The Impact of Septic Effluent on Groundwater Quality, Buttermilk Bay Drainage Basin, Massachusetts

PART II: NUTRIENTS



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Submitted to: The Buzzards Bay Project U.S. Environmental Protection Agency, Region I Massachusetts Executive Office of Environmental Affairs

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by

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### ABSTRACT

#### Part II: Nutrients

Buttermilk Bay, located at the head of Buzzards Bay in Bourne and Wareham, Massachusetts, has an unsewered watershed underlain by highly permeable sand and gravel deposits. Several of the most densely populated areas in the watershed are near the shore; septic systems are suspected to be a major source of the dissolved nitrogen and phosphorus now causing eutrophication in the bay. The present study was undertaken to assess the impact of septic systems on nutrient concentrations in the aquifer underlying Indian Heights, one of the densely populated sub-basins of the watershed.

Background dissolved inorganic nitrogen (DIN) and phosphatephosphorus ( $PO_4$ -P) concentrations beneath the pristine, upgradient portion of the sub-basin were quite low (about 1.9 and 0.75 uM, respectively). The mean DIN and phosphate concentrations of septic effluent discharged to the sub-basin were 2640 uM and 165 uM, respectively.

Nutrient levels and specific conductance in groundwater downgradient of the neighborhood cannot be explained by simple dispersive mixing of effluent with upgradient groundwater. Rather, we estimate that over 99% of the effluent-PO<sub>4</sub> and between 2 and 26% of the effluent-DIN is removed from solution during transport to the downgradient end of the sub-basin. Most of the phosphate removal, and probably much of the DIN removal takes place in the first few meters of transport from septic systems. To the extent that primary production in the fresh and marine waters of the Cape Cod/Buzzards Bay region is P-limited, septic systems contribute little to eutrophication. To the extent that these waters are N-limited, septic systems are probably a major contributor to eutrophication.

# TABLE OF CONTENTS

Ac	knowledgments	, i					
AJ	Abstract						
Ta	ble of Contents	111					
Li	t of Figures	iv					
Li	t of Tables	v					
1.	NTRODUCTION	1					
2.	THE STUDY AREA	1					
	2.1 Regional Setting 2.2 Buttermilk Bay and the Indian Heights Sub-basin						
	L.E. Dutter mirk bay and the indian heights Sub-basin						
з.	METHODS:	3					
	3.1 Effluent and Onsite Groundwater Sampling						
	3.2 Offsite Groundwater Sampling						
4.	SUB-BASIN HYDROGEOLOGY	5					
	4.1 Geology						
	4.2 Groundwater Hydrology						
5	RESULTS AND DISCUSSION FEEL HENT AND ONSITE GROUNDWATER	11					
0.	51 Discolved Inorganic Nitrogen (DIN)	<b>T</b> T					
	5.2 Phosphate_Phosphorus (POP)						
	5.2 Discussion						
	5.5 DISCUSSION						
6.	RESULTS: OFFSITE GROUNDWATER	17					
	6.1 Water Table Observation Wells						
	6.2 Multilevel Samplers						
7.	DISCUSSION: NUTRIENT REMOVAL DURING TRANSPORT	21					
	7.1 Estimated Removals						
	7.2 Comparison with Other Studies						
	7.3 Phosphate Removal Processes						
	7.4 Nitrogen Removal Processes						
٩	CONCLUSIONS	25					
0.	J. COROLOSIONS						
9.	). REFERENCES CITED						

# LIST OF FIGURES

1.	The location a	nd regional	geologic	setting	of	the
	Buttermilk Bay	drainage ba	asin.			

- 2. The Indian Heights sub-basin.
- 3a. Observation well and sampler locations, Indian Heights sub-basin (northern portion).
- 3b. Schematic geologic cross section, Indian Heights sub-basin.
- 3c. Land use/land cover, and mean water table elevations (November 1986-January 1988), Indian Heights sub-basin.
- 4. Lithologic log, observation well IH-1.
- 5. Grain size frequency curves, samples A-H, well IH-1.
- Water table elevations, Indian Heights, November 1986-January 1988 (meters above mean sea level).
- Box-plot of DIN concentrations, all effluent and onsite groundwater samples.
- Mean DIN concentrations, effluent and onsite groundwater samples, Sites 1-4.
- Box-plot of PO<sub>4</sub>-P concentrations, all effluent and onsite groundwater samples
- Mean PO<sub>4</sub>-P concentrations, effluent and onsite groundwater samples, Sites 1-4.
- 11. N:P ratio versus mean infiltration distance, Sites 1-4.
- 12. NOx/DIN versus mean infiltration distance, Sites 1-4.
- Frequency distribution of DIN concentrations, non-background multi-level groundwater samples.
- 14. Mean DIN concentrations, effluent, onsite groundwater, and multilevel groundwater samples (+/- the Standard Error of the Mean).

# LIST OF TABLES

 Specific conductance and nutrient data, water table observation wells.

#### 1. INTRODUCTION

Buttermilk Bay, located at the head of Buzzards Bay in southeast Massachusetts (Figure 1), has a history of water quality problems (Buchsbaum, 1988). The bay is eutrophic, or nutrient-enriched, and since 1984 shellfishing has been periodically restricted due to the bacterial contamination of its waters (Heufelder, 1987; Valiela and Costa, 1988). Up to 90% of the fresh water influx to Buttermilk Bay is derived from groundwater, either via direct discharge or from the baseflow of major tributary streams (Williams and Tasker, 1974; Moog, 1987). It is vital, therefore, to consider the possible role of groundwater-borne contaminants when assessing the present and future water quality status of Buttermilk Bay.

Because the drainage basin of the bay is presently unsewered, domestic septic systems have been suspected to be a major contaminant source to both the groundwater system and the bay itself (Heufelder, 1987; Valiela and Costa, 1988). The pupose of this study is to test this hypothesis, particularly with regard to the groundwater system. In Part I of this study, the microbial impact of septic effluent was assessed. In the present report (Part II), we assess the nutrient impact of septic effluent on the groundwater of the basin. Dissolved inorganic nitrogen (DIN) and dissolved phosphate-phosphorus  $(PO_{\mu}-P)$  were determined in septic effluent samples from the basin, "onsite" groundwater samples (collected concurrently with the microbial samples described in Part I), and "offsite" samples from monitoring wells and sampling devices installed in the Indian Heights sub-basin on the western shore of Buttermilk Bay.

# 2. THE STUDY AREA

#### 2.1 Regional Setting:

The study area is located in southeast Massachusetts, at the southern end of the Wareham Outwash Plain (Figure 1). The plain was deposited by braided, meltwater streams during the retreat of the Buzzards Bay and Cape Cod Bay lobes of the Laurentide Ice Sheet, ca. 14,000 yrs. B.P. (Larson, 1982; Stone and Peper, 1982). The plain consists of fine to coarse sands derived from glacial erosion of the underlying granite of Proterozoic age (Williams and Tasker, 1974). Silt and clay lenses of variable size are distributed throughout the deposit. The aquifer formed by these unconsolidated sands (the Plymouth-Carver Aquifer) has an



Figure 1. The location and regional geologic setting of the Buttermilk Bay drainage basin (after Larson, 1982).

2

average saturated thickness of about 30 meters and total storage of about 1.9 billion m<sup>3</sup>. The recharge rate is approximately 50 cm/yr (Williams and Tasker, 1974; Hansen and Lapham, in press).

# 2.2 Buttermilk Bay and the Indian Heights Sub-basin:

Buttermilk Bay, located at the head of Buzzards Bay, occupies a pair of kettles (ice block depressions) which were drowned by rising sea level subsequent to deglaciation (Figure 1). The shoreline of the bay is characterized by steep slopes of probable ice-contact origin, many of which terminate in narrow, fringing salt marshes.

Located on the western shore of Buttermilk Bay in East Wareham (Figure 2), the Indian Heights sub-basin is a highdensity residential area. The sub-basin supports 493 houses and mobile homes on a developed area of 53.2 hectares; mean housing density is 9.2 houses/hectare (3.7 per acre). The neighborhood is served by a public water supply and private septic systems. The northwest portion of the sub-basin (extending upgradient of the neighborhood to the groundwater divide) is overlain by a pristine area of pine/oak forest. The shoreline of the sub-basin is underlain by a narrow, "fringing" salt marsh which has been artificially filled with sand and gravel over most of its 1 km length (A. Sarkisian, personal communication, 1987).

# 3. METHODS:

#### 3.1 Effluent and Onsite Groundwater Sampling

Samples of septic effluent and onsite groundwater were collected concurrently with indicator bacteria samples, according to the protocol described in Part I of this report (pp. 11-13). The specific conductance of all samples was determined in the field with a YSI Model 30 S-C-T meters. All samples were stored in acid washed, 200 ml plastic bottles at 4 degrees C; all analyses were performed at the Woods Hole Oceanographic Institution. All samples were filtered (0.45 um Millipore) prior to analysis. Ammonium and phosphate analyses (U.S. EPA, 1979; Methods 350.1 and 365.1) were performed within 6 hours of collection, after which samples were frozen. Nitrate + nitrite (NO<sub>X</sub>) analyses (U.S. EPA, 1979, Method 353.2) were performed on thawed samples within one week.



Figure 2. Buttermilk Bay and the Indian Heights sub-basin. The position of the groundwater divide is approximate, and based on the regional data of Moog (1987) and Hansen and Lapham (in press).

### 3.2 Offsite groundwater sampling

"Offsite" samples were obtained from 5.1 cm (2") water table observation wells installed throughout the Indian Heights subbasin, and from multilevel samplers installed downgradient of all houses, but upgradient of the filled marsh sediments at the edge of Buttermilk Bay (Figure 3a). The wells and samplers were sited so as to avoid, as much as possible, the effects of individual septic system plumes. The 5.1 cm wells were installed according to standard solid stem and hollow stem auger drilling methods. Well screens were 3.3 m in length (except for a 6.2 m screen at IH-1), and were installed so as to straddle the mean water table position.

Three pairs of multilevel samplers were installed. Originally designed for use in large scale natural gradient tracer tests (Pickens et al., 1981; LeBlanc et al., 1987), the samplers were constructed of 3.8 cm I.D. PVC casing, 0.6 cm polyethylene tubing, and nylon mesh screen. The vertical spacing between ports was 25 cm. Samplers (or sampler pairs) had up to 24 ports each. A hollow stem auger drilling rig was used to advance each borehole to the required depth (which ranged from 6 m to 12 m below the water table, or approximately 5 to 11 meters below mean sea level). Each sampler was then lowered in 3.3 m sections down the 12.5 cm annular space afforded by the augers. Subsequent withdrawal of the augers allowed the saturated portion of the formation to collapse around the sampler casing and ports..

Groundwater samples (60 ml) were drawn with a peristaltic pump after purging three bore volumes (approximately 150 ml, depending upon the depth of the port). Samples were collected on four dates between June 1988 and July 1989. Sample storage and nutrient analysis methods were identical to those described above.

## 4. RESULTS AND DISCUSSION: SUB-BASIN HYDROGEOLOGY

#### 4.1 Geology:

Medium-to-coarse sands comprise the bulk of the stratigraphic section at all drilling sites. Split spoon samples collected from boring IH-1 at 1.5 m depth intervals show a moderate degree of stratification, with sample median grain sizes ranging from 0.190 to 0.785 mm (Figures 4 and 5). Sorting was found to be typical of fluvial sands, and ranged



Figure 3a. Observation well and sampler locations. • observation well. • multi-level sampling site. Section line is keyed to Figure 3b.

6



Figure 3c. Land use/land cover and mean water table elevations during the Nov 1986-Jan 1988 period, Indian Heights sub-basin. All elevations in meters above mean sea level; contour interval = 0.3 meters.

7



Figure 4. Lithologic log, well IH-1. Median grain size (D<sub>50</sub>) and sorting versus depth.



Figure 5. Cumulative frequency distribution of grain size, 8 split spoon samples, well IH-1. (vf, f, m, c, and vc = very fine, fine, medium, coarse, and very coarse sand; gr = granule; p = pebble-sized grains. Diameter in phi units = -log<sub>2</sub>D; when D is expressed in mm.)

from poor to moderate (according to the criteria of Folk, 1974). At multilevel sampling sites ML-1 and ML-2, a clay/silt layer was encountered approximately 6 m below the water table (5 m below mean sea level; see Figure 3b, cross section). The layer was 3 m thick at ML-2, and was underlain by a fining upward sequence of medium to very fine sands, which continued to the bottom of the borehole, at 11 m below mean sea level. The exact areal extent of the layer is not known. It was not encountered at site ML-3, the only other site where drilling was continued to a depth of 11 meters below mean sea level.

#### 4.2 Groundwater Hydrology:

The total saturated thickness of the unconfined aquifer averages about 30 m in the vicinity of the Indian Heights subbasin (Williams and Tasker, 1974). This estimate could not be confirmed, because none of the borings were continued to refusal. Mean depth to groundwater is 12 to 14 meters in the topographically flat portions of the sub-basin upgradient of the steep, nearshore zone. The aquifer is recharged by the infiltration of precipitation and septic effluent. Red Brook and Buttermilk Bay serve as discharge boundaries, and control the mean water table configuration of the sub-basin (Figure 3c). Due to the accretion of natural and effluent recharge in the direction of groundwater flow, the mean water table sloep steepens considerably toward the bay (Figure 3c).

The observation wells showed marked seasonal variations in water level during the November 1986 to January 1988 period (Figure 6). Seasonal variations were greatest in the wells furthest from the bay, as is typical in coastal aquifers (Frimpter and Fisher, 1983). The magnitude of the annual variation was observed to be directly proportional to the mean water table elevation at each well site (except for the beach wells). In mathematical terms, the coefficient of variation (COV = standard deviation divided by the mean) was nearly constant, and equal to a value of about 20%. Wells screened in the beach sediments were tidally influenced, though IH-3S showed clear seasonal effects as well (Figure 6). The upland wells were apparently not affected by the Buttermilk Bay tidal cyle in a significant way. All of the upland wells show the effects of a major precipitation event in the early days of April, 1987, which caused major flooding in New England watersheds underlain by less permeable deposits.





# 5. RESULTS AND DISCUSSION: EFFLUENT AND ONSITE GROUNDWATER

# 5.1 Results: Dissolved Inorganic Nitrogen (DIN)

The box plots of Figure 7 show the observed frequency distribution of DIN concentration for all effluent and onsite groundwater samples. The overall mean effluent concentration was 2641 uM/L (as N; Standard Error of the Mean = +/-12%). The mean DIN concentration in the onsite groundwater samples was 1720 uM/L (SEM = +/-18%). Attenuation (i.e., reduction in DIN concentration due to both solute removal and dispersive mixing with ambient groundwater) from the effluent samples to the groundwater samples was therefore approximately 35%, on average. Over 99% of the DIN in the effluent samples was in the ammonium (NH<sub>4</sub>) form, while only 25% of the groundwater DIN occurred in this form.

Effluent and groundwater DIN concentrations varied considerably at each site, and between sites (Figure 8). The greatest attenuation (89%) was observed at Site 2, which also had the thickest unsaturated zone (mean infiltration distance = 3.5 m). Groundwater samples from Site 3, by contrast, actually had higher DIN concentrations, on average, than the corresponding effluent samples. The reason for this anomaly is not clear, but may be due to difficulties in obtaining a representative sample at this site, which is served by a very small, narrow septic tank (see Figure 11 in Part I of this report).

#### 5.2 Results: Phosphate-Phosphorus

The frequency distributions of effluent and groundwater phosphate concentration are summarized in Figure 9. The mean phosphate concentration in the effluent samples was 165 uM/L (SEM = +/-8%). In the groundwater samples, the mean  $PO_4$ -P concentration was 42.6 uM/L (SEM = +/-23%); mean attenuation was therefore approximately 74%. As with the DIN data, there is variability from site to site (Figure 10). The highest degree of attenuation was observed at Site 2 (99.6%), while the least attenuation occurred at Site 4 (54%).

# 5.3 Discussion: Effluent and Onsite Groundwater

Figures 8 and 10 suggest major differences in the subsurface behavior of DIN and phosphate adjacent to the four septic systems. Unfortunately, the small number of samples and the variability in the DIN, phosphate, and specific conductance



Figure 7. Box-plot of dissolved inorganic nitrogen (DIN) concentrations, all effluent and onsite ground-water samples. (90th, 75th, 50th, 25th, and 10th percentiles shown for each sample set.)



Figure 8. Mean DIN concentrations, effluent and onsite groundwater samples, Sites 1-4 (+/- the Standard Error of the Mean).

12



Figure 9. Box-plots of phosphate-phosphorus (PO<sub>4</sub>-P) concentrations, all effluent and onsite groundwater samples (See Fig. 7 for key).





13

data preclude quantitative evaluation of their actual removal from the septic effluent during the initial phase of transport (i.e., vertical infiltration through the unsaturated zone and early transport with flowing groundwater to the i meter well). The net effect of N and P removal during initial and longterm transport will be considered in detail in Section 6 of this report.

Neverthless, the mean molar ratio of N to P in the effluent and onsite groundwater samples shows important features. First, it should be noted that the mean N:P ratio of the effluent samples is 16.4 to 1. This is very close to the "Redfield ratio" of 16:1, which was determined from bulk laboratory analyses of marine phytoplankton and has predictive value in marine ecological studies (Redfield et al., 1963; Ryther and Dunstan, 1971)

Second, the N:P ratio in the groundwater samples was observed to increase exponentially with increase in the mean distance between the base of the effluent leaching system and the water table (Figure 11). At the "best case" site, where the mean infiltration distance is 3.5 meters, the N:P ratio is over 500. Clearly, phosphate is being depleted relative to DIN during early transport. If we assume, for the moment, that DIN attenuation is due strictly to dispersive mixing with ambient groundwater, the relative change in N:P ratio between the effluent and the onsite well gives a high estimate of onsite phosphate breakthrough to the saturated zone. At Site 2, for example, we estimate that onsite P breakthrough is no more than 3%; removal is therefore at least 97%. Possible mechanisms of subsurface P removal will be considered in Section 6 below.

In addition to the N:P ratios, one should note the striking change in the nitrate fraction  $(NO_X-N/DIN)$  between the effluent and the samples from the onsite wells. The mean nitrate concentration in the effluent samples was observed to be 9.8 uM, or 0.37% of the DIN in the samples. The 1 meter well samples had a mean  $NO_X$  concentration of 1292 uM, or 75% of the total DIN. The respective ammonium fractions change from 99.6% to 25%, on average. The degree of conversion to nitrate, or "nitrification", was observed to be related to the infiltration distance at each site (Figure 12). The nitrification process will be discussed more fully in Section 6 below. The reason for the anomalously high nitrate fraction at Site 3 is not known; it may be related to the unique character of the tank at this site, as noted above.



Figure 11. N:P ratio versus mean infiltration distance, Sites 1-4. (Error bar = SEM of the N:P ratio at each site.)



Figure 12. NO<sub>x</sub> fraction (NO<sub>x</sub>/DIN) versus mean infiltration distance, Sites 1-4. (Error bar is SEM of NO<sub>x</sub> fraction.)

#### 6. OFFSITE GROUNDWATER: RESULTS AND DISCUSSION

#### 6.1 Water Table Observation Wells

Upgradient wells. A total of 17 samples were collected from the water table observation wells located upgradient, downgradient, and in the midst of the developed portion of the sub-basin (Table 1). As expected, DIN and PO<sub>4</sub>-P concentrations in the upgradient samples were quite low (4.0 and 0.75 uM, respectively), as was the mean specific conductance (37 uS/cm). These values are comparable to the data of the U.S. Geological Survey for groundwater in undeveloped areas of Cape Cod (Frimpter and Gay, 1979; Persky, 1986). The low specific conductance (about 50% lower than typical USGS data) is probably due to the unusually young age of the groundwater samples, which were collected at the water table, in what is presumably a recharge area (judging from the position of the wells relative to the groundwater divide). It is also important to note that these samples have a DIN concentration 80% lower than precipitation of the Cape Cod region, which averages about 20 uM (Teal and Howes, 1989; Frimpter et al., 1988). It would appear that the pine/oak forest native to the region (and the underlying soils) are efficient scavengers of precipitation-borne nitrogen.

<u>Midgradient wells.</u> The mean DIN concentration of the "mid-gradient" samples was 616 uM, though the sample set is small in size, and the concentrations varied widely between wells. This represents a 300-fold increase over the background DIN concentration.  $NO_X$  comprised 99.4% of this DIN. Phosphate concentrations in the mid-gradient samples were not significantly different from background levels (mean concentration = 0.17 uM). The N:P ratio of these samples was therefore the highest of any of the sample sets (3620:1).

<u>Downgradient wells</u>. Though limited in size, the set of samples from the downgradient observation wells shows significant trends. Three of the wells (Wells IH-3S, 9, and 10) are screened in the marsh sediments which underlie the artificial fill comprising Indian Heights beach. Two of these wells (Wells 9 and 10) yielded by far the highest ammonium concentrations found in the offsite groundwater samples, while their nitrate concentrations were by far the lowest (excluding the background wells). Well IH-3D, by contrast, which was screened in the outwash sand and gravel underlying the marsh sediments, had an  $NO_X$  and  $NH_4$  concentration more typical of the mid-gradient wells discussed above.

The low  $NO_X$  and high  $NH_4$  concentrations observed in Wells IH-6 and 10 are probably due to a combination of factors.

WELL #	S.C. uS/cm	NH4-N uM/L	NOX-N uM/L	DIN uM/L	PO4-P uM/L
Ungnadient	Wolls:				
opgradient	WEIIS.				
1H-5	40	0. 7	1.6	2.3	1.0
IH-6	34	0.7	0.8	1.5	0.5
Midgradien	t Wells:				
IH-1	270	<0.1	917.	917.	0.3
IH-4	188	0.4	1060.	1060.4	0.3
IH-11	104	1.5	89.0	90.5	0.5
IH-12	114	0.4	186.	186.4	0.2
Downgradie	nt Wells:				
IH-3S	120	1.9	272.	273.9	1.4
IH-3D	215	0.8	622.	622.8	1.1
IH-9	5900	149.	1.0	150.0	4.1
IH-10	475	55.3	0.68	56.0	1.6

Table 1. Specific conductance and nutrient data, water table observation wells. Values given for upgradient and midgradient wells represent mean values from two sampling dates: 21 Jan 88 and 9 Jun 88. Values for downgradient wells are from samples collected on 21 Jan 88. Given the presence of organic carbon and probable reducing conditions associated with the marsh sediments, some dissolved  $NO_X$  could be removed from the aqueous phase by denitrification. Conversely, the high NH<sub>4</sub> concentrations could result from the reduction of organic-N in marsh sediments or the dissimilatory reduction of groundwater nitrate. However, the occurence of high-nitrate groundwater in the sand and gravel at depth, below the marsh deposit, suggests that not all of the nitrate in the aquifer is removed (or transformed) by bacterial activity during transport to the bay.

#### 6.2 Multilevel Samplers

Introduction. While the above questions deserve further study, the limited scope of our investigation constrained us to focus on the impact of septic systems on the main aquifer system. In order to characterize that impact, it became evident that we would need to direct our sampling efforts to that portion of the aquifer downgradient of the septic systems, yet upgradient of the possible N source (and sink) represented by the fringing marsh sediments underlying the beach (Figures 3a, b, c).

We elected to install a small number of multilevel samplers along this upland strip for two reasons. First, it was not feasible to install a large number of conventional monitoring wells on the private properties just upgradient of the beach. Second, given the relatively uniform areal distribution of septic system N sources in the sub-basin, we postulated that variability in solute concentration should largely depend upon the dispersive characteristics of the aquifer itself. Recent large-scale, natural gradient tracer experiments in stratified glaciofluvial settings have observed solute dispersion in the transverse-horizontal (y) direction to be 10 to 20 times greater than in the vertical (z) direction (i.e., for a given groundwater flow velocity in the longitudinal (x) direction; Garabedian et al., 1987; Sudicky et al., 1987). Because vertical dispersion is very limited, one can expect the spatial variability in solute concentration to be greatest in this direction. Multilevel samplers allow intensive sampling of this variability.

<u>DIN results</u>. A total of 230 samples were analyzed for DIN. Concentrations ranged from background levels (1-4 uM) to 1720 uM; samples exceeded background in 192 (83%) of the samples. The 192 non-background samples were distributed normally over the 3 to 550 uM range, with a relatively small number of high values (Figure 13). The mean DIN concentration of the non-background samples was 379 uM; the standard error of



Figure 3b. Schematic geologic cross section, Indian Heights sub-basin (see Fig. 3a for location of section line).







# Sample Type



20

the mean was +/-5.5%. Sampling Site ML-2 yielded the highest DIN concentrations, on average, while Sites ML-1 and ML-3 yielded somewhat lower values (Figure 14). Differences in DIN concentration between sampling sites were small relative to their differences with the effluent and onsite sample sets (Figure 14). Over 99.5% of the DIN, on average, occurred as nitrate; ammonium was at background levels (0.7 uM) in 70% of the samples.

Phosphate results. Phosphate-P was at or below the upgradient "background" levels (0.75 uM) in 90% of the 157 samples analyzed for phosphate. The median sample contained 0.12 uM of phosphate-P. The sample set is non-normally distributed, as shown by the high mean to median ratio (5.84:1). The 16 above-background samples, which averaged 5.9 uM in concentration, account for the skewed character of the distribution.

<u>N:P results</u>. The mean N:P ratio in the 141 multilevel samples with a phosphate concentration above the detection limit (0.03 uM) was 3656:1, and the median was 1812:1. Because the N:P distribution is also skewed by a small number of very high values (caused by samples with extremely low phosphate concentrations), the median is a more representative value than the mean.

7. DISCUSSION: NUTRIENT REMOVAL DURING TRANSPORT TO SAMPLERS

7.1 Estimated Removal

The Approach. The large number of offsite samples allows a quantitative estimate of N and P removal during transport from the septic systems of the sub-basin to the downgradient samplers. The relative change in the mean nutrient:specific conductance ratio from the effluent to the multilevel sampling sites (after correcting for background levels) is a measure of the nutrient fraction which "breaks through" to those sites:

$$BF = \begin{bmatrix} \frac{1}{n} & \sum_{i=1}^{n} & \frac{C_{gw-i}-C_{b}}{SC_{gw-i}-SC_{b}} \end{bmatrix} \stackrel{\bullet}{\bullet} \begin{bmatrix} \frac{1}{n} & \sum_{i=1}^{n} & \frac{C_{eff-i}-C_{b}}{SC_{eff-i}-SC_{b}} \end{bmatrix} \quad (Eq. 1)$$
where,

BF = the mean nutrient breakthrough fraction

 $C_{gw-i}$ ,  $C_{eff-i}$ ,  $C_{b}$ = the nutrient concentration of the ith offsite groundwater and effluent sample, respectively, and the mean background nutrient

#### concentration.

 $SC_{gw-i}$ ,  $SC_{eff-i}$ ,  $SC_b$  = the specific conductance of the ith offsite groundwater and effluent sample, respectively, and the mean background specific conductance.

This approach assumes the following:

1. Specific conductance can be considered a conservative property in both the effluent and groundwater. While certain ionic species (e.g. nutrients) may be removed during transport, the net effect on the specific conductance is assumed to be small.

2. Septic effluent is the only significant source of (nonbackground) specific conductance and nutrients to the samplers; all other solute and nutrient sources in the basin (e.g., weathering of the aquifer matrix, road salt, and lawn fertilizer leaching) are assumed to be small by comparison with septic effluent.

We would argue that both of these assumptions are valid in the Indian Heights sub-basin. Assumption #2 is supported by the high degree of correlation between the specific conductance and DIN concentration of the offsite groundwater samples  $(r^2= 0.89)$ . Major solute contributions from silicate weathering, lawn fertilizer, and road salt would presumably lead to more scatter in the data. Assumption #1 is reasonable, given the fact that DIN and phosphate comprise only about 10% of the total dissolved solids in septic effluent (Canter and Knox, 1985). (To the extent that Assumption #1 is violated, this method tends to underestimate the actual nutrient removal.)

<u>The Results</u>. Approximately 86% of the DIN and 0.34% of the phosphate in the septic effluent is transported to the multilevel samplers. The standard error range (SEM) is 74% -98% for the DIN breakthrough estimate, and 0.19% - 0.49% for the phosphate estimate. Note that the rather large error associated with the phosphate breakthrough estimate (+/-43%) appears trivial because the actual mean value is so low. Likewise, the relatively small error in the DIN breakthrough estimate (+/-14%) appears large, because the mean value is quite high. The corresponding removal ranges are 2 - 26% for DIN and 99.5 - 99.8% for phosphate.

7.2 Comparison with Other Studies:

The nutrient removal estimates obtained above agree closely with the observations of other researchers in similar hydrogeologic settings (Fetter, 1977; Reneau and Pettry, 1976). Septic system plume mapping studies have also shown extremely limited phosphate transport relative to DIN at the micro-scale (Childs et al., 1974; Robertson et al., 1989).

In an extensive study of nutrient removal during early transport in a glacial outwash setting, Alhajjar et al. (1989) report phosphate removals of over 99.5% in the first few meters of transport from all septic systems studied; nitrogen removals ranged from 4 to 49%. Ironically, the poorest nitrogen removals (90% confidence interval = 4-8%) were associated with houses using strictly non-phosphate detergents (which were originally introduced to help prevent the eutrophication of surface waters). Those houses using strictly phosphate detergents showed much higher rates of N removal (90% C.I. = 43-49%). The investigators suggest that phosphate-rich effluent stimulates the growth of denitrifying bacteria in the clogging mats below septic leaching systems. (The use of phosphate detergent had no effect on groundwater phosphate concentrations.)

# 7.3 Phosphate Removal Processes

The highly efficient removal of dissolved phosphate during subsurface transport can be attributed to a variety of adsorption and precipitation reactions. Because phosphate ions (which occur primarily as  $H_2PO_4^-$  and  $HPO_4^-$  over a pH range of 4-10) are negatively charged, it is sometimes asserted that adsorption is not an important process of phosphate removal (e.g. Freeze and Cherry, 1979, p. 422). While it is true that the net negative surface charge common to *clay* minerals does not favor phosphate adsorption, phosphate has a strong affinity for the oxides of iron and aluminum (Barrow, 1983; Goldberg and Sposito, 1984). As is the case with most adsorption reactions, this process is reversible (Van der Zee et al., 1987).

The granite-derived sand and gravel materials underlying the aquifers of the Cape Cod region are relatively rich in oxides of Fe and Al, and extremely low in clay minerals (less than 0.1%; Barber, 1987). These metal oxides occur both as primary mineral grains of igneous origin, and as secondary coatings on other grains. Hence, in the Cape Cod geologic setting, adsorption is probably an important mechanism of phosphate removal.

Precipitation, the second removal mechanism, is important because phosphate is highly insoluble with respect to dissolved species of ferric iron (Fe<sup>+++</sup>), aluminum (Al<sup>+++</sup>), and calcium (Ca<sup>++</sup>), and will combine with extremely low concentrations of these cations to form the minerals strengite, varisite, and hydroxlapatite, respectively (Freeze and Cherry, 1979, p. 423). A process known as "diffusion precipitation", whereby phosphate ions convert metal oxides into phosphate minerals by means of bulk ionic substitution, has also been identified (Van der Zee et al., 1989). Unlike simple adsorption, this process is considered to be essentially irreversible.

### 7.4 Nitrogen Removal Processes

Our data confirm the frequently asserted statement (e.g. Frimpter et al., 1988, p. 21) that DIN removal is minimal in the sand and gravel aquifers of the Cape Cod/Buzzards Bay region. There are several reasons why dissolved nitrogen is so ubiquitous in the groundwater systems of the region:

1. The glaciofluvial sediments which comprise the major aquifers are very low in clay (0.1%; Barber, 1987). Hence, adsorption of ammonium cations to clay minerals during early (onsite) transport of effluent is minimal.

2. The pH of both pristine and sewage contaminated groundwater in the region ranges from neutral to acid (LeBlanc, 1984). Because dissolved ammonia gas  $NH_3(aq)$  is unstable with respect to ammonium ion  $(NH_4+[aq])$  below a pH of 9 (Hem, 1985, p. 126), ammonia volatilization is not a significant N removal mechanism.

3. The near surface groundwaters of the Cape Cod region are rich in dissolved oxygen (Frimpter and Gay, 1979). This is due to the high recharge rate, the relatively non-reactive silicate minerals of the aquifer matrix, and the extremly low organic carbon content of the matrix (about 0.01%; Barber, 1987).

In unsewered areas of the Cape Cod region, the biochemical oxygen demand (BOD) associated with sewage disposal is dispersed across a large number of small discharge points (septic systems). The high dissolved oxygen content of the ambient groundwater, in concert with the dispersed character of the effluent-imposed BOD facilitates bacterial nitrification of effluent ammonium. The nitrification process is oxygen limited, and its net stoichiometry can be expressed as follows (Fenchel and Blackburn, 1979):

 $NH_4^+ + 2O_2 = NO_3^- + 2H^+ + H_2O$ 

Our data indicate that nitrification of septic effluent occurs very rapidly in the Indian Heights study area. Nitrification is promoted in the Indian Heights sub-basin by the substantial thickness of the unsaturated zone (average depth: 12-14 meters except near the beach).

4. Nitrate is a stable species which is easily advected with flowing groundwater. Unlike phosphate, it does not form insoluble precipitates with metal cations. Like chloride, it has both a negative charge and a large ionic radius and is therefore not easily adsorbed to mineral surfaces (Fetter, 1988, p. 346).

5. Denitrification (the bacterial reduction of nitrate to  $N_2(g)$  or  $N_2O(g)$  under reducing conditions, in the presence of organic carbon) is not generally favored by well oxygenated, low organic-C, sand and gravel aquifers.

These five factors explain why DIN, as nitrate, is so widespread in the groundwater of the Cape Cod region. To the extent that it occurs at all, removal of anthropogenic nitrogen takes place in distinct micro-environments where the above conditions do not prevail. For example, what could be called "early denitrification" may be important beneath some septic systems, as suggested by Alhajjar et al. (1989). Our data suggest that such onsite denitrification is minimal in the Indian Heights study area, perhaps because phosphate detergents are no longer in general use in this country. In addition, what could be called "late denitrification" probably affects groundwater during its final stage of transport through or beneath fringing salt marshes or freshwater wetlands, as well as through lacustrine and subtidal bottom sediments. A great deal more field research on the complex hydraulics and biogeochemistry of these micro-environments is needed.

#### 7. CONCLUSIONS:

1. The dissolved inorganic nitrogen and phosphatephosphorus concentrations beneath the undeveloped, upgradient portion of the Indian Heights sub-basin are quite low (about 1.9 and 0.75 uM, respectively), and similar to those from other pristine areas in the Cape Cod/Buzzards Bay region.

2. The observed DIN concentration increases by a factor of 200 (to 379 uM) by the time the groundwater reaches the downgradient end of the sub-basin, some 300 meters from the edge of the pristine area. The average groundwater phosphate concentration remains at background levels. 3. The DIN and phosphate concentrations of septic effluent discharged to the sub-basin are approximately 2640 uM and 165 uM, respectively.

4. Virtually all (over 99.5%) of the effluent phosphate is removed from solution during transport from septic systems to the downgradient sampling points. Between 2% and 26% of the effluent DIN is removed over this same path. Large depths to groundwater (12-14 meters) do little to promote nitrogen removal in this setting.

5. The virtual elimination of effluent-derived phosphate, much of which occurs during early transport, can be attributed to its physical chemistry. The persistence of dissolved inorganic nitrogen, as nitrate, can be attributed partly to its physical chemistry, and partly to the low clay, low organic-C, and highly oxidizing character of the sand and gravel aquifer underlying the sub-basin.

6. To the extent that the fresh and marine waters of the region are P-limited in their primary production, eutrophication from septic systems poses little threat. To the extent that these waters are N-limited, septic systems pose a major eutrophication threat.

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