

Surface water nitrogen attenuation from the Accomack County, VA southern landfill groundwater discharge, final report.

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The Issue. Previous sampling of the stream crossing Bobtown Road (Rt 178) near the intersection of Hollies Church Road (Rt. 620), had indicated high levels of nitrogen in the stream flow (Snyder and Ross, 2019a). The proximity of the retired Accomack County Landfill upstream of the site triggered a higher resolution sampling of the stream in an attempt to isolate a source of the nitrogen loading (Snyder and Ross, 2019b). Accomack County has requested repeated sampling of this stream segment to monitor nutrient attenuation trends from the site, and stations were established for that purpose. This Final Report provides a summary of three years of sampling at the site (2018-2020).

Methodology. The initial sampling in 2018 was used to define groundwater loading sites along the stream East of Bobtown road. With an identified hotspot of high nitrogen and low dissolved oxygen discovered near the stream head (Figure 1). Sample sites were then established from that point designed to define an attenuation in nitrogen concentrations with distance downstream to a point where the stream reached tidal waters of a branch of Pungoteague Creek. (Figure 2). These stations were established with PVC pipe markers and the locations recorded by a Garmin handheld GPS meter (~12 ft accuracy). Distance downstream was determined with a measuring tool on an ESRI ArcMap GIS software plot of the stations, following the stream channel course with a Bayside NHDFlowline layer. An additional sample was taken of the ponds at the landfill site, midway down the berm separating the two basins (Figure 2). Surveying and sampling personnel included Richard Snyder VIMS ESL, Anna Hart VIMS Volunteer, and John Lauer Accomack County.

Standard water quality sampling procedures were followed. The field technician used latex gloves to prevent contamination of samples. For each sampling event, a 125 ml polypropylene bottle was filled and rinsed three times with site water before final filling, capping, and placing on ice for transport to the laboratory. This sample was analyzed for Total Nitrogen and Total Phosphorous (methods for analysis are included in Appendix I). A 60cc polypropylene syringe was rinsed three times with site water and then used to pass water through a Whatman 25 mm GF/F glass fiber filter held in a Millipore stainless steel swinnex into a 60 ml polypropylene bottle. This sample was analyzed for Dissolved ammonia and dissolved $\text{NO}_2 + \text{NO}_3$ (NO_x ; methods for analysis are included in Appendix I). Rainfall data was obtained from <https://weatherspark.com/h/m/147126/2019/12/Historical-Weather-in-December-2019-at-Melfa-Accomack-Airport-Virginia-United-States> and the Community Collaborative Rain, Hail, and Snow network (CoCoRaHS; <https://www.cocorahs.org/Content.aspx?page=watershedmap>).

A field data sheet recorded the number of the sample, station number, date and time of collection. Temperature, salinity, pH, and dissolved oxygen of the water were recorded from a handheld YSI meter. Flow rates at two culverts were estimated by timing the transit of a visual marker in the culvert as insufficient depth was available to use a SonTek Flowtracker. Field collection data were transferred to a MS Excel spreadsheet and is presented as Table 1. Water samples were frozen at -20 deg C at VIMS ESL until transport to VIMS Gloucester Point Analytical Services for analysis of nutrients. Samples were delivered still frozen during custody transfer. The analytical data were combined with the field data in an MS Excel spreadsheet, presented as Table 1. Data were plotted using ESRI Arcmap GIS mapping software and Kaleidagraph software.

Results and Discussion

Table 1 presents the accumulated data for determining attenuation of the landfill groundwater discharge. Table 2 presents all sample events from Table 1 at the Bobtown Road stream crossing, plus additional samples that were taken in a separate investigation into stream water quality in Accomack County. These latter data show rainfall events on 20 April 2019 and 8 September 2020 depressing the ammonia and TN values with storm water runoff, confirming the groundwater source of nitrogen to the stream. Loading rates (flow x concentration) provide estimates of the amount of nitrogen being transported downstream (Table 2)

Ammonia and TN concentrations decreased with distance downstream of the landfill groundwater discharge site for all sampling events (Table 1; Figure 3). NO_x was a very minor component of the nitrogen in the stream flow (Table 1; Figure 3). Ammonia represented 86%, on average, of the total nitrogen load (Figure 4), and little difference was noted between ammonia and total nitrogen attenuation values (data not shown).

A small increase above the attenuation trend in NH₃ concentration is seen between 150-200 m downstream (Figure 3), reflecting additional groundwater emerging along the stream bank East of Bobtown Road. West of Bobtown Road at >600 m there is a larger increase above the attenuation trend in NH₃ concentrations reflecting additional ground water contributions in the swamp between Bobtown Road and Country Club Road. This additional groundwater input is also reflected in the increased flow rate of the stream between these two road crossings. There are several stream branches from the south joining with the stream from the landfill that are not in the NHDFlowline database layer, and numerous seepage areas into the swamp between Bobtown Road and Country Club Road that contribute a significant volume of water to the system. The increase in water flow noted in the estimated flows between Bobtown Road and Country Club Road culverts was consistent over multiple sampling events (Table 2). The increase in flow appears to be due to ground water discharge into this wooded swamp area, and the increase in NH₃ concentrations suggests a landfill contribution here as well.

The attenuation of TN fit to exponential loss curves with distance is shown in Figure 5. The extinction coefficients from regression analysis for these data are shown in Table 3. The June sampling event had a greater attenuation rate and higher overall values. The higher concentrations may be due to temperature dependent microbial activity degrading organic matter. The faster attenuation rate in June may be related to greater uptake of ammonia within the stream system with greater biological activity, but overall attenuation may be mostly by dilution.

Similar analysis for total phosphorous (TP) is shown in Figure 6. The data indicate that the landfill is also a source of phosphorous to the stream, consistent with idea that microbial degradation of organic material in the landfill is the nutrient source. Phosphorous is typically highly insoluble in fresh waters, reflected in its rapid attenuation in the stream, but it does tend to be mobilized under low oxygen conditions, consistent with the low oxygen readings in the stream at the discharge location.

Despite differences in concentration of ammonia at the loading point, the stream nitrogen values all reach ~10 mg/L where tidal waters are met, which is consistent with some regional

groundwater values. However, ground water nitrogen tends to be in the form of nitrate, whereas the stream draining from the landfill is dominated by ammonium. Currently, the attenuation of the nitrogen and phosphorous with distance from the landfill does not appear to represent undue harm to the receiving waters of Pungoteague Creek.

References

Snyder, RA and PG Ross. 2019a. Water quality in southern Accomack County watersheds. VIMS ESL technical report #2. 21 pp. <https://doi.org/10.25773/cmm4-m650>

Snyder, RA and PG Ross. 2019b. Water quality in an unnamed branch of Pungoteague Creek, Bobtown road and Hollies Church Road, VA. VIMS ESL technical report #3. 9 pp. <https://doi.org/10.25773/bhz7-8h64>

Snyder, RA and PG Ross. 2020. Surface water nitrogen attenuation from the Accomack County, VA southern landfill groundwater discharge. VIMS ESL technical report #5. 7 pp. <https://doi.org/10.25773/7xqy-3n14>

Table 1. Field and analytical data for the stream samples taken to determine attenuation rates.

Date	Time	Station	Lat	Long	Dist. meters	Temp deg C	DO mg/L	Salinity PSU	pH	NH mg/L MDL: 0.0062	NOx mg/L MDL: 0.0055	TN mg/L MDL: 0.0285	TP mg/L MDL: 0.0095
11-Mar-19	9:50	LF1	37.6473	75.7895		8.7	13.12	0.14	9.28			0.490	
11-Mar-19	9:55	LF2	37.6475	75.7892		8.2	5.90	0.21	8.12			1.006	
11-Mar-19	10:12	LF3	37.6498	75.7944	347.0	9.8	8.14	0.36	7.85			17.546	
11-Mar-19	10:20	LF4	37.6494	75.7936	235.6	10	8.06	0.35	7.71			19.396	
11-Mar-19	10:25	LF5	37.6493	75.7932		10.2	8.72	0.25	7.54			20.164	
11-Mar-19	10:27	LF6	37.6493	75.7929	199.7	10	6.56	0.36	7.43			26.240	
11-Mar-19	10:31	LF7	37.6493	75.7929		10.6	9.84	0.31	7.56			18.998	
11-Mar-19	10:36	LF8	37.6490	75.7928	147.6	10.2	10.56	0.34	7.72			19.232	
11-Mar-19	10:50	LF9	37.6491	75.7920	110.8	10.3	5.97	0.33	7.67			24.004	
11-Mar-19	10:56	LF10	37.6488	75.7915	53.9	10.5	6.41	0.34	7.4			28.120	
11-Mar-19	11:00	LF11	37.6490	75.7915	53.9	9	6.58	0.37	7.28			37.820	
11-Mar-19	11:04	LF12	37.6487	75.7911	0.0	10.8	1.85	0.49	7.09			49.520	
11-Mar-19	11:10	LF13	37.6484	75.7913		10.09	9.82	0.1	7.63			0.610	
11-Mar-19	11:15	LF14	37.6484	75.7905		10	7.58	0.15	7.32			2.882	
11-Mar-19	11:24	LF15	37.6487	75.7907		12.2	7.96	0.33	6.96			18.062	
10-Dec-19	9:20	LFA1	37.6488	75.7909	0.0	13.5	0.97	0.64	6.68	45.360	0.030	54.030	0.036
10-Dec-19	9:27	LFA2	37.6488	75.7912	24.7	13	0.73	0.47	6.89	30.540	0.010	40.320	0.112
10-Dec-19	9:33	LFA3	37.6489	75.7915	53.9	14.4	0.8	0.33	6.92	22.960	0.006	25.010	0.093
10-Dec-19	9:42	LFA4	37.6491	75.7921	110.8	12.3	0.68	0.34	7.04	19.065	0.010	22.695	0.201
10-Dec-19	9:50	LFA5	37.6493	75.7924	147.6	13.4	1.62	0.38	7.06	20.185	0.071	21.865	0.083
10-Dec-19	9:57	LFA6	37.6493	75.7930	199.7	13.6	0.71	0.4	7.11	19.325	0.045	19.915	0.060
10-Dec-19	10:04	LFA7	37.6494	75.7936	235.6	13.6	1.19	0.38	7.27	14.715	0.016	18.445	0.047
10-Dec-19	10:21	LFA8	37.6498	75.7944	347.0	14.2	2.28	0.36	7.06	10.950	0.011	13.100	0.045
10-Dec-19	10:40	LFA9	37.6502	75.7950	415.4	14	2.08	0.34	7.46	9.465	0.063	11.695	0.033
10-Dec-19	11:03	LFA10	37.6512	75.7975	664.5	14.5	4.61	0.36	7.25	12.665	0.026	15.485	0.013
10-Dec-19	11:22	LFA11	37.6526	75.7990	885.9	14.5	5.05	0.28	7.24	9.510	0.046	10.930	0.019
10-Dec-19	11:32	LFA12	37.6531	75.8005	1061.8	14.6	5.92	0.24	7.22	6.190	0.706	8.360	0.028
10-Dec-19	15:50	LFP	37.6478	75.7432		13.1	9.13	0.41	7.79	18.150	0.602	24.955	0.010

Table 1. Concluded.

Date	Time	Station	Lat	Long	Dist. meters	Temp deg C	DO mg/L	Salinity PSU	pH	NH mg/L MDL: 0.0062	NOx mg/L MDL: 0.0055	TN mg/L MDL: 0.0285	TP mg/L MDL: 0.0095
4-Jun-20	14:35	LFP	37.6478	75.7432		29.2	7.12	0.37	8.22	15.700	1.670	20.890	0.010
4-Jun-20	15:00	LFA1	37.6488	75.7909	0.0	21.1	0.77	0.59	6.88	55.520	0.001	62.960	0.088
4-Jun-20	15:10	LFA2	37.6488	75.7912	24.7	23.5	0.52	0.21	6.83	7.110	0.000	8.340	0.259
4-Jun-20	15:20	LFA3	37.6489	75.7915	53.9	21.4	0.56	0.6	6.96	32.410	0.005	40.200	0.260
4-Jun-20	15:30	LFA4	37.6491	75.7921	110.8	21.6	2.22	0.42	7.07	27.870	0.088	31.200	0.059
4-Jun-20	15:40	LFA5	37.6493	75.7924	147.6	21.8	0.78	0.45	7.19	26.910	0.067	27.360	0.049
4-Jun-20	15:45	LFA6	37.6493	75.7930	199.7	23.3	2.8	0.42	7.32	23.630	0.155	24.230	0.084
4-Jun-20	16:00	LFA9	37.6502	75.7950	415.4	21.2	1.11	0.4	7.13	20.050	0.260	20.310	0.046
4-Jun-20	16:10	LFA10	37.6512	75.7975	664.5	21.7	3.77	0.45	7.12	23.550	0.039	24.270	0.023
4-Jun-20	16:15	LFA11	37.6526	75.7990	885.9	21	2.8	0.38	6.92	18.520	0.122	17.850	0.029
4-Jun-20	16:30	LFA12	37.6531	75.8005	1061.8	21.6	4.46	0.28	7.15	10.860	1.132	10.580	0.028
10-Dec-20	10:05	LFP	37.6478	75.7432		7.6	12.6	0.31	7.68	4.665	0.890	5.980	0.030
10-Dec-20	10:15	LFA1	37.6488	75.7909	0.0	8	1.7	0.5	7.06	41.670	0.006	46.250	0.099
10-Dec-20	10:20	LFA2	37.6488	75.7912	24.7	7.7	2.07	0.41	6.82	27.790	0.010	34.460	0.082
10-Dec-20	10:25	LFA3	37.6489	75.7915	53.9	7.1	2.95	0.27	6.97	20.290	0.012	26.570	0.091
10-Dec-20	10:30	LFA4	37.6491	75.7921	110.8	6.4	3.48	0.29	6.97	14.600	0.024	20.930	0.113
10-Dec-20	10:32	LFA5	37.6493	75.7924	147.6	7.7	4.35	0.32	6.93	15.070	0.087	21.420	0.061
10-Dec-20	10:35	LFA6	37.6493	75.7930	199.7	8.7	6.24	0.31	7.11	15.070	0.083	18.720	0.055
10-Dec-20	10:40	LFA9	37.6502	75.7950	415.4	8.7	6.47	0.29	7.12	12.240	0.103	16.180	0.041
10-Dec-20	10:45	LFA10	37.6512	75.7975	664.5					9.950	0.106	12.320	0.055
10-Dec-20	11:12	LFA11	37.6526	75.7990	885.9	9.9	6.43	0.29	7.18	8.500	0.133	10.620	0.048
10-Dec-20	11:25	LFA12	37.6531	75.8005	1061.8					10.400	0.120	12.980	0.043

Table 2. Results from repeated samples at the Bobtown Road stream crossing. Shading indicates samples following rainfall events, >1” for 20 April 2019 and >2” for 18 September 2020. The 4 June 2020 and 9 July 2020 samples were during a prolonged drought period and reflect ground water (base) flow into the stream.

date	Temp	DO mg/L	Salinity	pH	turbidity	flow L/min	NH3 mg/L	NOx mg/L	O-PO4 mg/L	TN mg/L	TP mg/L	Loading NH3 Kg/hr	Loading NOx Kg/hr	Loading TN kg/hr	Loading TP Kg/Hr
25-Jul-18							8.680	0.618	0.022	9.560	0.100				
9-Nov-18							17.500			18.260	0.044				
11-Mar-19	9.8	8.14	0.36	7.85						17.546					
20-Apr-19	19.1	6.1	0.15	6.95	turbid					6.650	0.410				
10-Dec-19	14	2.08	0.34	7.46			9.465	0.063		11.695	0.033				
1-May-20	14.4	6.01	0.23	7.06	38.1		8.945	0.247		12.720	0.135				
4-Jun-20	21.2	1.11	0.4	7.13		16	20.050	0.260		20.310	0.046	28.06	0.36	28.43	0.06
9-Jul-20	22.8	4.36	0.38	7.31	2.32	47	18.030	0.765		19.030	0.048	72.87	3.09	76.92	0.20
18-Sep-20	19.9	6.83	0.11	6.69	30.7	486	0.540	1.070		3.290	0.370	22.66	44.91	138.08	15.53
0-Dec-20						66	9.950	0.106		12.320	0.055	56.74	0.60	70.25	0.31
Geomeans							8.408	0.299		11.685	0.089	40.27	2.35	67.86	0.50

Table 3. Extinction/dilution coefficients for total nitrogen the attenuation curves presented in Figure 1.

Sample Date	Extinction coefficient	R ²
11 Mar 19	-0.00538	0.588
10-Dec-19	-0.00349	0.835
4-Jun-20	-0.00471	0.939
10-Dec-20	-0.00417	0.848



Figure 1. Identification of a groundwater discharge area by low dissolved oxygen recording in 2019 (red arrow).

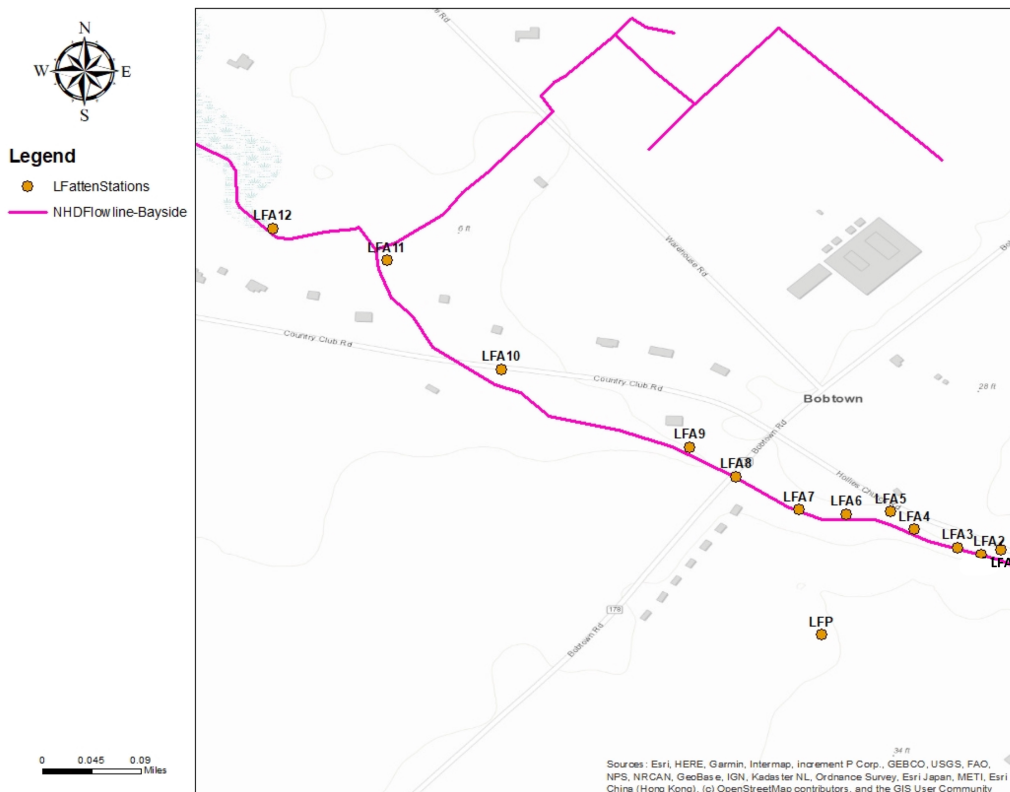


Figure 2. Surface water sample locations downstream of the Accomack Southern Landfill site to determine attenuation rates (LFA#) and the station between the ponds on the landfill site (LFP)

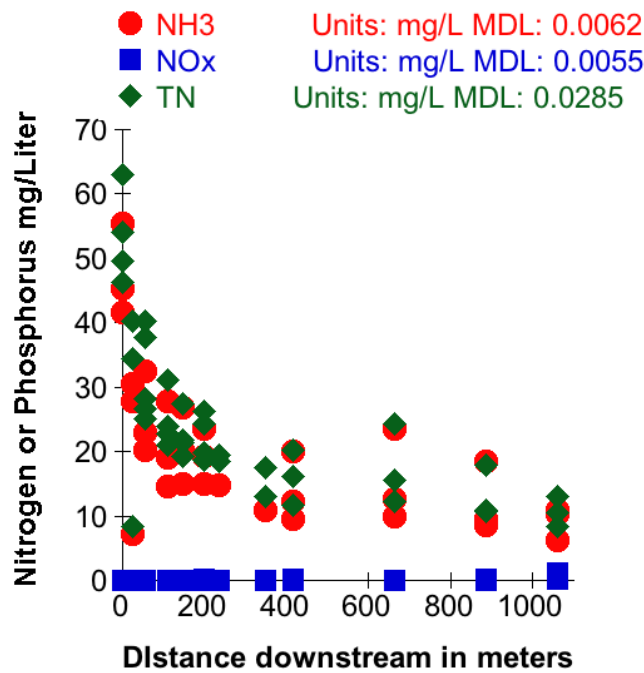


Figure 3. Nitrogen species in stream water as a function of distance from the Landfill discharge. Very little nitrite plus nitrate (NOx) is found in the system, resulting in a close tracking of ammonia NH₃ with total nitrogen (TN).

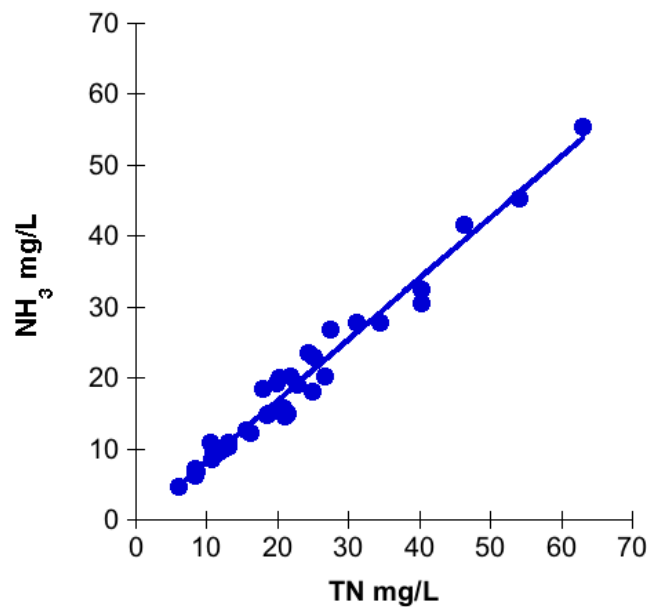


Figure 4. An analysis of Ammonia (NH₃) to total nitrogen (TN) for each sample reveals that an average of 86% of the total nitrogen in the system is present as ammonia ($R^2 = 0.967$).

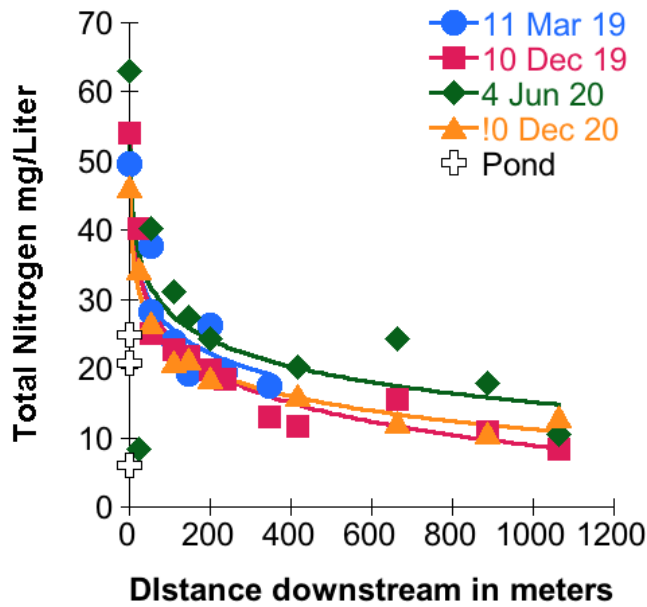


Figure 5. Attenuation of stream flow total nitrogen (TN) with distance from the landfill groundwater discharge for each sampling event. Zero meters was established at 37.6488° latitude and -75.7909° longitude at the low oxygen and high ammonia area of the stream.

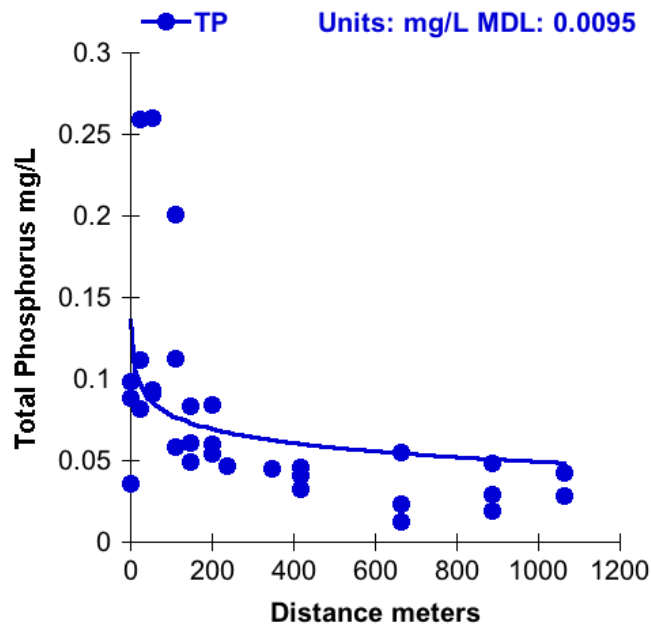


Figure 6. Total phosphorous (TP) in the stream with distance from the landfill discharge. The TP extinction coefficient for these data was -0.0014; $R^2 = 0.524$. The low R^2 value likely reflects the variance and high values recorded near the discharge site.

Appendix I. Analytical methods for nutrient analyses.

Determination of Ammonia by Skalar Auto Analyzer

ASC METHOD: 3000

Document Control Number: 00072

1.0 SCOPE AND APPLICATION:

1.1 This method is for the determination of Ammonia by Skalar Autoanalyzer. The applicable range is 0.005-2.0 mg/l.

2.0 SUMMARY OF METHOD:

2.1 Automated Continuous flow, segmented stream, no bubble gating.

2.2 Dual wavelength detection and matrix correction.

2.3 Alkaline phenol and hypochlorite react with ammonia to form indophenol blue that is proportional to the ammonia concentration. The blue color formed is intensified with sodium nitroprusside. Reaction is heat catalyzed at 37°C.

Determination of Total Dissolved Nitrogen and Total Dissolved Phosphorous by Skalar Auto Analyzer

ASC METHOD: 3005

Document Control Number: 00076

1.0 SCOPE AND APPLICATION:

1.1 This method describes the digestion procedure for total dissolved nitrogen (TDN) and total dissolved phosphorus (TDP) in fresh and estuarine surface waters by the alkaline persulfate oxidation technique. The dissolved fraction are aliquots of sample which have passed through a filter to remove particulates. The method is suitable for the determination of total nitrogen (TN) and total phosphorus (TP) with necessary precautions to ensure that particulates are fully digested. The applicable range for TDN and TN is 0.09-0.90 mg/L. The applicable range TDP and TP is 0.01-0.40 mg/L.

2.0 SUMMARY OF METHOD:

2.1 The persulfate oxidation technique for nitrogen in water is performed under heated alkaline conditions, where all organic and inorganic forms of nitrogen are oxidized to nitrate. As the reaction proceeds, NaOH is consumed and the pH drops to < 2.2, which allows the oxidation of all phosphorus compounds to orthophosphate.

2.2 An aliquot of digested sample is analyzed for nitrate and orthophosphate using automated colorimetric methods (Method 3001 and Method 3003, respectively) to produce total nitrogen and total phosphorus concentrations.