Section 5 – Surface Water Chemistry in Subwatersheds *(Scope of Services 1.c)*

During the 2005-06 study period, all surface water quality samples were analyzed for numerous parameters as outlined in Table 16. Parameters analyzed included temperature (^{o}C), pH, conductivity (µs/cm), dissolved oxygen (mg/L), turbidity (NTU), color (PCU), total suspended solids (mg/L), chlorophyll-a (µg/L), total P (µg/L), total N (mg/L), nitrate (mg/L), chloride (mg/L) and sulfate (mg/L). Appendix C contains a summary of the water quality analysis results during the study period. Flow measurements were also collected at each site when possible and those results are presented later in this report in Section 9. Fecal coliform bacteria and *E. coli* were also analyzed at 10 sites for each sampling period.

It should be noted that due to the low summer rainfall conditions, the Skug River and its tributaries in the upper reaches of the watershed exhibited very low or no flow conditions during some sample periods in later summer and early fall 2005, so neither complete surface water nor flow samples could be taken on some sample dates.

5.1 – Components of Turbidity in Martins Pond *(Scope of Services 1.h)*

Turbidity is a physical property of water and is defined as a reduction in clarity caused by suspended particles in the water column. Turbidity is measured in nephelometric turbidity units or NTUs. Turbidity typically consists of both inorganic and organic particles. Inorganic particles are often the products of soil erosion and resuspension of inorganic bottom sediments. Organic particles include decaying plant matter and algae. In order to assess the parameters influencing turbidity levels in Martins Pond, the organic and inorganic proportion of the total suspended solids (TSS), chlorophyll-a levels and overall turbidity (NTU) data were summarized from 2004 to 2006. Figure 16 shows the mean levels of organic and inorganic TSS for each sample period. Organic solids are clearly the dominant component of TSS in the pond. Over the 2005-06 study period, the mean organic percentage of the total TSS was 78.9% (SE = 2.45). The likely sources of this organic component are resuspended bottom sediments, suspended sediment loading from the Skug River inlet and runoff. The relatively high organic content of the sediments (Figure 13) are thus a logical source of resuspended organic particles in the water column in Martins Pond.

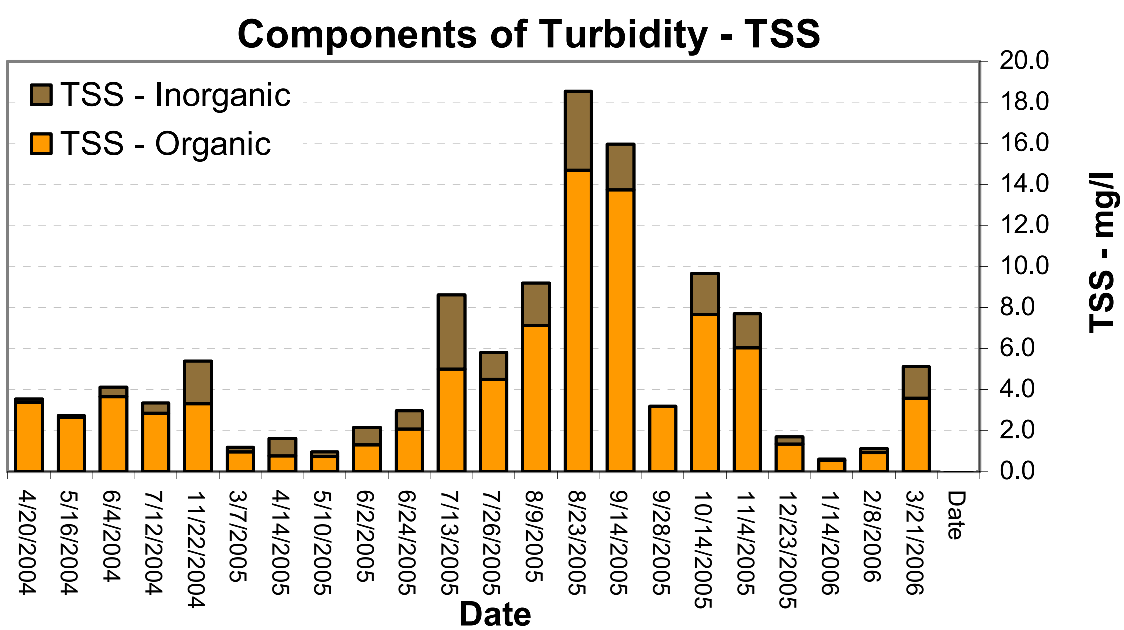

Figure 16. The mean levels of inorganic TSS (brown bars) and organic TSS (orange bars) in Martins Pond from 2004 to 2006. Organic suspended sediment is clearly the largest component of potential turbidity in the pond. Inorganic fractions were highest in the summer.

Figure 17 shows the mean levels of chlorophyll-a in Martins Pond on the same time scale as Figure 16. The scale of the Y-axis has been changed to reflect the lower overall concentrations of chlorophyll-a relative to TSS. While the absolute TSS levels vastly exceed absolute chlorophyll-a levels both parameters exhibited the same seasonal patterns.

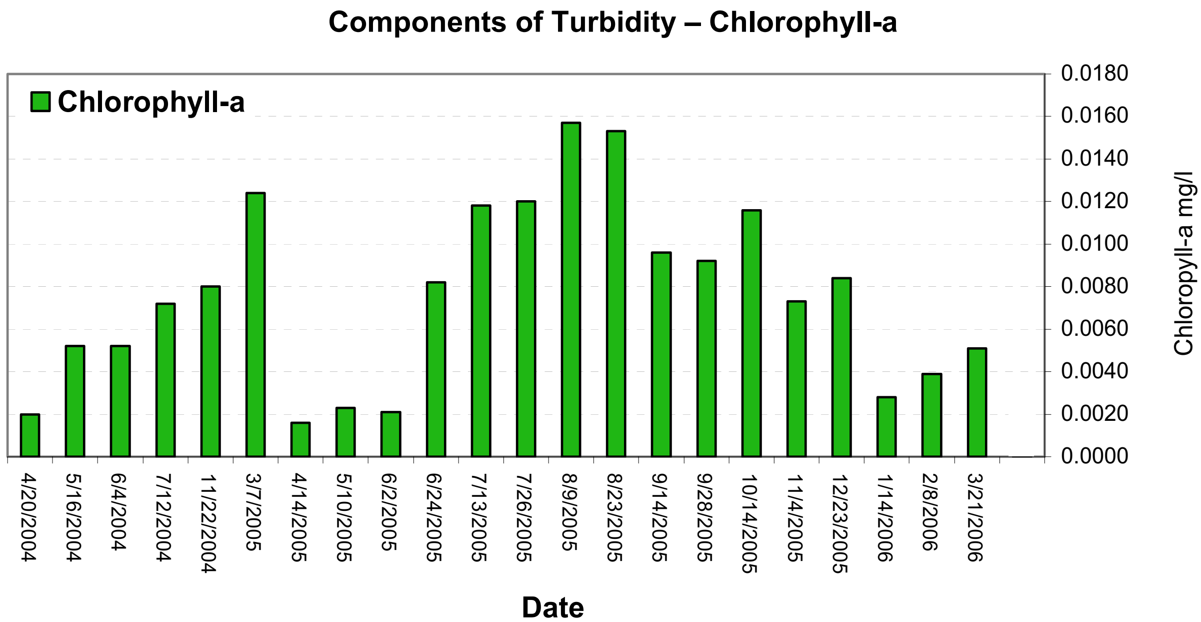

Figure 17. The mean levels of chlorophyll- in Martins Pond from April 2004 to March 2006. Chlorophyll-a levels were variable, but exhibited seasonal peaks in summer 2005 and relatively high levels in winter 2004 samples.

In addition to investigating the components of turbidity, the relationship between turbidity (NTU) and the sum of turbidity components (inorganic and organic TSS + chlorophyll-a) was also explored. Figure 18 is a double plot of NTU and the sum of the turbidity components for Martins Pond over time from 2002 to 2006. Brakke et al. (1988) report a median NTU value of 0.9 for lakes in the southern New England subregion. The median NTU value for Martins Pond based on 2002-2006 data was 1.9 NTU (mean = 4.6; range 0.4 to 25.3), over double of the subregion median values.

Overall, NTU was positively and significantly correlated ($r = 0.78$; $P < 0.001$) with the sum of the components of turbidity analyzed. Regression analysis showed that chlorophyll-a, TSS-organic and TSS-inorganic accounted for (predicted) 70.8% of the variability in NTU. Best subsets multiple regression analysis in Minitab 14.1 (Minitab 2003) showed that using the variables TSS-organic and chlorophyll-a provided the best fit subset model for the NTU data (r^2 = 72.1%; Mallow C-p = 2.1). In addition, the significant correlation between NTU and the sum of the turbidity components indicates that the sources of turbidity have been reasonably identified in Martins Pond. There was no significant correlation between NTU and Color (P = 0.478) and adding color to the best subsets regression analysis provided no improvement. However, the relatively high apparent color in Martins Pond is clearly limiting light penetration in the water column (see Section 5.4) and needs to be considered when interpreting light attenuation profiles and Secchi depths in the pond.

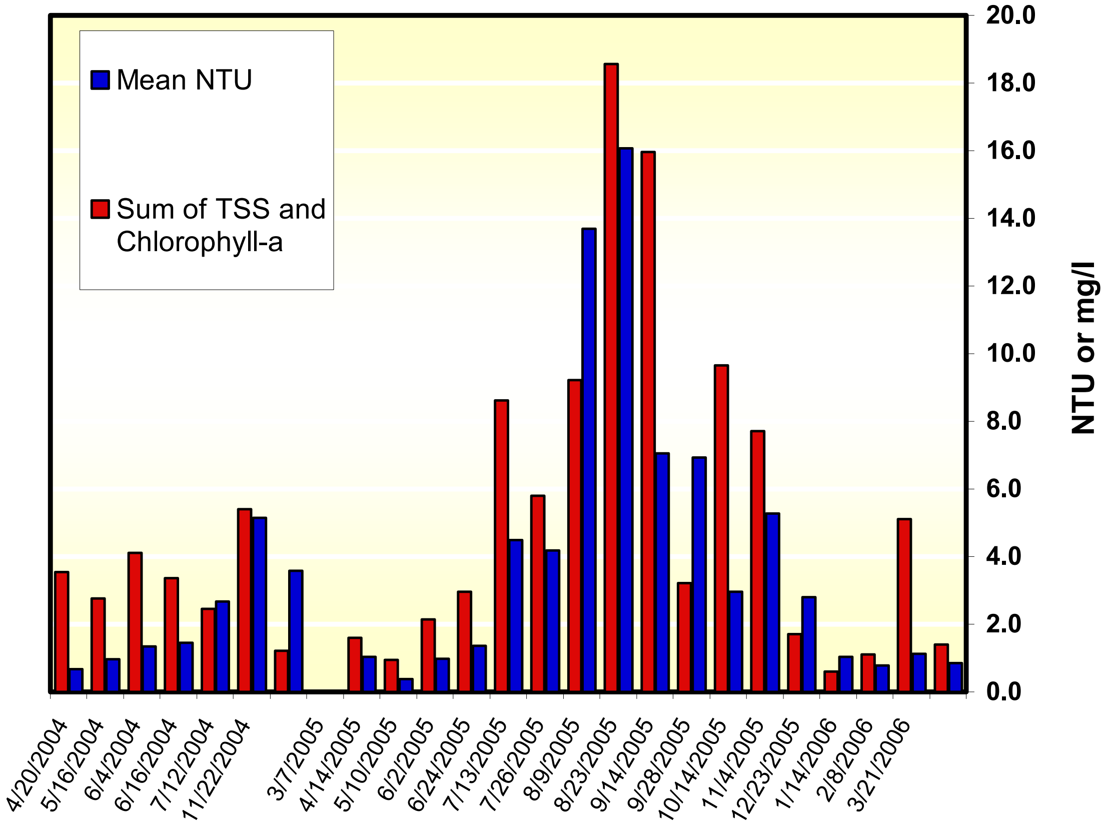

Figure 18. A comparison of NTU versus the sum of turbidity components (inorganic TSS + organic TSS + chlorophyll-a) in Martins Pond from April 2004 to March 2006. There was a significant positive correlation between the sum of turbidity components (concentration values) and NTU values. The three component measures account for some 70.8% of the variability in NTU values.

5.2 -- Total Suspended Solids Across the Watershed

Results of mean TSS levels across the 13 sampling sites are shown in Figure 19. The results show similar overall annual mean TSS levels across sample sites, although the WW1 site (headwater wetland site) showed significantly higher TSS levels (P = .006) than the other sites, including the other wetland site WW-NB.

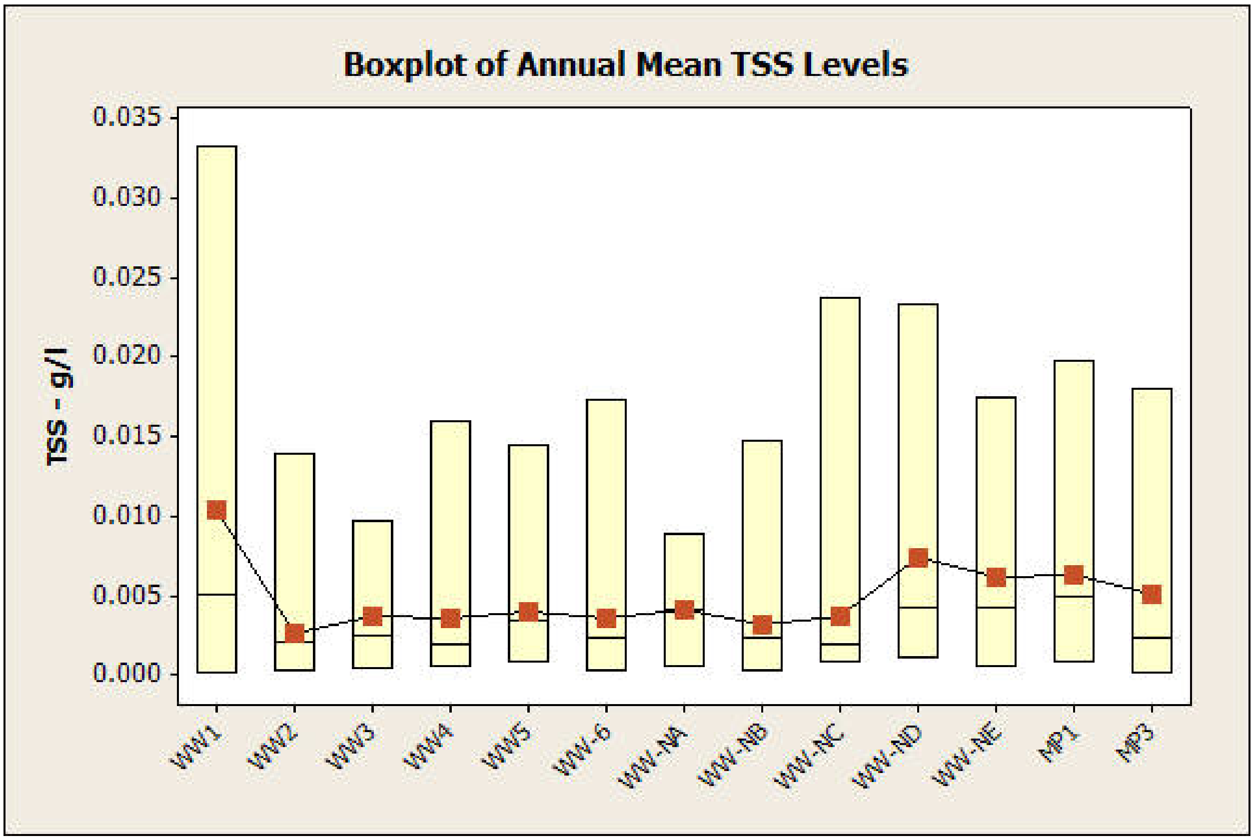

Figure 19. Boxplot of mean Total Suspended Solids (TSS) levels across sites during the March 2005-March 2006 sampling period. Means (■) are shown (and connected by lines) as are medians (—) and the range of values (extent of yellow bars).

The observed TSS levels at all sampling sites over the entire 2005-06 sampling period are shown in Figure 20. Except for site WW1, TSS levels were relatively low throughout the watershed in winter and spring, but increased in the summer and into the early fall. Site WW1 exhibited the highest TSS levels and those were in the fall. TSS levels at the Martins Pond inlet (MP1) and outlet (MP3) showed similar seasonal patterns.

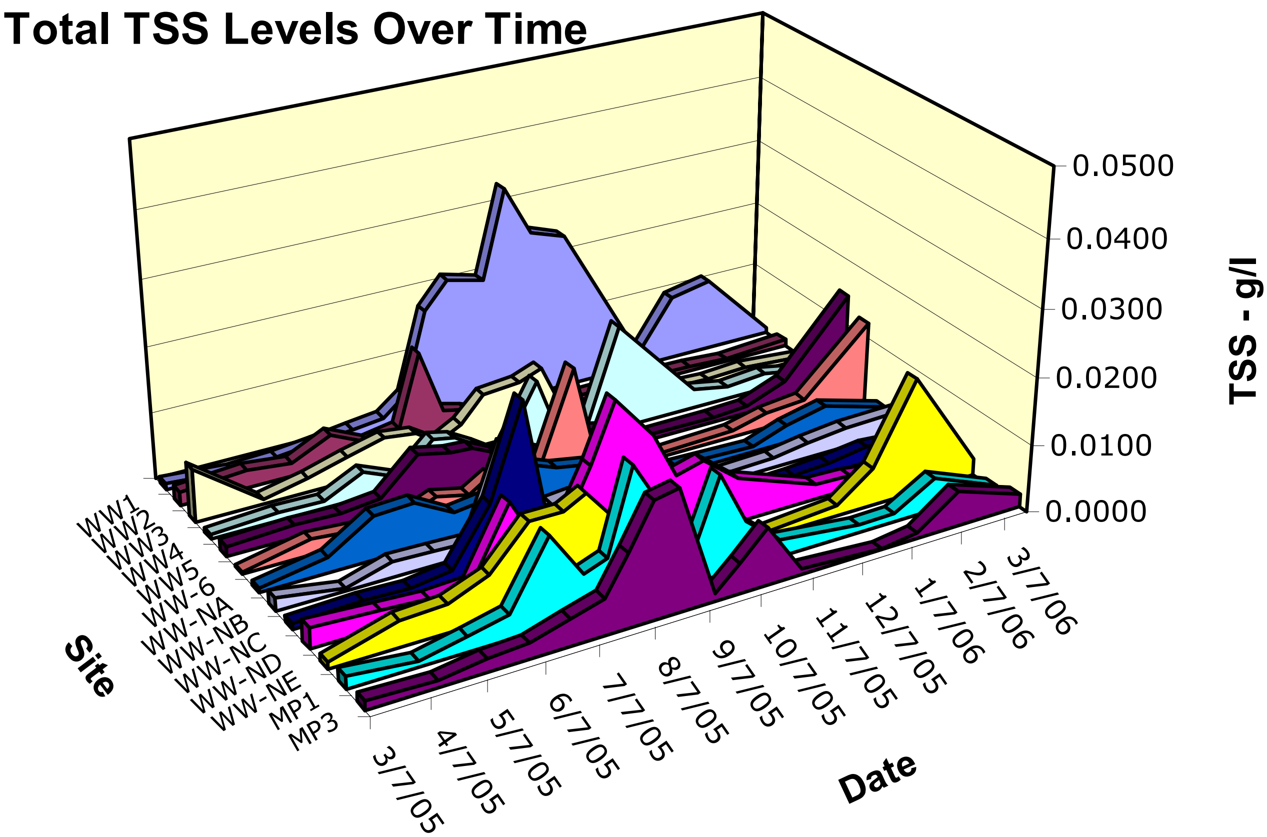

Figure 20. A comparison of total TSS levels (g/L) over the March 2005 to March 2006 Martins Pond watershed study. Low spring TSS levels were followed by high summer and early fall levels.

The mean percent organic matter content of the TSS samples at the different sampling sites is shown below in Table 18. The % organic fraction medians were very close to the mean in all cases. Overall, the majority of the suspended sediments were organic in Martins Pond (MP1 and MP3) and throughout the entire watershed, although the % organic fractions in Martins Pond were higher than in any other portion of the watershed. We attribute this high organic matter content to several factors, including the prevalence of wetland and forest detritus, suburban lawn and leaf materials from residential areas and the resuspension of sediments in the pond itself. Given the high color of surface waters in the watershed (Section 5.3), it is also not surprising that this could be linked with the level of organic suspended sediments, even though there was a weak positive correlation ($r = 0.246$) between color and TSS-organic in Martins Pond.

Table 18. A comparison of the mean organic content of TSS samples across all sample sites during the 2005-06 study.

Site	% Organic	SE	CV	Range	
WW1	83.0	3.4	17.1	54.6 - 100.0	*Wetland Sites*
WW-NB	68.9	6.3	37.8	13.6 - 100.0	
WW2	78.2	4.5	23.7	43.2 - 100.0	*Skug River Sites*
WW3	52.5	5.2	40.6	18.2 - 100.0	
WW4	86.4	3.4	16.3	54.6 - 100.0	
WW5	66.7	5.5	33.8	62.1 - 100.0	
WW6	67.8	6.5	39.7	0.0 - 100.0	
MP1	72.9	3.7	20.9	43.9 - 100.0	*Martin Pond*
MP3	80.8	3.9	19.9	81.5 - 100.0	
WW-NA	53.7	6.6	51.0	58.9 - 100.0	*Skug Tributaries*
WW-NC	76.8	2.8	14.7	62.1 - 100.0	
WW-ND	70.6	4.7	27.5	44.2 - 100.0	
WW-NE	59.1	5.3	36.6	9.5 - 100.0	
Overall Mean	70.6	2.9	15.2	0.0 - 100.0	

% Organic = mean annual organic matter content of TSS;
SE = standard error; CV = coefficient of variation.

There were no discernible seasonal patterns in the organic/inorganic components of TSS across sample sites; fluctuations occurred throughout the year on all sites and the fluctuations were not significantly correlated between sites or with season.

5.3 – Color

Color, also known as 'true color', is a measure of the color of water from which the turbidity has been removed. Color is influenced by the presence of both dissolved organic compounds and naturally occurring soluble metal ions (e.g., iron and manganese). Color has also been shown to be one of the contributing factors leading to attenuated light penetration in the water column.

Mattson et al. (1992) report a median color level of 29 PCU for Massachusetts lakes within the Boston region. Brakke et al. (1988) report a median level of 24 PCU for lakes in the southern New England subregion. Figure 21 shows the surface water color results for all monitoring/sample sited during the 2005-06 study. Except for the reference subwatershed (WW4 – subwatershed J), the color values exceeded the median values reported by Mattson et al. (1992) and Brakke et al. (1988).

In addition, there were clear seasonal patterns in color level across the watershed; color levels showed a steady increase over the spring and summer and then began to decline by early fall. Overall, color exhibited a similar seasonal pattern to that of turbidity (Figure 18). Sampling site WW-4 (reference watershed J) exhibited the lowest overall color levels - the relatively high forest cover in this watershed combined with the relatively low cover of wetlands and residential areas may be responsible for the low color levels. The extent of wetlands (see Table 17) has also been shown be positively correlated with color level and dissolved organic carbon compounds (Williams et al. 2005).

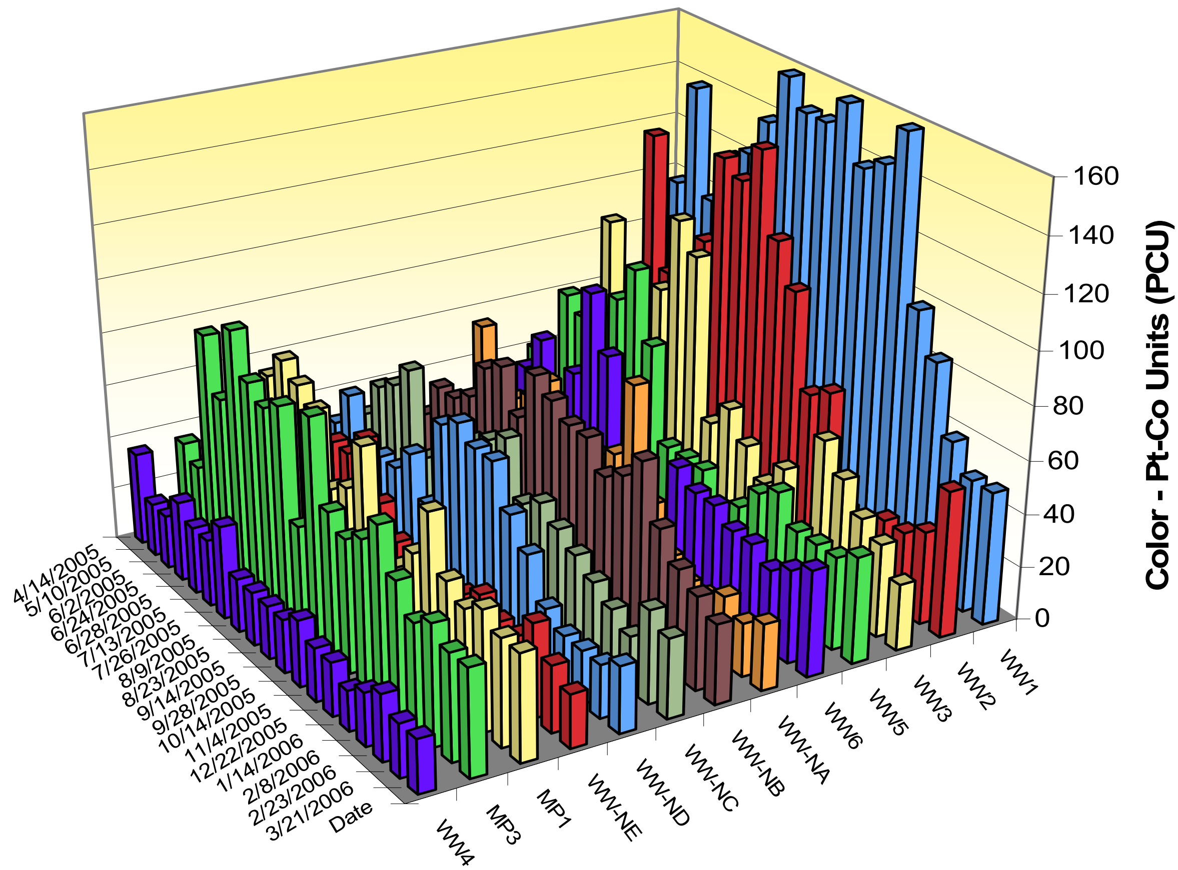

Figure 21. A comparison of color (Pt-Co Units) in surface waters in the Martins Pond Watershed during the 2005-06 sampling period. Some seasonal patterns are evident on most sites.

Iron and Manganese Levels

Figure 22 shows mean Fe and Mn levels at the sampling sites within the watershed during the 2005-06 study. The median Fe and Mn concentrations reported for southern New England Lakes were 84 and 19 µg/L, respectively (Brakke et al. 1988). Mattson et al. (1992) report Fe and Mn median concentrations for Boston region lakes as 250 and 30 µg/L, respectively. The concentrations of Mn and Fe in the surface waters in the Martins Pond watershed are at the high end of the levels noted for the region. The relatively high Mn and especially the Fe levels are contributing to the relatively high color levels throughout the watershed and especially in Martins Pond (MP1). However, Fe and Mn concentrations alone do not explain the variation in color across the watershed. For example, samples site WW1, WW2 and WW3 showed the highest color values during the study period (Figure 21), but some of the lowest Fe and Mn levels (Figure 22). The three sites are in the northern half of the watershed. The IEP (1977) study on Martins Pond reported mean in-pond Fe and Mn concentrations of 950 µg/L and 120 µg/L, respectively, considerably higher than the levels found in the current study. Overall, Fe and Mn are important factors influencing light attenuation and visibility in Martins Pond.

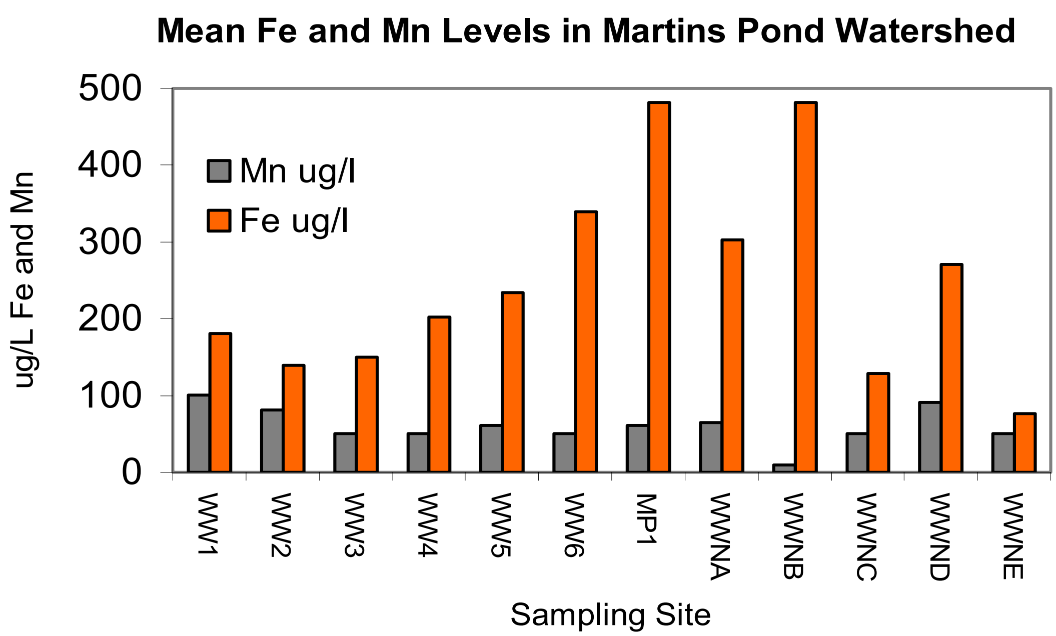

Figure 22. Mean Fe and Mn concentrations in surface waters at sampling points within Martins Pond watershed from March 2005 to March 2006. Fe concentrations generally increased moving downstream from WW1 (headwaters) to Martins Pond (MP1) along the Skug River.

5.4 – Light Attenuation Profiles – *(Scope of Services 1h.)*

To assess the impact of turbidity on light attenuation in Martins Pond, a series of *in situ* light penetration profiles were conducted using a Li-Cor 250 Light Meter (measuring photosynthetically active radiation - PAR) in July 2002, 2003, 2004 and 2005. The results were remarkably similar. The euphotic depth (depth beyond which the light level falls below 1% of surface light) was 4.3 ft (four year mean = 4.331 ft; SE = 0.051 ft). The mean summer Secchi depth over the same four-year period was 1.09 m or 3.58 ft (median 1.10 m or 3.61 ft). The 1985 D/F Study (Anderson-Nichols and Lycott 1985) reported a mean Secchi depth of 0.94 m (range 0.9 to 2.0).

To determine the relative contributions of TSS versus algae versus organic acids, a simple laboratory experiment was also conducted. A series of externally blackened, cylindrical water tanks, approximately 1.5 m deep and 0.7 m in diameter, were filled with filtered tap water and then treated at one of three levels (low, medium and high) of one of three parameters, TSS, algae (chlorophyll-a) and tannic acid (color). There were three replicate tanks used for each level of each treatment in the study. Martins Pond water was also collected and analyzed. The experiments were conducted in April and May 2005. Low, medium and high levels were determined using the 25th, 50th and 75th percentiles for each respective parameter based on means from data collected from Martins Pond prior to May 2005. The treatments were as follows:

	25th	50th	75th
TSS – mg/L	1.4	2.7	5.0
Chlorophyll-a $\mu g\ L^{-1}$	3.6	8.0	13.0
Color - PCU	40	50	70

TSS was simulated using fine clay particles added to filtered tap water. Chlorophyll-a (algae) levels were created by adding various amounts of stock green algae (Chlorophyta) to filtered tap water in the tanks. Powdered tannic acid stock solution ($C_{76}H_{52}O_{46}$ – Hach 79114) was used to achieve the desired color to the filtered tap water. Filtered tap water was used as a control. A Li-Cor 250 Light Meter was used to measure photosynthetically active radiation (PAR) in the tanks at different depths. PAR is a light intensity measure across the wavelengths of light that can actually be used for photosynthesis. Thus, it represents the amount of light available to photosynthetic organisms to perform photosynthesis. The results presented in Figure 23 are over the top 0.4 m (40 cm) of water surface in the experimental tanks. The depth 0.0 refers to light levels above the water surface and a depth of 0.01 corresponds to light levels just beneath the surface. The additional depth classes are in 0.05 m (5 cm) increments.

Relative to the control (filtered tap water), the rank of the three parameters impact on light attenuation in this experiment were as follows: TSS < Algae < Tannic Acid. The 25th, 5oth and 75th percentile tannic acid treatments correspond to color levels of 40, 50 and 70 PCUs, respectively. While this experiment is not a direct measure of the factors contributing to light attenuation in Martins Pond, it suggests the importance of all three factors in reducing light penetration in the water column. In particular, the role of dissolved organic acids, such as tannic acid in this study, at color levels typical of those found in Martins Pond indicate they the most important contributor to light attenuation. The impact of tannic acid at color levels of 70 PCUs was particularly pronounced as shown in the 75th percentile graph in Figure 23.

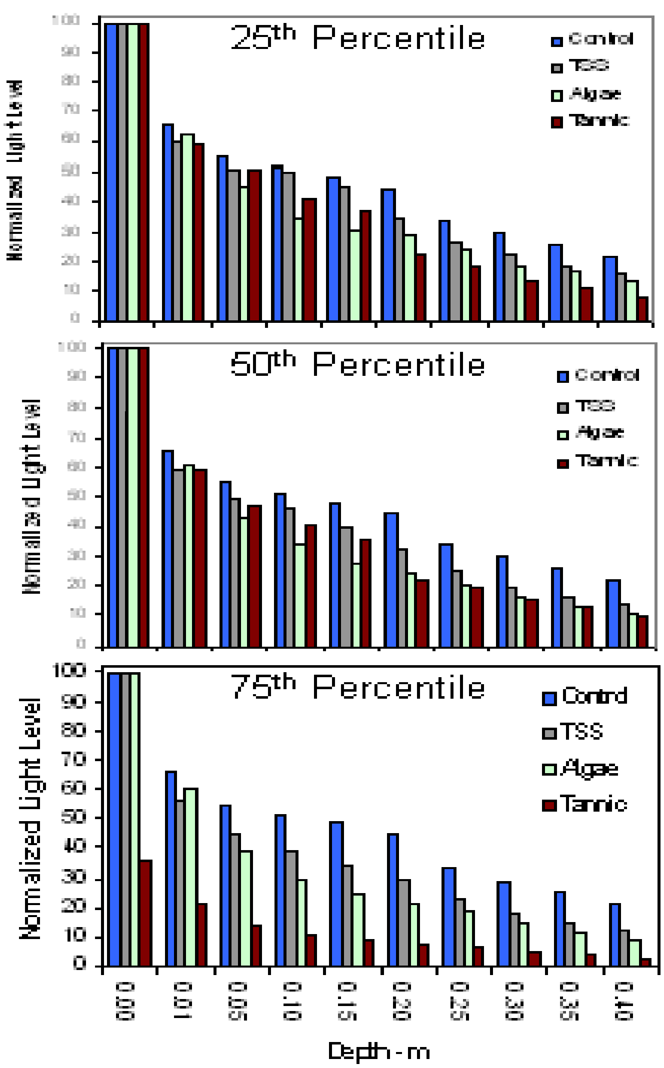

Figure 23. A summary of the light attenuation results for the laboratory experiment conducted using the 25th, 50th and 75th percentile levels for each of the three parameters used in this study: TSS, algae (chlorophyll-a) and tannic acid (color). All three figures are shown at the same scale for comparison. Relative to the control (filtered tap water), the parameters impacted light attenuation as follows: TSS < Algae < Tannic Acid. The 25th, 5oth and 75th percentile tannic acid treatments correspond to color levels of 40, 50 and 70 PCUs, respectively. While this experiment is not a direct measure of the factors contributing to light attenuation in Martins Pond, it suggests the importance of all three factors in reducing light penetration in the water column. In particular, the role of dissolved organic acids, such as tannic acid in this study, at color levels typical of those found in Martins Pond indicate they the most important contributor to light attenuation. The impact of tannic acid at color levels of 70PCUs was particularly pronounced as shown in the 75th percentile graph on the left.

Table 19 provides an overall summary of light attenuation across the top 0.4 m of the water column in the study. Mean light levels across the water column in the raw sample from Martins Pond were some 29.5% of the control, thus indicating that the combination of color and the components of turbidity produced a 29.5% of potential light penetration into the water column.

Table 19. A summary of laboratory light attenuation results comparing the relative contributions of TSS, algae and organic acids (color) to light level reductions in the top 0.4 m of the water column.

% Light reduction in Martins Pond versus control: 29.5			
	25^{th}	50^{th}	75^{th}
% Light reduction due to TSS treatments relative to control	13.9	19.7	21.7
% Light reduction due to algae treatments relative to control	27.1	30.9	35.5
% Light reduction due to organic acid (color) relative to control	30.5	33.6	75.2

The importance of organic acids and color in attenuating light in Martins Pond and other surface waters throughout the Skug River watershed should not be underestimated. Given the color results presented in Figure 21 and the components of turbidity results summarized in Figures 16 through 20, light, and more specifically the attenuation of light, is a major limiting factor that influences the activity of all photosynthetic organisms in Martins Pond.

5.5 – pH

The Commonwealth of Massachusetts standard for pH in Class B waters is that pH:

> '*shall be in the range of 6.5 through 8.3 standard units and not more than 0.5 units outside of the background range. There shall be no change from background conditions that would impair any use assigned to this Class*.'

Figure 24 summarizes the 2005-06 pH results from this study. pH values in the Martins Pond watershed varied with subwatershed. Over the course of the 2005-06 study, the pH values at the Martins Pond inlet and outlet were as follows:

Inlet	annual mean = 7.01	median = 6.72	std Error = 0.14	range: 6.15 to 8.71
Outlet	annual mean = 6.82	median = 6.74	std Error = 0.09	range: 5.94 to 7.86

Based on the results above, the range of pH values both were under and exceeded the standard, although the means and medians were within the standard range. The highest pH levels were observed at the inlet (MP1) in summer. Similar late summer/early fall increases in pH were noted in Martins Pond in 2003 and 2004. The cause of this pH increase is not known, but may be due to reduced CO_2 levels and biologically mediated redox reactions. The percent saturation of dissolved oxygen was at or over 100% during the noted pH increase period. The 1985 D/F Study (Anderson-Nichols and Lycott 1985) reported mean pH value of 6.6 in Martins Pond (range 6.3 to 7.2).

Wetland site WW1, located in the headwaters area of the watershed, exhibited significantly lower pH values than all other sites (2005-06 mean = 5.89; SE = 0.056; range 5.57 - 6.62). There was no significant pH difference among the other sample sites, although the lower Skug River (WW-6) exhibited high pH levels in late summer 2005. The low pH in the headwaters is likely linked to the reducing conditions, high color and high organic acid content in the waters draining from the extensive wetland complex in that watershed (21.9% wetland land cover).

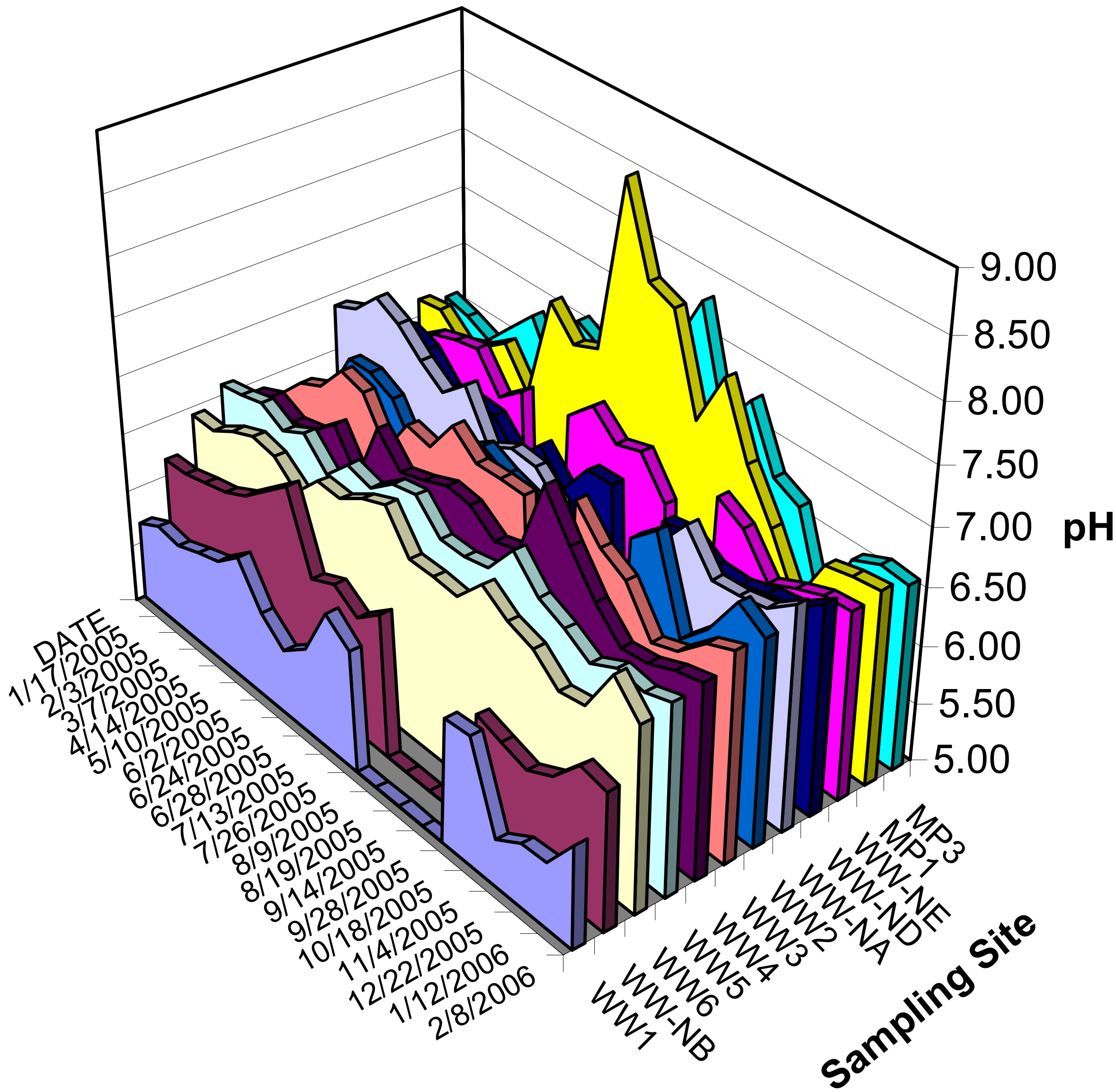

Figure 24. pH levels over time at each sample site in the Martins Pond watershed. pH values were lowest at WW1 (subwatershed G) and WW-NB (within subwatershed H), both in the upper portions of the watershed.

5.6 – Conductivity

Conductivity is the measure of the resistance of a solution to electrical flow. Thus, the lower the conductance, the 'purer' the water and the lower its dissolved salt content. Brakke et al. (1988) report the median conductance value for the southern New England region was 81.5 μs/cm. The conductivity results for the 2005-06 Martins Pond study are presented in Table 20.

Overall, and other than for site WW-1, the conductivity levels in the Martins Pond watershed were substantially higher than the median value reported by Bakke et al. (1988); yearly means ranged from 91.8 μs/cm (WW1 – subwatershed G) to 346.6 μs/cm (NWW-NA – subwatershed F). Site WW1 had significantly lower conductivity than all other sites (subwatershed G). There were no significant differences in conductivity between the Skug River sites and the Martins Pond inlet (MP1) and outlet (MP3). The tributaries to the Skug River exhibited some of the highest conductivity levels. High levels of both road salt and dissolved organic acids are likely contributing to the generally high conductivity levels in this watershed.

Mean conductivity at the Martins Pond inlet and outlet was 277.7 μS/cm and 276.2 μS/cm, respectively. In contrast, the mean conductivity in-pond level reported in the 1985 D/F Study (Anderson-Nichols and Lycott 1985) was only 126 μS/cm (range 88 to 205). In addition, the 1985 study reported that conductivity "virtually followed the patterns exhibited by the chloride ion," a result that was not supported in the current study (see Section 5.7). There is thus evidence that the dissolved ion content in Martins Pond has increased in the past twenty years and that this increase can likely not be solely attributed to increased chloride levels alone.

Table 20. Conductivity levels over time at each sample site in the Martins Pond watershed. All units are μS /cm. Conductivity was lowest at WW1 (subwatershed G). Two Skug River tributary subwatershed sites, WW-NA (subwatershed F) and WW-NE (subwatershed D), exhibited the highest conductivity levels. Cells with no data available are designated by nd.

	WW1	**WW2**	**WW3**	**WW4**	**WW5**	**WW6**	**MP1**	**MP3**	**WW-NA**	**WW-NB**	**WW-NC**	**WW-ND**	**WW-NE**
Date	**Conductivity** μS/cm												
3/7/2005	107	322	302	251	277	273	275	279	433	72	212	325	380
4/14/2005	95	313	291	274	260	308	339	341	425	61	201	339	341
5/10/2005	86	205	256	246	256	265	305	309	430	268	189	356	344
6/2/2005	88	155	245	240	252	258	308	291	405	299	165	316	320
6/24/2005	99	108	241	247	250	265	309	282	389	320	186	314	317
6/28/2005	87	208	235	251	257	268	312	319	420	328	156	327	325
7/13/2005	79	142	205	245	230	232	305	307	418	271	198	402	337
7/26/2005	114	156	162	265	191	178	335	339	395	334	201	356	135
8/9/2005	101	145	267	330	267	268	299	308	308	310	146	224	106
8/19/2005	nd	nd	97	260	252	272	298	297	325	nd	111	113	129
9/14/2005	nd	129	156	250	259	272	311	312	289	nd	152	126	158
9/28/2005	nd	nd	178	250	242	341	299	273	225	206	138	141	167
10/18/2005	151	153	166	219	195	265	225	250	277	169	157	125	138
11/4/2005	121	260	150	205	178	180	178	169	287	60	169	154	120
12/22/2005	100	165	245		250	266	285	294	404	333	82	150	349
1/14/2006	35	123	100	219	97	104	192	188	174	154	74	138	166
2/8/2006	36	116	107	95	92	92	99	102	170	140	105	140	189
3/21//2006	78	302	293	242	254	289	324	312	465	333	196	289	370
Mean	91.8	187.6	205.3	240.5	225.5	244.2	277.7	276.2	346.6	228.6	157.7	240.8	243.9
Median	95.0	155.5	220.0	247.0	251.0	265.5	302.0	295.5	392.0	269.5	161.0	256.5	253.0
	Skug River						Martins Pond		Skug Tributaries				

nd – no data available

5.7 – Chloride

Chloride is a common constituent of surface waters in New England. This is frequently attributed to the use of road salts during the winter months. Godfrey et al. (1996) noted that in the Boston Region, median Cl levels were 22.4 mg/L (666 μeq/L) in lakes and 24.9 mg/L (702 μeq/L) in streams. Godfrey et al. (1996) also concluded that most of the sodium and chloride in Massachusetts streams is due to the application of road salt during winter weather events. The authors used a simple mass balance model of road salt and stream runoff and determined that salt in precipitation, even given coastal influences in the eastern portion of Massachusetts, can account for only some 4% of the observed stream concentrations.

Figure 25 shows the concentration of chloride (mg/L) in surface waters in the Martins Pond watershed from March 2005 to March 2006. Not surprisingly there were high levels in the winter and early spring followed by declines over the late spring and summer into early fall. The influence of road salting is clearly evident, however the seasonal peaks well exceed the regional median values noted above. The only subwatershed with consistently and relatively low chloride levels was WW1 (headwater wetlands) where there are few roads influencing water quality and no transport of chloride from upstream locations. Interestingly, the drop in chloride levels in the summer months were not accompanied by lower conductivity levels (Table 20). Thus, chloride is not the primary source of the high summer conductivity readings.

The IEP (1977) study reported mean chloride levels in the summer 1976 of 20 mg/L at site WW-6 in the current study, 22 mg/L at the inlet to Martins Pond (MP-1) and 29 mg/L at the outlet (MP-3). In the current study, mean summer 2005 chloride levels (samples between 6/24 and 8/23) were 26.7, 26.5 and 25.0 mg/L at site MP-1, MP-3 and WW-6, respectively. Thus little difference was noted between the two studies. However, the mean yearly concentration of chloride at sites MP-1, MP-3 and WW-6 in the current study were 47.7, 48.6 and 44.7 mg/L, respectively.

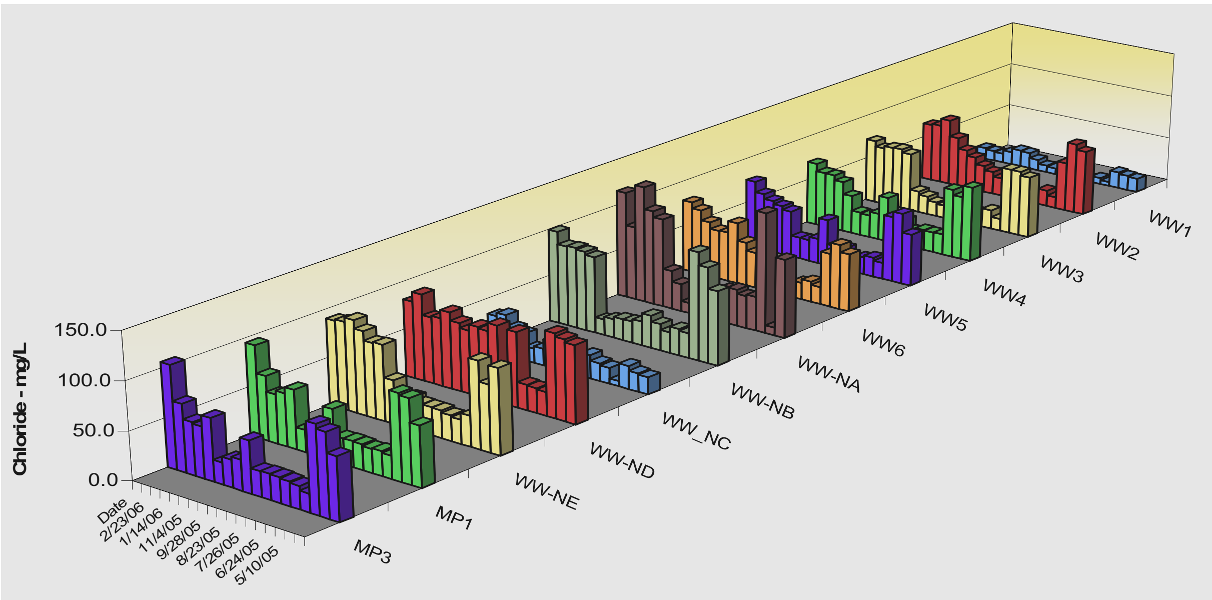

Figure 25. A site comparison over time of the concentration of chloride in surface waters in the Martins Pond watershed from March 2005 to March 2006.

5.8 – Sulfate Levels in the Martins Pond Watershed

Potential sources of sulfate (SO_4^{2-}) include dry and/or wet deposition, terrestrial source of sulfate within the watershed, sulfate adsorption dynamics and/or evapoconcentration. In addition, sulfate can become mobilized during post-drought rainfall events resulting in a sulfate pulse (Devito and Hill 1997). In addition, sulfate reduction can occur under low flow scenarios and behind beaver dams (Rittmaster and Shanley, 1990).

The sulfate levels in the watershed for the 2005-06 sampling period are presented in Figure 26. Godfrey et al. (1996) report median sulfate levels of 3.59 mg/L (224 µeq/L) in lakes and 4.73 mg/L (295 µeq/L) for streams in the Boston region. In a broader geographic context, Wetzel (2001) noted the range of sulfate in surface waters is usually between 5 – 30 mg/L with a mean of around 11 mg/L.

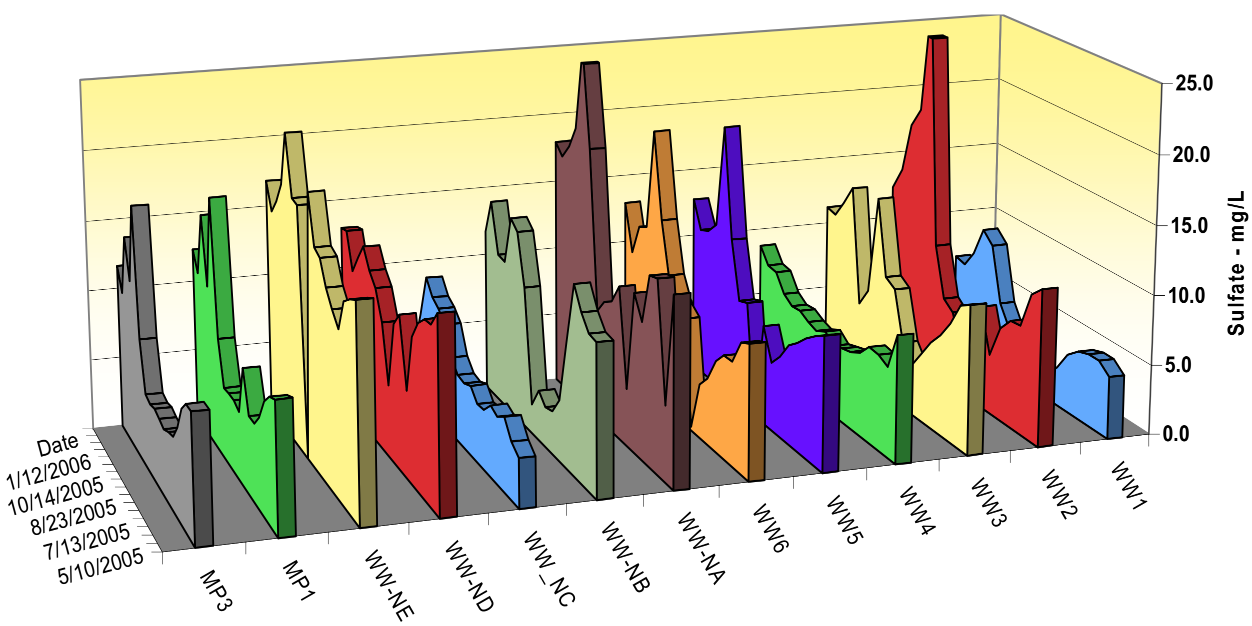

Figure 26. A comparison of sulfate levels (SO_4) in the Martins Pond watershed during the 2005-2006 study period. Overall sulfate levels where generally high and generally showed summer decreases followed by fall and winter increases. The Martins Pond inlet (MP1) and outlet (MP3) showed very similar seasonal patterns.

Overall, sulfate levels in the Martins Pond watershed study were at or above levels expected for this part of New England. Similar to the total N results, there was a pattern of decreasing SO_4

levels from March to July at all sites. This pattern was also noted by Williams et al. (2005) in their assessment of the relationships between land use and stream solute concentrations across the Ipswich River basin. High late winter/early spring values likely reflect relatively high concentrations in snowmelt runoff embedded with wet and dry SO_4 deposition. A comparison of seasonal sulfate levels in Martins Pond compared to wet deposition of sulfate at the NADP/NTN Monitoring site in Lexington, MA (site MA13) is shown in Figure 27.

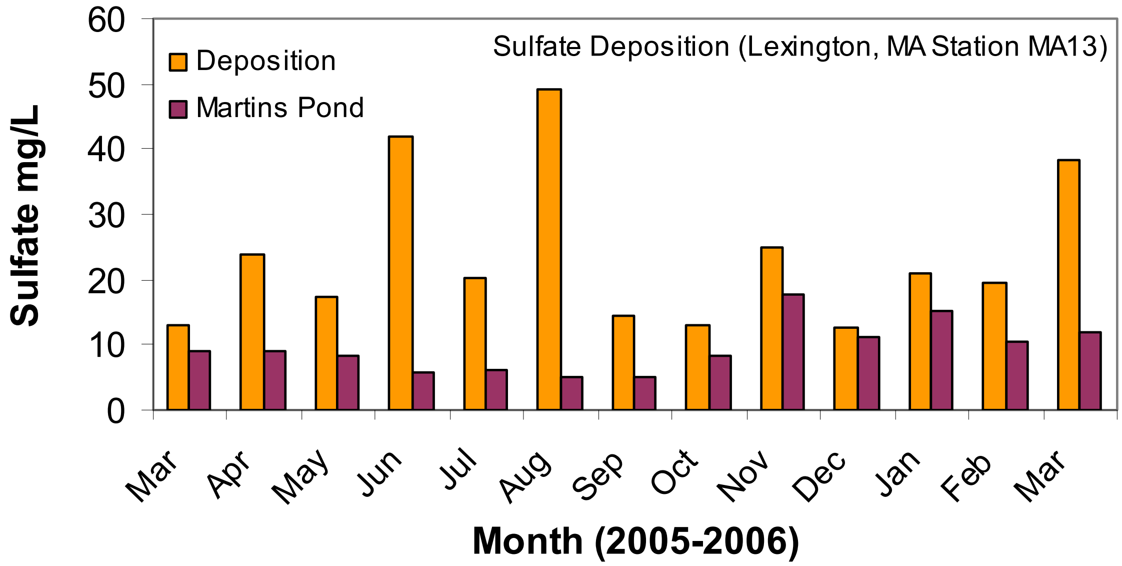

Figure 27. Mean sulfate levels found in surface waters in Martins Pond versus wet deposition values reported from the NADP/NTN Monitoring Location in Lexington, MA. There was no discernible pattern between the two measurements. Values from the Lexington station represent precipitation weighted mean concentrations.

Three tributary sites to the Skug River, WW-NA (subwatershed F), WW-ND (subwatershed E) and WW-NE (subwatershed D), exhibited higher levels than the other sites. These subwatersheds also have higher housing densities than other portions of the watershed and thus higher septic system densities. Septic effluent can make large contributions of sulfate to surface waters.

Sulfate levels at the inlet (MP1) and at the outlet (MP3) of Martins Pond were very similar. Prior to reaching Martins Pond, some of the SO_4 may be taken up by SO_4 reducing bacteria in deoxygenated sediments and wetlands. However, overall the relatively high SO_4 levels observed were not anticipated in this study. The winter SO_4 peaks, generally between 10 to 15 mg/L SO_4^{-2}

(620 – 940 μeq/L) indicate very high levels relative to other surface waters not only in the region but at a much broader geographic scale (Baker et al. 1990). In addition, some of the high SO_4 levels are likely due to the relatively high level of Fe is soils combined with S-deposition and lower soil pHs can result in the formation of $FeSO_4$ and $Al_2(SO_4)^3$ that readily dissolve and enter surface waters (Johnson and Todd 1983). Also, nutrient-poor soils with low SO_4 adsorption, especially coniferous forest covers of white pine (*Pinus strobus* L.) in the watershed may also be contributing to higher sulfate levels. These factors in combination with the high septic densities in portions of the watershed and depositional inputs may account for the high SO_4 levels observed in surface waters in the watershed.

5.9 – Dissolved Oxygen

Dissolved oxygen (DO) is a measure of the amount of gaseous oxygen (O_2) dissolved in an aqueous solution, in this case surface water. Oxygen gets into water by diffusion from the surrounding air, by aeration (rapid movement by waves or currents) and via photosynthesis. The level of DO depends on several factors including temperature, respiration levels, photosynthetic activity, mixing and elevation. The DO standards for Class B waters are:

Dissolved Oxygen

(a) Shall not be less than 6.0 mg/L in cold water fisheries nor less than 5.0 mg/L in warm water fisheries unless background conditions are lower;

(b) natural seasonal and daily variations above these levels shall be maintained; levels shall not be lowered below 75% of saturation in cold water fisheries nor 60% of saturation in warm water fisheries due to a discharge; and

(c) site-specific criteria may apply where background levels are lower than specified levels, to the hypolimnion of stratified lakes or where the Department determines that designated uses are not impaired.

Percent saturation is another measure of dissolved oxygen. Percent saturation refers to the dissolved oxygen concentration expected from gas solubility at a given temperature and pressure. Saturation values can thus exceed 100%. Table 21 summarizes the percent saturation of oxygen calculated at the different samples sites during 2005-06. The percent saturation was less than 60% at many sites over extended periods of time. In contrast to the Martins Pond and Field Pond, the Skug River, sites, particularly WW1, WW6 and WW2 (corresponding to subwatersheds G, B and H, respectively), were the most oxygen deficient.

Oxygen depletion has been a concern for many decades in Martins Pond. McCabe (1949) notes in his extensive survey of lakes and ponds that winter-fish kills were a very real possibility in Martins Pond, although there is no solid evidence to support this contention.

Table 21. A comparison of percent oxygen saturation at the sample sites during the 2005-06 study. Clear seasonal and between-site variation is evident with the highest levels occurring during summer and early fall. Saturation fell below 60% in many instances along the Skug River (values in yellow). Overall, saturation levels in ponds (MP1, MP2, WW-4) were much higher than levels in the Skug River and its tributaries.

	Sampling Sites												
	MP1	**MP3**	**WW6**	**WW5**	**WW4**	**WW3**	**WW2**	**WW1**	**WW-NA**	**WW-NB**	**WW-NC**	**WW-ND**	**WW-NE**
	Percent Oxygen Saturation												
3/7/2005	79	76	78	75	80	72	71	66	89	51	62	53	73
4/14/2005	86	97	98	103	105	111	114	91	79	93	79	109	73
5/10/2005	96	99	91	105	88	101	93	55	82	60	96	85	48
6/2/2005	74	80	86	94	49	117	102	53	117	39	103	34	34
6/28/2005	85	87	89	97	67	102	92	36	78	49	75	27	23
7/13/2005	108	107	43	69	79	99	91	31	95	32	65	52	80
7/26/2005	188	116	28	68	81	114	*	29	80	19	89	29	33
8/9/2005	112	105	27	59	93	82	*	22	66	33	34	22	30
8/19/2005	111	103	35	54	93	105	*	*	*	*	68	75	41
9/14/2005	110	89	19	49	100	*	48	*	*	*	*	*	*
9/28/2005	109	92	55	77	99	*	*	*	*	*	77	*	*
10/18/2005	93	100	64	65	100	70	98	39	90	58	*	67	46
11/4/2005	115	111	53	113	110	80	109	37	62	52	49	48	45
12/22/2005	95	92	63	*	91	75	95	55	89	86	89	62	43
1/8/2006	88	86	70	68	75	82	86	65	75	56	91	75	*
2/8/2006	75	79	68	75	78	82	69	78	71	42	*	74	48
3/21/2006	82	80	85	92	119	112	87	96	63	49	79	60	62

5.10 – Total Phosphorus Concentrations in Surface Waters

Phosphorus (P) is one of the most important nutrient measures in freshwater studies. Phosphorus is considered a major cause of eutrophication in freshwater systems because this essential nutrient is typically at very low ambient concentrations (short supply) in surface waters and thus can control primary productivity in algae and aquatic macrophytes (Wetzel 2001). Measuring and quantifying phosphorus can be problematic owing to the many different pools of P, including soluble and insoluble fractions and organic and inorganic forms. The use of total P (sum of all P fractions determined using a digested water sample) has been shown to be a better indicator of trophic state and available P levels than other less comprehensive P measures, such as soluble reactive P (Hudson et al. 2000; Dodds 2003). Thus, total P was quantified in the current study.

The median Total P levels for lakes reported for Brakke et al. (1998) in the southern New England region where Martins Pond is located is 0.014 mg/L. Median total P values for other regions in the northeastern U.S. range from 0.005 to 0.022 mg/L. Figure 28 is reproduced from the ENSR (2000) study and shows the frequency distribution of total P values for 1,155 lakes, ponds and reservoirs in New England and provides a powerful context for the total P levels observed in the Martins Pond watershed.

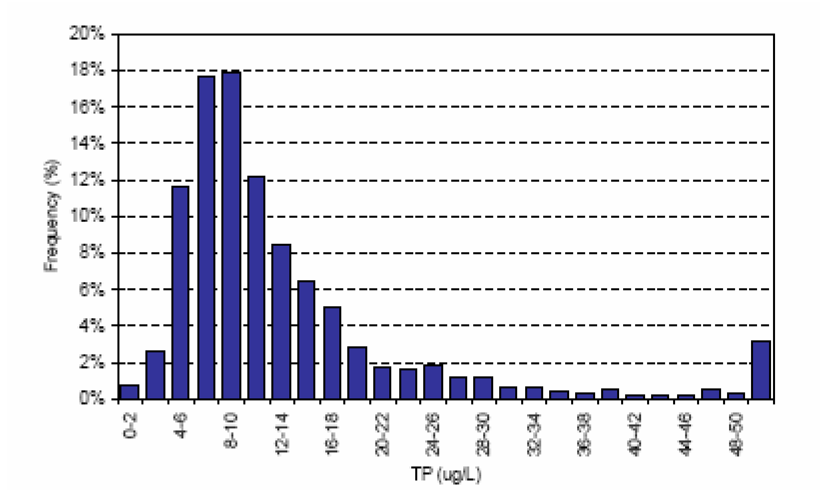

Figure 28. The frequency distribution of total P levels in summarized for 1,155 lakes, ponds and reservoirs in New England. This Figure is taken from the ENSR (2000) C*ollection and Evaluation of Ambient Nutrient Data for Lakes, Ponds and Reservoirs in New England, Data Synthesis Report*. The 2005-06 mean total P level in Martins pond was 63 µg/L, thus putting it on thee high tail of the distribution show in the Figure.

Total P levels were summarized for the five different sampling sites along the Skug River and Martins Pond from which there were data collected from 2003 to 2006. The total P level results for the seven sites are presented in Figure 29. All sites, ranging from the headwaters of the Skug River (WW1) to the Martins Pond watershed outlet (MP3) showed very similar seasonal patterns: relatively low levels in winter and early spring, followed by steadily increasing total P levels through summer, followed by declines in autumn. The unified rise and fall of total P levels throughout the entire watershed indicate two important total P dynamics: (1) the release of P into surface waters is a watershed-wide phenomenon occurring simultaneously in the Skug River and Martins Pond; and (2) there appears to be no downstream increase in total P concentration along the Skug River (sites WW1 to WW6) or in Martins Pond (MP1 and MP3). Upper watershed sites WW1 (subwatershed G) and WW2 and WW3 (subwatershed H) exhibited some of the highest overall total P levels. Site WW4 (subwatershed J), the reference watershed for this study, showed generally low total P levels throughout the year relative to the other sites.

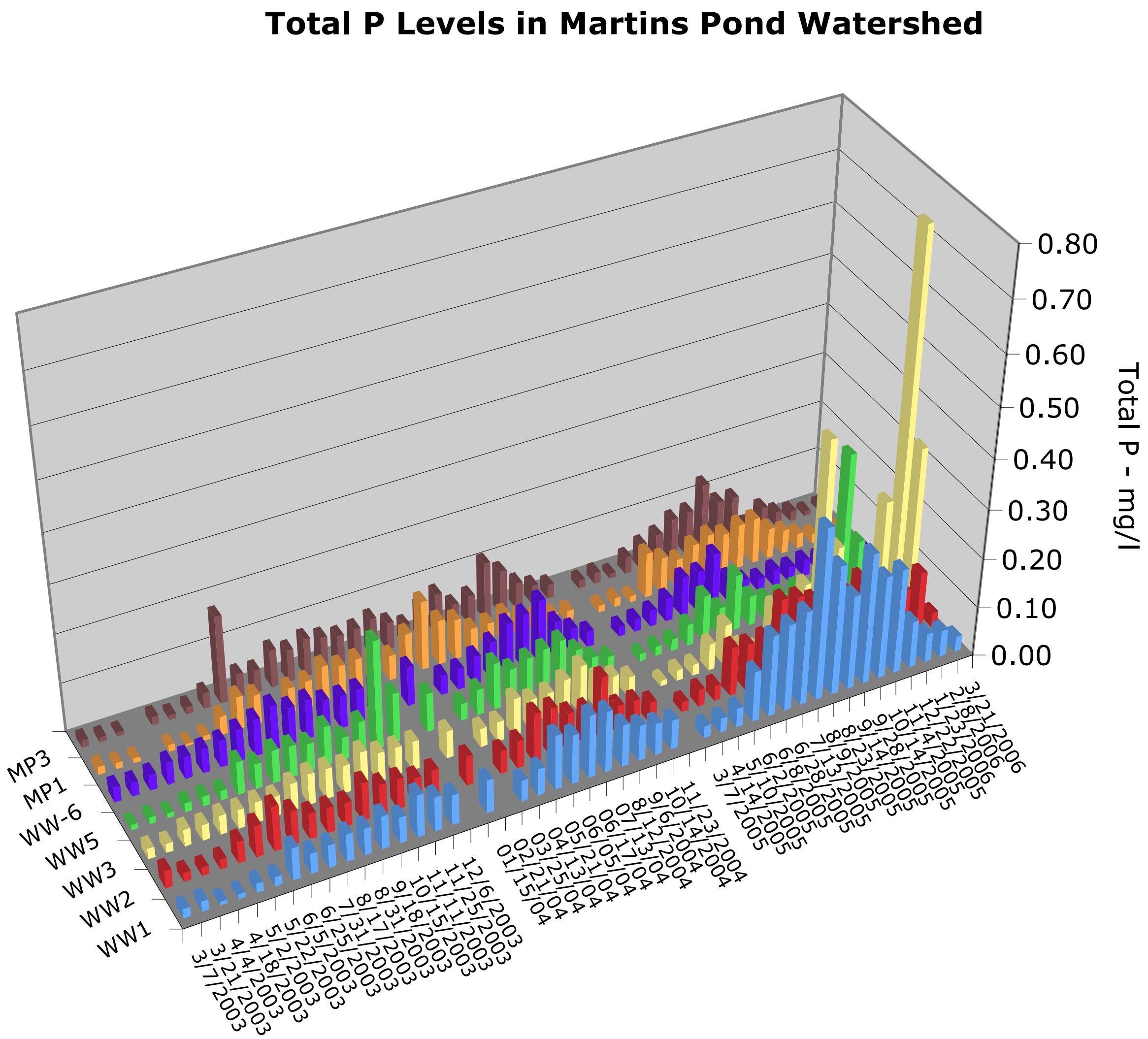

Figure 29. A comparison of total P values from 2003 to 2005 at five Skug River sample sites (WW1 to WW6) and the Martins Pond inlet (MP1) and outlet (MP3).

As noted above, in 2005-06, total P values were higher in the upper portions of the Skug River, namely sites WW1 (wetland site) and WW2. The relative similarity and seasonal pattern in total P levels in the lower reaches of the watershed, including Martins Pond highlight that P concentrations remain somewhat constant along the low gradients of the lower Skug River. The consistent spatial and temporal patterns in total P concentration indicate the presence of multiple and watershed-wide sources of total P rising and falling in a synchronous fashion.

Total P levels in five additional tributary sample sites along the Skug River, in addition to those shown in Figure 29, are presented in Figure 30. Overall for these tributary sites, there was a clear seasonal pattern with total P values peaking over the summer and early fall at most sites. There was great variability in total P levels across the different tributaries with sites WW-NA and the wetland site WW-NB showing the highest overall P concentrations. These patterns are in parallel with the results presented in Figure 27; the highest total P values were noted in the northern portion of the watershed at sites WW-NA and WW-NB. In addition, total P concentrations were the highest in the two wetland sites analyzed in this study.

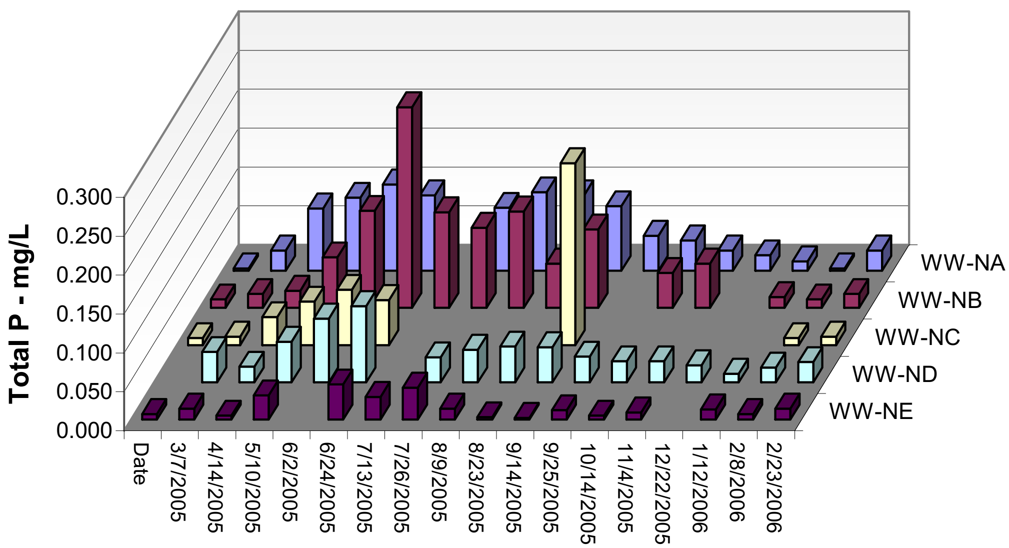

Figure 30. A comparison of surface water P values for additional sampling sites in 2005-06 in the Martins Pond watershed. Trends of increasing total P in spring and summer were noted at all sites and parallel the results in Figure 29.

5.11 – Historic Trends in Total Phosphorus Levels in Martins Pond

To provide context for the current study results and to investigate any historical trends in total P levels in Martins Pond, all of the available total P data for the pond were summarized over the past four decades. The results of that historic compilation are presented in Figure 31 along with more recent total P values from 2002 to 2005. All values in Figure 31 represent mean total P values in Martins Pond only. As has been noted in previous studies on Martins Pond, total P levels have been consistently high in Martins Pond since the 1970's. The 2005-06 total P values (mean = 0.063 mg/L) are representative of surface water quality in the pond since the mid 1970's. The pond total P values in 2005-06 ranged from 0.011 to 0.137 mg/L and were similar to total P values for the past two years.

The source of the extremely high total P levels observed in Martins Pond (and the lower Skug River) in 2002, were not determined. However, potential sources could have been a relatively low benthic P influx during low oxygen conditions at the water-sediment interface, evapoconcentration or a watershed source. In addition, prolonged calm (low wind) periods in that summer and fall in Martins Pond were observed that even resulted in the formation of a temporary thermocline. These issues are discussed in more detail in Section 9.0 of this report.

Density stratification can prevent the efficient mixing of surface and deeper water layers, resulting in a prolonged residence time of the near-bottom water. This prolonged residence time in combination with the high sediment O_2 consumption caused by the high sediment organic matter content noted in Martins Pond, can lead to anoxia at the sediment-water interface, thus triggering the release of relatively large quantities of P (Scheffer 1998). This process may have at least contributed to the very dramatic rise in total P levels noted in 2002 and accounted, in part, for the extremely high observed total P values observed in the Pond. Because the various abiotic conditions that might have triggered the large P release are somewhat rare in Martins Pond, strongly developed anoxia and high evapoconcentration, it is likely this was a rare event. Nonetheless, the large pool of P in the sediments in the pond, P sources in the Skug River watershed represent a large capacity for P loading that can be triggered whenever a specific set of anoxic and abiotic conditions are met at the sediment-water interface (Welch and Cooke 1995).

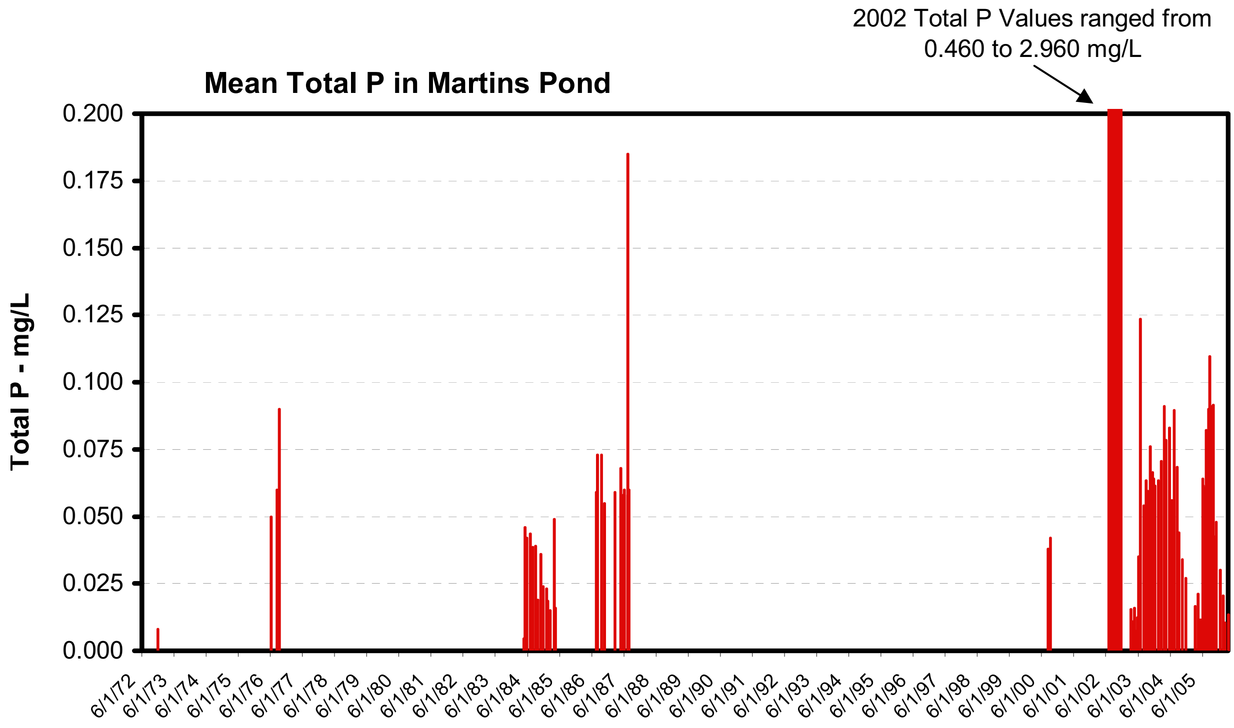

Figure 31. A comparison of mean total P values (mg/L) reported in Martins Pond over time from 1972 to 2006. There were very high total P results from 2002 as follows: 7/12 - 0.460; 7/124 – 0.520; 8/13 – 1.460; 8/29 – 2.960; 9/12 – 0.590; 9/26 – 0.590; 10/17 – 2.39; 11/14 – 1.102 mg/L. See Figures 29 and 30 for more detailed results for 2004 to 2006.

5.12 -- Nitrogen Levels in Surface Waters

Forms on Nitrogen – Nitrogen dynamics and chemistry are functionally complex. Given the many and dynamic components of the nitrogen cycle, it is difficult to get a handle on all the sinks, sources and transformations of nitrogen compounds, including dissolved molecular N_2, ammonia (NH_4^+), nitrate (NO_3^-), nitrite (NO_2^-) and dissolved organic N (DON). In addition, nitrogen can be transformed into nitrogen gas N_2 under anaerobic conditions through the process of denitrification and some cyanobacteria (blue-green algae) can use N_2 as a nutrient – algae and plants cannot. Ammonia is readily available to plants and algae. In addition, NH_4 can be transformed by microbes to nitrate (NO_3) via the process of nitrification. Neither ammonia nor nitrate bind well to pond sediments, thus in some lakes and ponds undergoing eutrophication, nitrogen may or may not accumulate in the sediment (Scheffer 1998).

Major sources of nitrogen in freshwater systems are nitrogen fixation in the water and sediments, decomposition occurring at lake and pond bottom sediments, inputs from groundwater, inputs from surface water inflows and both wet and dry atmospheric deposition. Additional factors contributing to total N levels include extensive wetland complexes, stream slopes, soils, septic density and efficiency and residential N inputs via fertilizers.

Nitrogen losses can occur via outflow, reduction of nitrate to N_2 (dentrification) and sediment binding. Studies have shown that some 60-80% of N inputs into temperate watersheds in the northeastern US are either retained and/or lost through denitrification (Howarth et al. 1996, Boyer et al. 2002). Filoso et al. (2004) noted that a combination of wetland, riparian and in-stream processes are responsible for N processes and transformations in the Ipswich River basin. The authors found that lateral N processing was positively correlated with the cover of wetlands and low elevation riparian areas – two landscape characteristics that are found in many of the subwatersheds in the Martins Pond system, especially along the lower Skug River. Other studies have shown that nitrogen loss in aquatic systems is highest in shallow ponds and this is likely due to denitrification at the sediment surface (Windolf et al. 1996). Given that Martins Pond is a shallow and eutrophic system with high organic content sediments, it is potentially prone to denitrification. Similar abiotic and biotic conditions exist along the low gradient, lower Skug River corridor.

Nitrogen Deposition - In this study no direct measure of either wet or dry nitrogen deposition was made. However, N deposition data were available for the NADL/NTN site (MA 13) in Lexington, MA (http://nadp.sws.uiuc.edu/sites/siteinfo.asp?net=NTN&id=MA13). Based on their dataset, N deposition measured during the study period is noted in Table 22.

	NH_4 kg ha^{-1}	NO_3 kg ha^{-1}
Spring 2005	0.67	3.22
Summer 2005	0.93	3.77
Fall 2005	0.27	1.70
Winter 2005	0.25	3.09

Table 22. A summary of N deposition during the 2005-2006 study period.

These results illustrate the importance of N loading into watersheds in the northeast. These results will be discussed in more detail in the nutrient loading sections of this report.

5.13 Nitrate Levels (NO_3^-)

Brakke et al. (1988) reported a median value of 0.80 mg/L nitrate for ponds in this region of New England. Nitrate was monitored at the thirteen sample sites throughout the 2005-06 study. A summary of the nitrate results by season is presented in Table 23. ANOVA results indicate there were both significant site ($P < .001$) and seasonal ($P < .001$) differences in nitrate levels. The seasonal nitrate means across sites were as follows:

Spring: 2.38 mg/L NO_3 Summer: 1.63 mg /L NO_3 Fall: 2.48 mg/L NO_3 Winter: 3.77 mg/L NO_3

The results in Table 23 show that the lowest nitrate concentrations were found in summer and the highest in winter as has been shown in other freshwater systems (Barica 1990). During summer, nitrate in surface waters is often taken up by algae and macrophytes and converted to organic nitrogen, whereas during the late winter and early spring, nitrate is not taken up by algae and macrophytes and so constitutes a larger proportion of the total nitrogen load. Interestingly these nitrate results are the inverse of the seasonal patterns in total P concentrations (Figures 29 & 30).

The most distinct seasonal differences in nitrate concentrations occurred on sites WW-6, MP1, MP3 and WW-NA. Overall, spring and summer nitrate means were lower than fall and winter means across sites in the watershed. These seasonal nitrate reductions have occurred despite chronic N deposition and the presence of many maturing forest stands within the watershed (Goodale et al. 2003). The presence of ponded areas and wetland complexes along the Skug River, coupled with the relatively shallow depth of most of the surface waters in the watershed, represent conditions where (1) water residence time is sufficient to allow NO3 to diffuse into benthic sediments, (2) anoxic conditions are more likely to occur, and (3) dentrification potential is high. The dissolved oxygen results presented in Table 21 show that the lowest oxygen saturation levels along the Skug River occurred in the headwater wetlands (WW1) and along the lower Skug River (WW5 and WW6).

The reference watershed J (site WW-4) showed some of the lowest overall nitrate levels. This may be in part, due to the sequence of ponds through which the surface water flows (Delano → Brackett → Fields) resulting in sequential denitrification and/or due to the presence of large extent of coniferous forests, which has been shown to retain nitrate even during baseflow conditions (Jones and Mulholland 2000, Mulholland et al. 2000).

Table 23. A seasonal comparison of nitrate levels at the 13 sample sites during the 2005-06 study. Means, medians, standard errors (SE), coefficient of variations (CV), minimum (Min) and maximum (Max) values are shown.

Site	Season	Mean	SE	CV	Min	Median	Max	
WW1	Spring	**0.19**	0.069	83.26	0.02	0.25	0.34	
	Summer	**0.72**	0.425	145.42	0.02	0.07	2.13	
	Fall	**1.46**	0.824	97.57	0.34	0.98	3.07	
	Winter	**0.72**	0.344	95.47	0.02	0.73	1.41	Wetland Sites
WW-NB	Spring	**3.71**	1.710	103.18	0.13	2.12	8.36	
	Summer	**0.33**	0.236	173.08	0.02	0.09	1.49	
	Fall	**1.07**	0.093	15.04	0.94	1.02	1.25	
	Winter	**4.21**	1.650	78.51	1.92	2.93	9.04	
WW2	Spring	**1.62**	0.432	59.63	0.85	1.27	3.21	
	Summer	**1.89**	0.467	60.60	0.75	1.65	3.53	
	Fall	**2.85**	0.122	7.40	2.67	2.79	3.08	
	Winter	**2.97**	0.398	26.82	2.15	2.88	3.96	
WW3	Spring	**0.92**	0.105	25.43	0.70	0.91	1.27	
	Summer	**1.84**	0.721	95.84	0.69	1.11	5.32	
	Fall	**1.04**	0.376	62.70	0.42	0.98	1.72	
	Winter	**2.36**	0.197	16.66	0.96	2.30	2.89	
WW4	Spring	**0.27**	0.115	95.77	0.02	0.14	0.56	
	Summer	**0.05**	0.025	116.40	0.02	0.02	0.17	
	Fall	**0.49**	0.350	123.73	0.13	0.15	1.19	
	Winter	**0.86**	0.319	73.95	0.26	0.72	1.76	
WW5	Spring	**1.85**	0.278	33.54	1.16	1.84	2.84	
	Summer	**2.13**	0.215	24.71	1.65	1.92	2.98	
	Fall	**2.32**	0.301	22.46	1.98	2.06	2.92	
	Winter	**2.73**	0.127	9.33	2.43	2.74	3.00	
WW6	Spring	**1.67**	0.339	45.36	0.94	1.71	2.81	
	Summer	**0.59**	0.259	107.04	0.02	0.39	1.77	Upstream Tributary Sites
	Fall	**1.13**	0.313	48.14	0.54	1.23	1.61	
	Winter	**2.42**	0.118	9.78	2.12	2.45	2.67	
WW-NA	Spring	**2.39**	0.648	60.73	0.74	2.57	4.32	
	Summer	**2.63**	0.849	78.98	1.31	1.94	6.80	
	Fall	**5.96**	0.947	27.52	4.29	6.03	7.57	
	Winter	**6.30**	0.428	13.58	5.46	6.18	7.37	
WW-NC	Spring	**0.65**	0.442	152.95	0.02	0.02	2.28	
	Summer	**0.23**	0.148	155.01	0.02	0.04	0.92	
	Fall	**0.95**	0.156	28.55	0.67	0.96	1.21	
	Winter	**1.55**	0.428	55.11	0.68	1.42	2.69	
WW-ND	Spring	**6.47**	1.061	36.57	3.25	6.83	9.65	
	Summer	**2.74**	1.162	103.40	0.37	1.24	6.52	
	Fall	**5.83**	3.980	118.22	1.58	2.13	13.79	
	Winter	**6.45**	2.003	62.06	3.29	5.18	12.16	
WW-NE	Spring	**9.19**	1.286	31.04	6.16	9.47	13.45	
	Summer	**7.88**	0.736	22.87	4.60	8.10	10.00	
	Fall	**7.32**	1.294	30.42	5.13	7.24	9.58	
	Winter	**12.01**	2.657	44.17	6.58	1.65	18.15	
MP1	Spring	**1.09**	0.382	78.42	0.13	0.85	2.36	
	Summer	**0.06**	0.016	62.10	0.02	0.07	0.11	
	Fall	**1.15**	0.513	77.44	0.22	1.23	1.99	
	Winter	**3.11**	0.584	37.53	2.01	2.85	4.75	In-Pond Sampling Sites
MP3	Spring	**0.93**	0.306	73.84	0.190	0.58	1.80	
	Summer	**0.07**	0.025	88.49	0.02	0.06	0.17	
	Fall	**0.71**	0.330	80.05	0.07	0.91	1.16	
	Winter	**3.39**	0.713	42.08	2.04	3.06	5.40	

The IEP Study (1977) reported mean nitrate concentrations in Martins Pond ranging from undetectable to 0.4 mg/L. The 1985 D/F Study (Anderson-Nichols and Lycott 1985) reported nitrate levels from undetectable to 1.5 mg/L in Martins Pond. The same study reported Skug River concentrations up to 4.63 mg/L. Overall, the 1985 D/F Study reported mean in-pond nitrate concentrations of 0.05 mg/L and 0.34 mg/L at the Pond outlet at Burroughs Road. In the current study, the mean concentration at the pond inlet (MP-1) was 1.21 mg/L and 1.15 mg/L at the Pond outlet (MP-3). Thus, there is some evidence that nitrate levels have increased over the 20-30 year period between studies.

5.14 – Total Nitrogen Levels in Surface Waters in the Martins Pond Watershed

Total nitrogen (Total N) is a measure of all forms of nitrogen in a sample, including the sum of nitrate, nitrite, different forms of ammonia N and organic nitrogen. Total N thus represents all the various forms and pools of organic and inorganic N present in any given water sample. Nurnberg (1996) categorized summer epilimnetic total N concentrations of < 0.35 mg/L as reflective of oligotrophic conditions, between 0.35 and 0.65 mg/L as mesotrophic, between 0.651 and 1.20 mg/L as eutrophic and > 1.20 mg/L as hypereutrophic.

Total nitrogen levels were monitored for the current study in 2005-06. The results are presented in Table 24. The total N levels observed in the watershed varied across a relatively large range (0.41 to 21.68 mg/L; corresponding to 6.61 μM to 349.65 μM) both spatially and temporally. Overall, the values found in the current study are consistent with other studies conducted in northeastern Massachusetts. The total N levels in the 2005-06 study were generally in the range of those reported within the larger Ipswich River watershed; Williams et al. (2005) reported a mean total N concentration of 60.8 μM (3.77 mg/L) across the Ipswich River basin in 2000-01.

Overall, the highest total N levels across the different subwatersheds occurred at various times of year. The mean subwatershed total N values shown at the bottom of Table 24 indicated that the highest means were at sample site WW5 along the Skug River and that three of the four tributaries had similarly high means (WWNA, WWND, WWNE). The coefficient of variation for all samples sites was relatively high except for WWNC (range 51.1 to 112.6) indicating high levels of variability across all sites. The two wetland site, WW-1 and WW-NB, exhibited very low and high total N-levels, respectively.

The IEP Study (1977) reported summer 1976 total Kjeldahl-Nitrogen levels of 0.47 mg/L at their Route 28 site (WW-6), 0.44 mg/L at the inlet (MP-1), 1.10 mg/L at an in-pond station and 3.8 mg/L at the Martins Pond outlet (MP-3). The Martin Pond values are not substantially different than the yearly means found in the 2005-06 monitoring. The concentrations at the WW-6 site, however, were substantially higher in the current study (yearly mean 2.4 mg/L) that found in the IEP Study.

Table 24. A comparison of Total N values across sample sites and dates. Sites with an * denote samples where total N could not be analyzed. Sample dates with total N values > 1.20 mg/L are noted in yellow corresponding to Nurnberg's (1996) hypereutrophic category.

	SAMPLING SITES												
Date	**MP1**	**MP3**	**WW6**	**WW5**	**WW4**	**WW3**	**WW2**	**WW1**	**WW-NA**	**WW-NB**	**WW-NC**	**WW-ND**	**WW-NE**
All Values are in mg/L													
3/7/2005	*	3.360	3.240	2.140	2.250	3.170	2.510	1.290	14.800	*	*	16.400	*
4/14/2005	*	5.120	*	*	*	3.780	*	*	*	*	*	2.250	*
5/10/2005	*	3.740	*	3.430	4.230	0.570	*	1.340	6.910	3.980	1.580	11.720	23.420
6/2/2005	1.930	*	1.650	2.270	*	2.330	1.950	1.380	12.700	14.590	1.510	9.810	*
6/24/2005	0.580	0.390	3.510	14.610	1.890	*	*	0.390	*		*	*	*
7/13/2005	*	0.730	2.670	21.680	0.710	3.080	2.780	0.750	4.660	7.600	*	3.680	2.290
7/26/2005	*	0.950	0.470	3.670	*	0.680	6.390	0.770	4.100	1.630	*	2.450	10.690
8/9/2005	*	10.600	*	*	*	*	*	*	7.340	1.140	*	2.360	*
8/23/2005	0.380	3.030	2.640	9.860	0.820	16.220	*	*	*	*	*	13.170	*
9/14/2005	0.680	0.410	1.760	25.470	0.610	*	8.710	1.620	*	*	*	*	*
9/28/2005	0.680	1.120	0.670	9.110	5.540	1.850	*	0.560	1.690	*	*	15.300	14.690
10/14/2005	*	2.130	*	*	*	*	*	1.123	*	*	*	*	*
11/4/2005	*	1.265	4.473	*	*	0.993	*	*	8.49	0.720	*	*	1.265
12/22/2005	*	3.576	2.755	2.093	*	5.474	*	*	5.281	2.611	*	*	3.576
1/12/2006	*	*	*	*	*	*	*	*	*		*	*	
2/8/2006	*	6.912	0.728	6.215	1.646	4.924	2.652	0.492	6.309	13.375	*	14.140	6.304
2/23/2006	*	*	*	*	*	*	*	*	*	*	*	*	*
3/21/2006	2.839	1.812	4.191	2.383	1.143	1.972	*	0.252	9.386	0.768	*	*	1.812
Mean mg/L	**1.182**	**3.010**	**2.396**	**8.580**	**2.093**	**3.750**	**4.17**	**0.906**	**7.420**	**5.16**	**1.545**	**9.130**	**8.01**
[1] **SE**	0.401	0.724	0.391	2.320	0.569	1.220	1.120	0.140	1.150	1.82	0.035	1.850	2.770
[2] **CV**	83.1	93.2	56.5	93.9	81.6	112.6	65.7	51.1	51.3	105.7	3.2	64.0	97.7

[1] SE = Standard Error
[2] CV = Coefficient of Variation

5.15 – Nitrogen:Phosphorus (N:P) Ratios in the Martins Pond Watershed

The ratio of N:P has important implications for the productivity and eutrophication of surface waters. Dodds (2003) noted that total N and total P are the best values to use for indication of trophic status and nutrient limitation rather than dissolved inorganic N and soluble reactive P. In freshwater systems, algal growth (phytoplankton) requires both N and P in an approximate molar ratio of 16:1 to 23:1, also known as the Redfield ratio (Wetzel 2001). N or P limitation in an aquatic system is considered to occur when the availability of N relative to P is well below or above this ratio, respectively (Howarth 1988). In general, if the N:P ratio ~ > 16-23, there is a possibility that P may be limiting. If the N:P ratio < 16-23, then N may be limiting. Generally, water bodies with short residence times, including ponds and streams (and Martins Pond), generally exhibit N:P ratios < 26 (Hecky et al. 1993). The 1985 D/F Study (Anderson-Nichols and Lycott 1985) reported N:P ratios in the range of 39.0 to 63.5, indicating P limitation. Interestingly, the report also mentioned the possibility that conditions could exist in Martins Pond where N was limiting.

The N:P molar ratios found at the sample sites in the current study are presented in Table 25. In looking at the Martins Pond inlet (MP1) and outlet (MP3) results, an interesting pattern emerges. During most of the winter and spring, the N:P ratios were all well over 30:1 (in some cases an order of magnitude higher) indicating the potential for P limitation in Martins Pond. However, during the summer and early fall sampling dates (June through September), with the exception of 8 August 2005, the N:P ratios were less than 16:1, indicating the potential for N limitation. Thus, based on the N:P ratios observed in the current study, it appears that Martins Pond may be shifting from P limiting conditions to N limiting conditions over the course of the year. The observed seasonal patterns of total P (Figures 29 and 30) and total N concentrations (Table 24) reflect complex seasonal dynamic of P and N sources and sinks. Similar seasonal patterns in N:P ratios have been observed in other shallow, eutrophic systems (Barica 1990; Matthews et al. 2002). This point will be discussed further in the nitrogen and phosphorus budget discussion (Sections 7 and 8).

Some of the Skug River sample sites exhibited similar N:P ratio seasonal changes as those observed in Martins Pond, namely sample sites WW6, WW3 and WWNB. Other sites in the watershed exhibited N:P ratios substantially different from Martins Pond. Sites WW5, WW4 (the reference watershed) and Skug River tributary sites WWND and WWNE had consistently high N:P ratios indicating likely P limitation. Water quality in the reference watershed (WW4) was indicative of P limitation conditions over most of the sample dates. This shows that at least one pond in the watershed (Fields Pond) had N and P levels that were more typical of the ecoregion.

Table 25. A summary of N:P molar ratio results for all sample sites over the 2005-06 study period. Ratios that exceed 30:1 are noted in red and ratios that are less than 16:1 are noted in green indicating potential P and N limitations, respectively. N:P ratios between 16:1 and 30:1 are shown in yellow. Molar ratios were calculated by dividing the observed concentration values (mg/L) by the formula weights of $N\text{-}NO_3$ and $P\text{-}PO_4$ and then dividing molar N by molar P values. Sample sites and dates where a ratio could not be calculate are denoted by an *.

	Sampling Sites												
	MP1	MP3	WW6	WW5	WW4	WW3	WW2	WW1	WW-NA	WW-NB	WW-NC	WW-ND	WW-NE
	Molar N:P Ratios												
3/7/2005	*	93.2	77.1	71.3	160.6	132.0	62.7	25.8	2464.4	*	*	*	*
4/14/2005	*	111.2	*	*	*	85.8	*	*	*	*	*	28.8	*
5/10/2005	*	169.8	*	74.5	422.6	12.4	*	17.6	43.1	90.4	21.9	292.7	2339.8
6/2/2005	10.4	*	17.2	25.8	*	21.2	9.7	6.7	67.5	112.1	13.5	94.2	
6/28/2005	4.0	3.8	21.6	78.5	36.3	*	*	*	*	*	*	*	*
7/13/2005	*	5.9	16.3	190.0	11.1	54.9	14.0	2.1	24.0	14.7	*	18.8	25.4
7/26/2005	*	5.6	2.2	15.9	*	28.3	19.2	2.0	*	6.6	*		184.1
8/9/2005	*	58.8	*	*	*	*	*	*	45.3	5.5	*	36.8	*
8/19/2005	2.3	11.0	40.0	109.5	29.3	114.1	*	*	*	*	*	156.6	*
9/14/2005	3.7	2.3	33.8	295.9	101.6		28.8	4.2	*	*	*	*	*
9/28/2005	3.7	6.2	9.8	94.8	1383.7	2.3		1.1	10.2	*	*	169.8	3669.1
10/18/2005	*	46.3	*	*	*	*	*	2.7	*	*	*	*	*
11/4/2005	*	13.2	65.7	*	*	22.5	*	*	108.7	8.0	*	*	126.4
12/22/2005	*	61.6	49.2	3.6	*	52.6	*	*	101.5	22.9	*	*	198.5
1/8/2006	*	*	*	*	*	*	*	*	*	*	*	*	*
2/8/2006	*	345.3	36.4	77.6	63.2	3.2	10.8	4.6	262.6	477.2	*	642.1	242.2
3/21/2006	94.5	50.3	99.7	79.4	81.6	82.1	*	5.0	180.3	21.3	*		64.7

It is important to note that total P levels, although high relative to other regional watersheds, need to be evaluated relative to the N:P ratio. High total P levels do not always translate into N limitation or *vice versa*. Either nutrient may be limiting given the changing dynamics of the N:P ratio in the surface waters analyzed in this study. To test if algal growth were N or P limited, two nutrient limitation bioassays were conducted in June and September 2006 using raw water samples from Martins Pond. The methods and results of those bioassays are presented in Section 5.16.

5.16 - Nutrient Limitation Bioassays

To determine if nitrogen or phosphorus were the nutrient(s) limiting algal growth in Martins Pond during the summer and fall, two seasonal bioassay experiments were run. Companion laboratory and field assays were conducted. The results presented here are based on the laboratory assays and the laboratory results. There was some difficulty in maintaining *in situ* bioassay containers at the Martins Pond site due to problems with wave action disturbance, vandalism and other damage to the bioassay apparatus.

In the laboratory assays, 800 ml, clear polyethylene containers were used to monitor algal growth responses to nitrogen and phosphorus additions as well as light level. A basic experimental design was employed where controls were given no additional N or P additions and a sequential increase of N and P, respectively, in a series of replicates was employed. The basic set-up is outlined in Table 26. The nutrient addition levels chosen in both the N and P treatments reflect a range in total P and total N values that were likely to be encountered in Martins Pond during the course of a given year.

Table 26. Experimental design of nutrient bioassay experiments.

Experimental Design of Bioassay Study				
N Treatments	N Addition NH_4NO_3 mg/L N	P Treatments	P Addition K_2HPO_4 mg/L P	Bioassay Dates 2006
Full Light Conditions				
Nutrient Control	0.0	Nutrient Control	0.00	June, October
Nitrogen-A	1.0	Phosphorus-A	0.01	June, October
Nitrogen-B	2.0	Phosphorus-B	0.02	June, October
Nitrogen-C	5.0	Phosphorus-C	0.03	June, October
Nitrogen-D	10	Phosphorus-D	0.05	June, October
30% Light Reduction				
Nutrient Control	0.0	Nutrient Control	0.00	June, October
Nitrogen-A	1.0	Phosphorus-A	0.01	June, October
Nitrogen-B	2.0	Phosphorus-B	0.02	June, October
Nitrogen-C	5.0	Phosphorus-C	0.03	June, October
Nitrogen-D	10	Phosphorus-D	0.05	June, October

Raw water samples were collected directly from Martins Pond. A 30 L Nalgene Carboy was filled with water and transported to the Merrimack College Campus. The assay was conducted in the climate-controlled, Merrimack College greenhouse. The raw pond water was filtered through a sterilized cheesecloth to remove any larger-sized particles and/or organic debris in the water. The water was then mixed and distributed to the 800 ml assay containers. Prior to any nutrient additions, all assay containers were analyzed for chlorophyll-a, dissolved oxygen, temperature, conductivity and pH using a YSI 6820ES Multi-Parameter Probe. Total P was also measured in all containers at the start of the bioassay.

The various treatments were added by pipetting appropriate volumes of each nutrient level solution into the assay containers. Two sets of controls were used, neither received any nutrient additions. The 'light control' was placed with the set of N and P addition assay containers on a bench under 9-hour per day growth lamps. The light intensity (photosynthetically active radiation – PAR) under the grow lights was some 600 µmol cm^{-1}. A low-light control group was also established that received ambient sunlight under a 30% shade cloth to better mimic light conditions in Martins Pond (~400 µmol cm^{-1}). Samples were placed in the greenhouse for a total of 8 days and the chlorophyll-a concentration in each assay container were measured each day during the 8 day period to track any algal growth responses. Three replicates were used for each treatment.

Total P and Total N concentrations at the start of the bioassays were as follows:

	Total P	Total N
June:	0.035 mg/L	0.726
October:	0.044 mg/L	0.689

Nutrient Bioassay Results

The chlorophyll-a results from the June bioassays are shown in Figure 32. The October assay results are note shown but they closely follow the results shown in Figure 32. Clearly, both light and N were limiting growth in each of the assays (June and October). The controls in the full-light N treatments (A) and P treatments (B) both showed increases over the 8 day period. There was clearly a more significant algal growth response to N relative to P. Similar results were found in the 30% light reduction treatments (C and D). The algae still responded to the N additions but to a lesser extent than the full light treatment indicating a clear light limitation in addition to the N limitation.

Overall, these results support the contention that at certain times of year, N is limiting algal growth in Martins Pond. Following the bioassays, water samples from each treatment were observed under the microscope to identify the relative proportions of diatoms, Chlorophyta or Cyanophyta. In the case of the June bioassay, green algae dominated the algal communities in the bioassay jars. In October, diatoms dominated the algal communities.

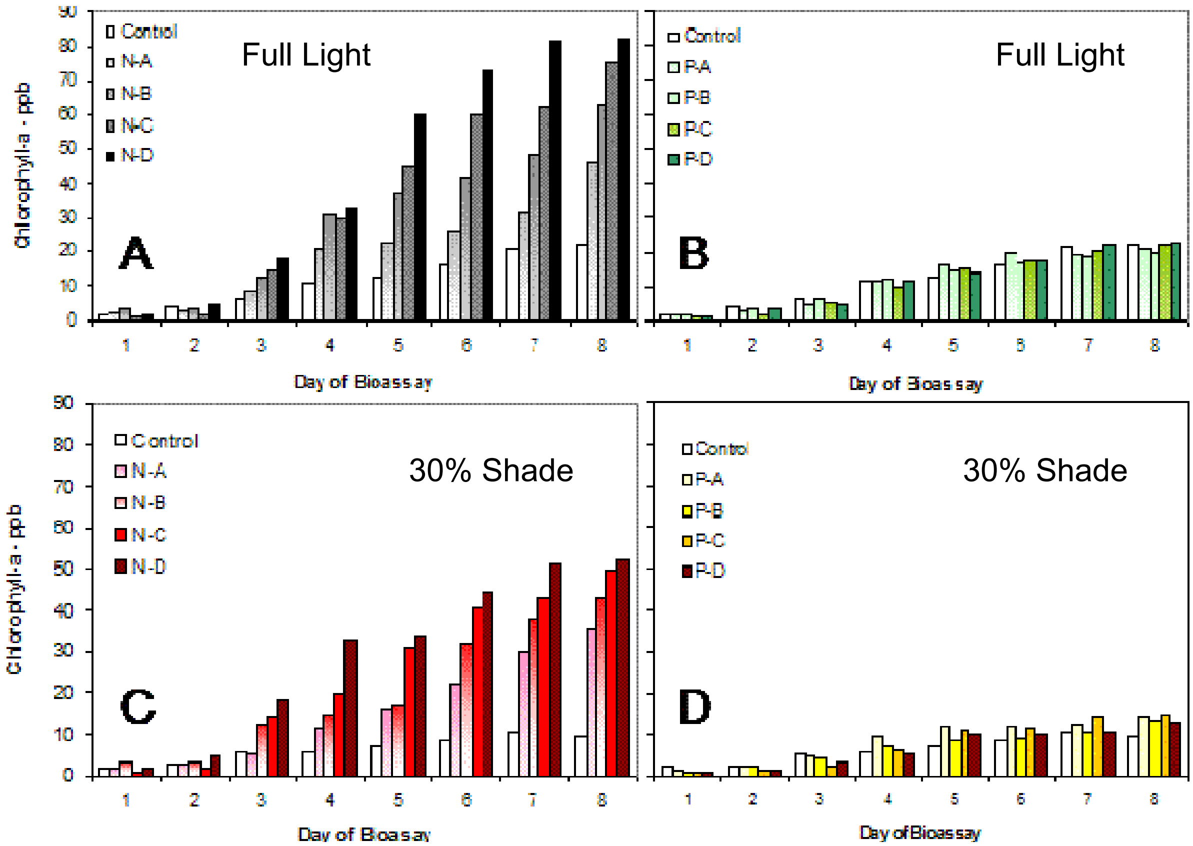

Figure 32. A comparison of chlorophyll-a concentration change over the 8-day nutrient bioassay period. Graph **A** represents the 9 hr day-1 full light treatment with N treatments and **B** shows results for P treatments; **C** shows the ambient light conditions under a 30% shade cloth with N treatments and **D** shows results for P treatments. Overall, both light and Nitrogen were limiting algal growth (as represented by chlorophyll-a concentrations). All graphs are shown on the same Y-axis scale for comparison. Mean values are plotted based on 3 replicates per treatment.

5.17 - Water Quality Chemistry Data Summary and Comparison

To put all the water quality results for Martins Pond in a regional context, Table 27 was created to summarize many of the water quality parameters analyzed in this study relative to published regional water quality summary data. Table 27 shows median parameter values from three regional studies/data compilations (Brakke et al. 1998; Mattson et al. 1992; Rohm et al. 1995; ENSR 2000). The median results for both Martins Pond and Fields Pond are also shown. Fields Pond was included because it is the main outlet of the reference watershed in this study (J) and provides somewhat of a reference condition for evaluating the eutrophic status and conditions in Martins Pond.

Based on the results and relative comparisons in Table 27, the use of Fields Pond as a reference watershed is justified. Fields Pond, overall, arguably has much higher water quality and exhibited parameter values closer to regional medians, than Martins Pond. This is not all together surprising given the recent origin of Fields Pond in the 1930s and the fact that it is found in the least developed sub-basin in the Martins Pond watershed.

Given the summary of yearly median results presented in Table 27, Martins Pond should be considered somewhat atypical with respect to the physical, abiotic and biotic conditions found in this geographic region of New England. The median values for Martins Pond exceeded all the median parameter values published by the three studies, save for Secchi depth which was lower than the regional medians. Fields Pond is more representative of the region and thus its usage as a reference watershed for the study would appear to be justified.

Table 27. A summary of median water quality parameter comparisons between regional summary studies and Martins and Field Ponds.

	Regional Summary Study				
	Brakke et al. 1988	Mattson et al. 1992	ENSR 2000		
	Southern New England	Boston Region	North Eastern Coastal Zone	Martins Pond [1]	Fields Pond [1]
Parameter	**Median**	**Median**	**Median**	**Median**	**Median**
Color PCU	24	29	-	50	20
Turbidity NTU	0.90	-	-	2.80	0.96
Secchi Depth m	1.6	-	2.34	1.1	1.6
Conductivity µs/cm	81.5	-	-	297.5	248.5
pH	-	6.73	-	6.73	6.66
Cl ueq/L	382	633	-	1216	1044
Fe µg/L	84	250	-	508	271
Mn µg/L	19	30	-	91	71
SO_4 µg/L	141	224	-	508	374
NO_3 mg/L	0.80	-	-	0.67	0.15
Total P mg/L	-	0.008	0.014	0.045	0.014
Total N mg/L	-	-	447.8		
Chloro-a µg/L	-	-	4.06	8.15	2.30

[1] Based on yearly median values from samples collected from March 2005 to March 2006.

Section 6 - Hydrological Modeling and Hydraulics *(Scope of Services 1.d)*

The charge under the Scope of Services was to create a yearly phosphorus, nitrogen and hydrologic water budget. We have used the EPA Storm Water Management Model (SWMM) for our hydrological modeling and to support the development of nutrient budgets. SWMM is a dynamic rainfall-runoff simulation model used for single event or long-term (continuous) simulation of runoff quantity and quality. The runoff component of SWMM operates on a collection of subcatchment areas that receive precipitation and generate runoff and pollutant loads. The routing portion of SWMM transports this runoff through a system of conduits, pipes, channels, storage/treatment devices, pumps, and regulators. SWMM tracks the quantity and quality of runoff generated within each subcatchment, and the flow rate, depth, and quality of water in conduit during a simulation period comprised of multiple time steps (James et al. 2005).

SWMM accounts for various hydrologic processes that produce runoff, including rainfall, evaporation of standing surface water, rainfall interception from depression storage, infiltration of rainfall into unsaturated soil layers, percolation of infiltrated water into groundwater layers and interflow between groundwater and the drainage system. Spatial variability in all of these processes is achieved by dividing a study area into a collection of smaller, homogeneous subcatchment areas, each containing its own fraction of pervious and impervious sub-areas. Overland flow can be routed between sub-areas, between subcatchments, or between entry points of a drainage system.

In order to both assess the quantity and dynamics of water flow through the Martins Pond watershed, hydrological and hydraulic modeling using SWMM and PCSWMM were used in this study. The objectives in conducting this modeling were threefold:

(1) get a better understanding of water flow through the different subwatersheds in the Martins Pond watershed

(2) Develop the model via calibration and validation so that gauge-discharge relationships could be used for future studies

(3) To assist in the development of nutrient budgeting for the entire Martins Pond watershed