Nitrogen Loading and Attenuation in the West Falmouth Harbor Watershed

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Abstract

West Falmouth Harbor has started to show signs of eutrophication in which have been attributed to the increase in nitrogen loading due to the opening of the wastewater treatment plant and increased septic inputs. There is currently a plume of high nitrogen concentration moving through the groundwater from the plant to the harbor's edge. We measured NO_3, NH_4, TDN of samples around the harbor as well as town monitoring wells, septic inputs and treatment plant inputs to look at the total load to the harbor. We also measured all samples for boron and fluorescent whitening agent concentrations to determine the possibility of using multiple tracers to distinguish between near shore and far sources of nitrogen. Using N:B and N:FWA ratios we attempted to determine where the plume enters the harbor. We found the travel time of the plume to be approximately 7 years from the plant to the shore. We also found that boron is a conservative tracer, whereas FWAs are non-conservative, and a combination of these two tracers may be useful in distinguishing between near and far sources. We were able to determine a new potential path for the plume which has the plume entering up along the river feeding into the harbor rather than at snug harbor.

Key Words

Attenuation, nitrogen loading, nitrogen plume, conservative/non-conservative tracer

Introduction

Nitrogen loading has become a widespread problem for estuaries all over the United States, causing symptoms of eutrophication in many estuaries. (National Research Council, 2000) As more nitrogen is introduced into the system from outside sources the system experiences a fertilization effect and becomes more productive, often resulting in eutrophication or over production. Characteristic signs of eutrophication include loss of eelgrass or other submerged aquatic plants and increases in algae production leading to harmful algal blooms. (National Research Council, 2000) Hypoxic and anoxic waters due to excess productivity can result in fish kills and an alteration of migration patterns of fish and harmful algal blooms have been connected to deaths of marine mammals.

West Falmouth Harbor, a local estuary on the western coast of Cape Cod, has started to show signs of eutrophication including a large decrease in eelgrass cover (Costa, 1997). This is as a result of the opening of the treatment plant and increases in septic inputs which are the two major inputs of nitrogen to the system. There also used to be septage lagoons at the town landfill that was also a source of nitrogen, but has now been capped.

The inputs of nitrogen from the West Falmouth Wastewater Treatment Plant (WWTP) and septic tanks arrive in the form of plumes of higher nitrogen concentration in the groundwater moving from the treatment plant or septic tank to the harbor's edge. The treatment plant provides secondary treatment to the incoming wastewater but is not designed to provide tertiary treatment and remove nitrogen in the process. The plant is however about to switch over to an upgraded system that will denitrify the wastewater before exporting it to decrease the amount of nitrogen in the effluent. After treatment this water is divided up and 75% of it is sprayed onto plots in the adjacent forest in hopes that the nitrogen will be sequestered by the forest and stimulate its growth. The other 25% of the water is sent to sewage infiltration beds where the water is leeched into the ground. (Jordan, 1997) The treatment plant plume is deeper and more spread out than the septic plumes, due to the area that the wastewater is sprayed over and its distance from the harbor. It has not yet been identified exactly where the plume is entering the harbor, although he current hypothesis is that the plume is entering the harbor at Snug Harbor on the northeast corner of West Falmouth Harbor.

The treatment plant began operating in December of 1986 and began spraying effluent on the forest in 1988. (Jordan, 1997) The plume has an assumed travel time from the plant to the shore of between 7 and 10 years, and is assumed to have reached the harbor around 1997. The nitrogen export of the plant steadily increased from its opening until 1997 when the plant was upgraded, so the nitrogen loading to the harbor due to the treatment plant should continue increasing until 2007. (Costa, 1997) This predicted increased loading will aggravate current conditions in the harbor.

This paper looks at these nitrogen plumes in more depth. One of our aims was to determine whether a combination of conservative and non-conservative tracers could be used to locate where the plume was entering the harbor and distinguish between the treatment plant plume and the near shore septic plumes. Determining where the plume enters the harbor would be useful for mitigation efforts, allowing efforts to be concentrated to a specific area. For this paper we chose to use boron and fluorescent whitening agents (FWAs) as tracers since both are found in laundry detergent. We hypothesized that boron was a conservative tracer and FWAs were non-conservative tracers that sorbed slightly to soil. Also we tried to learn more about what the nitrogen was doing as it traveled through the groundwater, including how long the travel time is, and how much of the nitrogen was lost in transit.

Methods

In order to address the above questions we sampled the groundwater around the harbor using multi-depth wells and well point sampling. We installed 2 new multi-depth wells along the edge of the harbor and sampled from one existing multi-depth well. These were located in three different places along the harbor's edge, one on Snug Harbor, one on the river feeding into the harbor and the third by the local dock. Locations for well point samples, multi-depth wells and town monitoring wells are provided in Figure 1. At the multi-depth wells we took water samples from three depths from two wells and one sample from the third well which only yielded water at one depth. We also took 8 samples using well point sampling along the edge of the harbor.

In order to look at what is happening in the plume between plant and the harbor's edge we sampled sources and monitoring wells located along the projected path of the plume. We sampled influent and current effluent from the wastewater treatment plant as well as the future effluent after the plant's upgrade to look at outputs from the plant. We also sampled from different places in a septic tank and field at the Massachusetts Alternative Septic System Testing Center (MASSTC) to determine the initial outputs from septic systems. We also sampled from seven town monitoring wells at various sites up gradient of the harbor along the projected path of the plume from the treatment plant to the harbor. Well 1 was installed up-gradient of the spray irrigation plots, wells 15 and

16 are within the spray irrigation plots and all other wells are at various locations between the treatment plant and the harbor.

Total dissolved nitrogen (TDN), nitrate (NO_3), and ammonium (NH_4) were analyzed in all collected water samples. Each nutrient sample was filtered using a GFF filter (0.7um) in the field to remove any phytoplankton or other particulates in the water and then stored on ice until returning to lab where they will be divided and prepared for analysis of TDN, NO3, and NH4 by freezing the TDN and NO3 samples and acidifying the NH4 samples. TDN samples were analyzed using a modification of D'elia et al. and run using a Lachet QuikChem 8000 flow injector analyzer. In the TDN run we ran multiple sample types as spikes to test their retention rates. Of the spiked samples the MASSTC and treatment plant samples showed incomplete recovery. From this we were able to determine percent retention and used this to adjust the concentrations. NO_3 analyses were run using a Cd-Cu reduction on a Lachet QuikChem 8000 flow injector analyzer. (Wood et al, 1967) The NH_4 analysis was run as per Solarzano (1969). The concentrations obtained from samples from multi depth wells were also used to attempt to distinguish between septic plumes and the wastewater plume.

The NO3 and NH4 analyses for groundwater samples from the harbor's edge were used with a water budget model of the watershed modified by Chuck Hopkinson and a running two year average of annual recharge to determine the total nitrogen loading to the system. Average concentrations measured by past students at the harbor's edge were also used with a running two year average to determine past loading which was then compared to the amount of nitrogen leaving the treatment plant yearly to determine the travel time. (Townsend-Small, Arling, Angeloni et al., Yum et al., Thoms, Alexander et al., Nolan et al., Akullian et al.)

The fluorescent whitening agent analysis was run according to the methods in Poiger et al. (1996) with a few alterations. The samples used for fluorescent whitener analysis were collected in dark BOD bottles to keep light from degrading the samples, and put on ice until they could be refrigerated. The samples from the Massachusetts Testing Center were filtered with a GFF (0.7 um) filter in the lab. Two hundred ml of all groundwater and well samples were then run through a hydrophobic Oasis filter while only 100 ml of all septic samples and effluent samples and 10 ml of unfiltered influent were used. These filters were then extracted with 0.05M TBA in MeOH. The liquid was then blown off using N2 gas and a warm sand bath leaving a small amount of residue. 1 ml of DMF/H2O (1:1) was added at the end to re-liquefy the sample and were then passed through a 0.45 um filter in order to run it in the high pressure liquid chromatography machine (HPLC). We also used a post-column UV reactor with the HPLC in order to convert all isomers to the E,E isomer before reaching the detector. FWA samples were used with analyses of TDN, NO3 and NH4 to look at N:FWA. FWA samples taken in the leach field were also used to determine the conservative nature of FWAs.

All samples were analyzed for boron concentrations as well. All boron samples were filtered in the field using a GFF (0.7um) filter and then stored in the refrigerator until processing. The B analysis was run as a colorimetric analysis according to methods outlined in Grindstead and Snider (1967), with all reactions occurring in 60 ml plastic nalgene bottles. The analyses of nitrogen and boron were also used to determine a N:B ratio in order to examine whether reductions in nitrogen concentrations were due to dilutions or attenuation of the nitrogen as it moves from the treatment plant to the harbor. These ratios were used in conjunction with N:FWA ratios to attempt to determine where the treatment plant plume might enter the harbor. Boron concentrations of samples taken from the leach field were used to look at the conservative nature of boron.

Results

Locations for well point sampling sites and wells 6, 11B and 18A are shown on Figure 1. Sites for the multi depth well and the other town wells were not included as I did not get GPS coordinates for them.

TDN and DIN (NO3 and NH4) were measured for each site. Well point samples at the harbors edge were averaged with multi depth well samples to give an average value for samples at the harbor's edge. All Mass TC samples were averaged to give a value for septic systems. Town well values were averaged to give a value for samples between the treatment plant and the harbors edge. (Figure 2) The largest amount of TDN and DIN was found in the septic system samples(1805 uM DIN), followed by the treatment plant's effluent (436 uM DIN), the monitoring wells (297 uM DIN) and, then the harbor's edge samples (90 uM DIN). TDN and DIN were also measured individually for the town monitoring wells. (Figure 3) The highest concentration was measured in well #15 (527 uM DIN) and the lowest concentration in Well #1 (3.9 uM DIN). In all cases TDN was nearly equal to DIN.

Nitrogen loading to the watershed due to the treatment plant has been tracked by the plant, and the amount of nitrogen leaving the plant over time was graphed showing an increase in loading over time with some variation (Figure 4) (Town of Falmouth Wastewater Treatment Facility). Figure 6 shows the calculated loading of nitrogen to the harbor along with the nitrogen leaving the plant using first a 10 year travel time and then a 7 year travel time. The nitrogen loading to the harbor excludes a base input of 3237 Kg N/yr estimate for loading to the harbor due to septic systems. Current loading of 12985 Kg N/yr with the septic input included was calculated using a recharge value of 9.79×10^6 and an average nitrogen concentration of 94.7 uM which included concentrations measured in SES lab 7/8 2005 as well as the measured concentrations from our samples. Appendix 1 shows all measured nitrogen concentrations.

Figure 7 shows the basic structure of fluorescent whitening agents although it is only the E,E isomer that fluoresces. (Poiger 1996) When using the HPLC the two types of FWAs came off of the column at 19.5 minutes (CBS) and 20.5 minutes (AMS) (Figure 8)

Both FWA and boron concentrations were plotted against depth in a Mass TC leach field, using the D-box sample as 0m in order to look at each tracer's conservative nature. The boron concentrations stay relatively stable as the wastewater moves down through the soil while FWA concentrations show a very apparent decrease as the water leaches through the soil. (Figure 9)

Boron and FWA concentrations were also measured and averaged according to type of sample. (Figure 10) The highest concentrations for both tracers were again in the septic tanks followed by the treatment plant effluent. The samples at the edge of the harbor showed higher concentrations than those in the town monitoring wells in both cases with the FWA concentrations showing a difference of 12.6 ppt between shore points and town wells, and boron concentrations showing a difference of 1.1 uM.

The concentration of FWAs was plotted against the concentration of boron in all samples. The MASSTC and WWTP samples clustered out showing high concentrations of both tracers (Figure 11). The shore points and town wells show a large amount of variation in both FWA and boron concentrations.

DIN concentrations were plotted against both tracers and color coded by sample type (Figure 12). In both cases the sources clustered out with high nitrogen and tracer concentrations. The town monitoring wells showed higher nitrogen concentrations than the samples taken along the shore. However in both cases the monitoring wells showed similar ranges of tracer concentration as the shore points.

DIN:FWA ratios were also calculated for all harbor's edge samples. Results were scattered, with Grace 6.5m showing the largest ratio of 5.4. Sample 2 and Sample 6 also showed larger ratios of 2.8 and 3.0 respectively. (Figure 13)

DIN:B ratios were calculated for every sample taken at the harbors edge. Results were relatively scattered with a range of 894-1.0, with especially high N:B ratios at Hill 6.2m, Dock 2m, and Sample 8 (894, 660, 371 respectively). (Figure 14)

Discussion

We observe a decrease in nitrogen when moving from the treatment plant to the harbor. (Figure 2) This is due to the attenuation of nitrogen as it moves through the ground and denitrifies or is adsorbed by the soil. The small difference in TDN and DIN is attributed to a very small amount of organic nitrogen, but since the difference is so small DIN is used for all subsequent nitrogen concentrations.

The town monitoring wells do not show a clear trend in nitrogen concentrations (Figure 3). Well 1 is up gradient of the spray irrigation plots and should show very little nitrogen which it does. Wells 15 and 16 are in the spray irrigation plots and should show the most nitrogen. Wells 2 and 6 are slightly down gradient of wells 15 and 16 but are still on the treatment plant's grounds. These wells should show a decrease in nitrogen from the previous wells. Wells 18A and 11B are further towards the harbor and should show even less nitrogen. The actual data shows well 15 with the most nitrogen, but well 16 which should be comparable shows substantially less nitrogen. Similarly well 6 shows a mid range concentration of nitrogen which is less than well 15, and well 2 should show similar results, but instead shows very low concentrations. This is a recurring trend and Costa explains it by suggesting that wells 2 and 16 are being diluted by rain or groundwater. (Costas, 1997) Well 18A shows much higher nitrogen concentrations than expected, suggesting a potential outside source on nitrogen for that well.

The nitrogen loading to the watershed has generally increased over time with variations in the years (Figure 4). The graph of nitrogen entering the harbor fits best with the measured load to the watershed when using a 7 year travel time rather than a previously predicted 10 year travel time. This also shows less attenuation than previously predicted.

The leach field at the Mass TC provides a good initial look at the conservative nature of FWAs. We were able to sample from 1, 3 and 5m depths in the leach field. We were also able to use the D-box samples as a 0m point since the D-box distributes the water to the leach field, but has not yet passed through soil. This allows us to get an idea of what happens when FWAs and boron pass though soil. In a graph of boron vs. depth, there is little variation of boron concentrations with depth, which is consistent with the assumption that boron is a conservative tracer. (Figure 9) The graph of FWA concentration vs. depth however, shows a distinct decrease in concentration with increasing depth, indicating that FWAs are not conservative but instead interact with the soil they move through and attach to cellulose as we originally hypothesized.

Both boron and FWA concentrations showed a decrease in concentration from the both the septic and treatment plant sources to the harbor. (Figure 10) This is indicative of a dilution of the effluent by groundwater. At the shore however there was an increase in boron concentrations. This is likely due to boron inputs from septic plumes at the harbor's edge. In the FWAs, this increase is less apparent than the increase in boron, which is likely indicative of the semi-conservative nature of FWAs. There may be more FWAs at the shore because of the septic systems of the houses on the harbor, but there may not be as strong of an increase because the FWAs react a little with the soil as the septage moves from the septic tank to the shore.

A graph of FWA concentration vs boron concentration shows a clustering of the sources with high concentrations of both tracers. The points at the shore show a variation of tracer concentrations which can be used to distinguish near shore sources from far sources. One shore point (Hill 3.25m) shows comparatively high FWAs and average boron concentrations. This suggests that this point might be a septic plume since the FWAs would have less distance to travel, resulting in less attenuation. Two shore points are outliers showing higher boron concentrations than any septage or sewage. This may be indicative of an outside input of boron, or a problem with the analysis. Boron concentrations may increase if the samples are contaminated with salt water, but this increase is very slight for any immeasurable salt contamination and can likely be discounted as a reason these two points are so high in boron.

Graphs of DIN vs. each tracer show clustering of sources with high nitrogen and tracer concentrations. The higher nitrogen in the monitoring wells shows attenuation of nitrogen as it moves through the groundwater to the harbor. The range of tracer concentrations in the monitoring wells and the shore points shows a range in dilution of all points, indicating that dilution needs to be corrected for when looking at nitrogen and FWA concentrations.

The graphs of N:B and N:FWA are designed to get a feel for where the treatment plant is entering the harbor. If FWAs are a semi-conservative tracer, then the concentration of FWAs will diminish with distance from the source. They will diminish less quickly than the nitrogen will however, allowing for their use as a tracer. The treatment plant plume therefore should show higher N:FWA ratios than septic plumes as more of the FWAs will have been lost in the treatment plant plume. In Figure 13 the samples at Grace 6.5m show a very high N:FWA ratio, which may indicate that this is a good place to start looking for the plume. However, this needs to be looked at in conjunction with the samples N:B ratio as this is indicative of the dilution factor of the sample. This can show whether the sample has low nitrogen of FWA concentrations due to attenuation or dilution. The N:B ratios at the shore have a large range, but most notably the Grace 6.5m sample shows a lower (though not the lowest) N:B, indicating lower levels of dilution. This implies that the low FWA concentrations are due to attenuation rather than dilution suggesting that the Grace site is one that should be looked at more closely in terms of finding the plume.

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West Falmouth Harbor Sampling Locations

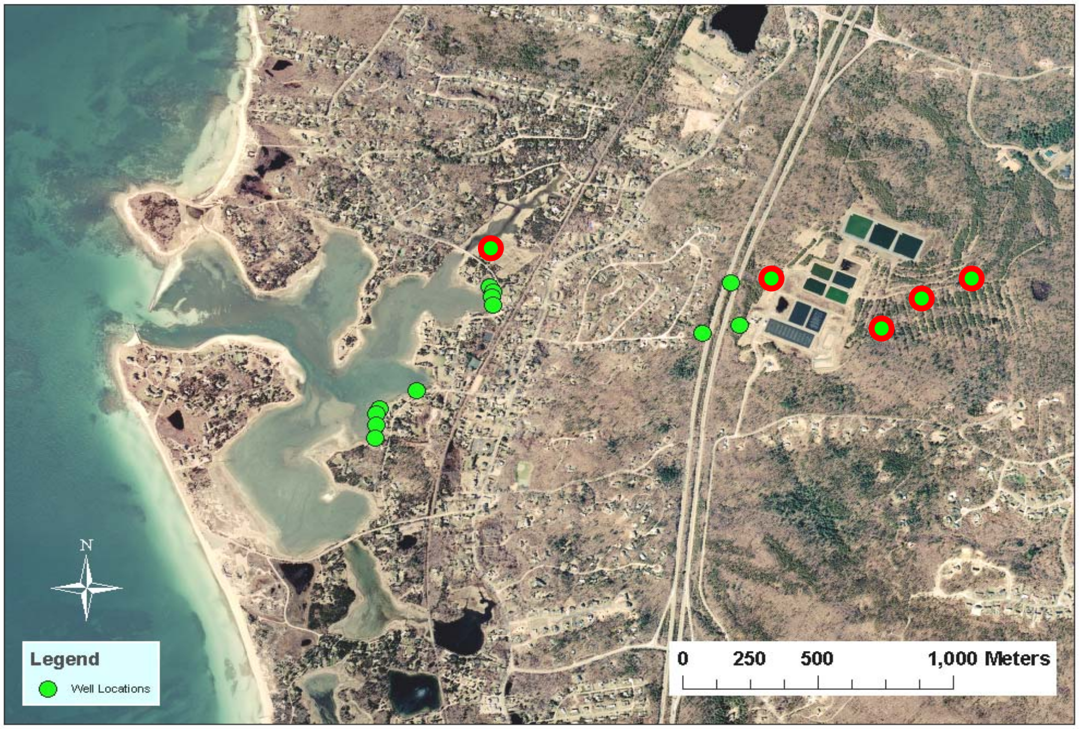


Figure 1: Well point and monitoring well sampling locations at West Falmouth Harbor. Red outline denotes estimated locations. All other wells located by GPS coordinates.

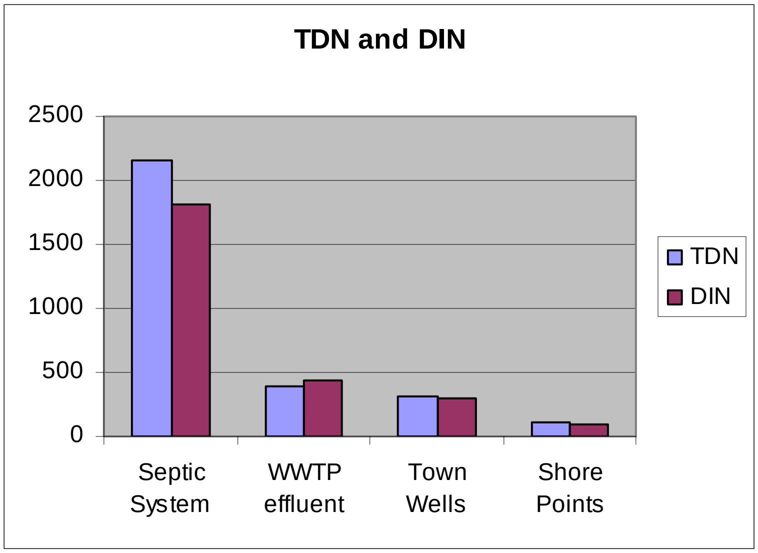


Figure 2: TDN and DIN concentrations averaged by sample type

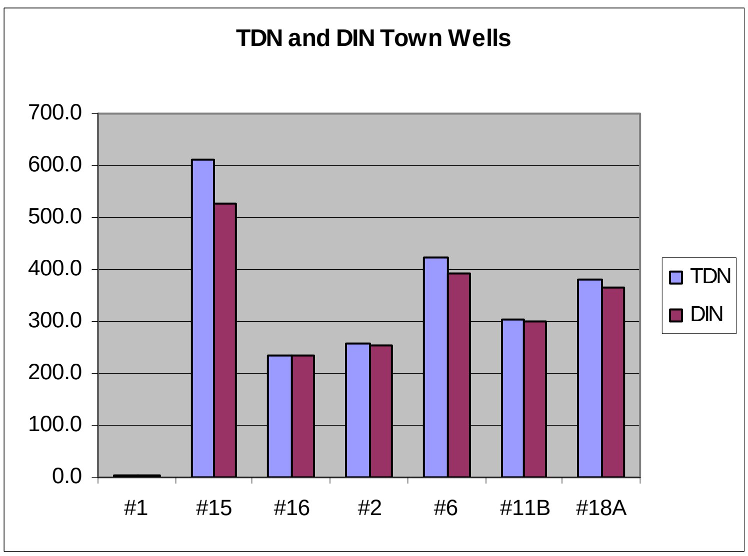


Figure 3: TDN and DIN concentrations of town monitoring wells arranged by distance from plant

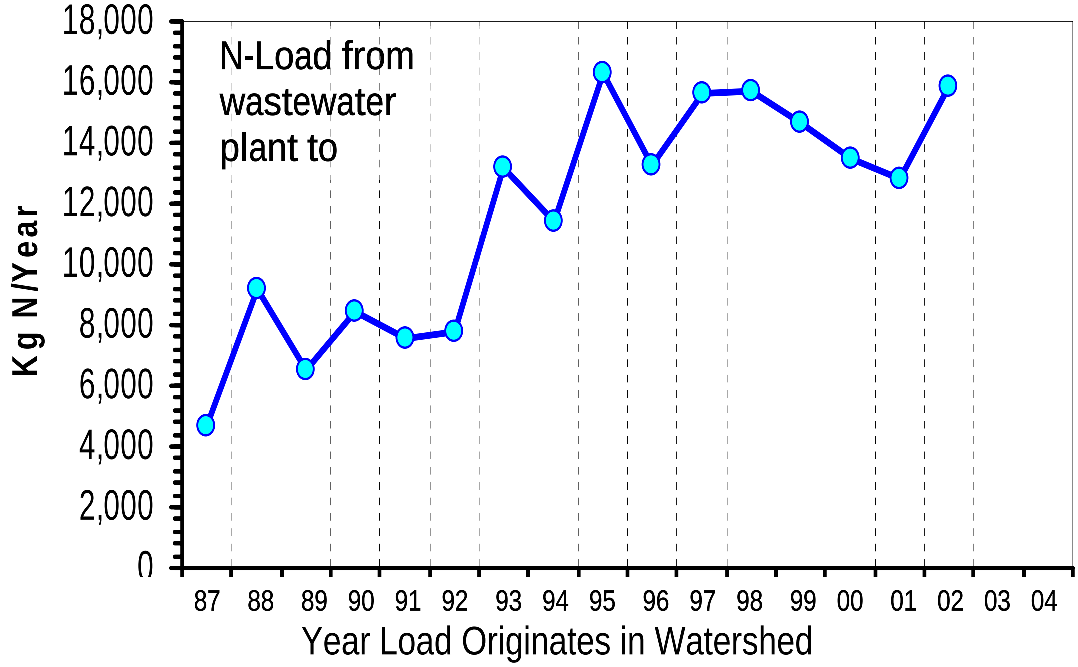
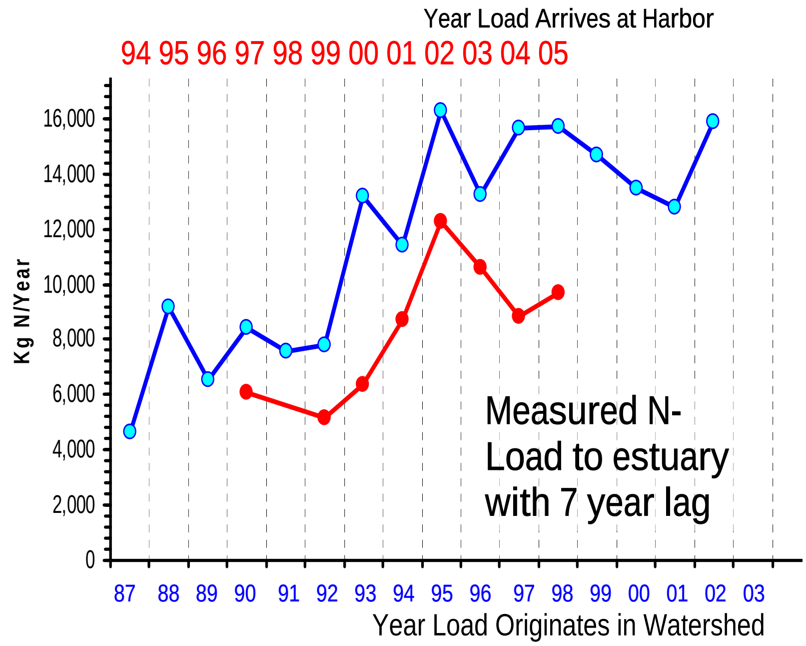


Figure 4: Yearly load to watershed by Treatment Plant

$$94.7\frac{umolN}{L}\times\frac{9.79\times10^{6}m^{3}}{yr}\times\frac{1mol}{1000000uM}*\frac{1000L}{m^{3}}\times\frac{14.01g}{1mol}\times\frac{1Kg}{1000g}=\frac{12984KgN}{yr}$$

Figure 5: sample calculation of yearly load to harbor using 94.7 uM N and 9.79 m^3/yr recharge



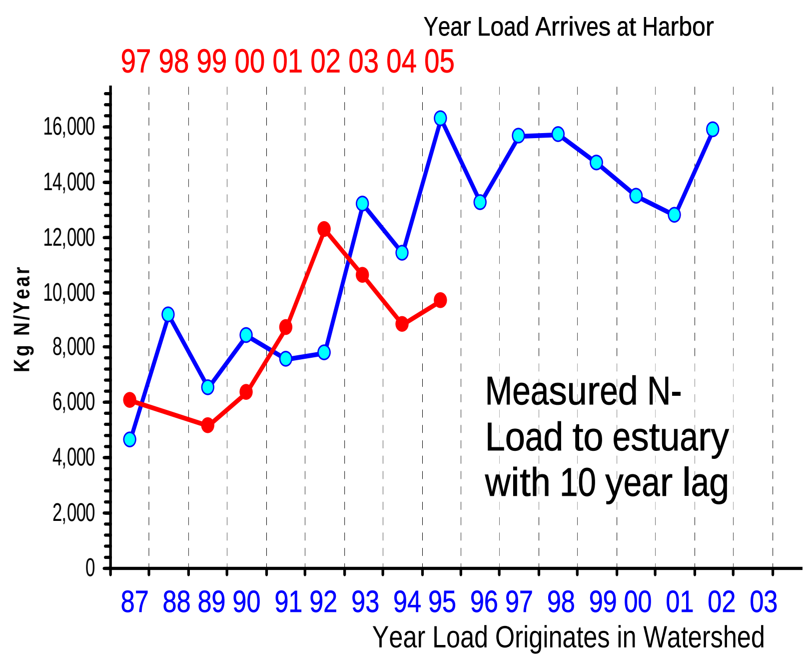
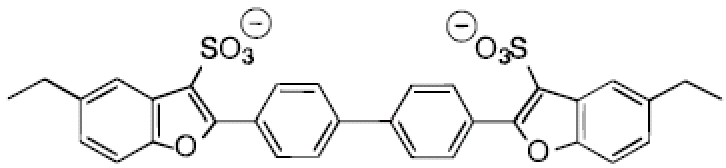


Figure 6. Load to watershed graphed with load to harbor using 7 year and 10 year lag times.



FWA 5 (Internal Standard)

Figure 7: structure of a FWA

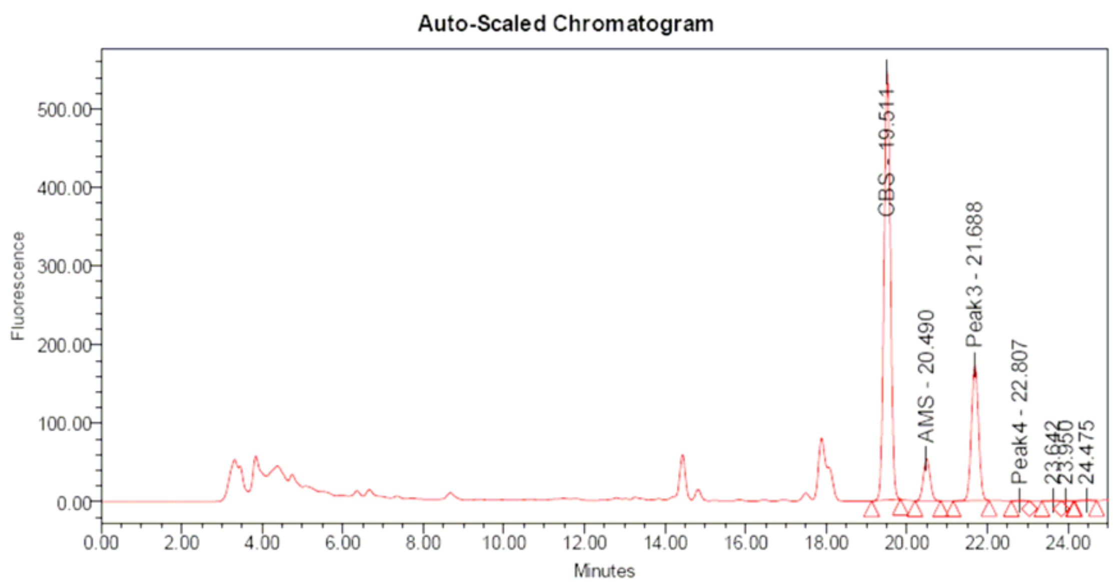


Figure 8: Sample FWA Chromatogram of Trench sample.

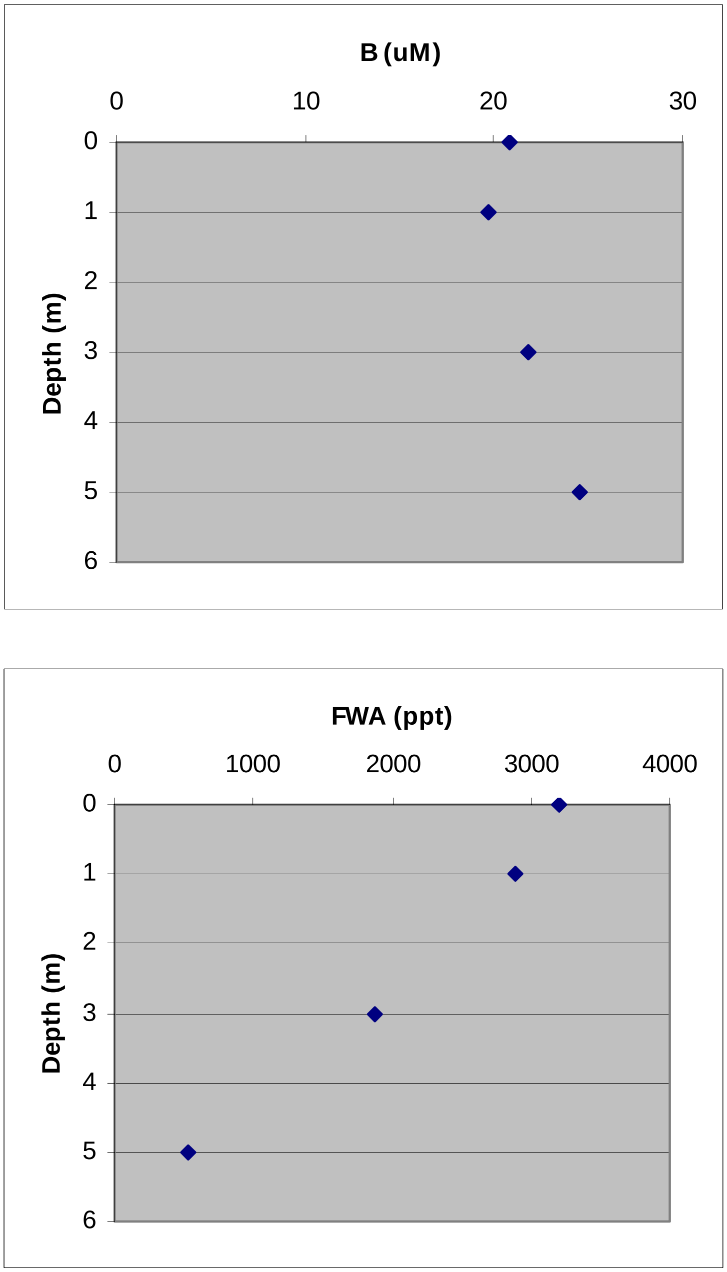
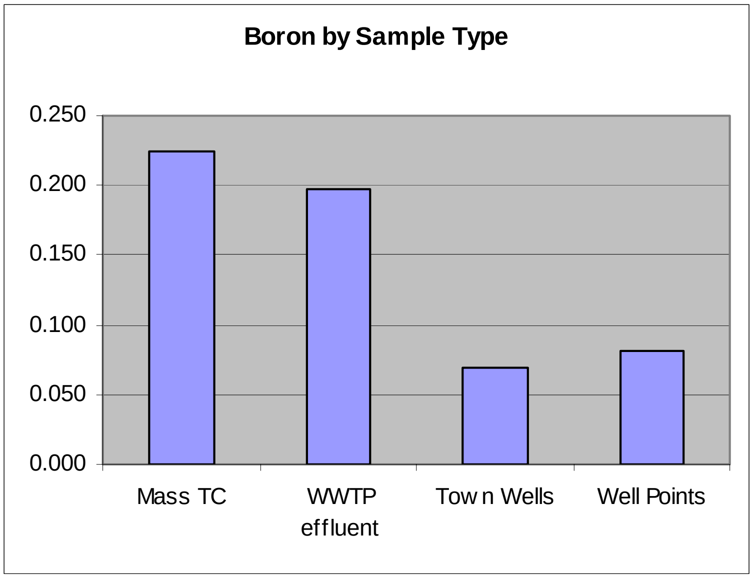


Figure 9. B and FWA concentrations by depth in leach field at MASSTC



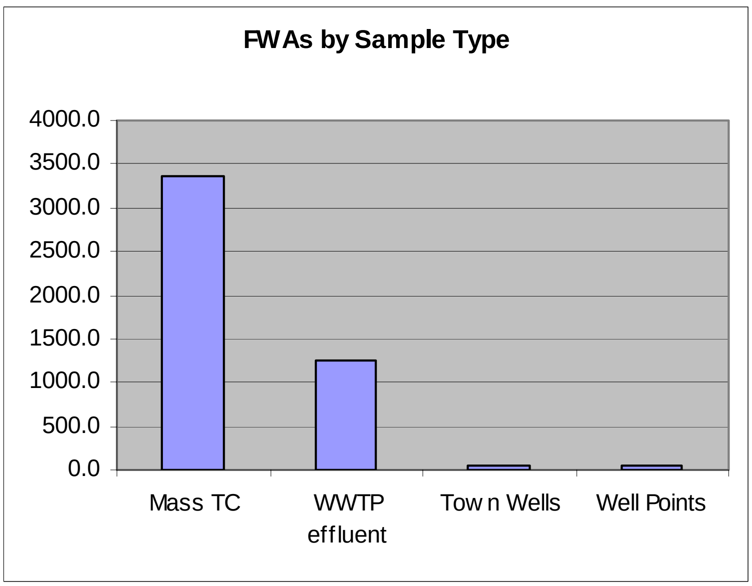


Figure 10: Boron and FWA concentrations averaged by sample type

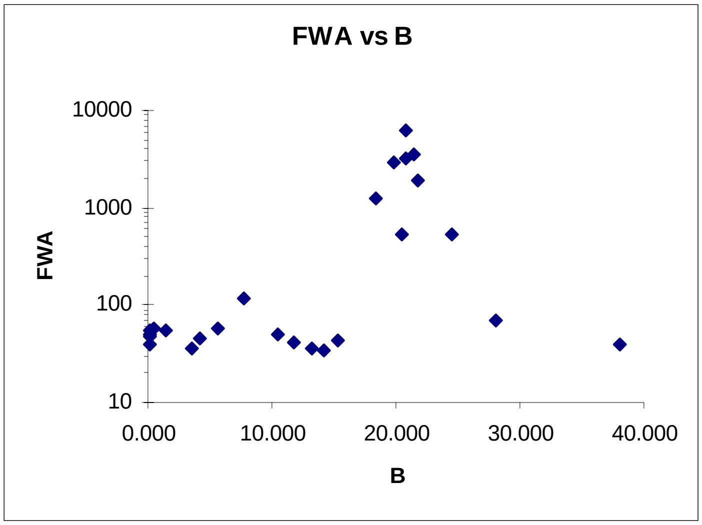
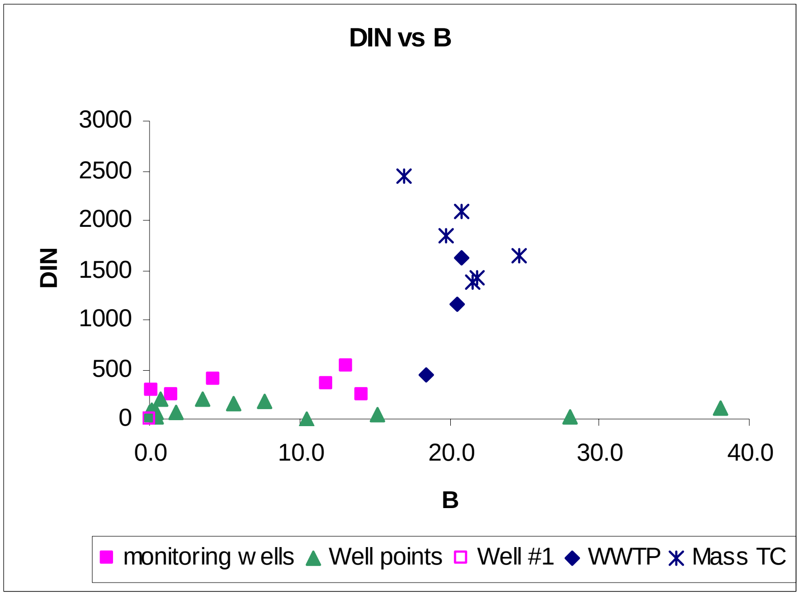


Figure 11: FWA concentration vs. boron concentrations. Log scale.



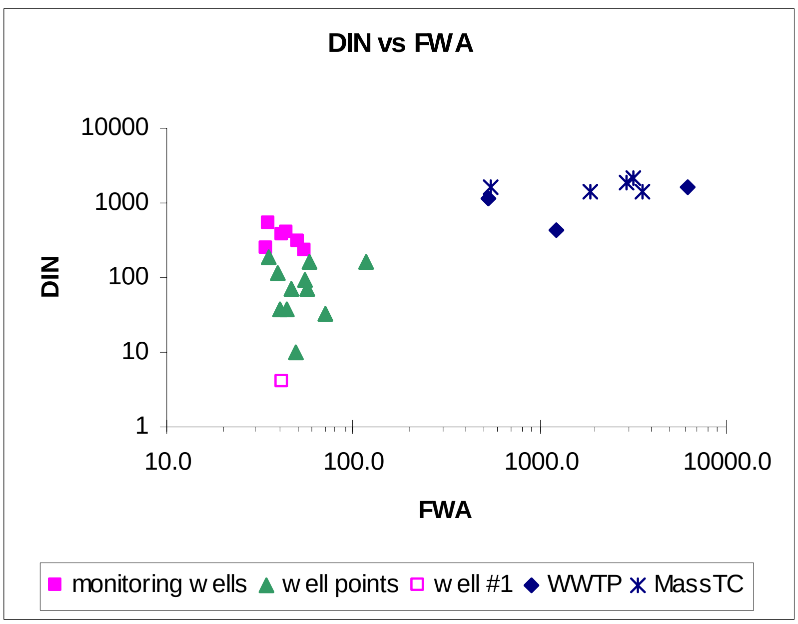


Figure 12: DIN vs tracer concentrations. DIN vs. FWA plotted on a log log scale

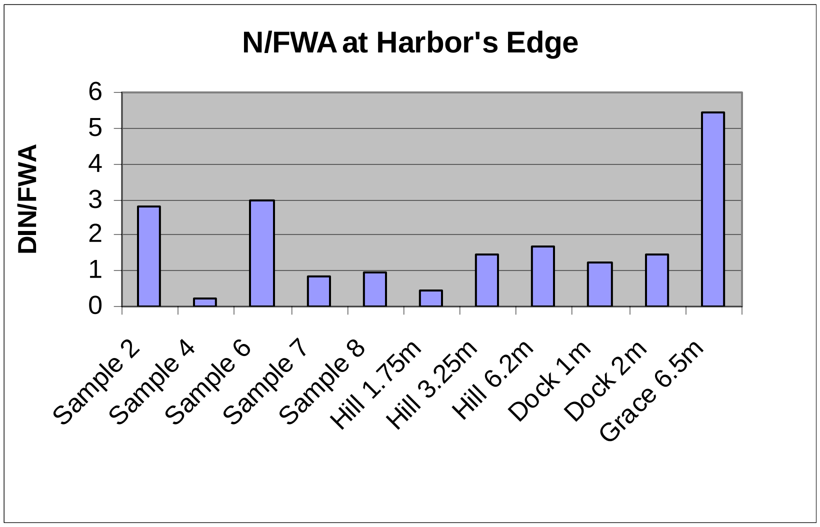


Figure 13: N/FWA for all analyzed samples taken at harbor’s edge

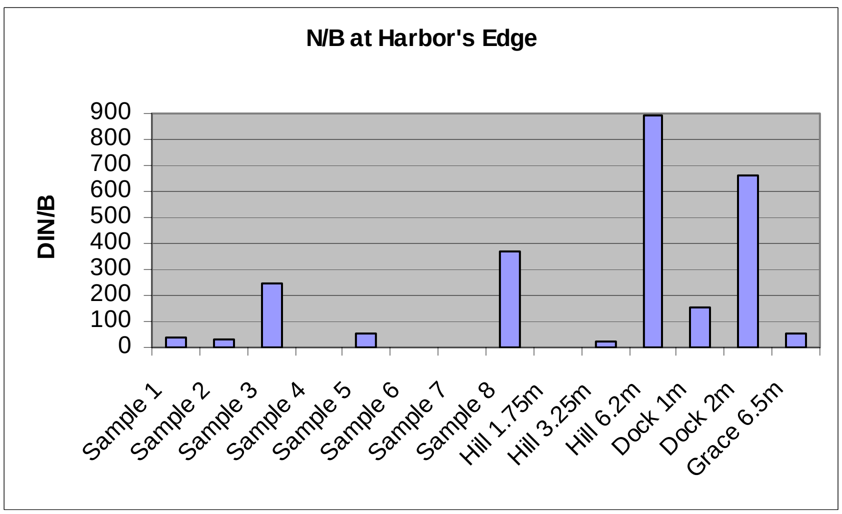


Figure 14: N/B for all samples taken at harbor’s edge

Appendix 1: concentrations of NO_3, NH_4, TDN, B and FWA for all samples taken

Sample name	**NO_3 (uM)**	**NH_4 (uM)**	**TDN (uM)**	**B (uM)**	**FWA (ppt)**
influent	3	1615	1478	20	6132
Old effluent	189	247	194	18	1240
New effluent	73	1076	72	21	530
Trench	3	1380	1573	21	3534
Settling tank	3	2445	2405	17	-
D-Box	2	2093	2809	21	3199
Leach 1m	48	1803	1442	20	2884
Leach 3m	774	637	2295	22	1882
Leach 5m	1637	3.9	2440	25	539
Well point 1	70	2.6	85	1.8	-
Well point 2	165	0	168	5.6	59
Well point 3	194	0.9	189	0.8	-
Well point 4	1	9.5	27	10	49
Well point 5	25	0.2	37	0.4	-
Well point 6	118	0	113	38	40
Well point 7	37	0	56	15	44
Well point 8	38	0	52	0.1	40
Town Well 1	4	0	4	0	42
Town Well 2	254	0	257	14	34
Town Well 6	393	0	422	4.2	45
Town Well 11B	300	0	304	0.1	50
Town Well 15	527	0	612	13	35
Town Well 16	234	0	235	1.5	55
Town Well 18A	360	4.4	382	12	42
Hill 1.75m	16	17.4	47	28	70
Hill 3.25m	168	0	198	7.7	116
Hill 6.2m	91	1.6	124	0.1	55
Dock 1m	70	0	81	0.4	57
Dock 2m	68	0	79	0.1	47
Dock 5m	62	0	60	0.0	-
Grace 6.5m	192	0	233	3.5	35