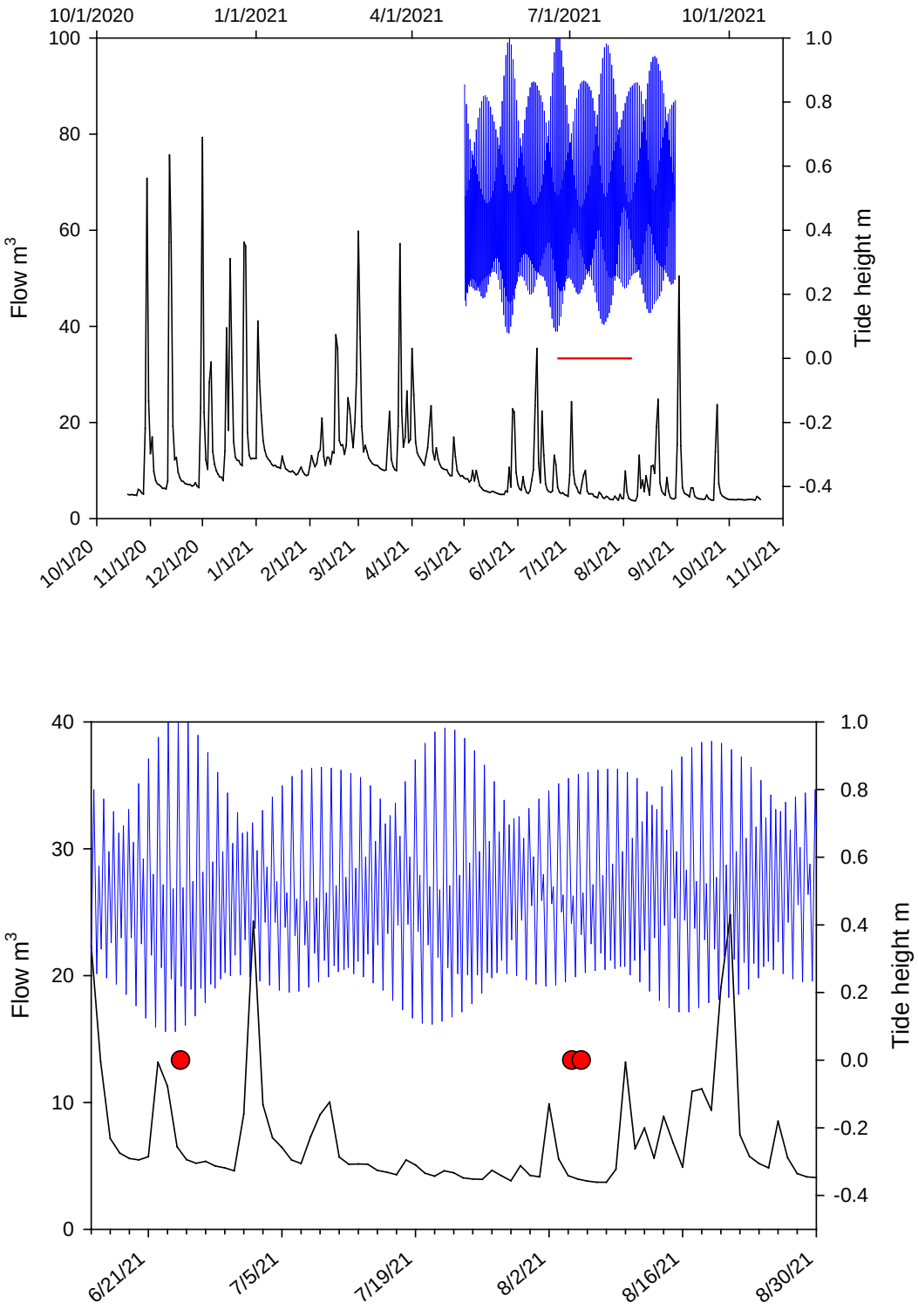

Figure 2. Flow conditions in the Patuxent River. Flows are taken from the USGS gauging station 01594440. Tides are from Benedict Bridge.

Chemical analysis

Water samples were analyzed for nutrients, ammonia, nitrate, nitrite, total nitrogen and total phosphorus. The analysis was performed by the Nutrient Analytical Services Laboratory at the Chesapeake Biological Laboratory (CBL). The water was also analyzed for a series of chemical compounds known to be released in human wastewater. To analyze these compounds in water, a process called solid phase extraction is required. Water is passed over a resin contained in a cartridge, which temporarily binds the chemicals, which are released when a solvent is passed over the resin (Agilent PPL Bond Elut resin). This method allows us to concentrate the compounds and desalt the sample. This approach allows for very low detection limits if paired with liquid chromatography mass spectrometry (LC-MS). Analysis of the extracts were undertaken using an Agilent 6420 qqq mass spectrometer and the so-called isotope dilution approach. The compounds tested and quantified are listed in table 2.

Chemistry Results

Nutrient Data

Concentrations of nitrogen are higher in the shallow groundwater of Benedict than the Patuxent River, the exception being one creek sample near the Marsh (Site 12) in June. Most of the nitrogen occurs as nitrate + nitrite (NO23) in the wells whereas half the nitrogen in the Patuxent River is organic nitrogen (ON). Organic nitrogen is determined by subtracting the inorganic nitrogen species from the total dissolved nitrogen (TDN) Ammonium (NH4) was only significant in well 7 adjacent the water and the surface water site near the Marsh. Phosphorus concentrations are variable and generally the same in shallow groundwater and surface water. Phosphorus in well and surface water is dominated by phosphate. Given the concentration gradient in nitrogen (Examples in Figure 3) we would expect Benedict to be a source of nitrogen especially nitrate to the River.

Site	Date	description	NH4	NO2	NO23	TDN	ON	PO4	TDP
			mg N/L	mg N/L	mg N/L	mg N/L	mg N/L	mg P/L	mg P/L
Well 1	6/24/2021	Inland Yard	0.009	0.001	2.430			0.005	
Well 1	8/4/2021	Inland Yard	0.012	0.001	1.960	2.130	0.158	0.026	0.047
Well 3	6/24/2021	Inland County fallow	0.009	0.002	1.390	1.450	0.051	0.032	0.063
Well 3	8/4/2021	Inland County fallow	0.077	0.014	0.977	1.330	0.276	0.006	0.029
Well 4	6/24/2021	Inland Boat Yard	0.010	0.165	0.802	0.960	0.148	0.004	0.024
Well 4	8/4/2021	Inland Boat Yard	0.009	0.046	1.680	1.640	0.000	0.019	0.031
Well 6	6/24/2021	Upland new House	0.009	0.001	2.570	2.610	0.031	0.003	0.005
Well 6	8/4/2021	Upland new House	0.009	0.001	1.880	1.930	0.041	0.003	0.007
Well 5	6/24/2021	Yard by water	0.009	0.001	0.621	1.050	0.420	0.155	0.185
Well 5	8/4/2021	Yard by water	0.030	0.007	1.480	1.700	0.190	0.087	0.124
well 7	6/24/2021	New House by water	0.294	0.001	0.018	2.370	2.058	0.021	0.126
well 7	8/4/2021	New House by water	0.677	0.001	0.005	2.040	1.358	0.013	0.174
Surface 8	6/24/2021	Pax off transect 5	0.038	0.003	0.089	0.390	0.263	0.027	0.041
Surface 8	8/4/2021	Pax off transect 5	0.009	0.038	0.043	0.380	0.328	0.080	0.113
Surface 9	6/24/2021	Pax off transect 6	0.018	0.001	0.009	0.310	0.283	0.021	0.035
Surface 9	8/4/2021	Pax off transect 6	0.009	0.047	0.057	0.370	0.304	0.078	0.103
Surface 10	6/24/2021	Pax Upstream	0.009	0.001	0.009	0.290	0.272	0.022	0.036
Surface 10	8/4/2021	Pax Upstream	0.009	0.037	0.056	0.370	0.305	0.081	0.109
Surface 11	6/24/2021	Pax Downstream	0.009	0.001	0.009	0.270	0.252	0.020	0.038
Surface 11	8/4/2021	Pax Downstream	0.009	0.005	0.011	0.340	0.320	0.064	0.094
Surface 12	6/24/2021	Back Creek Marsh	0.403	0.011	0.396	1.140	0.341	0.214	0.316
Surface 12	8/4/2021	Back Creek Marsh	0.009	0.001	0.004	0.350	0.338	0.057	0.087
Surface 13	6/24/2021	Back Creek mouth	0.009	0.001	0.002	0.280	0.269	0.012	0.029
Surface 13	8/4/2021	Back Creek Mid	0.009	0.001	0.004	0.250	0.237	0.033	0.054
Surface 14	6/24/2021	Back Creek Head	0.064	0.003	0.069	0.520	0.387	0.039	0.064
Surface 14	8/4/2021	Back Creek Head	0.009	0.001	0.005	0.370	0.356	0.105	0.137

Table 1. Nutrient data in shallow groundwater (well) and surface water from Benedict Maryland. Ammonium (NH4), nitrite (NO2), Nitrate + Nitrite (NO23), TDN (Total Dissolved Nitrogen), Organic Nitrogen (ON = TDN – NH4 – NO23), Phosphate (PO4) and Total Dissolved Phosphorus (TDP). The June 24th well 1 sample for TDN and TDP was lost in the laboratory.

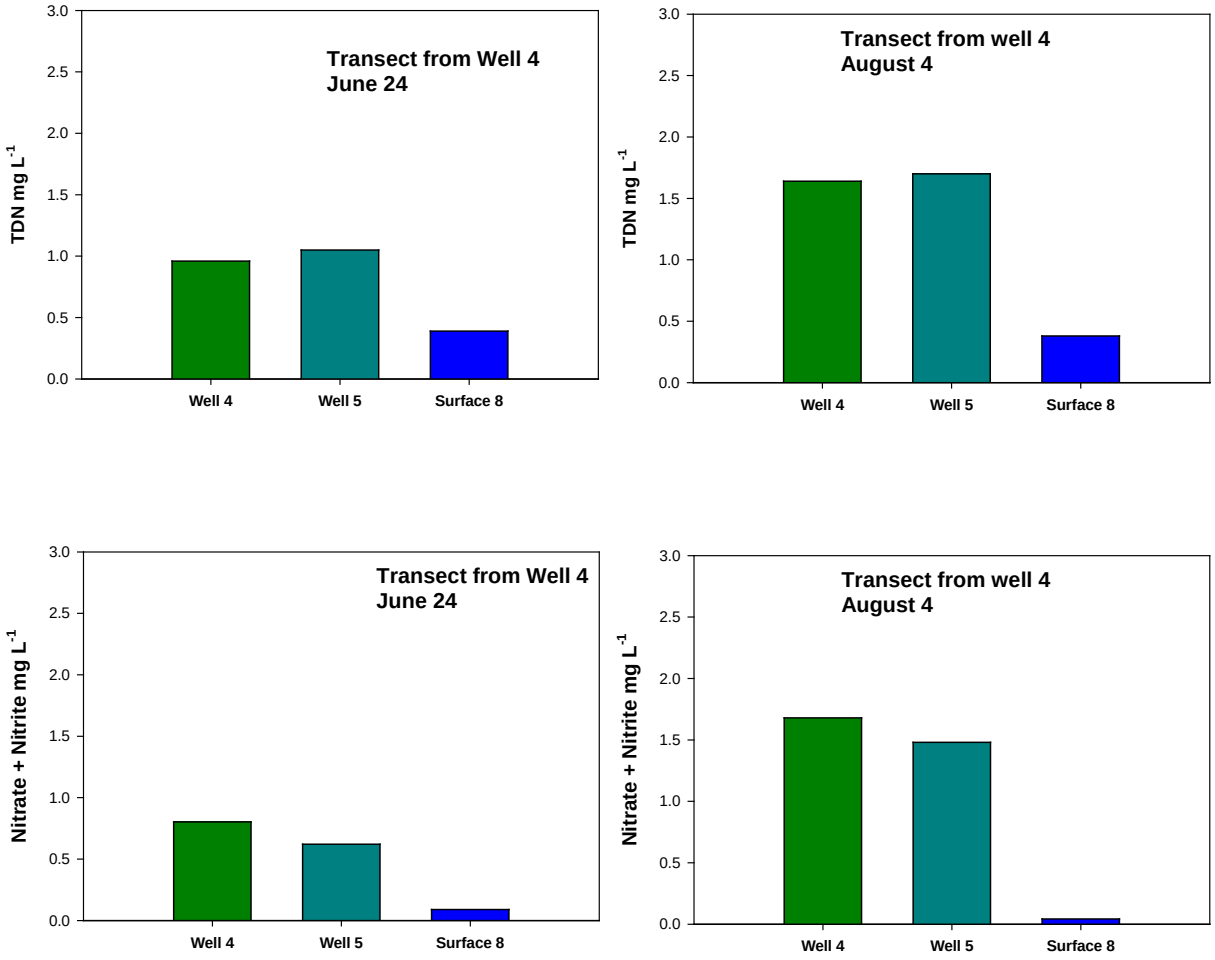

Figure 3. Total Dissolved Nitrogen (TDN) in the well 4, well 5 and surface water 8 transect on June 24, 2021 (upper left), August 4, 2021 (upper right), Nitrate + Nitrite on June 24, 2021 (lower left) and August 4th, 2021(lower right).

Tracer chemistry

The full tracer chemistry data set is provided in Table 2. We found a number of the target compounds in both the Benedict groundwater and Patuxent surface water. Probably the most striking result was the high concentration of some compounds in the Patuxent River. A number of compounds are of limited use, because of few to no detections hence and for this reason we will not discuss Acetaminophen, Sulfamethoxazole, Ibuprofen, Estrone, Diclofenac, Dichlorvos, Cotinine, Atorvastatin. We will focus on the discussion on sucralose, Paraxanthine, DEET, Carbamazepine and Caffeine.

While detection of these compounds where expected, such high concentrations in surface water of the Patuxent River were not. DEET (N,N-diethyl-meta-toluamide) is used as an insect repellent and is found in higher concentrations in the groundwater (0.013 ng L^{-1}) and detected in

nearshore waters (0.008 ug L^{-1}), but only at one time and one location in deeper waters (0.008 ug L^{-1}). DEET is highly hydrophobic and adsorbs to particles. It is degraded by sunlight and likely released from wastewater treatment plants. The pattern observed for DEET is consistent with its use and suggests a land source which was expected. Carbamazepine was not detected in the upland wells, detected in the near shore wells (0.005 ug L^{-1}), but was common in all Patuxent River water samples (0.012 ug L^{-1}). Carbamazepine is a drug which might not be common in Benedict and has limited use, but would be a common compound in wastewater from a larger community. There are numerous wastewater sources from which it could originate from along the upper Patuxent River. Its presence in the near shore wells suggests some mixing of river and groundwater and is evidence for water exchange. The most useful compounds are caffeine and one of its breakdown products paraxanthine, along with sucralose. Sucralose is elevated everywhere, averaging 2 ug L^{-1} in the Patuxent River samples. Being highly stable, sucralose can be transported long distances with minimal degradation and in our case overwhelms the signal from Benedict. The highest concentrations of caffeine are found in groundwater (0.06 ug L^{-1}) and decrease steadily in groundwater (0.05 ug L^{-1}) toward the Patuxent river (0.02 ug L^{-1}) (figure 4). This is similar to what we see with nitrogen, in fact a strong relationship between the two is apparent (Figure 5) and indicate that nitrogen detected in the wells is likely derived from septic system effluent. We could only quantify paraxanthine in 2 “upland wells” although we could detect its presence more frequently.

Site	Date	description	Acetaminophen		sucralose 2		Sulfamethoxazole		Paraxanthine		Ibuprofen		Estrone		Diclofenac	
			ug/L	stderror	ug/L	stderror	ug/L	stderror	ug/L	stderror	ug/L	stderror	ug/L	stderror	ug/L	stderror
Well 1	6/24/2021	Inland Yard	BLD		1.668	0.325	0.003	0.000	BLQ		BLD		BLD		BLD	
Well 1	8/4/2021	Inland Yard	BLD		0.390	0.006	BLQ		BLQ		BLD		BLD		BLD	
Well 3	6/24/2021	Inland County fallow	BLD		1.541	0.783	0.003	0.001	BLQ		BLD		BLD		BLD	
Well 3	8/4/2021	Inland County fallow	BLD		2.097	0.645	0.003	0.001	0.064	0.044	BLD		BLD		BLD	
Well 4	6/24/2021	Inland Boat Yard	BLD		0.163	0.034	BLQ		BLQ		BLD		BLD		BLD	
Well 4	8/4/2021	Inland Boat Yard	BLD		0.226	0.058	BLQ		BLQ		BLD		BLD		BLD	
Well 6	6/24/2021	Upland new House	BLD		0.153	0.012	BLQ		0.046	0.009	BLD		BLD		BLD	
Well 6	8/4/2021	Upland new House	BLD		BLQ		BLQ		BLQ		BLD		BLD		BLD	
Well 5	6/24/2021	Yard by water	BLD		1.285	0.682	0.005	0.002	BLQ		BLD		BLD		BLD	
Well 5	8/4/2021	Yard by water	BLD		0.911	0.061	0.003	0.000	BLQ		BLD		BLD		BLD	
well 7	6/24/2021	New House by water	BLD		0.862	0.514	0.004	0.001	BLQ		BLD		BLD		BLD	
well 7	8/4/2021	New House by water	BLD		0.452	0.102	0.003	0.001	BLQ		BLD		BLD		BLD	
Surface 8	6/24/2021	Pax off transect 5	BLD		3.631		0.008		BLQ		BLD		BLD		BLD	
Surface 8	8/4/2021	Pax off transect 5	BLD		1.653	0.041	BLQ		BLQ		BLD		BLD		BLD	
Surface 9	6/24/2021	Pax off transect 6	BLD		1.699	0.240	0.006	0.001	BLQ		BLD		BLD		BLD	
Surface 9	8/4/2021	Pax off transect 6	BLD		1.555	0.127	BLQ		BLQ		BLD		BLD		BLD	
Surface 10	6/24/2021	Pax Upstream	BLD		2.147	0.032	0.008	0.000	BLQ		BLD		BLD		BLD	
Surface 10	8/4/2021	Pax Upstream	BLD		1.537	0.132	0.002	0.000	BLQ		BLD		BLD		BLD	
Surface 11	6/24/2021	Pax Downstream	BLD		1.782	0.057	0.008	0.000	BLQ		BLD		BLD		BLD	
Surface 11	8/4/2021	Pax Downstream	BLD		1.165	0.004	0.003	0.000	BLQ		BLD		BLD		BLD	
Surface 12	6/24/2021	Back Creek Marsh	BLD		0.290	0.056	BLQ		BLQ		BLD		BLD		BLD	
Surface 12	8/4/2021	Back Creek Marsh	BLD		1.080	0.041	0.003	0.000	BLQ		BLD		BLD		BLD	
Surface 13	6/24/2021	Back Creek mouth	BLD		1.602	0.050	0.008	0.000	BLQ		BLD		BLD		BLD	
Surface 13	8/4/2021	Back Creek Mid	BLD		1.180	0.121	0.004	0.000	BLQ		BLD		BLD		BLD	
Surface 14	6/24/2021	Back Creek Head	BLD		1.075	0.091	0.003	0.001	BLQ		BLD		BLD		BLD	
Surface 14	8/4/2021	Back Creek Head	BLD		1.053	0.014	0.003	0.000	BLQ		BLD		BLD		BLD	
	Limit of Quantification		0.050		0.050		0.002		0.040		0.130		0.060		0.020	

Site	Date	description	Dichlorvos		DEET		Cotinine		Carbamazepine		Caffeine		Atorvastatin	
			ug/L	stderror	ug/L	stderror	ug/L	stderror	ug/L	stderror	ug/L	stderror	ug/L	stderror
Well 1	6/24/2021	Inland Yard	BLQ		BLQ		BLQ		BQL		0.035	0.019	BLD	
Well 1	8/4/2021	Inland Yard	BLQ		0.009	0.001	BLQ		BQL		0.057	0.013	BLD	
Well 3	6/24/2021	Inland County fallow	BLQ		0.024	0.010	BLQ		BQL		0.024	0.002	BLD	
Well 3	8/4/2021	Inland County fallow	BLQ		0.057	0.034	BLQ		BQL		0.117	0.068	BLD	
Well 4	6/24/2021	Inland Boat Yard	BLQ		BLQ		BLQ		BQL		0.018	0.000	BLD	
Well 4	8/4/2021	Inland Boat Yard	BLQ		0.011	0.001	BLQ		BQL		0.040	0.002	BLD	
Well 6	6/24/2021	Upland new House	BLQ		BLQ		BLQ		BQL		0.138	0.034	BLD	
Well 6	8/4/2021	Upland new House	BLQ		BLQ		BLQ		BQL		0.080	0.043	BLD	
Well 5	6/24/2021	Yard by water	BLQ		BLQ		BLQ		0.005	0.005	0.050	0.037	BLD	
Well 5	8/4/2021	Yard by water	BLQ		0.020	0.008	BLQ		0.006	0.001	0.045	0.004	BLD	
well 7	6/24/2021	New House by water	BLQ		BLQ		BLQ		0.005	0.005	0.026	0.007	BLD	
well 7	8/4/2021	New House by water	0.012	0.005	BLQ		BLQ		BQL		0.082	0.043	BLD	
Surface 8	6/24/2021	Pax off transect 5	BLQ		0.015		BLQ		0.021		BQL		BLD	
Surface 8	8/4/2021	Pax off transect 5	BLQ		0.008	0.000	BLQ		0.013	0.000	BQL		BLD	
Surface 9	6/24/2021	Pax off transect 6	BLQ		BLQ		BLQ		0.013	0.001	BQL		BLD	
Surface 9	8/4/2021	Pax off transect 6	BLQ		BLQ		BLQ		0.012	0.000	BQL		BLD	
Surface 10	6/24/2021	Pax Upstream	BLQ		0.008	0.000	BLQ		0.015	0.000	0.015	0.002	BLD	
Surface 10	8/4/2021	Pax Upstream	BLQ		BLQ		BLQ		0.012	0.000	0.024	0.000	BLD	
Surface 11	6/24/2021	Pax Downstream	BLQ		BLQ		BLQ		0.013	0.000	0.022	0.011	BLD	
Surface 11	8/4/2021	Pax Downstream	0.008	0.005	BLQ		BLQ		0.011	0.000	BQL		BLD	
Surface 12	6/24/2021	Back Creek Marsh	BLQ		BLQ		BLQ		0.008	0.000	BQL		BLD	
Surface 12	8/4/2021	Back Creek Marsh	BLQ		BLQ		BLQ		0.010	0.000	BQL		BLD	
Surface 13	6/24/2021	Back Creek mouth	BLQ		BLQ		BLQ		0.013	0.000	0.051	0.031	BLD	
Surface 13	8/4/2021	Back Creek Mid	BLQ		BLQ		BLQ		0.011	0.000	BQL		BLD	
Surface 14	6/24/2021	Back Creek Head	BLQ		BLQ		BLQ		0.010	0.000	0.012	0.000	BLD	
Surface 14	8/4/2021	Back Creek Head	BLQ		BLQ		BLQ		0.011	0.000	0.011	0.003	BLD	
	Limit of Quantification		0.007		0.009		0.004		0.040		0.010		0.02	

Table 2. Concentration of the target compounds in shallow groundwater (wells) and in surface waters. Limit of Detection (LD) is based on instrument detection whereas the limit of quantification (LQ) is based on the ability to quantify the compound, thus BLQ does not mean the compound isn't present.

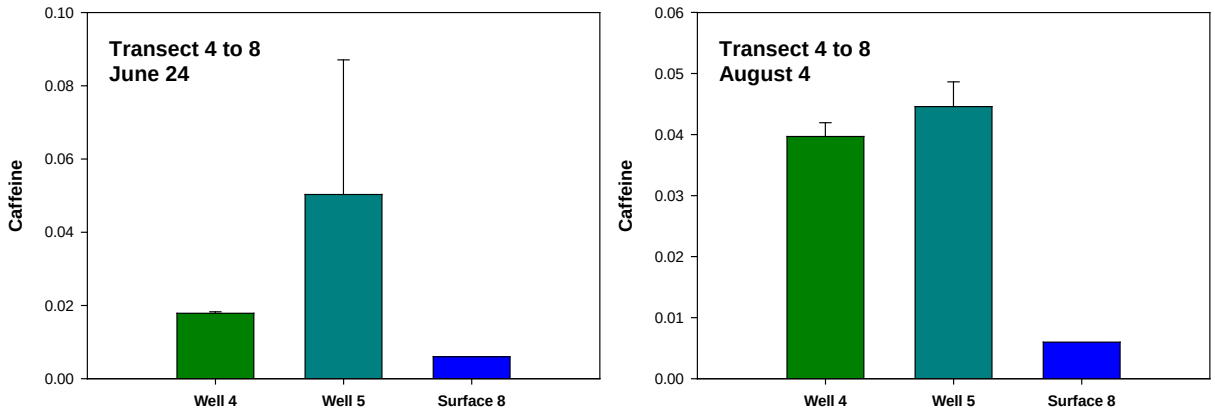

Figure 4. Concentrations of caffeine in the 6 to 9 transect on June 24th and August 4th 2021.

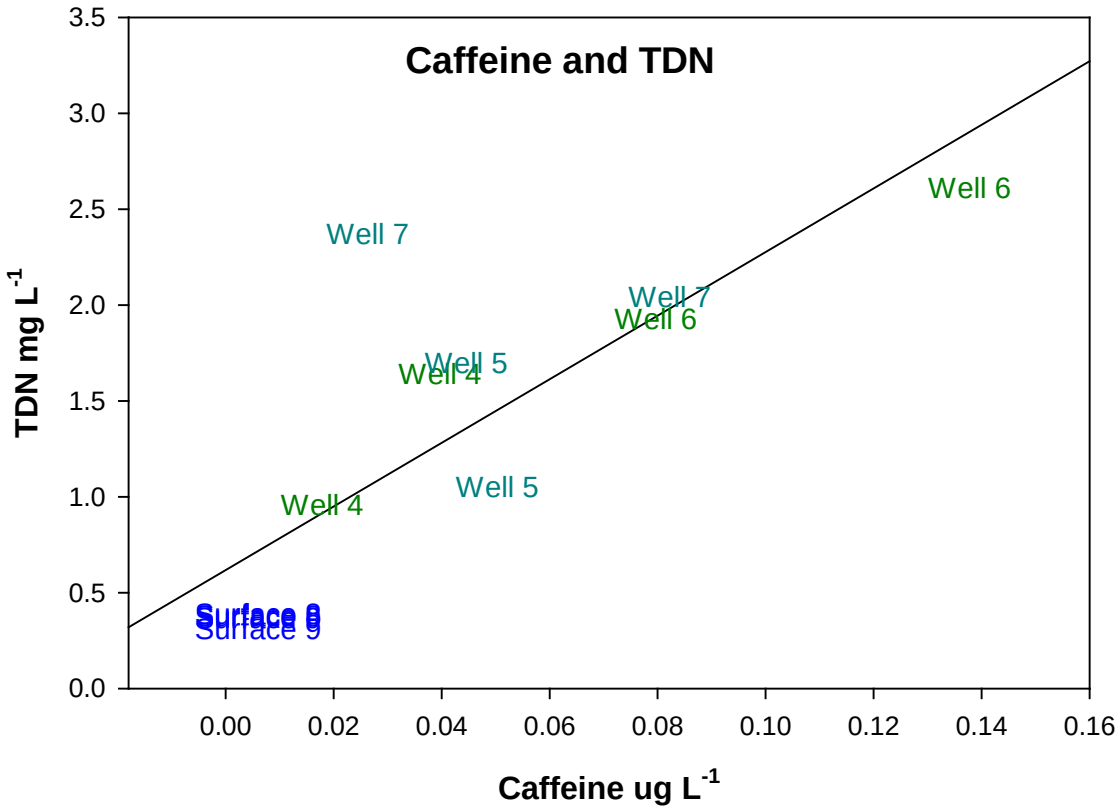

Figure 5. Relationship between Caffeine and TDN well and surface water transects.

Since caffeine degrades over time and sucralose is recalcitrant lasting months in groundwater, the ratio of sucralose (conservative) to caffeine provides an indication of the freshness of the wastewater. This ratio between the two increases dramatically between the groundwater and the Patuxent River water. This same pattern is present in the ratio of sucralose to paraxanthine, a breakdown product of caffeine (Table 3). The back Creek samples have ratio's (83± 42) lower than the River (151± 60), the fresher signal may reflect a greater influx of septic system effluent.

Site	Date	description		
			Suc:Caf	Suc:Para
Well 1	6/24/2021	Inland Yard	48	92
Well 1	8/4/2021	Inland Yard	7	17
Well 3	6/24/2021	Inland County fallow	64	124
Well 3	8/4/2021	Inland County fallow	18	33
Well 4	6/24/2021	Inland Boat Yard	9	17
Well 4	8/4/2021	Inland Boat Yard	6	22
Well 6	6/24/2021	Upland new House	1	3
Well 6	8/4/2021	Upland new House	0	1
Well 5	6/24/2021	Yard by water	26	50
Well 5	8/4/2021	Yard by water	20	43
well 7	6/24/2021	New House by water	33	72
well 7	8/4/2021	New House by water	5	12
Surface 8	6/24/2021	Pax off transect 5	218	294
Surface 8	8/4/2021	Pax off transect 5	177	208
Surface 9	6/24/2021	Pax off transect 6	160	256
Surface 9	8/4/2021	Pax off transect 6	236	222
Surface 10	6/24/2021	Pax Upstream	139	250
Surface 10	8/4/2021	Pax Upstream	65	172
Surface 11	6/24/2021	Pax Downstream	82	145
Surface 11	8/4/2021	Pax Downstream	129	184
Surface 12	6/24/2021	Back Creek Marsh	35	67
Surface 12	8/4/2021	Back Creek Marsh	113	202
Surface 13	6/24/2021	Back Creek mouth	32	60
Surface 13	8/4/2021	Back Creek Mid	136	195
Surface 14	6/24/2021	Back Creek Head	90	164
Surface 14	8/4/2021	Back Creek Head	95	147

Table 3. Sucralose to Caffeine Ratios determined for all the sampling sites in 2021.

Discussion

A number of the target compounds examined were not detected, which is a similar finding to our study of Calvert County streams. These non-detected compounds were also not necessarily expected, due to their intended use. Comparing concentrations of detected compounds in Benedict to those of Calvert County, we see similar values. Concentrations of sucralose in Calvert County streams draining a variety of developments averaged 2.8 ug L^{-1} which is not much greater than the 1.9 ug L^{-1} in the Patuxent main stem samples and 0.85 ug L^{-1} in groundwater. Concentrations of sucralose in septic tanks sampled in Calvert County averaged 33 ug L^{-1}. Caffeine concentrations in Calvert streams averaged 0.05 ug L^{-1} which is higher than the 0.02 ug L^{-1} in the Patuxent but similar to Benedict's average concentration in shallow groundwater of 0.06 ug L^{-1}. Caffeine concentrations in Calvert septic tanks averaged 4.2 ug L^{-1}. The Calvert County data yields "freshness" ratios of 7.8 for the septic tanks and 62 for the streams placing Benedict groundwater of 19 between the two with the Patuxent River's average of 121 being the highest. Some Benedict ratios in groundwater were even less than the Calvert Septic tanks (Table 3). This suggests that the shallow groundwater under Benedict is likely to be dominated by Septic waste water.

What is difficult to assess is the impact of this water on the Patuxent River because it also has high concentrations of conservative tracers such as sucralose. The Patuxent River appears to be highly impacted. While Benedict is undoubtable a source, the only feasible way to measure success from removing septic systems would be by monitoring changes in the groundwater concentrations of the tracers over time and comparing them to conditions in the Patuxent River.