# HUZZARDS BAY

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# CRANBERRY BOG INFUT STUDY

## Prepared By

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# SPECIAL WATER QUALITY STUDY 1986

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## ABSTRACT

The Commonwealth of Massachusetts's is the nation's largest producer of cranberries. Production is concentrated in a broad band of glacial outwash deposits located in the low-lying coastal plains bordering Buzzards Bay and Cape Cod Bay. More than 55 percent of the total 4856 hectares under production can be found within the Buzzards Bay drainage basin. The Division of Water Pollution Control conducted a study of a commercial cranberry bog operation located within the Buzzards Bay coastal drainage basin. The objectives of the study were to evaluate several suspected water quality impacts: Excessive Nutrient Export; Residual Levels of Pesticides and Herbicides in Sediments; and Qualitative Changes to Benthic Macroinvertebrate Communities Within and Downstream of the Bog Outlet.

Variations in nutrient levels in the discharge were found to coincide with agricultural activities as well as with hydrological events with significantly greater concentrations of total phosphorous being exported to receiving waters than a comparative fresh water wetland. Trace amounts of the pesticide, chlorpyrifos and the herbicide, glyphosate were recovered in sediments within the bog discharge stream well after the reported last application. The relative abundances of macroinvertebrates within the detrital shredding community appeared reduced within the outlet stream below the bog. TABLE OF CONTENTS

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# 1.0 Introduction

#### 1.1 <u>General</u>

The American cranberry (<u>Vaccinium macrocarpon</u> Ait.) grows wild in the wet bogs and swamps of the New England and Great Lakes regions. Cranberries have been harvested since pre-colonial times. However, the production and quality from the wild vines is unreliable and would not meet today's market demands. Commercial production of cranberries requires a temperate climate, acidic soils and an ample source of fresh water. The Commonwealth of Massachusetts is the nation's major producer of cranberries, accounting for 50 percent of the total 1984 harvest (N.E.C.R.S. 1984).

During the latter part of the 19th and early 20th centuries considerable portions of the Buzzards Bay basin's freshwater wetlands, bogs and bordering vegetated wetlands were altered and converted to the commercial production of cranberries. Using SCS published estimates of related soil types in the basin, roughly 13 percent of the estimated 21,195 ha (52371 acres) of wetlands have been converted to commercial cranberry production. Most of the conversion has occurred in the northeastern portion of the basin. The ability to manipulate large volumes of water on relatively short notice has become an important economic advantage to cranberry bog operators. These largely non-consumptive demands may be used to distribute fertilizers, to control certain pests during the harvesting period and to protect the vines during the winter from desiccation and freezing.

In a recent survey of water usage within the industry, (SCS, unpublished report 1986), the Cape Cod Cranberry Growers Association in cooperation with the USDA, Soil Conservation Service and U.S. Geological Survey (USGS), reported that over 76 percent of the acres surveyed were wet harvested and 97 percent of the bogs had some form of sprinkler system. Estimates place the current average requirement at 454 cu.m/ha (300,000 gals/acre of bog/year) (SCS, 1986).

These agricultural practices have largely supplanted the meteorological and hydrological events as the primary factors in determining when the altered wetland functions as a nutrient sink or exporter.

Essential nutrients have been shown to have "cycles" or turnover rates which can be measured in minutes to days rather than months or years (Harrison and Hobie, 1974). Further, the reversal of nutrient release and retention patterns within wetlands has also been shown to be subject to rapid change (Barsdate and Alexander, 1975; Gardiner, 1975). While such episodic events may be relatively short lived they could contribute substantial volumes of nutrient laden water to the estuary over the long-term.

#### 1.2 Buzzards Bay Estuarine Study

In 1984, Buzzards Bay was one of four estuaries in the country chosen to be part of the National Estuary Program. The Buzzards Bay Project was initiated in 1985 to protect water quality and the health of living resources in the bay by identifying resource management problems, investigating the cause of these problems and recommending actions to

protect the resources from further degradation. The Buzzards Bay Project identified three priority problems: the closure of shellfish beds; contamination of fish and shellfish by toxic metals and organic compounds; and excessive nutrient inputs.

Studies in Chesapeake Bay (Flemer et al., 1983) and Pamlico Sound (Harrison and Hobie, 1974) have identified nonpoint sources, particularly from agricultural sources as being a major source of nutrients and pesticides. They also established some evidence of adverse effects in the form of eutrophication and possible reproductive losses to shellfish and fish stocks within the bay.

The Division of Water Pollution Control proposed, as part of a much larger research effort for Buzzards Bay, a study to examine several of the suspected impacts attributed to cranberry culturing: the introduction of nutrients to the bay thereby contributing to eutrophication, the contamination of sediments with residual levels of pesticides and herbicides, and degradation of natural populations of macroinvertebrates due to cranberry culturing practices.

## 1.3 Buzzards Bay

Buzzards Bay is a prominent coastal embayment on the New England coast nestled between Cape Cod and the southern Massachusetts mainland. The mouth of the Bay opens south into Rhode Island Sound. On its western shore, the drainage basin is formed by seven coastal rivers basins with a total drainage area of approximately 906.5 sq. km. (350 square miles). On its easterly shore from the Cape Cod Canal to Woods Hole, Falmouth small rivers and streams provide an additional 90.6 sq. km. (35 square miles) of drainage area (Figure 1).

## 1.3.1 <u>Geology</u>

Geologically, the Buzzards Bay Drainage Basin is characterized as being a low granitic upland with glacial till and outwash deposits forming the soils. The terrain can be described as low and gently rolling with numerous lakes and marshes.

The glacial events which formulated surface deposits in the northeast quadrant of the bay are described by Moog; (Masters Thesis, 1987). The irregular retreat of the Buzzards Bay ice lobes resulted in the formation of moraines at Hog Rock and Ellisville and an interlobate outwash plain, the Wareham pitted plain. This plain slopes southward from the southern quarter of the Plymouth and Manomet quadrangles to the northern part of the Onset and Marion Quadrangles. Buried ice blocks, later melted to form collapsed outwash areas with kames, kettles and ice contact slopes next to the encapsulated outwash. Post glacial modifications included stream dissection, alluvial deposition, and the formation of marshes, bogs, and swamp deposits in the kettles and other low lying areas.

#### 1.3.2 <u>Climate</u>

The climate of Massachusetts is characterized by moderately warm summers, moderately cold winters, ample year round rainfall (ranging



from 104 to 119 cm (41 to 47 inches), and rapid changes in weather conditions (Upham et al., 1969). The prevailing westerly winds contain air masses from both the Arctic and the Tropics. The interaction of these cold dry air and warm moist air masses produces large storm systems which frequently pass over the state. The climate is also influenced by the proximity of Cape Cod Bay, Buzzards Bay and the Atlantic Ocean. In the summer the immediate coastline is most affected by cooling sea breezes. In the winter the coastal climate more closely resembles that of the mainland because the winds are more often from the westerly or northwesterly direction. Temperatures differ widely from winter to summer and from day to On clear nights, as the air is exposed to radiational night. cooling, it becomes heavier and drains to the low areas which contain As a consequence, frost damage often the wetlands and bogs. threatens the cranberries even into the summer months (Upham et al., 1969).

#### 1.3.3 <u>Soils</u>

Soils within the study area are best described as being within the Carver-Peat association for Plymouth County (Upham et al., 1969). This soil group is reported to occupy roughly 15% of Plymouth County and a larger percentage within the south-central portion of the county. It consists of a large, nearly level, sandy outwash plain that is pitted with kettle holes and dissected by southward flowing In most places the elevation is less than 30 m. (100 streams. feet). Carver soils occupy about 70 percent of this association and peat about 10 percent. The Carver soils consist of droughty coarse sands that formed in deep deposits of sand, on the nearly level plain and along steep sides of kettle holes and stream channels. Peat occurs on the bottom of drainage ways and in some of the deeper kettle holes. The droughty gravelly Hinckley soils and the sandy Gloucester soils make up the balance of secondary soils. The upland portions are covered predominantly with pitch pine and scrub oak woodlands.

#### 1.3.4 Wetlands

Wetlands are generally considered to occupy an early seral stage in vegetation succession from an aquatic to terrestrial environment (Ohm, 1971). Despite documented cases of long-term stability, most wetlands tend to be short-lived. The general direction of wetland succession being to a reduction in water level and to a drier state. Natural changes in water level can be brought about by autogeneic processes i.e., the raising of the wetland surface due to the accumulation of litter deposition and by external causes such as siltation from flowing waters. Changes in water levels can also be brought about by anthropogenic processes such as, drawdowns or damming. These changes can be expected to either accelerate or retard the transformation to upland as well as cycling of nutrients through wetlands.

Odum describes three general stages to nutrient cycling in wetlands: a high flow-through system relative to storage (nutrient cycles are dominated by inorganic forms); succession progress as more nutrients become tied up in biomass and detritial matter; a low flow-through system where large amounts of nutrients are stored relative to inputs and exports.

The role of wetlands as either nutrient exporters or as sinks has been discussed by a number of researchers (Harrison and Hobie, 1974; Gardiner, 1975; Williams, 1985; Wolaver and Spurrier, 1988). Nutrient release and retention patterns within wetlands have been shown to be subject to rapid changes (Barsdate and Alexander, 1975; Gardiner, 1975). The rate of change can be measured in minutes to days. Under normal conditions, wetlands in temperate climates tend to serve as nutrient exporters during the colder months when surface water and ground water levels are high and assimilation by plants and microorganisms is low. During the summer the opposite conditions generally hold true and wetlands tend to retain nutrients.

As previously described, most of the Commonwealth's cranberry bogs were constructed within existing freshwater wetlands and bogs. The natural vegetation within these habitats ranges from sites dominated by mosses to reeds and grasses through woody shrubs. Cranberry bogs as wetlands could be described using the terms formalized by (Cowardin et al., 1979) as occupying areas where the water table is at or close to the surface for long periods during the year, as wetlands subject to periodic inundation, seasonal freezing and where the vegetation is rooted versus floating.

#### 1.3.5 <u>Wetland Soils</u>

Sediment in rooted wetlands plays a major role in nutrient cycling (Williams, 1985). The soil in commercial cranberry bogs is described as "sanded muck" which consists of muck, peat, and very poorly drained mineral soils overlaid by coarse sand (Upham et al., 1969). Soils such as peat and muck are classified as Histosoils (soils which formed in accumulations of organic matter) (Upham et al., 1969).

Peat is an organic soil consisting of partially decomposed organic remains which accumulate in water or under wet conditions. The water and organic content of this soil type has been found to vary considerably with depth and location. Cowardin (1984) reported findings by Whigham and Simpson (1975) of a range in organic matter in the marsh soils along the tidal freshwater portion of the Delaware River of 14 percent to 40 percent (dry weight), while Bowden (1982) found a range of 50 to 75 percent in the north River marsh of Massachusetts. Brady (1984) in his book "The Nature and Properties of Soil" reported that organic matter in bogs ranged between 59.7 and 94.2 percent (d.w.) with corresponding respective ranges for nitrogen, phosphoric acid  $P_2O_5$  and potassium  $K_2O$ , of 1.20 -3.53 percent, 0.10 - 0.43, and 0.04 - 0.28.

# 1.3.6 Nutrient in Wetland Soils

The five principal sources of inorganic nitrogen to the bog are from surface waters flowing through the bog, ground water, nitrogen fixation, decomposition of plant tissue and the application of fertilizers containing nitrogen. Decaying materials are a relatively

large repository for organic nitrogen, however, remineralization is quite high acidity and low oxygen conditions within the sediments. Experiments using isotopically tagged nitrogen have shown only 2 to 3 percent of the immobilized nitrogen remineralized annually (Brady, The availability of inorganic forms of nitrogen (NO3 and 1984).  $NH_A$ ) are low due to a number of factors. First, the saturated nature of the soils effectively reduces the availability of oxygen needed to carry on the nitrification reaction, second, the low pH is not conducive to the most common forms of nitrifying bacteria, third, the temperate climate produces low temperatures which reduce the activity of the nitrifying bacteria within the bog, and fourth, the high carbon/nitrogen ratio selects for hetrotrophic microorganisms such as fungi, bacteria and actinomycetes as opposed to strict nitrifyers (Brady, 1984). As a consequence of these factors, concentrations of the reactive forms, ammonia and particularly nitrate within a wetland were expected to be low.

The availability of inorganic phosphorus is largely determined by the pH of the soil, the presence of soluble forms of iron, manganese and aluminum, available calcium and calcium minerals, the amount of organic matter and the activities of microorganisms (Brady, 1984). The first four factors are interrelated since soil pH drastically influences the reaction of phosphorus with these minerals. Thus under the acidic conditions of the bog, available phosphorus is readily "fixed" in very complex and insoluble salts of iron, Richardson and Marshall (1986) examined the manganese, etc. processes controlling the movement, storage, and export of phosphorus in a fen peatland. They suggest that soil adsorption and peat accumulation control long-term phosphorus sequestration. However, microorganisms and small sediments control initial uptake rates, especially during low nutrient concentrations and standing water. Phosphorus levels have been found in bog soils at levels of 36 to 85 ppm (Deubert, 1974). Phosphorus has also been shown to migrate through cranberry soils. At pH levels over 5 phosphorus becomes more soluble and is made available to higher plants.

The availability of potassium, the third major nutrient is influenced by the nature of the soils colloids, wetting and drying, freezing and thawing and the presence of lime (Brady, 1984). In most peaty soils potassium is comparatively low and held in exchangeable forms within the organic colloids. In addition, available potassium is readily lost from the soil through leaching. Peaty soils are also deficient in trace elements particularly when there is an active removal process i.e., harvesting.

#### 1.3.7 Eutrophication

In 1840, Justus Liebeg developed an hypothesis based on his study of various factors effecting the growth of plants which may be stated as follows: the total amount of growth in a population is limited by that essential growth factor present in least supply. A second hypothesis by V.E. Shelford in 1913 (Odum, 1971) developed the concept of the limiting effect of maximum as well as minimum which has been incorporated into the "law of tolerance". The law states that an animal, plant, or population's success will be dependent upon its ability to tolerate a given factor(s).

The term eutrophication is used to describe a complex increased rate of supply of plant nutrients through the water column (Vallentyne, Under unaltered conditions it is generally a slow moving 1974). process resulting in a change in the shape and depth of that body of When induced by man it is a comparatively rapid process water. brought about by an increase in the rate of supply of nutrients (Flemer et al., 1982). The excessive discharge of dissolved nutrients primarily in the form of organic carbon, phosphorus and nitrogen has been shown to cause low concentrations of dissolved covvgen, and blooms of blue-green algae in aquatic systems (Flemer et al., 1983) (Figure 2). Additional evidence of nutrient enrichment within the Chesapeake Bay Basin was formed from observations on the once extensive beds of submerged aquatic vegetation (SAV's). During the period from 1965 to the present many of the beds have shown a significant decline in abundance (Flemer et al., 1983). The likely explanation for this decline appears to be related to an observed increase in nutrient levels and a corresponding decrease in the amount of light penetration in the water column. They apparently block the ability of the SAV's to properly photosynthesize.

The source of the nutrients varies with location and nature of the aquatic system. Within the Potomac River point sources are implicated as the principal nutrient sources while nonpoint sources such as agricultural runoff from the Susquahanna River drainage basin have been identified as the dominant source in the upper reaches, (Flemer, et al., 1983). A study on eutrophication and nutrient inputs to coastal lagoons in Rhode Island (Lee and Olsen, 1985) identified suburban development within the coastal zone as the principal sources of nitrogen to the coastal lagoons. Nitrogen primarily in the form of nitrates from septic systems and garden fertilizers is thought to be entering the ground water discharge resulting in the profusion of macrophytic growth. They also noted some significant changes in the patterns of eutrophication exhibited in these shallow poorly flushed salt ponds. Overlying waters were found to be clear, had relatively low concentrations of nutrients and did not support large populations of plankton. The evidence for eutrophication was established by the presence of dense mats of green algas such as <u>Ulva</u> sp., <u>Enteromorpha</u> sp., and <u>Gracilaria</u> sp., the differences are attributable to the shallowness of the lagoons and their salinity.

The role of the estuaries and the coastal embayments as nutrient importers or exporters is dependent upon a number of factors: salinity, redox characteristics of the sediments, presence of absence of upland sources, tidal input and the magnitude and stability of nutrient flux (Odum, 1984). Estuaries and coastal embayments are usually highly productive areas as evidenced by the abundance of homographic growth, benthic microphytes and phytoplankton (Odum, 1971). Coastal wetlands generally act as sinks for nutrients during the growing season and as exporters during the fall and winter.



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Nitrogen is as essential to plant and animal growth in the marine environment as it is in aquatic systems. Nitrogen exists in the ocean as elemental nitrogen and more commonly in organic or inorganic forms in particulate or dissolved phases. Physical and biological components within oceans such as the sediments, the flora and fauna recycle the nitrogen introduced into the system. The relative concentrations of each form and phase varies with the time of year and degree of biological activity. In temperate climates the concentrations of the inorganic forms, nitrate  $(NO_3^-)$  and ammonium ion  $(NH_4^+)$  are typically higher in the winter months and declines as water temperature and biological activity increases.

Within aquatic regimes, phosphorus is generally accepted as the limiting factor to net organic carbon production in freshwater while in the marine environment nitrogen appears to be most often the limiting factor to specific growth rates of natural populations of phytoplankton grown in cultures (Smith, 1984). Smith, however, sees an inherent problem with these determinations since they measure factors which effect the growth rate of individual populations and not the net limiting factors of the entire ecosystem. "The evolution of optimal ratios for phytoplankton growth may not be able to occur in estuaries due to their short residence times and domination by physical processes. Nitrogen fixed from the atmosphere or returned from the sediments is swept into the open ocean so rapidly that it cannot accumulate to the degree which is common in freshwater The implications is that the "discrepancy" between lakes." phosphorus limitation in lakes and nitrogen limitation in the coastal marine environment lies with the difference between relative rates of biochemical reactions of nitrogen and water exchange in the environment. Water exchange may be fast relative to internal fluxes in coastal marine ecosystems.

In the absence of direct data, nitrogen limitation is inferred from the deviation of N"P concentration of loading ratios from the composition of primary producers in the system (Smith, 1984). The accepted ratio of N:P which supports the growth of algae is considered to be 16:1 (the Redfield ratio). Dominance by nitrogen-fixing organisms in lakes with low N:P ratios has been well documented (Schindler, 1977; V.H. Smith, 1983) these observations suggest that nitrogen fixation hence nitrogen availability in the marine environment can be high but that it can be regulated by the availability of phosphorus. Work within the Chesapeake Bay suggests that phosphorus controls phytoplankton biomass in the tidal-fresh reaches and low low salinity areas throughout the year while nitrogen controls phytoplankton biomass during the summer and in areas of higher salinity (Flemer et al., 1983).

Buzzards Bay is a relatively shallow embayment with an estimated total mean inflow of freshwater of only  $15.4 +/- 3.9 \text{ m}^3$  s (Signell, 1987). The dominant source of freshwater to the bay is from stream flow but this is heavily influenced by precipitation and evaporation. A comparison of the ratios of basin volume to inflow shows that the influence of freshwater is low (Signell, 1987). Given the relatively low inputs of freshwater Buzzards Bay and hence input sources of nitrogen, Buzzards Bay is likely to be nitrogen limiting.

An assessment of nutrient discharges to 17 estuaries in the Northeast found Buzzards Bay ranked 11th in estimated nitrogen loadings per square mile of estuary surface area. Spatial variations within the bay are attributed to higher loadings from the more urbanized sections and are associated with discharges from municipal sewage treatment facilities (Warsh, et al., 1988). A recent publication by Fisher et al., (1988) cited atmospheric deposition of nitrates from combustion sources a s a major source to Atlantic Coastal Estuaries.

Phosphorus levels in Buzzards Bay were found to be comparatively high to other northeastern estuaries (Warsh et al., 1988). Principal sources identified included treatment plant effluents and nonpoint source discharges from agricultural lands and urban runoff. A Redfield ratio of 4.8 is cited a s evidence of nitrogen being the limiting nutrient in the bay.

The evidence for eutrophication within Buzzards Bay and more specifically Buttermilk Bay are reports of algae blooms, fish kills and reductions in eelgrass beds <u>Zostera marina</u> (Valiela and Costa, draft report 1987). Actual documentation of such events is sparse. A two year survey of water quality conditions throughout the basin disclosed no instances of anoxic conditions (Gil, 1986). Declines in eelgrass from the deepest portions of Buttermilk Bay and in some of the poorly flushed coves is attributed to nutrient loading or increased turbidity (Costa, 1988). Areas with the highest nutrient concentrations are reported to correlate with the absence of eelgrass (Costa, 1988).

#### 1.4 Cranberry Production in Massachusetts

1.4.1 General

The Commonwealth's cranberry production is concentrated in a broad band of glacial outwash deposits located in the low-lying coastal sections of Norfolk, Plymouth, Barnstable, and Dukes counties bordering Buzzards Bay and Cape Cod Bay. More than 55 percent, or 2671 of the total 4856 hectares (6600 of the total 12,000 acres), can be found within the Buzzards Bay drainage basin (personal communication J. Wesoloski SCS, 1986), (Figure 2). Cranberry bogs within the Buzzard Bay drainage basin have generally been constructed within existing freshwater wetlands and bogs (Artman, 1930; Cooperative Extension Service, 1982). Golet and Larson (1974) in their "Classification of Freshwater Wetlands in the Glaciated Northeast" report that man created cranberry bog reservoirs in former wooded and shrub swamps.

Over the decades the adjacent waterbodies were gradually dammed, altered or converted to reservoirs to meet the needs of the growers. In 1925, 5261 ha (13,900 acres) were reported under production (Artman, 1930).

Ownership began to shift into the hands of a few large individual holders and corporations. Assessments made during this time reported nearly 2100 individual owners with nearly one-half of the total acreage and more than 50 percent of the total harvest concentrated in the hands of a relatively small number of individuals or corporations (Artman, 1930). By 1930, further expansion of the acreage was held in check by the requirements of large capital outlays for developing the bogs, land clearing, and installation of equipment for flooding.

During the past thirty-five years the yield per acre has shown a substantial increase. Production levels increased from 41 barrels/acre in 1950, to 64.5 barrels in 1965, to an estimated 148.5 in 1984 (N.E.C.R.S., 1985). Conversely the amount of land under production has declined 25 percent from a high of 6071 ha in 1950 to 4533 ha in 1984 (15,000 acres to 11,2000) (Figure 3). Increased productivity can be attributed to several factors: the increased use of sprinkler systems, a shift to water harvest, improved marketing, use of pesticide/herbicide controls, and the use of fertilizers.

Typically commercial cranberry bogs are prepared by first clearing the surface of it's surface vegetation. Next a layer of sand is applied to serve as the rooting medium for the new cranberry vines. Succeeding years of growth are then laid down over alternating layers of sand and partially decomposed organic matter (primarily cranberry leaf litter). Sand is applied every two or three years to rejuvenate the plants and as a pest control management practice (Deubert, 1982; Demoranville, 1982). Cranberry soils have been described by (Deubert, 1982) as an artificial soil containing a relatively low percentage of organic matter. He found that the soil content from 12 Massachusetts cranberry bog soil (2mm) consisted of 92 (86-94) percent sand, 6.6 (1.1 - 8.4) percent silt and clay, and 2.6 (0.9 -5.17) percent organic matter. An earlier estimate by Deubert (1974) reported the percentage of organic matter at 10 percent.

The typical depth of the growing media (sand) as reported by several researchers shows considerable variation, (Deubert, 1982) reports the average depth of 230 soil samples was 3.8 - 5 cm (1.5 - 2 in.), while (Upham, 1969) reports cm (12 inc.) of coarse sand as the typical depth. The differences are important since in shallow sand the role of the organic layer and the processes which transform nutrients would be expected to dominate while in a deeper sand layer the physical processes would be dominant.

Characterizing nutrient concentrations in a cranberry bog based on the sand growing media yields low results since the sand is largely composed of relatively inert coarse crystalline feldspar and quartz. The high acidity and coarse nature of the media in a deep sand favors leaching and downward migration out of the sand layer and into the organic layer. The relationship of the crop and this underlying reservoir of nutrients is not well established. In a study of the ombrothrophic Thoreau Bog (Chapman and Hamond, 1981) reported an upward gradient of ammonium concentrations in the subsurface waters. They also reported findings by others of processes which recycle nutrients to the upper portions of the Sphagnum peat. Williams (1985) states "that in any habitat, a total pool of nutrients is present in a number of forms, some of which are unavailable. In a



steady state when nutrient input = output, and when plant growth = mortality, if the nutrient inputs from the outside the system are less than consumption rates the available pool..." In a cranberry bog with multiple applications of highly available nutrients the mechanisms by which the plants would draw on to assimilate less available forms of essential nutrients are likely to be under utilized.

# 1.4.2 Fertilizer Applications

The role of fertilizers in the development of agriculture can be traced back to th earliest records of man's activities. Through the use of animal and human excrement, man has extended the fertility of soils. The use of mineral salts to enhance fertility, however, is a relatively new development having been in use systematically and extensively for little more than 100 years (Brady, 1984). Plants require at least 14 essential nutrient elements with calcium, magnesium and sulfur being supplied in variable amounts based on the soil chemistry and the nature of the plant to be grown. Aside from the trace elements, the application of various forms of the elements of nitrogen, phosphorus and potassium are crucial to maintaining the high yields exhibited by most of the commercially grown plant matter in the world.

The amount of Massachusetts land under active cranberry cultivation exceeds 4500 ha (11,200 acres) with 55 percent of the total lying within the Buzzards Bay Drainage Basin (New England Crop Reporting Service, 1985 and S.C.S. 1986).

Demoranville (1982) reports the first records of experimentation with fertilizers and cranberries from New Jersey in 1885, while in Massachusetts some early work was conducted in the 1920's and 30's.

Note B of the "Cranberry Fertilizer Chart" (U.Mass. Agric. Exp. Sta. Bull., 1984) state "A crop of 100 barrels per acre plus one ton of vegetative material removes 23 pounds of nitrogen, 10 pounds of phosphorus and 18 pounds of potassium from the soil. Applying 230 pounds of 10-20-10 or comparable amounts of other analyses replaces the nitrogen. Much of the phosphorus is unavailable to the plant because of the nature of cranberry soils and petticoats leaches out very rapidly." Fertilizer applications of 5.5 kg/ha/year (30 pounds/acre/year) on a fen peatland (Richardson and Marshall, 1986) resulted in no significant increase in growth or nutrient uptake by emergent macrophytes. Agronomists from Oregon State University (Shaw et al., 1984) have estimated the removal of essential nutrients by the harvesting of cranberries at a yield of 370 barrels per ; hectare to be 79 Kg (36 lgs) of nitrogen, 3.3 Kg (1.5) of phosphorus, and 21 Kg (9.6 lbs) of potassium.

The use of fertilizers in conjunction with improved harvesting techniques and pest control measures has played a major role improving the yield per acre from 41 barrels per acre in 1950 to over 140 barrels per acre in 1984 (NECRS, 1985). Applications of fertilizers are generally timed to specific stages of plant growth. Consequently agronomists recommend multiple applications over the course of the year to provide more uniform distribution. Applications of fertilizers to optimize growth can be expected to meet or exceed the crop requirements. The preferred formulations include balanced ratios which introduce nitrogen in the form of ammonium ion. Sources include urea, urea formalydehyde, ammonium nitrate and ammonium sulfate (U. Mass. Agri. Exp. Sta. Bull., 1984). The common methods of application include distribution in dry form using cyclone spreaders or in liquid formulations through irrigation systems. Water applied through the sprinkler system may be retained within the bog system, returned to the reservoir or released downstream.

The amounts of fertilizers applied to cranberries are comparatively low, e.g. corn yielding at a comparable rate of 100 bushels per acre, plus five tons of cobs and other vegetative material requires 130 lbs of nitrogen, 50 lbs of phosphoric acid and 110 lbs of potash (Demoranville, 1982). The close association of cranberry bogs to surface waters and the high volume requirements are sufficient justification for examining the role of cranberry bogs as s potentially significant source of nutrients to Buzzards Bay.

The cranberry industry has been identified as a likely source of nutrients (Whittaker, 1980) and of toxics (DMF, 1985; Williams, 1987). The intensive use of insecticides over the past few decades is cited as one of the main factors to have increased yields per acre to their present levels (EPA, 1978). The use of pesticides and herbicides to control pests has also been implicated as the causative factor in several reported fish kills (DMF, 1985). The database to support or refute the significance of the industry on the environment is limited. In 1974, Deubert published a study which examined the relative impacts of cranberry production, automobile traffic and population density on surface and ground water quality in Cape Cod. He concluded that "neither automobile traffic nor cranberry production appears to have a measurable impact on quality of water." Unpublished studies in Wisconsin, the nation's second largest cranberry producer also have looked at the industry's impact on nutrient loading within receiving waterbodies, the effect of pesticide discharges as well as the impact of wetlands modification (personal communication, K. Schreiber, D.E.S., Wisconsin). In the Wisconsin studies phosphorus loading from the bogs generally was found not to be significantly affecting the conditions in the lakes examined but could be important where the acreage of the lake was small and where other potential sources were of minor importances (personal communication, K. Schreiber, D.E.S., Wisconsin).

# 1.4.3 <u>Pesticide Applications</u>

The general laws regulating the use of pesticides are contained within state and federal jurisdictions. In Massachusetts that law is the Massachusetts Pesticide Control Act. It is administered by the Massachusetts Pesticide Board which is a division of the Massachusetts Department of Food and Agriculture. Under its authority all pesticides are required to bear a label with directions and warnings concerning usage. The Board has developed regulations for the storage handling and disposal of pesticides and their containers. The Board also certifies the pesticides used and the training of applicators.

As noted in the introduction, the role and significance of the cranberry growing industry as a likely source of contamination to the region's surface and ground waters has been an issue of volatile concern for a number of years. The use of highly toxic chemicals in relative proximity to ground water, surface waters, and dwellings places all of these resources at potential risk. Cranberries during a typical growing year may be exposed to a host of insect pests and receive unwanted competition from weeds and grasses. The successful control of pests through the use of pesticides and herbicides has undoubtedly been a principal factor in improving harvest yields and berry quality Devilin et al., (1987), reported a 5 percent reduction in cranberry yields due infestations of long-stemmed weeds such as spike rush (Juncus effusus L), and narrow-leaf goldenrod (Solidago tenuifolia).

Pesticides exhibit a wide variety of structures and properties. They range from relatively simple inorganic salts such as lead arsenate to very complex organic compounds such as DDT and Diquat. The widespread use of organochlorine pesticides such as DDT and Dieldrin during the 1950's and 60's became a cause of nationwide concern during the 1970's. The same attributes which made these compounds attractive as pest control agents i.e., persistence/killing power, resulted in the accumulation and bioconcentration of the parent compounds and metabolites and subsequent migration out from the application sites through various pathways into the environment.

The extent of the migration is dependent upon the physiochemical properties of each compound and the nature of the media. There are three major pathways for pesticide degradation, photochemical, chemical and microbial transformations. The principal migration pathways for the organochlorine group are volatilization and adsorption since organochlorines generally have low solubilities in water and are immobile in soil systems where organic content is high, (Weber, 1972).

A factor in assessing the relative toxicity of certain compounds is the extent and amount of time necessary to degrade such compounds to nontoxic forms. Rao and Davidson (1979) discuss classifying pesticides based on their half-lives in soils: nonpersistent (t 1/2 < 20 days), moderately persistent (20 </t 1/2 </100 days). For example, the parent compound DDT and its metabolites are known to be extremely resistant to degradation. Further many of the DDT metabolites retain some of the same toxicological influences as the parent compounds. Due to a favorable partition coefficient onto fats and lipids, DDT and its metabolites have been shown to move through the food chain by partitioning to lipidal biological fractions and concentrating at the top of the food chain with significant adverse impacts. Goring et al., (1975) reports that available information on the loss of pesticides in soils is limited and cites many of the aforementioned factors. Additional losses are attributed to the effects of leaching and plant uptake. The authors do however, state that the few attempts at predicting losses under field conditions to have been surprisingly good. Goring further reports that (Hamaker et al., 1967) had developed a statistical correlation with the climatic conditions of temperature and rainfall for explaining roughly half of the variability in the disappearance of the pesticide picloram.

Comparable studies on the long-term stability of the modern organophosphate based pesticides used in the cranberry industry are limited. Most study researchers looked for residual levels of the parent compounds in the water column shortly after applications. There are some exceptions, the Environmental Protections Agency's National Enforcement Investigations Center (NEIC) (EPA, 1978) conducted an unpublished study in October of 1977 before and during a cranberry harvest on the Tremont Bog in Wareham. :They reported recoveries of ethyl parathion from bog soils ranging from 0.6 to 5.6 mg/g 90 days after the last application. Examinations of sediments and fish downstream proved negative. Miller et al., 1966 reported the detection of parathion S35 at concentrations of 0.007 ppm 6 days after application under laboratory conditions.

# 2.0 Study Objectives

The Division's study as proposed had three objectives: to estimate the levels of nutrients discharge from a commercial cranberry bog operation into an estuary; to analyze sediments within and immediately downstream of a commercial cranberry bog for residual levels of selected herbicides and insecticides; to qualitatively examine the composition of macroinvertebrates communities within and downstream of the cranberry bog.

# 2.1 Design and Rationale

The primary concerns in the early development of the study plans were: to identify a study area with a minimum of confounding nutrient inputs from upstream sources; to locate a site which where typical agricultural practices were employed and finally to select several blocks of time when agricultural practices could be monitored with relative ease. A secondary issue of concern was to locate a suitable control site on which to base comparisons in nutrient loadings and pesticide residues.

A decision was made to focus site selection within the Buttermilk Bay area to take advantage of existing and proposed studies under the Buzzards Bay Program. In order to account for hydrological as well as agricultural practices a monitoring plan which measured nutrient exports over (2) three day periods was chosen; late May-early June to coincide with a seasonal application of fertilizers and mid-October immediately after the harvest.

# 2.2 Study Area

Buttermilk Bay is a shallow water embayment located along the northwestern side of Buzzards Bay (Figures 2,4). It has a surface drainage basin of some 42.83 sq. km. (17 sq. miles) much of which is located within the "pitted plain" described by (Moog, 1987). It is comprised of extensive sand and gravel outwash deposits interspersed with streams, ponds, lakes and kettle holes which are ideally suited for the production of cranberries. Within the basin an estimated 137 ha (338.4 acres) of land are devoted to the commercial production of cranberries.

A commercial cranberry bog operation with 36.4 ha (90 acres) of producing bogs was selected as the study site. The study site is located approximately 1.2 km (0.7 m) east of Red Brook, the principal freshwater source to Buttermilk Bay (Figure 4). Surface drainage is largely contained within the 182 ha (450 acres) property bounds. Additional contributing nutrient sources were considered to be minimal, they included two residential dwellings, one located in the upper half of the watershed, and the second located roughly 610 m (2000 feet) east of the bog outlet stream. Two street drains located along Head of the Bay road also discharge to the bog during rain events (see Figures 5 and 6).

At this site the owner has the option of drawing or storing water from several waterbodies located on the property. The first, Weeks Pond is the major surface waterbody on the property. It serves as the principal reservoir for the upper 23 ha (57 acres) of active bogs (Garland Bogs). The second, Nyes Reservoir, serves as the major surface water source for the lower series (Nye Bog), which has a total of 13.3 ha (33 acres) under production. Additional water sources include North Pond, a 0.30 ha (3/4 acre) kettle pond located along the northern limits of the property. It provides water for several of the individual bogs located in the upper Mares Pond serves as secondary supply for the lower bogs and series. Bennetts Pond, a largely unaltered waterbody can provide water during periods of high water discharge to the lower Nye Bog. Additional water is supplied by two large capacity wells located in the upper and lower reaches which pump groundwater as needed to the bogs. The flexibility in water sources allows the owner to manage the upper and lower bogs as separate units.

The owner during the sampling period withdrew water from the groundwater wells and pumped the tailwaters back into the reservoirs. This is standard practice during most situations other than periods of extreme high water when storage capacity becomes limited.

#### 2.3 <u>Monitoring Network</u>

The owner's flexibility in meeting his water demands made it impossible in this limited study to monitor the entire system as simple inputs and outputs. In selecting the location of the stations within the active bog it was necessary to take into account the management practices of the bog owner.







# 2.3.1 Flow

Sites within the active bog and inactive bog identified as being suitable for flow monitoring were inspected one week prior to the initial sampling period of June 2-5, 1986. Criteria for determining suitability is included in the Standard Operating Procedures developed by the Engineering Section of the Division's Technical Services Branch. The pertinent criteria being; a minimum depth of 13 cm (5 inches) 1.5 - 1.8 m (5 to 8 feet) of straight reach, a stable stream bed free of large rocks, weeds and protruding obstructions which could create turbulence, and a flat stream bed profile to eliminate vertical components of velocity.

The first site selected was in the outlet stream of the active bog roughly 1.2 m (4 feet) upstream of the 91.4 cm (36") culvert (see Figures 5 and 6). The second site Station C, which was to originally serve as the control was located roughly 3 m (10 feet) downstream of the outlet weir of the Robbins Bog. This site was later abandoned due to inadequate flow. A third station, Station D, was established at the outlet of Bennetts Pond which at the time of the initial sample period, was contributing to the outlet discharge (see Figures 5 and 6).

# 2.3.2 <u>Nutrients</u>

Three nutrient monitoring stations were selected (Figures 5 and 6). The first (Station A) was located at the outlet of the North Pond: water from this kettle pond located in the upper reaches of the It was assumed that its water chemistry approximated watershed. groundwater quality and received minimal contributions of nutrients. The second site (Station B) was located at the outlet end of the 13 ha Nyes Bog complex. It served as the principal monitoring station since all flow from the entire site eventually discharged to this A third (Station C) was located off site and drained the stream. abandoned "Robbins Bog." This bog which is located within the Red Brook drainage basin was taken out of production 20 - 30 years ago when the property was acquired by the Town of Wareham for use as a public water supply (personal communication, William Tatlow). It was originally selected for this study to provide a comparison of nutrient outputs from an active versus an inactive bog. This site was subsequently abandoned as a water guality monitoring station due to low flow. A fourth, (Station D) was located at the outlet of Bennetts Pond prior to its discharge to the Nyes Bog. It provided the basis for comparing the nutrient outputs from an unaltered freshwater wetland with the active cranberry bog.

#### 2.3.3 <u>Sediments - Pesticide Residues</u>

The influence of pesticides and on the resources downstream of the bog and to the receiving estuary is a complex issue involving many interrelated physical and biological processes such as the chemical nature of the agent, the influences of soil particles through absorption, water, temperature, pH, sunlight, microbial action; all affect the agent in the rate of decomposition and its persistence in the environment. This study addresses one aspect of the problem by examining sediments within and downstream of the commercial bog for pesticide residues to determine the extent of pesticide translocation.

The selection of which pesticides to look for was determined after reviewing the list of recommended pesticides issued by the Massachusetts Agricultural Experiment Station for 1984 and polling the grower as to his usage during 1985 - 1986. These samples were collected in the fall to coincide with the end of the growing season and hence reflect the applications of the agents during that growing season. Collection times were coordinated with a low tide event to facilitate collection of sediments within the estuarine portion of the outlet stream.

Sediments were collected from three (3) stations, the first, Station B was located within a stagnant portion of the stream discharging from the bog. The second, Station C at the outlet of the abandoned Robbins Bog served as a control. The third, Station E was located at the mouth of the outlet stream where it discharges into Buttermilk Bay.

# 2.3.4 <u>Macroinvertebrates</u>

As a corollary to the examination of the sediments for pesticide/herbicide levels the Division also conducted a qualitative examination of the aquatic macroinvertebrate communities at several locations. The purpose of which was twofold: 1) to identify family to the predominant invertebrates in each segment and 2) to determine whether there is sufficient biomass of a single taxon to meet analytical requirements for tissue analysis.

The bog/stream system was divided into four segments for sampling purposes. Segment "E" which included the estuarine portion of the outlet stream was not sampled. Segment "1" covered approximately 90 m (295 feet) from Segment "E" to "Head of the Bay Road." Segment "2" was approximately 100 m (328 feet) long, running from "Head of the Bay Road" to the dirt road which crosses the outlet stream. Segment "3" was approximately 5 m (16 feet) long and ran from the outlet structure at the end of the bog along the central outlet channel (see Figures 5 and 6 for segment locations).

# 3.0 <u>General Field Sampling Procedures</u>

Field sampling procedures were developed after reviewing methodologies included in the Standard Operating Procedures document developed by the Massachusetts Division of Water Pollution Control's Technical Services Branch, guidelines provided by the Environmental Protection Agency (EPA, 1983) and through the development of a Water Quality Assurance Project Plan specifically designed for this study. Copies of these documents are on file the Divisions Technical Service Branch Office, Westview Building, Lyman School, Route 9, Westborough, Massachusetts 01581.

Field work was conducted by sampling crews supervised by the author. Each crew was provided with a "Survey Preparation Report" which detailed the sampling station locations, the type of samples to be collected and the time of collection. All field work was supervised by the author. Field crews collected and preserved all samples in accordance with details provided in the "Survey Preparation Reports."

#### 3.1 Flow Measurements

In order to convert the nutrient levels found in the sampling scheme to a loading function it was necessary to obtain an estimate of the volume of water discharging from the bog and the wetlands. Flow measurements were made by the "wading rod method." The wading rod method is a standardized method suitable for estimating flow in shallow, relatively slow moving streams. The equipment included a "Pygmy Current Meter" No. 625 manufactured by Gurley Co, Troy, New York. As the bucket wheel rotates electrical contact is made on a single contact cam producing a signal each time the bucket wheel completes a revolution. The velocity at the point of the current meter is measured by counting the number of signals in a specified time interval with a headset attached to the contact post.

A Current Meter Digitizer (CMD) (Software Version 1.2) manufactured by Scientific Instrument Co., mounted on the wading rod provided a digital display of the number of revolutions per time interval and the velocity in feet per second (fps).

Readings were taken at 15 cm (6 inch) intervals across the width of each stream during the June 1986 sampling period. During the October 1986 sampling period, flow measurements were restricted to the outlet stream 6 m (20 feet) downstream the bog outlet. Further discussion of the conditions and flow measurements taken during this time period can be found in the Results Sections (5.1.4 and 5.2.4) of this report. Copies of the original flow measurements as well as the flow calculation sheets, are included in the master file stored at the TSB office in Westborough.

#### 3.2 <u>Nutrients and Water Chemistry</u>

Twenty-four 150 ml. samples, two each hour, were collected at each of the three (3) nutrient stations, using an automatic sampler manufactured by Instrumentation Specialities Co. of Lincoln, The ISCO Model 1680 Wastewater Sampler is a portable Nebraska. device designed to collect up to 28 separate sequential samples of a predetermined volume. The controls and electronics are housed in a water tight stainless steel container which sits over a sampling well containing two rings of 14 bottles per ring (see Appendix). Nutrient samples and physical chemistry samples were collected hourly using the unit's programmable circuitry. The interval in minutes remaining until the next sample is displayed on an LED readout. Cross contamination of the samples was minimized by the automatic purging of the Tygon (tm) suction line before and after each sample. The central well within the sampler was periodically filled with ice to

keep samples chilled thereby reducing biological activity. Nutrient samples, (TKN,  $NH_3^+$ ,  $NO_3^-$ , TP and  $PO_4^+$ ) were assigned to the outer ring of bottles and those were for physical chemistry assigned to the inner ring. Prior to the time of collection with 2 mls of 1 N  $H_2SO_4$  were added to each nutrient bottle. The individual hourly samples were manually composited at 1800 hours June 2, 1986 and thereafter at the 0600 and 1800 hours for the balance of the study.

At each of the nutrient stations, grab samples for total iron and hardness were collected once each day and preserved in the field with 2 mls of 1 N  $HNO_3$ . In addition, pH, temperature and dissolved oxygen measurements were made at each station during the early morning, midday and late afternoon of each sampling day.

All glassware used in the study was washed in phosphate free detergent (Thomas liquid detergent (tm)) and rinsed with 30 percent HCl followed by three (3) successive rinses of dionized distilled water.

At the conclusion of each sample period the individual samples were composited to make up a one (1) liter sample. Samples were tagged and packed in wet ice coolers for transport to the Lawrence Experiment station for analysis.

Specific information concerning sample preservation for each parameter, sample volume requirements, containers, preservation and holding times is presented in Table 1.

#### 3.3 <u>Sediment Collections For Pesticide Residues</u>

The sediment collections were made on November 12, 1986, roughly 30 days after harvest flood waters had been pumped back into the reservoirs. Collection times were coordinated with a low tide event to facilitate collection of sediments within the estuarine portion of the outlet stream. The actual sample locations within each station were selected after locating sediments which appeared to contain a high percentage of organic matter.

Collections originally were to be made using a hand coring device manufactured by Wildco but the sediments within the outlet stream proved to be too watery to maintain a discrete sample. As an alternative the top 10 cm (4 inches) of sediments were scooped-up using a stainless steel bucket which had been previously rinsed with successive washes of distilled water, reagent gradacetone and reagent grade hexane. Core samples were obtained from Stations C and E. Approximately 300 grams of sediment from each station were then transferred to glass jars which had been previously rinsed with successive washes of distilled water, reagent grade acetone and reagent grade hexane. The jar caps were equipped with teflon septums. The jars were then tagged and transported in wet ice to the Massachusetts Pesticide Analytical Laboratory at Amherst,

# TABLE 1

# SUMMARY OF WATER QUALITY PARAMETERS, VOLUME REQUIRMENTS, CONTAINERS, PRESERVATION AND

# MAXIMUM HOLDING TIMES

DADAMETED	REQ (ml)		DRCFDMMTM	HOLDING
	VOLUME			
Acidity	100	G	Cool, 4 Deg C	14 days
Total Alkalinity	100	G	Cool, 4 Deg C	14 days
Ammonia	400	G	Cool, 4 Deg C H <sub>2</sub> SO <sub>4</sub> to pH<2	28 days
Chloride	50	G	None Reg	28 days
Color	50	G	Cool, 4 Deg C	48 hrs.
Dissolved Oxygen	300	NA	None Req	in situ
Hardness	100	G	Cool, 4 Deg C $H_2SO_4$ to $p[H<2$	6 mon.
Nitrate	100	G	Cool, 4 Deg C H <sub>2</sub> SO <sub>4</sub> to pH<2	48 hrs.
Ortho-Phosphorus	50	G	Cool, 4 Deg C H2SO4 to pH<2	48 hrs.
pH	25	NA	None Reg	in situ
Specific Conductivity	7 100	G	Cool, 4 Deg C	28 days
Temperature	1000	NA	None Req	in situ
Total Dissolved Solids	100	G	Cool, 4 Deg C	7 days
Total Iron	100	G	HNO, to pH<2	6 mon.
Total Kjeldahl- Nitrogen	500	G	Cool, 4 Deg C $H_2SO_4$ to pH<2	28 days
Total Phosphorus	50	G	Cool, 4 Deg C H <sub>2</sub> SO <sub>4</sub> to pH<2	28 days
Total Solids	100	G	Cool, 4 Deg C	7 days
Total Suspended Solids	100	G	Cool, 4 Deg C	7 days

Foot Note:

G = Glass

NA = Not Applicable

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Massachusetts for subsequent analysis. Sediment samples were frozen upon receipt and thawed by refrigeration 24 hours prior to analysis. All samples were analyzed under the direct supervision of Dr. J. Marshall Clark.

#### 3.4 <u>Macroinvertebrates</u>

TSB freshwater biologists surveyed the bog outlet/stream from its terminus along the northern shore of Buttermilk Bay, known locally as "Hideaway Cove," to the cranberry bog outlet. The length of the stream was sectioned then divided into four reaches for sampling purposes. Segment "E", which included the estuarine portion of the outlet stream, was not sampled. Segment "1" covered approximately 90 m (295 feet) from Segment "E" to "Head of the Bay Road." Segment "2" was approximately 100 m (328 feet) long, running from "Head of the Bay Road" to the dirt road which crosses the outlet stream. Segment "3" was approximately 5 m (16 feet long) upstream of the outlet structure along the central outlet channel (see Figure 5 for segment locations). D-nets were used to collect aquatic macroinvertebrates from different micro-habitats within each segment. Taxa were identified in the field to the best possible level without the aid of magnification (usually family level). Some specimens were brought back to the laboratory for confirmation of field identifications. A list of the taxa collected from the various segments is listed in Table 13.

# 4.0 Quality Assurance Quality Control Procedures

# 4.1 Data Quality Field Procedures

Variability within the sampling system and the water column was estimated by: 1) splitting the final nutrient composite samples collected at Station B during the June 4-5 and October 22-23, 1986 collection periods; and 2) by collecting two (2) liter grab samples from Station B and making duplicate splits of these grab samples and a field blank. During the March 23, 1987 sampling period three replicate grab samples were collected from Station B.

The results were then evaluated for outliers and basic statistics: mean, standard deviation and coefficient of variation. All results are presented in Table 2.

#### 4.2 Data Quality Laboratory procedures

Upon transfer of the water samples to the Lawrence Experiment Station (LES), the samples are logged in accordance with the Standard Operating Procedures developed by the laboratory and approved by the Environmental Protection Agency (EPA). This generally verifies the information presented on the tag and an assignment of a laboratory identification number which is then entered into a bound log book. These log books are available for inspection at LES. Table 3 presents the parameters, the analytical methodology, the units of measure, references and maximum holding times for each parameter.
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# SUMMARY OF FIELD VARIABILITY WITHIN NUIRIENT

## SAMPLES OBTAINED FROM STATION B

6/5/86

	Rep A	Rep B	SPLIT 1	SPLIT 2	SPLIT 3	SPLIT 4
TKN	0.77	0.45	0.70	0.73	0.54	0.55
NH <sub>2</sub>	0.21	0.07	0.04	0.10	0.13	0.13
NO	1.20	0.10	<0.1	0.1	<0.1	0.1
TP	0.12	0.14	0.06	0.10	0.09	0.09
P04	0.08	0.19	0.04	0.07	0.07	0.06
10/23/86	5					
	Rep A	Rep B	SPLIT 1	SPLIT 2	SPLIT 3	SPLIT 4
TKN	0.59	0.60	0.56	0.45	0.45	0.54
NH <sub>3</sub>	<0.02	0.06	0.03	0.10	0.12	0.05
NO3	<0.1	<0.1	<0.1	0.1	0.1	<0.1
TP	0.51	0.53	0.58	0.56	0.58	0.58
P04	0.33	0.33	0.40	0.40	0.41	0.40

10/23/86 Field Blank

TKN	0.18
NH <sub>3</sub>	<0.02
NO3	0.1
TP	0.13
P04	0.07

3/23/87

Rep A	Rep B	Rep C	
0.85	0.84	0.59	
0.11	0.04	0.02	
0.1	0.4	<0.1	
0.21	0.15	0.18	
0.11	0.03	0.03	
	Rep A 0.85 0.11 0.1 0.21 0.11	Rep A Rep B   0.85 0.84   0.11 0.04   0.1 0.4   0.21 0.15   0.11 0.03	

DATE		6/5	/86		LO/23/8	6		3/23/87	
	/X	SD	SX	<u>/X</u>	SD	SX	/X	SD	S/X
				-			· · ·		
REPS	0.61	0.23	0.38	0.60	0.01	0.01	0.76	0.15	0.19
SPLITS	0.63	0.10	0.16	0.50	0.06	0.12			
NH3 REPS	0.14	0.10	0.71	<0.04			0.06	0.05	0.79
SPLITS	0.10	0.04	0.42	0.08	0.04	0.52			<del></del>
NO3 REPS	0.65	0.78	1.20	<0.1			<0.2		
SPLITS	<0.1			<0.1		-			
TP REPS	0.13	0.01	0.11	0.52	0.01	0.03	0.18	0.03	0.17
SPLITS	0.19	0.02	0.19	0.58	0.01	0.02			
PO4 REPS	0.14	0.08	0.56	0.33	0	0	0.06	0.05	0.83
SPLITS	0.06	0.01	0.24	0.40	0.01	0.01			-

# TABLE 2 (CONTINUED)

X = MEAN

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- SD = STANDARD DEVELATIONS/X = COEFFICIENT OF VARIATION
- -- = NOT SAMPLED

# SUMMARY OF WATER QUALITY PARAMETERS, METHODOLOGY,

# REPORTING UNITS, ANALYTICAL PROCEDURES AND

# LIMITS OF DETECTION

PARAMETER	METHOD	UNITS	REFERENCE	DENECT LIMITS
Acidity	Titrimetric	meg/1	EPA 1983 Method 305.1	
Alkalinity	Titrimetric	mg/l	SM 16th ed.,	
Total	pH 5	CaC03	Sec. 40	
Ammonia	Automated Phenate Method	mg/l NH <sub>3</sub> -N	SM 15th ed., Sec. 417F	0.02 mg/l
Chloride	Argentometric with AgN0 <sub>3</sub>	mg/l Cl	SM 15th ed., drv/407A	0.5 mg/l
Color	Visual Comparison	Color Units	SM 1th ed., Sec. 204A	
Dissolved Oxygen	Membrane Electrode	mg/l D.O.	Yellow Springs Inst. Co.	0.05 mg/l
Hardness	by Calculation	mg, eq. CaCO <sub>3</sub>	SM 18th ed., Sec. 314	
Nitrate	Colonnetric Automated Hydrazine Red	mg/1 N0 <sub>3</sub> -N	EPA Met. 353.1	983 0.1 mg/l
Orthophosphorus	Ascorbic Acid Met.	mg/l P	SM 16h ed., Sec. 424 F	0.01 mg/l
pH	Electrometric	pH log Units	Orion Research Model 211	
Specific Cond.	Wheatstone Bridge	umhos/cm	Yellow Spring In Co.	st.
Temperature	Thermometric	Deg. C	WWR brand Cat No. 61157	
Total Dissolved Solids	Dried 180 deg. C	mg/1	SM 6th ed., Sec. 209B	10 mg/l

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# TABLE 3 (CONTINUED)

PARAMETER	METHOD	UNITS	સ્ટાફાર્ટ્સર્ટ્સ્ટ્ર	DEPECT LIMITS
Total Iron	Atomic Absorption Direct Aspiration	<b>mg/1</b>	EPA 1983 Meth. 236.1	0.03 mg/l
Total Kjeldahl Nitrogen	Colormetric Semi-automated Block Digester	mg/ln	EPA 1983 Meth. 351.2	<1 mg/l
Total Phosphorus	Colormetric Technicon BD-40 Block Digester Technicon Auto Analyzer II	mg/l	EPA 1983	<.02
Total Solids	Dried at 103-105 Degrees	mg/l	SM 16th ed., Sec. 209A	5 mg/l
Total Suspended Solids	Filtrate Dried at 1103-105 Deg. C	mg/l	SM 16th ed., Sec. 209C	5 mg/l

10

Footnote:

SM = Standard MethodsN/A = Not Applicable

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#### 4.2.1 Lawrence Experiment Station Quality Assurance Quality Control

Information regarding analytical accuracy and precision is included in the following: Standard Operating Procedures, Inorganic Chemistry Laboratory, Lawrence Experiment Station 1984 and the SOP developed for the Wastewater Laboratory at the Lawrence Experiment Station.

The Lawrence Experiment Station employes the following measures to ensure quality control within the laboratory. In order to ensure precision during analysis, one out of every ten samples were selected and run in duplicate. This sample was analyzed immediately. After the set of ten it was selected from and prior to the next set of ten. It was recorded in the work book in the order it was run. The duplicate data were then used in the following manner:

- a. The difference between the original sample and the duplicate was determined.
- b. The standard deviation of the differences was determined from at least 20 such samples.
- c. A Quality Control Chart was generated from these data using one (1) and two (2) standard deviations around zero. Two (2) standard deviations determined the upper and lower control limits. If a duplicate was out of control the analysis was stopped and the analyst checked for error. When the problem was solved, that set of ten (10) samples was reanalyzed.

In order to insure accurate analytical data, the following two methods were employed.

- a. An EPA reference standard was run after every ten (10) samples. These known concentrations indicated whether the working standards were good or bad, and whether the instrument settings had been properly set up.
- b. To insure the accuracy of actual field samples, one out of every 10 samples (the duplicate sample) was spiked with a known amount of analyte.

After the analysis, the percent recovery of the spike was determined and used as follows:

- 1. The mean (at least 20 samples) of the percent recoveries was determined.
- 2. The standard deviation of the percent recoveries was determined.
- 3. A quality control chart was generated from this data using two (2) and three (3) standard deviations around the mean percent recover; two (2) standard deviations around the percent recovery determined the upper and lower control limits. If a spike was found to be out of control the analysis was stopped and the analyst checked for error. When the problem was solved that set of ten was reanalyzed.

A typical run would include the following: Standard, blank, EPA reference, ten samples, blank, duplicate, spike, EPA ref., etc. All of the Q.C. data generated was recorded on the Q.C. charts and in a separate Q.C. data book.

The calculations used to determine the percent recovery are as follows:

Tables 4-8 present the aforementioned QA/QC nutrient data. Additional information regarding the other water quality parameters is on file at the Lawrence Experiment station, Lawrence, MA.

#### 4.3 Laboratory Procedures Pesticide Analysis

The pesticide and herbicide analysis was conducted by Matthew Brooks, residue chemist under the direction of Professor J. Marshall Clark. The details of the methodologies were kindly provided by Mr. Brooks in a series of three reports, which are included here with only minor editorial changes.

A ten gram aliquot of each sample was heated to 105°C overnight to determine water content. Results of analyses were reported on a total wet weight basis. Two spike samples were run for each sample for each group of analyses (e.g. a group constituted a set of compounds analyzed in a single analyses, such as diazoxon and parathion as a group, dichlobenil, diazinon, methyl parathion and chlorpyifos as a group, the lone compound p-nitrophenol as a group, etc.) and an average percent recovery The value was influential in determining the individual determined. detection limits of each compound for each sample. A reagent blank was run for every ten samples analyzed. No extraneous peaks were noted. Site C was used as the soil blank (untreated cranberry sediment). Standards were injected with every site analysis (approximately every 5 All solvents were pesticide grand and all glassware was injections). prewashed before use.

#### 4.3.1 Parent Compounds

The following techniques were employed in the analysis of chlorphyrifos, methyl parathion, parthion, dichlobenil, diazinon. Organophosphate parent compounds were analyzed in soil and sediment according to the method provided by the National Enforcement Investigations Center, EPA Office of Enforcement. Approximately 50 gram samples from each site was analyzed in duplicate for the listed compounds. Samples were subjected to a hexane/acetone extraction followed by a water rinse to remove the acetone and polar soluble impurities. The hexane layer was dried over sodium sulfate, concentrated and analyzed by a Varian 3700 gas-liquid chromatograph (GLC) equipped with electron capture (ECD) and thermionic specific (TSD) detectors.

Analysis by ECD utilized a 15 m DB percent megabore column (J & W Scientific Inc., Palo Alto, CA) which was temperature programmed from 110°C at 15°C/min. The column was held at 110°C and 220°C for one minute. The injector and detector temperatures respectively were

## SUMMARY OF QA/QC PROCEDURES PERFORMED ON TOTAL KJELDAHL-NITROGEN

ANALYSIS FOR THE PERIOD 6/02/86 - 6/17/87 SAMPLE REFERENCE

NUMBERS R16483 THROUGH R23281

DATE	SAMPLE #	DUPLICATE 1	DUPLICATE 2	MEAN	SPIKE	SPIKE MEAN
Jun 02 86	R16483	3.2	3.0	3.1		
Jun 03 86	R16561	0.62	0.68	0.65	1.0	0.35
Oct 20 86	R22273	0.58	0.62	0.60	0.98	0.38
Mar 20 86	R22412	0.60	0.55	0.57	0.97	0.40
Mar 09 87	R23185	0.86	0.91	0.88	1.38	0.50
Mar 20 87	R23281	0.38	0.33	0.35	0.70	0.35

N = 6 samples Mean = 0.0750 Standard Deviation (S) = 0.0616 2S = 0.1231 3S = 0.1847 Coefficient of Variation (CV) = 82.08% TKN-N Spike - 0.45 mg/l N = 30 Mean = 0.4283 S = 0.0832 CV = 19.43% Spike Recovery 95.19% --- = Not Reported

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## SUMMARY OF QA/QC PROCEDURES PERFORMED ON AMMONIA NITROGEN

## ANALYSIS FOR THE PERIOD 5/29/86 - 3/23/87

## SAMPLE REFERENCE NUMBERS R16362 THROUGH R23341

DATE	SAMPLE	ORIGINAL	DUPLICATE	MEAN	SPIKE	SPIKE	\$ RECO
	#	·			SAMPLE	CONCENTRAT	ION
May 29 86	R16362	0.27	0.19	0.23	0.58	0.4	88
May 29 86	R16317	0.09	0.06	0.075	0.40	0.4	81
Jun 03 86	<b>R1638</b> 5	0.09	0.07	0.08	0.43	0.4	88
Jun 04 86	<b>R164</b> 31	0.22	0.22	0.22	0.58	0.4	90
Jun 05 86	<b>R16501</b>	0.12	0.12	0.12	0.43	0.4	78
Jun 05 86	<b>R16525</b>	0.07	0.06	0.065	0.41	0.4	86
Jun 06 86	<b>R16567</b>	0.13	0.13	0.13	0.37	0.4	60
Oct 17 86	R22344	0.01	0.09	0.095	0.41	0.4	79
Oct 17 86	<b>R22</b> 375	0.07	0.07	0.07	0.40	0.4	83
Oct 23 86	<b>R2244</b> 5	0.01	0.01	0.01	0.36	0.4	88
Oct 24 86	<b>R225</b> 03	0.03	0.03	0.03	0.46	0.4	108
Mar 20 87	<b>R23335</b>	0.22	0.22	0.22	0.55	0.4	<b>8</b> 5
Mar 20 87	<b>R2</b> 3341	0.06	0.06	0.06	0.40	0.4	85

\*\* 1 NH3-N Spike 0.4 mg/l; N = 13; Mean = 0.0169; S = 0.0295; CV = 174.63%; Spike Recovery 84.5%

\*\* 1 Calculations based on QA/QC data reported for sample # R16363 - R23341

## SUMMARY OF QA/QC PROCEDURES PERFORMED ON NITRATE-NITROGEN

## ANALYSIS FOR THE PERIOD 5/29/86 - 3/23/87

## SAMPLE REFERENCE NUMBERS R16362 THROUGH R23341

DATE		SAMPLE	ORIGINAL	DUPLICATE	MEAN	SPIKE	SPIKE	& RECO
		#				CONCEN- TRATION	SAMPLE	
May 29 8	B6	R16362	0.20	0.19	0.195	0.4	0.50	96
May 29 8	B6	R16317	0.01	0.01	0.01	0.4	0.43	105
Jun 03 8	B6	<b>R16385</b>	0.04	0.01	0.025	0.4	0.41	96
Jun 04 8	B6	R16431	0.52	0.52	0.52	0.4	0.88	90
Jun 05 8	B6	R16501	0.54	0.50	0.52	0.4	0.86	85
Jun 05 8	B6	R16525	0.34	0.34	0.34	0.4	0.73	98
Jun 06 8	B6	R16567	0.06	0.06	0.06	0.4	0.46	100
Sep 30 8	B6	R22134	0.03	0.02	0.025	0.4	0.42	99
Oct 23 8	B6	R22445	0.00	0.00	0.00	0.4	0.38	95
Mar 20 8	87	R23341	0.31	0.31	0.31	0.4	0.68	93

 $NO_3$ -N Spike - 0.4 mg/l; N = 10; Mean = 0.0090; S = 0.0145; CV = 161.1%; Spike Recovery 95.7%

\*\*1 Calculations based on QA/QC data reported for samples R16363 - R23341

## SUMMARY OF QA/QC PROCEDURES PERFORMED ON TOTAL PHOSPHOROUS

## ANALYSIS FOR THE PERIOD 6/01/86 - 6/17/87

## SAMPLE REFERENCE NUMBERS R16483 THROUGH R23281

DATE	SAMPLE #	DUPLICATE	DUPLICATE	MEAN	SPIKE	SPIKE MEAN	% RECO
Jun 01 86	R16483	0.46	0.45	0.45	0.65	0.20	89
Jun 03 86	R16561	0.03	0.03	0.03	0.24	0.21	93
Oct 20 86	R22273	0.06	0.06	0.06	0.28	0.19	84
Oct 21 86	R22412	0.06	0.05	0.05	0.27	0.22	98
Mar 09 87	R23185	0.04	0.05	0.04	0.27	0.22	98
Mar 20 87	R23281	0.02	0.01	0.01	0.23	0.22	98

\*\* 1

TP-P Spike 0.210 mg/l; N = 6; Mean = 0.0050; S = 0.0055; CV = 109.5%; Spike Recovery 93.3%

\*\* 1 QA/QC data summary i.e. a mean of 0.02 and S of 0.0247 etc based on data for the entire sampling period.

# SUMMARY OF QA/QC PROCEDURES PERFORMED ON ORTHOPHOSPHORUS ANALYSIS FOR THE PERIOD 6/03/86 - 10/23/86 SAMPLE REFERENCE NUMBERS R16362 THROUGH R23341

DATE	SAMPLE #	ml/SAMPLE	ABSORBANCE	CONCENTRATION	mg/l
Jun 03 86	BLANK	50	0.000		
Jun 26 86	R16597	50	0.042	0.1111	0.11
Jun 26 86	DUP 597	50	0.041	0.1085	0.11
Jun 26 86	5ug/50 mis		0.041	0.1085	5.43
Jun 26 86	15ug/50 ml s		0.115	0.2291	15.0
Oct 17 86	BLANK	50	0.000		
Oct 17 86	R22379	50	0.025	0.0679	0.07
Oct 17 86	DUP 379	50	0.026	0.0704	0.07
Oct 22 86	BLANK	50	0.000		
Oct 22 86	R22403	50	0.147	0.3778	0.38
Oct 22 86	DUP 403	50	0.149	0.3829	0.38
Oct 22 86	5ug/50 ml s	50	0.040	0.1060	5.3
Oct 23 86	15ug/50 ml	50	0.116	0.2991	14.95
Oct 23 86	BLANK	50	0.000		
Oct 23 86	R22474	50	0.154	0.3956	0.40
Oct 23 86	DUP 474	25	0.076	0.1975 x2	0.40
Oct 23 86	5ug/50 ml s		0.040	0.1060	5.30
Oct 23 86	15ug/50 ml		0.119	0.3067	15.33
Aug 26 86	BLANK	50	0.000	0.000	0.00
Aug 26 86	1 EPA WPO	50	0.008	0.0247	0.02
Aug 26 86	2 EPA 17	10	0.047	0.1238 x5	0.6188

250°C and 300°C. The carrier gas was nitrogen at 10 ml/min while the detector make up was argon/methane (95/5, v/v at 60 ml/min.). Samples measured by TSD were analyzed on a 1.8 m 4%0V101/6%0V210 packed metal column. The column was temperature programmed from 160°C to 210°C at 5°C/min. The column was held at 210°C for one minute. The injector and detector temperatures respectively were 220°C and 300°C. The TSD was supplied with hydrogen at 4 ml/min. and air at 160 ml/min. The nitrogen carrier gas was adjusted to 30 ml/min. The bead current was set at 3.6 amperes.

The ECD provided extremely sensitive residue analysis for aromatic and halogenated compounds (e.g., picadores to fentogram levels). This provided a low level of detection (e.g., 20 ppb). The TSD, although not as sensitive as the ECD, gave a second screen specifically for nitrogen and phosphorous compounds which provided an additional verification of questionable peaks as in the case for chlorpyrifos. Verification of positive compounds was by using a Hewlett Packard 5985b gas chromatograph/mass spectrometer (GC/MS Facility, College of Food and Natural Resources, MA. Agric. Exp. Station, Univ. of MA-Amherst, Thomas Potter, Director). A 3 ul aliquot was injected onto an 11m SE30 capillary column (J.& W. Scientific, Inc.) which was temperature programmed from 80°C to 220°C at  $10^{\circ}/min$ .

#### 4.3.2 Total Organic Carbon and Nitrogen Analysis

A representative ten gram aliquot of each sediment sample was analyzed for total organic carbon and nitrogen by the University of Massachusetts Microanalysis Laboratory using a Control Whitman mode 24TxA elemental analyzer (Control Whitman, Inc., Lowell, MA). Each aliquot was dried at 110°C for 24 hours. Any shell fragments larger than (>0.5 cm) were removed. The dried sediment was ground to a fine powder using a mortar and pestle. If sediment carbonates were significant they were removed. The powdered sediments were stored in vials at room temperature in a desiccator until further analysis. Prior to analysis 5 grams of soil from each site was dried overnight in a 105°C oven. The samples were then combusted and the carbon and thermal conductivity detector.

#### 4.3.3 <u>Metabolite Analysis</u>

The soil samples were also analyzed for the insecticide metabolites: aminoparathion, paraoxen, diazoxon, p-nitrophenol and p-aminophenol. aminoparathion, diazoxon, and paraoxen were analyzed according to the method for organophophate compounds in soil and sediment provided by the National Enforcement Investigations Center, EPA Office of Enforcement. Approximately 50 grams samples from each site were analyzed in duplicate for the listed compounds. Samples were subjected to a hexane/acetone extraction followed by a water rinse to remove the acetone and polar soluble impurities. The hexane layer was dried over sodium sulfate, concentrated and analyzed by a Varian 3700 gas-liquid chromatograph (GLC) equipped with electron capture (ECD) and thermionic specific (TSD) detector. The GLC was equipped; with a 1.8 m 4% 0V101/6% 0V210 packed metal column. The column was operated isothemally at 180°C. The injector and detector temperatures respectively were 220°C and 300°C. The TSD was supplied with hydrogen at 4 ml/min. and air at 160 ml/min. The nitrogen carrier gas was adjusted to 30 ml/min. The bead current was constant at 3.6 Amperes.

P-nitrophenol and p-aminophenol were analyzed by high performance liquid chromatography (HPLC) utilizing the methods of Diamond and Quebbeman (1977) for p-nitrophenol and Sakurai and Ogawa (1976) for p-aminophenol. Soil samples of approximately 15 gm wet weight were shaken for 10 min. in 10 ml of methanol water (MeOH:20, H20:80).

The solution was then filtered and analyzed by reversed phase HPLC. Both compounds were analyzed isocratically on a Waters liquid chromatograph (Millipore Co., Bedford, MA). A Spherisorb C18 column (25 cm length, 10 um particle size) was used at ambient temperature for both compounds (Spherisorb, Inc., United Kingdom).

P-nitrohenol was analyzed using a mobile phase of 10 mM K2HP04 containing 0.075% triethylamine at a flow rate of 1.0 ml.min. The pH was adjusted to 7.0 by addition of phosphoric acid. Detection was by UV absorption at 280 mm. P-aminophenol was extremely difficult to analyze due to its poor UV absorption and its rapid degradation (Merck, 1983).

#### 4.3.4 Glyphosate and AMPA Determinations

Soil samples were also analyzed for the herbicide glyphosate and its primary metabolite, aminomethyl phosphonic acid (AMPA), by methods of Lundgren, 1986; and Cowell, et al 1986).

Approximately 10 gr of soil (wet weight) were shaken for 15 min. in 30 ml of 0.1M triethylamine. This solution was filtered and the filtrate shaken 10 min. with 10 gr of AG 1-x8 resin (50-100 mesh, Bio-Rad Laboratories, Richmond, CA). The resin was pretreated with 10 ml of 6N HC1 and washed to neutrality with distilled water.

After shaking, the triethylamine extract was discarded and the resin was washed twice3 with 10 ml portions of distilled water. Glyphosate and AMPA was recovered from the resin by shaking with 10 ml of 6 N HCl for 5 min. An 80 ul aliquot of the resin extract was filtered through 0.45 um polyvinylchloride filters and analyzed.

The analysis was performed on a Perkin-Elmer liquid chromatograph (Perkin-Elmer Co., Norwalk, CT) equipped with a Kratos post column reaction system (PCRS, Kratos Analytical, Ramsey, NJ). Glyphosate and AMPA were separated on an aminex A-9 caution exchange column (25 um x 4 mm, Bio-Rad Lab.). The column temperature was maintained at 50°C. The mobile phase consisted of 5 mM  $KH_2PO_4$ : MeOH (96:4). The pH was adjusted to 1.9 by dropwise addition of phophoric acid. The flow rate of the mobile phase was 0.5 ml/min.

Glyphosate was oxidized to a primary amine for conjugation with 0-phythaladehyde (OPA) in a calcium hypochlorite oxidation solution

(10 mM  $\text{KH}_2\text{PO}_4$ , 200 mM NaCl, 10 mM boric acid, 28 mM mercaptoethanol, 1.1 mM OPA Pickering Lab., Mountain View, CA) in a 1.0 ml reaction coil. The flow rate for the OPA reagent was 0.3 ml/min. A Kratos Spectraflow 800 fluorescence detector (excitation wavelength 340 nm and emission wavelength 455 nm) was used to detect the conjugates.

Confirmation of positive samples was by gas liquid chromatography (GLC) utilizing an esterification and acylation process described by (Deyrup et. al, 1985). Soil samples were extracted as previously described. A 100 ul aliquot of the final extract was concentrated to dryness under N<sub>2</sub>. The residue was dissolved in 200 ul ethyl acetate and analyzed. Samples were analyzed using a Varian 3400 GLC equipped with an electron capture detector (ECD). A 15 m DBL megabore column (J & W Scientific, Palo Alto, CA) was temperature programmed from 100°C to 150°C at 10°C/min. The column was held at the initial and final temperatures for one min. The injector and detector were respectively maintained at 250°C and 300°C.

### 5.0 <u>Results</u>

#### 5.1 <u>Spring 1986</u>

The agricultural management practices as previously discussed and weather events largely determine when these altered wetlands will function as nutrient sinks or sources. The approach taken in the development of the sampling scheme used in this study was to select two blocks of time which coincided with times and activities likely to result in the active export of tailwaters from the bog. The first period selected was during the late spring. The timing was considered to be favorable since it coincided with a period recommended by the Agricultural extension Services for application of fertilizers (CES, 1984), and because groundwater and surface waters would be elevated due to the spring runoff. The owner reported that an application of fertilizer would be made to the lower 13.3 hectares (33 acres) of bog on May 28, 1986 (personal communication, Mr. David Mann).

"Spring 1", a fertilizer mix developed by Golden Harvest Agricultural services was manually applied to the lower Nye bog using "cyclone spreaders" at the rate of 21.65 kg/ha (118 lbs per acre) (personal communication, Mr. Joseph Pelis). The owner also reported that an application of the pesticide Parathion would also be made to the lower bog at the rate of 1.5 pints per acre through the sprinkler system (personal communication, D. Mann). Tailwaters were held within the bog until June 1, 1986. Retention of the tailwaters after such applications is as a matter of policy and sound agricultural practice. The monitoring equipment was in place by noon on June 2, 1986.

#### 5.1.1 Field Conditions

On day one (June 2, 1986), a quick moving cold front passed through the region bringing gusty winds, declining temperatures and rain squalls. Precipitation over the area was variable with the Cranberry Experiment Station recording 0.05 cm (.02 inches) of rain while a heavy downpour was experienced roughly 7 kilometers (4 miles) to the southeast. No rainfall was recorded at the Rochester station. No further precipitation was reported after 1300 hours on June 2nd.

### 5.1.2 Water Chemistry

The first ISCO unit #A-555-66#5 was set up at Station B located in the outlet stream of the Nye Bog on the upstream side of the 90 cm (36 inch) culvert. The intake line and probe were anchored in 0.3 meters (1 ft.) of water to a piece of plywood placed on the stream bed. The plywood was used to minimize the introduction of particulate matter from the stream bed into the sample. The second ISCO unit #A-773-2#7 was installed at Station A located at the North Pond. The probe was allowed to hang suspended in the water column 0.3 meters (1 ft.) from the bottom of the pond, in 0.6 meters (2 ft.) of water. A notation was made concerning the large amount of pollen covering the surface of the pond. Plans to locate a third nutrient monitoring station, station C, at the outlet of the abandoned Robbins Bog were cancelled due to insufficient discharge.

Both ISCO units were programmed to begin collecting hourly samples at noon of the first day (6-2-86) and to complete the first round of sampling at 0600 hours on 6-3-86 thereby effecting an 18 hours composite. Subsequent 24 hours composites began at 0600 hours and ended at 0600 hours of the following day. At 1800 hours of the first day each of the ISCO units was inspected. The unit at Station B was found to operating irregularly resulting in the loss of the first 6 hours of samples for that station. The control unit was replaced with a backup unit #555-58-#4 and no further problems were experienced. As a further precaution the Nicad battery pack for each unit was replaced every 18 hours.

During the night of June 2nd and early morning hours of June 3rd, temperatures dropped down to 0 to 2°C. As a precautionary measure against frost damage to the plants the grower activated the sprinkler system from midnight to 0600 hours on 6-3-86 (personal communication David Mann). At Station A water from the North Pond was pumped into the sprinkler system which services several hectares (acres) of bogs within the upper reaches of the Garland Bogs. This caused the water level in the North Pond to drop below the depth of the suspended ISCO problem and resulted in the loss of samples from 0300 hours 0600 hours of the first day.

A third ISCO unit #773-137#10 was installed in the outlet stream of Bennetts Pond during the early morning hours of 6-3-86 and was labeled Station D. The establishment of this station allowed comparisons to be made between the chemical outputs of the commercial bog and a largely unaltered freshwater wetland.

As noted previously, temperature, pH and dissolved oxygen readings were made three times a day at each station. Measurements of pH made with an Orion Model 211 digital meter equipped with a glass electrode displayed a persistent rising drift during each measurement period. The meter consistently registered an initial pH reading in the 4.3 to 4.8 range which gradually climbed and held steady at the levels reported in the data tables (a reading was recorded seconds). An explanation offered by a company representative for the drifting indicated that the low ionic strength of the stream discharge may have resulted in a poor signal response by the electrode.

All of the water quality data collected during this phase of the study is included in the Appendix.

#### 5.1.3 <u>Hydrology</u>

On June 2, 1986 at Station B, the first of the flow measurements was taken at 1530 hrs. A second flow monitoring station scheduled for the outlet of the Nye Reservoir was abandoned due to insufficient flow. The only source of surface water to the lower bog was found to be coming from Bennetts Pond. A flow monitoring station was established within its outlet stream upstream of its discharge point out the lower Nye bog (see Figure 6). Periodic inspections of the outlet structures at each of the reservoirs located on the property, particularly at the outlet of Nyes Reservoir, established no additional inputs of surface water to the lower Nye bog during the balance of this study period.

Flow and depth at Station B measured at mid-mornings of the second day exceeded the previous days measurements while flow remained essentially constant at Station D. Flow measured at Station B at midafternoon of the second day (June 3, 1986) declined from the high levels found in the morning and returned to levels which approximated the discharge reported for the first day. Flow gradually declined at each station during the balance of the study period (Table 9).

Using the flow measurements collected over the previous three days a hydrograph was constructed and the base flow was estimated. The base flow value was assumed to be constant over the study period and was subtracted from the total hydrograph leaving the response of the system to the rain event and additional flow provided by the sprinkler system. In this instance, base flow is a combination of surface and subsurface runoff while the shorter term event was assumed to be made up of the rain event which occurred on May 28, 1986 and the water passing through the sprinkler system during the early morning hours of June 3, 1986 (Figure 7).

#### 5.1.4 <u>Nutrients</u>

Variability between stations was assessed using a one way ANOVA for unequal sample sizes Model II (Sokal and Rohlf, 1969). The Model II ANOVA was chosen because the study did not consist of fixed treatments and because conditions at each station were only partly under the authors' control. The calculation sheets used to generate the statistics are included in the Appendix.

The first of the nutrient parameters measured was Total Kjeldahl-Nitrogen (TKN). TKN is defined as the sum of free-ammonia and organic nitrogen compounds, such as, amino acids, proteins and peptides converted to ammonium sulfate (NH4)2SO4 (EPA, 1983). The data presented in Table 10 compares the mean values of the composited

# SUMMARY OF FLOW DATA FOR CRANBERRY BOG INPUT STUDY

JUNE 2 - JUNE 5, 1986 SPRING SURVEY

STATION B	TIME	MEAN DEPTH	AREA	VELOCITY	DISCHARGE	
DATE		(ft)	(sq ft)	(fps)	(cfs)	
Jun 02 86	3:30 pm	0.71	3.31	0.39	1.28	
Jun 03 86	10:40 am	0.75	3.76	0.92	3.45	
Jun 03 86	5:45 pm	0.79	3.73	0.36	1.36	
Jun 04 86	10:25 am	0.77	3.66	0.31	1.13	
Jun 05 86	10:10 am	0.76	3.61	0.26	0.93	
STATION D						
Jun 02 86	4:15 pm	0.61	1.68	0.29	0.48	
Jun 03 86	11:10 am	0.54	1.46	0.33	0.48	
Jun 03 86	6:45 pm	0.54	1.48	0.26	0.39	
Jun 04 86	10:45 <sup>-</sup> am	0.52	1.49	0.23	0.34	
Jun 05 86	10:30 am	0.54	1.48	0.20	0.30	



TKN-N samples collected from the three monitored stations. The dual readings for the 6/4-6/5 composite at Station B was obtained by splitting that day's composite sample. The mean, standard deviation and coefficient of variation within each station is located to the right of the daily composite values. The data is also presented in histogram form in Figure 8. The initial TKN value of (0.51 mg/1) reported for Station A North Pond was higher than anticipated since the pond is spring fed. The high value may be related to the events which occurred during the early morning hours of 6/3/86. The speculation being that nitrogenous material from the bottom of the pond or from pollen litter floating on the surface was drawn into the ISCO intake as the level of the pond dropped. A 53 percent decline in the mean TKN values over the three day monitoring period (0.72 -0.34 x 100) at Station A lends supporting evidence that TKN concentrations in the pond are usually lower.

#### TABLE 10

## TOTAL KJELDAHL NITROGEN DATA FOR THE PERIOD JUNE 2, 1986 THROUGH JUNE 5, 1986 (ALL DATA IN mg/l)

	6/2-6/3	6/3-6/4	6/4-6/5	<u> </u>	<u>    S                                </u>	S/X	
A	0.72	0.4	0.34	0.51	0.19	0.37	
В	1.20	0.75	[0.77/0.45]	0.79	0.31	0.39	
D		0.60	0.70	0.65	0.07	0.11	

not samples

[ ] split composite

No significant difference was found between groups at the 5 percent level with  $F_S = 1.65$  where  $F_{.05}$  [2,5] = 5.79. An estimation of the variance components from these stations indicates that there was more variation within stations. Figure 8 shows a systematic decline in TKN levels at Stations A and B while at the outlet of the fresh water wetland, Station D, TKN levels increased slightly. The most likely explanation for the declines exhibited at Stations A and B being the introduction of nutrient poor groundwater to the North Pond and reduced runoff to the outlet stream after the sprinkler system was turned off. The differences seen at Station D probably reflect sample variability.

A comparison of the other two forms of nitrogen ammonia  $(NH_3)$  and nitrate  $(NO_3^-)$  at the three stations showed mixed results (Table 11).

The mean concentration of ammonia was 64 percent higher at the outlet of the bog than at Station A and 80 percent higher than the discharge from the fresh water wetland. Nitrate concentrations at Station B were 70 percent higher than Station D. Single classification ANOVA's

with unequal samples sizes established no significant differences in ammonia or nitrate nitrogen between stations with calculated  $F_s$ values of 3.75 and 0.85 respectively. This finding was disappointing since the histograms Figures 9 and 10 clearly show large differences in the ammonia levels between the stations. These differences are attributed to residual fertilizer being discharged from the bog. The annonia concentrations for Stations B and D were proportioned to estimated flow measurements and an ANOVA was conducted on the two means. The F statistic of 7.98 was found to be slightly below the F .05 of 10.13. A nonparametric procedure Kruskal - Wallis test (Sokal and Rohlf, 1969) was also employed on this data set. In the Kruskal - Wallis test the verities are first ranked from smallest to largest with each variate being assigned a numerical value equal to its frank from low to high values. The original data table is then reconstructed by replacing the data value with its rank and an "H" statistic calculated which is then compared to a chi value (Sokal and Rohlf, 1969). The results indicate no significant differences in annonia or nitrogen levels between the three stations. The strength of the data set was weakened by the low number of samples and the large variances observed at Station B.







NH <sub>3</sub> -N							
STATION	6/2-6/3_	6/3-6/4	DATE 6/4-6/5	- x	<u> </u>	CV	-
A	0.12	0.03	0.13	0.09	0.06	0.67	
В	0.26	0.46 [	0.21/0.07]	0.25	0.16	0.64	
D		0.05	0.04	0.05	0.01	0.14	
NO <sub>3</sub> -N							
STATION	6/2-6/3	6/3-6/4	DATE 6/4-6/5	- x	S	CV	-
A	0.20	0.09	0.10	0.13	0.06	0.46	
В	0.10	0.30 [	1.20/0.10]	0.43	0.53	1.23	
D	di kanga	0.70	0.09	0.40	0.43	1.08	

## AMMONIA (NH<sub>3</sub>-N) AND NITRATE (NO<sub>3</sub>-N) DATA FOR THE PERIOD JUNE 2, 1986 THROUGH JUNE 5, 1986 VALUES IN (mg/l)

X = Mean S = Standard Deviation CV = Coefficient of variation -- = No Data [ ] = Duplicate Split

The phosphorus series of data for this study period is presented in Table 12 and its companion histogram Figure 11. Highly significant differences in the total phosphorus levels were found between Stations  $F_s = 38.75$   $F_{.001}$  [2,5] = 37.12. Phosphorus levels also exhibited less day to day variability within each station. An estimation of the variability components established that 92% of the variation occurred between stations and only 8% within a station. Significance at the .05 level was also found for total phosphorus concentrations  $F_s = 11.72$ ,  $F_{.05}$  [1,3] = 10.13. The June data establishes the cranberry bog as exporter of ammonia and phosphorus as a result of this agricultural practice.

Figure 12 presents all of the mean composite values for the nitrogen series at each station during the June study period. The data while showing considerable variability does establish the bog and wetlands as exporters of various forms of nitrogen during periods of active discharge.

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# TOTAL PHOSPHORUS (TP-P) AND ORTHOPHOSPHORUS (P04-P) DATA FOR THE PERIOD JUNE 2, 1986 - JUNE 5, 1986

TP-P

STATION			DATE	-		
	6/2-6/3	6/3-6/4	6/4-6/5	X	<u> </u>	<u>CV</u>
A	0.05	0.02	0.02	0.03	0.02	0.67
В	0.12	0.11	[0.12/0.14]	0.12	0.01	0.08
D		0.06	0.06	0.06		

P<sub>04</sub>-P

STATION			DATE	-		
	6/2-6/3	6/3-6/4	6/4-6/5	<u> </u>	<u>S</u>	CV
A		0.02	0.02	0.02		
В		0.07	[0.08/0.08]	0.08	0.01	0.13
D		0.03	0.04	0.04	0.01	0.25

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X = Mean S = Standard Deviation CV = Coefficient of variation -- = No Data [ ] = Duplicate Split





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## 5.1.5 <u>Macroinvertebrate Survey</u>

On June 4, 1986, sampling was conducted for aquatic macroinvertebrates at the outlet of the lower bog and within two segments further downstream. At the time of sampling, Segment #3 (Figures 5 and 6) was a well defined channel flowing between the raised mats bearing the cranberry plants, as well as, a few riparian plant species. The channel bottom was predominately sandy to mucky substrate densely covered with submerged vascular plants and emergent species along the margins. These included <u>Vaccinium macrocarpon</u> (cranberry), <u>Potamogeton</u> sp. (pondweeds), <u>Callitriche</u> sp. <u>Mvriophyllum</u> sp. (water-milfoils), <u>Cyperus</u> sp. (umbrella sedges), and Scirpus cyperinus (woolgrass).

The macroinvertebrates from this segment were reasonably abundant, but not indicative of a particularly diverse community (Table 13). Segments #2, and further downstream segment #1, physically resembled first or second order woodland streams. Substrates varied from muck to gravel within each segment. Canopy coverage over these segment was estimated at 90 to 100%. In such streams allochthonous carbon loading in the form of leaf litter usually supports a community of shredders, or organisms adapted to utilizing coarse particulate organic matter (CPOM). Isopods which are shredders were present in both segments but not in abundance. This was particularly apparent in leaf packs snagged at debris or bends in the stream.

The abundance of macroinvertebrates in the cranberry bog channel segment #3 was surprising given an anticipated decline due to exposure due to pesticides. Scarcity of benthic fauna downstream while unexpected can be explained by manipulations in flow due to agricultural practices. Speculation as to influences exerted by transport of pesticides to downstream sites can not be evaluated given the limited amount of data and the aforementioned variability in flow regimes experienced by these benthic populations.

## CRANBERRY BOG INPUT STUDY

SEGMENT						
TAXON	#1	#2	#3			
Turbellaria		_	v			
Oligochaeta	v	v	v			
Hirudinea	М	ν	v			
Asellidae	v	<b>V</b>	v			
Hydracarina						
Collembola		M				
Coenargrionidae	м					
Haliplidae			v			
Chironomidae	v	v	v			
Ancyllidae	cs					
Lymnaedae	cs					
Physidae	cs					
Planorbidae	cs	-				
Sphaeriidae	cs	V	v			

## SUMMARY OF MACROINVERIEBRATE GROUPS ENCOUNTERED IN OUTLET STREAM JUNE 4, 1986

Habitat Types:	CS	=	Channel Substrates
	M	=	Stream Margins
	V	=	Various

Segment 1: Ninety meters long from a point above estuary to head of the bay road.

Segment 2: One-hundred meters long from Head of the Bay road east to dirt road crossing the bogs outlet stream.

Segment 3: Twenty meters long from dirt road east to junction of side ditches.

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## 5.2 Fall 1986

The second survey was conducted in October 1986. This time period was selected because it coincided with the harvest.

Beginning in the late 1960's, the harvesting of cranberries in Massachusetts shifted from a dry harvest process to the wet harvest method (Norton, 1982). In this method the bogs are flooded to a depth of several inches above the highest vines and a "water reel," a modified airboat equipped with beater bar is passed over the vines thereby stripping the berries off the vines. The berries float to the surface and are then corralled with floatable booms before being loaded onto trucks. Over 75 percent of the state's entire crop is now harvested in this manner (SCS, 1987).

Harvesting began in the upper Garland bogs in the last week of September and continued at a five acre per day pace through the week of October 15, 1986, when harvesting was completed.

### 5.2.1 Field Conditions

On October 20th the second round of sampling was initiated under substantially different field conditions. The owner had decided not to release the flood waters downstream but maintain flood conditions for several additional weeks before pumping the waters back to the reservoirs. Time constraints prevented rescheduling the sample period and a decision was made to sample the same three stations as they existed. The situation was in-effect the sampling of three impoundments. Climatological conditions were also different with maximum and minimum temperatures averaging five and ten deg F cooler than during the June period. Precipitation was not a factor with only a trace of rain reported on June 23rd. In general, the weather could be described as clear and sunny with light winds and a moderate warming trend occurring over the three day study period.

### 5.2.2 <u>Water Chemistry</u>

Several improvements were made to the sampling regime from the previous study period. First the flooded conditions allowed the ISCO intake probes to be suspended in the water column at each site 0.3 m (1 ft) from the bottom. Second and more significant was the use of two ISCO units at each of the three sites. After reviewing the procedures employed during the first round of sampling the possibility of cross contamination between samples could not be ruled out as a possible explanation for the wide variability exhibited in some of the parameters. The first step was to use separate ISCO units at each station for the collection of nutrient and physical chemistry sample. The last change was the addition of two parameters, (specific conductivity and chlorides) to the suite of measurements. In all other respects sampling was conducted in the same manner as the June period with thrice daily measurements of temperature, pH and dissolved oxygen levels and daily grab samples for total iron and hardness at each station.

### 5.2.3 <u>Hydrology</u>

During the fall survey the flow regimes at Stations (B and D) were completely different. In the case of Station D there was no discharge from Bennetts Pond to the lower Nye Bog and consequently no measurements were taken. At Station B a series of wood planks had been placed in the outlet structure to maintain a flooded condition thereby reducing the discharge to leakage. Since some flow was still occurring a flow measurement station was established some 6 m (20 feet) west and downstream of the outlet structure. In order to obtain a flow measurement, the stream was narrowed to a width of 20 cm (8 in.) with sand and rocks. The depth of the channel varied between 6 and 10 cm (0.2 and 0.3 feet). Five velocity measurements were taken from the center of the channel and the mean velocity was then multiplied by the area to determine the discharge (Table 14). During each of the sample collections potential sources of flow to the lower bog were inspected and in no case was a significant discharge noted.

#### TABLE 14

## SUMMARY OF FLOW DATA FOR CRANBERRY BOG INPUT STUDY

STATION B OCTOBER 20 - OCTOBER 23, 1986 FALL SURVEY

DATE	TIME (HRS.)	MEAN DEPIH (ft)	AREA (sa. ft.	VELOCITY	DISCHARGE (cfs)
<u></u>					
Oct. 20, 1986	1500	0.667	0.3	0.183	
				0.171	
				0.195	
				0.218	
			-	0.262	0.206
Oct. 21, 1986	1100	0.667	0.2	0.318	
•				0.313	
·				0.331	
				0.328	
				0.330	0.324
Oct. 22, 1986	1145	0.667	0.3	0.352	
·				0.345	
				0.366	
				0.351	
				0.336	0.350
Oct. 23, 1986	0700	0.667	0.2	0.231	
				0.219	
				0.218	
				0.255	
				0.215	0.228

### 5.2.4 Nutrients

The results obtained during the fall survey exhibited marked changes in water quality from what was observed in June. The overall mean for all composite TKN samples was 52 percent lower (0.35/0.67) in October. Ammonia and nitrate  $(NH_3^+ \text{ and } NO_3^-)$  concentrations also declined.

This was surprising because the effects of the harvesting operations was expected to increase both particulate and dissolved solids within the water column and consequently the concentrations of nitrogen. The data presented below for Station B (Table 15) compares mean concentrations of total solids, suspended solids and total dissolved solids (TS, TSS, TDS) from the two sampling periods and the surveyed nitrogen series.

#### TABLE 15

#### CRANBERRY BOG INPUT STUDY

#### COMPARISON OF MEAN CONCENTRATION FOR SOLIDS (TS, TSS, TDS)

AND NUIRIENIS (TKN, NH<sub>3</sub>, NO<sub>3</sub>) DATA (mg/1)

#### June 2-5, 1986

#### October 20-23, 1986

TS	83	TKN	.79	TS	112	TKN	0.54
TSS	4.8	NH3	.25	TSS	1.6	NH3	0.06
TDS	54.6	N03	.43	TDS	134.6	N03	0.09

Concentrations of total solids and total dissolved solids were respectively 26 and 59 percent higher than in the June discharge. While TKN,  $NH_3$  and  $NO_3$  levels declined 32, 76 and 79 percent.

Single classification ANOVA's using Model II equal size classes showed highly significant differences in TKN levels between all stations  $F = 15.95**, F_{.01}$  [2,6] = 10.92.

Statistical tests on the ammonia levels were hampered by values reported by the laboratory as less than detection limits (<) and did not show significant differences between stations F = .92.  $F_{.05}$  [2,6] 5.14

Nitrate levels were uniformly low at all stations with a mean of 0.09 mg/l the results are depicted in graph form along with TKN and  $NH_3^+$  levels (see Figure 13).

The most striking difference was found in the total and orthophosphorus data. Table 16 presents the mean, standard deviations, range and cv of the observed TP and  $P04^+$  data at each station during the fall sampling period 10/20-10/23, 1986.



Single ANOVA calculations of TP means between stations showed a highly significant difference at the 001 percent level (F = 268\*\*\* F.001 [2,6] = 27). Similar levels were reported by the State of Wisconsin in an unpublished study of flood waters from Wisconsin bogs where levels ranged between 0.0059 and 0.331 mg/l F. Figure 14 displays the mean concentrations of total and orthophosphorus at each station during the October sampling period.

## TABLE 16

#### TOTAL PHOSPHORUS (TP-P) AND ORTHOPHOSPHORUS $(P0_A - P)$ mg/1

STATION MEAN S RANGE CV Α TP 0.04 0.01 0.03-0.05 0.25 0.01 0.01 <0.01-0.02 1.0 P0\_ 0.58 0.03 В TP 0.51-0.61 0.05 0.33-0.41 PO<sub>4</sub> 0.38 0.03 0.08 D 0.09 0.03 TP 0.07-0.12 0.33 P04 0.01 0.01-0.02 0.01 1.0

DATA FOR THE PERIOD OCTOBER 20 - OCTOBER 23, 1986

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X = Mean S = Standard Deviation CV = Coefficient of Variation

## 5.2.5 Pesticide in Sediments

As described in previous sections, sediments obtained from three sites were analyzed for a suite of pesticide and herbicide compounds. Information describing degradation pathways of parent compounds and their metabolites was obtained from several sources, (Khan, et al, 1975, Matsumura, Klaassen, 1986 and personal communications with John Clark and Paul Gosselin).

Parathion, chemical name: 0,0-diethyl 0-P-nitrophenyl phosphoriate, has during the last decade become the most widely used organophosphorus insecticide (Gomaa and Faust, 1972 and Klaassen et al., 1986). Parathion is widely used in the cranberry growing industry (EPA, 1978; UMass Agri. Ext. Bull., 1985).

Its use is strictly regulated under provisions of the Massachusetts Pesticide Control Act. Parathion is commonly applied several times over the course of the growing season for a range of insect pest. EPA requirements published by the Cranberry Experiment Station and



Cooperative Extension Service include a maximum actual toxicant level of one pound per acre or less, restricting harvest to least 15 days after the last application.

Parathion was applied at the study site in the form of an emulsion or wettable powder through the sprinkler system four times over the last two growing seasons at the rate of one pint/acre. The last reported application was on 7/30/86, (Personal Communication, David Mann).

The results of the analysis for this pesticide and some of its metabolites is reported in Tables 17-19. Neither parent compound nor metabolites were recovered at any of the stations. A suspected recovery of the metabolite paroxon was found to be the pesticide chlorpyrifos. Metabolite recoveries were five to ten times lower than parent compounds, p-aminophenol recoveries were noticeably low due to poor UV absorption and its rapid degradation (analytical note, Matthew Brooks).

The insecticide chlorpyrifos, chemical name: 0,0-Diethyl 0-(3,5,6-trichloro-2-pyridyl)-phosphorothicate, trade name LORSBAN is recommended for use as a foliar insecticide to control infestations of fireworms, cutworms, sparganothis fruitworms, army worms and other boring insects (Farm Chemicals Handbook, 1984). Two reported applications at rates of three pints per acre via aerial spray during the summer of 1985 were reported (Personal Communication, David Mann).

Chlorpyrifos was found to coelute from the gas-liquid chromatograph with the parathion metabolite paroxon (Personal Communication, Matthew Brooks analyst). Confirmation of the presence of chlorpyrifos was made by thermionic detection and by gas chromatograph/mass spectrometer (GC/MS Facility, College of Food and Natural Resources, Mass. Agric. Exp. Station, Univ. of Mass-Amherst, Thomas Potter, Director). Chlorpyrifos was not recovered at either of the other two stations (Table 18).

The herbicide glyphosate chemical name: isopropylamine salt of N-(phosphonomethyl)glycine is widely used to control a wide range of annual and perennial grasses and broad-leaf weeds. A foliar-applied herbicide, it is translocated through the plant to the roots (Farm Chemicals Handbook, 1984). Applications were made throughout both summers by wiping the emergent plants (Personal Communication, D. Mann). The herbicide glyphosate and its primary metabolite aminomethyl phosphonic acid (AMPA) were recovered at Station B, the outlet of the active bog. Confirmation of positive samples was by gas liquid chromatography utilizing an esterification and acyllation process. Table 18 summarizes the results from the three stations.

Residues of the remaining compounds, diazinon, diazoxon and dichlobenil were not recovered at any of the stations.

## 5.3 <u>Spring 1987</u>

On March 23, 1987 a final round of sampling was scheduled to coincide with the height of the spring runoff period. The collection provided a comparison of nutrient concentrations during a period of high flow.
### CRANBERRY BOG INPUT STUDY

### SUMMARY OF PARATHION AND SELECTED METABOLITE LEVELS (ppb) IN SEDIMENIS

SAMPLE SITE	ANALYTE	RESULT (POS/NEG)	SPIKE RECOV (%)	CORRECTED DET. LIM*	AMT. FOUND
В				• •	
	Methyl Parathion	Neg	<b>95+</b> /7	22	
	Parathion	Neg	68+/-2	64	
	Paraoxon	**	**	**	**
	Amino Parathion	Neg	73+/-23	272	**
	p-Nitrophenol	Neg	77+/-3	32	
** coelu	tes with chlorpyrifos				
с					
	Methyl Parathion	Neg	99+/-1	22	
	Parathion	Neg	63+/-1	68	
	Paraoxon	Neg	30+/-13	889	
	Amino Parathion	Neg	<del>66+/-</del> 8	<b>3</b> 03	
	p-Nitrophenol	Neg	7 <del>9+</del> / <del>-</del> 6	23	
	p-Aminophenol	Neg	74+/-16	3014	
E		•			
	Methyl Parathion	Neg	78+/-2	25	
	Parathion	Neg	66+/-4	61	
	Paraoxon	Neg	22+/-5	770	
	Amino Parathion	Neg	71+/1	263	
	p-Nitrophenol	Neg	85+/-3	20	
	p-Aminophenol	Neg	88+/13	3439	

- \* Corrected detection limits refers to the division of instrument detection by spike recovery (i.e. if the instrument detection limit was 5 ppb and the spike recovery was 50% then the corrected detection limit would be 5/0.5 = 10 ppb.
- \*\* Coelutes is the term used to describe a situation when two more compounds separate (elute) at the same temperature and time.

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#### CRANBERRY BOG INFUT STUDY

### SUMMARY OF PESTICIDE CHLORPYRIFOS LEVELS (ppb) IN SEDIMENTS

SAMPLE SITE	ANALYTE	RESULIT (POS/NEG)	SPIKE RECOV (%)	CORRECTED DET. LIM*	AMT. FOUND	
В						
	Chlorpyrifos	Pos	81+/-12	25	245	
с						
	Chlorpyrifos	Neg	91+/-1	24		
Е						
	Chlorpyrifos	Neg	74+/-7	27		

-- Not Found

\* Corrected Detection Limit = Refers to the division of isntrument detection by spike recovery (i.e. if the instrument detection unit was 5 ppb and the spike recovery was 50% then the corrected detection limit would be 5/0.5 = 10 ppb.

### CRANBERRY BOG INFUT STUDY

#### SUMMARY OF THE HERBICIDE GLYPHOSATE

### AND METABOLITE AMPA (ppb) LEVELS IN SEDIMENTS

SAMPLE SITE	ANALYTE	RESULT (POS/NEG)	SPIKE RECOV (%)	CORRECTED DET. LIM*	AMT. FOUND	
В	· <u>······</u> ·····························		<u></u>	<u>, , , , , , , , , , , , , , , , , , , </u>		
	Glyphosate AMPA	Pos Pos	85+/-14 68+/11	112 124	258 156	
с						
	Glyphosate AMPA	Neg Neg	43+/-9 68+/-11	214 150		
E						
	Glyphosate AMPA	Neg Neg	57+/-9 50+/-7	130 196		

\* Corrected detection limit refers to the division of instrument detection by spike recovery (i.e. if the instrument detection limit was 5 ppb and the spike recovery was 50% then the corrected detection limit could be 5/0.5 = 10 ppb.

-- Not found.

Sampling was limited to the collection of three nutrient replicates at Station B. Flows at the time of sampling were estimated to be 3.9 cfs. The data set for the March collection is reported in Table 20. ANOVA calculations for ammonia (NH<sub>3</sub>-N) and total phosphorus (TP-P) weighted to flow were conducted on the Spring 86, Fall 86 and Spring 87 data sets. Differences in ammonia concentrations were found to be not significant at the F.05 [2,4] = 8.94 F<sub>g</sub> = 6.78, however the differences in total phosphorus were found to be highly significant F .001 [2,4] = 61.25 F<sub>g</sub> = 86.73. Figures 15 and 16 present the comparative mean concentrations in the nitrogen series and phosphorus series for the 3 sampling periods.

#### 5.4 Meteorological Data

Meteorological data reported in Table 21 were obtained from two NOAA weather stations closest to the study area. The first station is located at the Cranberry Experiment Station in West Wareham, MA at latitude 41°46' N, longitude 70° 40' W. The station is part of the National Cooperative Weather Service Network (NCWSN) and operated by the University of Massachusetts School of Agriculture. The station located roughly 6 km (3 miles) west of the study site served as the principal reference for meterological conditions during the study. Precipitation is presented as 24 hour totals, midnight to midnight.

Evapotranspiration rates are recorded at a second station located in Rochester, MA at latitude 41° 47' min N, longitude 70° 55 min W. Spatial differences in rates of evapotranspiration were assumed to be negligible.

#### 6.0 <u>Discussion</u>

Figure 17 provides some insight into the relationships between the hydrological conditons, agricultural practices and nutrient concentrations observed at the three stations during the June 1986 sampling period. At Station A nutrient levels for all parameters (TKN,  $NH_3-N$ ,  $NO_3-N$ , TP-P, and  $PO_4-P$ ) declined over the three day period as the pond was rechrged with relatively poor nutrient ground water. At Station B the unit hydrograph shows the response of the system to the activation of the sprinkler system followed by a sharp decline to base flow conditions. As water from the sprinkler system saturated the planted areas of the bog it picked up the uncombined ammonia and phosphorus. The resulting runoff was then added to the existing base flow. As the runoff from the planted areas declined annonia and organic nitrogen levels also declined. The reasons for the increase in nitrates is not clear but may reflect nitrification within the stream channels in response to the introduction of ammonia from the vegetated mats. Flow at Station D declined steadily over the three day monitoring period leading to the conclusion tht rainfall had a negligible influence on the discharge from the wetland. Organic nitrogen as measured by the TKN-N concentrations and ammonia exhibited little variation while a sharp decline in nitrate concentrations was not associated with any observed events. Total and orthophosphorus concentrations remained steady and held an intermediate position between the nutrient poor waters of the North Pond and the elevated concentrations exiting the bog.

### CRANBERRY BOG INPUT STUDY

# SUMMARY OF NUIRIENT DATA (mg/l)

MARCH 23, 1987 STATION B

3/23/87

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	REP A	REP B	REP C	X	SD	S/X
TKN	0.85	0.84	0.59	0.76	0.15	.19
NH3	0.11	0.04	0.02	0.06	0.05	.79
N03	0.1	0.4	<0.2	<0.2		
TP	0.21	0.15	0.18	0.18	0.03	.17
P04	0.11	0.03	0.03	0.06	0.05	.79

X = mean SD = standard deviation S/X= coefficient of variation -- = Not Calculated

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# CRANBERRY BOG INFUT STUDY

### SUMMARY OF METEOROLOGICAL DATA DURING STUDY PERIODS

LOCATION	DATE	MAX TEMP	MIN TEMP	RAINFALL	EVAPOIRANSP
		(F)	(F)	(IN)	(.00 IN)
E. WAREHAM	5/28/86	77	57		
ROCHESTER		79	45		0.16
E. WAREHAM	5/29/86	75	51	0.03	
ROCHESTER		83	52	0.20	0.18
E. WAREHAM	5/30/86	86	61		
ROCHESTER		80	60		0.32
E. WAREHAM	5/31/86	84	57		
ROCHESTER		90	63	т	0.32
E. WAREHAM	6/01/86	68	47	0.02	
ROCHESTER		83	60	0.06	0.24
E. WAREHAM	6/03/86	62	41	0.06	
ROCHESTER		69	43	0.03	0.11
E. WAREHAM	6/04/86	<b>6</b> 6	53		
ROCHESTER		66	45		0.20
e. Wareham	6/05/86	75	60		
ROCHESTER		72	53		

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# TABLE 21 (CONTINUED)

LOCATION	DATE	MAX TEMP	MIN TEMP	RAINFALL	EVAPOIRANSP
		(F)	(F)	(IN)	(.00 IN)
				0.57	
E. WAREHAM	10/15/86	60	40	0.57	
ROCHESTER		68	48	0.58	0.21
E. WAREHAM	10/16/86	57	35		
ROCHESTER		59	38		0.13
E. WAREHAM	10/17/86	57	36		
ROCHESTER		58	36		
E. WAREHAM	10/18/86	50	36	0.31	
ROCHESTER		54	40	0.16	0.03
E. WAREHAM	10/19/86	57	32		
ROCHESTER		49	32		0.05
E. WAREHAM	10/20/86	57	35		
ROCHESTER		58	31		0.05
E. WAREHAM	10/21/86	62	33		
ROCHESTER		57	34		0.08
E. WAREHAM	10/22/86	65	42	T	
ROCHESTER		64	35	Т	0.10
e. Wareham	10/23/86	65	53		
ROCHESTER		72	55		
E. WAREHAM	3/18/87	43	31	0.02	

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# TABLE 21 (CONTINUED)

LOCATION	DATE	MAX TEMP	MIN TEMP	RAINFALL	EVAPOIRANSP
		(F)	(F)	(IN)	(.00 IN)
ROCHESTER		36	25		
E. WAREHAM	3/19/87	43	28		
ROCHESTER		44	29		
E. WAREHAM	3/20/87	40	31		
ROCHESTER		42	32	0.01	
E. WAREHAM	3/21/87	38	30		
ROCHESTER		42	32	0.01	
E. WAREHAM	3/22/87	41	30	0.09	
ROCHESTER		40	31	т	
E. WAREHAM	3/23/87	41	32	0.12	
ROCHESTER		40	33	0.04	

FOOINOIE: Evapotranspiration data reported from Rochester Station only. Recordings discontinued after November 1986.

T = Trace --- = No Data

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Data obtained from the two closest NOAA weather stations (Table 21) reported rainfall averaged less than 0.15 cm per day (0.06 in) during the eight (8) day period 5/29/86 - 6/5/86. Evapotranspiration rates during the same time period averaged 0.56 cm per day (0.22 in). The data clearly establishes the acricultural practices employed during the monitoring period as the source of the increased nutrients in the tailwaters leaving the bog. The results obtained during the fall sampling period displayed marked differences in nutrient concentrations when compared with the June results. Mean concentrations of organic nitrogen, annonia and nitrate at all three stations were respectively 50, 64 and 62 percent lower than observed in June. Concentrations of the inorganic nitrogen forms during the fall sampling were essentially the same at all three stations. Since the last application of fertilizer occurred in early September (David Mann, personal communication) the low levels reflect the high assimilative nitrification processes. Mean concentrations of total and orthophosphorus the concentrations measured within the kettle pond (Station A). The increase reflects the additive sources of decomposing vegetation within the wetland.

STATION	JUNE 2-5	, 1986	OCTOBER 20-23, 1986		
	TP-P	P04-P	TP-P	Р0 <sub>4</sub> -Р	
A	0.03	0.02	0.04	0.01	
В	0.12	0.08	0.56	0.38	
D	0.06	0.04	0.09	0.01	

At Station B total and orthophosphorus concentrations increased 79 percent over the elevated levels found in June. The likely sources of the phosphorus are from unassimilated fertilizer applications sequestered in the sediments and phosphorus released by damaged fruit and leaf litter. The mechanism is the liberating of the complexed phosphorus into the water column through the flooding of the bogs.

Several studies (Deubert, 1974; Whittaker, 1980) point to elevated concentrations of phosphorus in cranberry discharge waters when compared to background conditions. Deubert measured the mean concentrations of phosphates along a 250 foot length of cranberry bog drainage ditch and found over an order of magnitude decline (0.256 ppm - 0.024 ppm). Whittaker examined water quality in nearby White Island Pond in Plymouth, Massachusetts and reported elevated levels of total phosphorus in the outlets of cranberry bogs draining into the pond when compared to the phosphorus levels measured in groundwater wells and from other stations within the pond. The Department of Natural Resources in Wisconsin has conducted a number of studies (unpublished) on the nutrient of cranberry marsh discharges waters (Kenneth Schreiber, Wisconsin DNR, personal communication). In 1971 and 1972 (Konrad, unpublished report, 1974) compared nutrient concentrations from 5 individual bogs during the fall harvest and winter flood release periods. Nutrient concentrations ranging from 0.18 to 0.46 kg/ha total P. 0.012 to 0.05 kg/ha  $NO_3$ -N and 0.011 to 0.09 kg/ha  $NH_3$ -N were noted with the highest levels associated with the winter flood release. The author concluded that nutrient losses from cranberry operations did occur

FIGURE 17 Flow Volumes vs Nutrient Concentration June 2–5, 1989



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but could not conclude that degradation of receiving waters had occurred. Another unpublished study in cranberry bog operations in the Thunder Lake region of Wisconsin (Maltbey, Dunst and Konrad, 1982) had as one of its objectives the determination of the average discharge of phosphorus from five individual beds. Influent concentrations averaged 0.06 mg/l and effluent concentrations averaged 0.14 mg/l with a range of (0.059 - 0.331 mg/l).

Data collected by (Gil, 1986) as part of the Buzzards Bay Program compiled water quality data from the outlet of the Mann bog (Station B) and from the outlets of two other bogs located on the Cape Cod side of the Bay. The data set while incomplete showed a degree of seasonality in nutrient concentrations (Figures 18 and 19). The nutrient peaks occur in the spring and fall collection periods which also correspond with periods of increased flow and active agricultural management practices. Richardson and Marshall (1986) report that in a fen peatland dominated by <u>Carex</u> sp. that 81 percent of the plant storage under high fertilizer applications resided within the roots and rhizomes. A fivefold increase in P flux to the water column was noted during seasonal dieback and leaching of P from above ground standing plant material on high fertilized plots.

#### TABLE 22

### SUMMARY OF NUIRIENT CONCENTRATIONS RECOVERED FROM CRANBERRY BOG OUTLET STREAMS DURING 1985, 1986 AND 1987 (TKN-N, N03-N, TP-P, P04-P) mg/1

STATION	DATE	TKN-N	<u>N03-N</u>	<u>NH3-N</u>	TP-P	<u>P04-P</u>
В	5/22/85	1.1	0.26	0.1	0.12	- 0.08
	8/13/85	0.86	0.07	0.1	0.08	0.06
	8/14/85	0.78	0.13	0.8	0.14	0.07
17	8/27/85	1.5	0.09	0.5	0.11	0.07
19	8/27/85	1.8	0.08	0.2	0.15	0.11
17	8/28/85	1.4	0.07	0.3	0.06	0.03
19	8/28/85	1.5	0.06	0.2	0.09	0.05
В	<b>6/2-5/8</b> 6	0.79	0.25	0.43	0.12	0.08
	10/20-23/86	0.54	0.06	0.09	0.56	0.38
	3/23/87	0.76	0.06	<0.2	0.18	0.06

Using the base flow, mean flow, and peak discharges measured during the June 1986 sampling period estimates of the loading rates of the inorganic nutrients ( $NO_3$ -N,  $NH_3$ -N, TP-P and  $PO_4$ -P) were calculated (see Table 23).





### CRANBERRY BOG INPUT STUDY ESTIMATED NUTRIENT LOADING RATES FROM A COMMERCIAL BOG IN POUNDS PER DAY

#### JUNE 2-5, 1986

BASE FLOW 0.93 cfs

0.93 cfs x 0.646 mgd x 8.34 lbs/gal.

X 0.25 mg/l NH<sub>3</sub>-N = 1.25 lbs per day X 0.43 mg/l NO<sub>3</sub>-N = 2.15 lbs per day X 0.12 mg/l TP-P = 0.60 lbs per day X 0.08 mg/l PO<sub>4</sub>-P = 0.40 lbs per day

X 0.25 mg/l NH<sub>3</sub>-N = 2.20 lbs per day X 0.43 mg/l NO<sub>3</sub>-N = 1.05 lbs per day

MEAN DISCHARGE 1.63 cfs

1.63 cfs X 0.646 mgd X 8.34 lbs/gal.

HIGH FLOW 3.45 cfs

3.45 cfs X 0.646 mgd X 8.34 lbs/gal.

X 0.12 mg/l TP-P = 3.78 lbs per day X 0.08 mg/l P0<sub>4</sub>-P = 0.70 lbs per day X 0.25 mg/l NH<sub>3</sub>-N = 4.65 lbs per day X 0.43 mg/l NO<sub>3</sub>-N =

7.99 lbs per day X 0.12 mg/l TP-P = 2.33 lbs per day X 0.08 mg/l PO<sub>4</sub>-P = 1.48 lbs per day

Dividing the loading rates by the acreage (33) the following estimates for total and orthophosphorus were obtained.

mean discharge TP-P = 0.03 lbs/acre  $P0_4$ -P = 0.02 lbs/acre

high flow TP-P = 0.07 lbs/acre  $PO_A - P = 0.04$  lbs/acre

These values were found to compare well with the results in the unpublished study by (Maltbey, Dunst and Konrad, 1982), who reported a range of 0.816 - 0.009 lb/acre of phosphorus exported from 4 individual bogs.

A daily mass balance for phosphorus was developed for the lower Nye Bog using the data generated during the June 2-5, 1986 survey period for peak and mean flow.

Lower Nye Bog = 33 acres, Nye Reservoir pump activated for 6 hours 6/2 2400 to 6/3 0600 hrs. Pump capacity 2000 gal/min gal applied through the sprinkler system. Total phosphorus concentration in Nye Reservoir water 0.08 mg/l (source: David Mann, IEP, 1986).

Bennetts Pond = 13 acres flows into lower Nye Bog. Flow measured on 6/3/86 at 1110 hrs = 0.48 cfs. Total phosphorus concentration 0.06 mg/l.

1 cfs = 646,317 gallons per day

INPUTS:

Base Flow	Sprinkler System	Bennetts Pond Discharge			
646,317 gal/day/cfs		646,317 gal/day/cfs			
x 1.28 cfs		x 0.48 cfs			
827,286 gal/day x 3.785 liters/gal	720,000 gal	720,000 gal 310,232 gal/day x 3.785 liters/gal			
3,131,277 liters x 0.12 mg/l P	2,725,200 liters x 0.08 mg/l P	1,174,228 liters x 0.06 mg/l P			
375,753 mg of P x 0.001 grams/mg	218,016 mg of P x 0.001 mg of P	70454 mg of P x 0.001 mg of P			
376 grams of P x 0.0022 lbs/gr	218 grams of P x 0.0022 lbs/gr	70 grams of P x 0.0022 lbs/gr			
0.83 lbs P/acre/day	0.48 lbs P/acre/day	0.16 lbs P/acre			
Summing the total inputs = $0.83 + 0.48 + 0.16 + 2.6$ lbs of P = 4.07 lbs/acre of bog converted to scientific units =					

4.07 lbs/2.2 lbs/kg = 1.85 kg x 0.4047 acres/hectare = 0.75 kg/ha

A daily mass balance for phosphorus was developed for the lower Nye Bog using the data generated during the June 2-5, 1986 survey period for peak and mean flow.

Lower Nye Bog = 33 acres, Nye Reservoir pump activated for 6 hours 6/2 2400 to 6/3 0600 hrs. Pump capacity 2000 gal/min gal applied through the sprinkler system. Total phosphorus concentration in Nye Reservoir water 0.08 mg/l (source: David Mann, IEP, 1986).

Bennetts Pond = 13 acres flows into lower Nye Bog. Flow measured on 6/3/86 at 1110 hrs = 0.48 cfs. Total phosphorus concentration 0.06 mg/l.

1 cfs = 646,317 gallons per day

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Base Flow	Sprinkler System	Bennetts Pond Discharge
646,317 gal/day/cfs x 1.28 cfs		646,317 gal/day/cfs x 0.48 cfs
827,286 gal/day x 3.785 liters/gal	720,000 gal	720,000 gal 310,232 gal/day x 3.785 liters/gal
3,131,277 liters x 0.12 mg/l P	<u>x 3.785 liters/gal</u> 2,725,200 liters x 0.08 mg/l P	1,174,228 liters x 0.06 mg/l P
375,753 mg of P x 0.001 grams/mg	218,016 mg of P x 0.001 mg of P	70454 mg of P x 0.001 mg of P
376 grams of P x 0.0022 lbs/gr	218 grams of P x 0.0022 lbs/gr	70 grams of P x 0.0022 lbs/gr
0.83 lbs P/acre/day	0.48 lbs P/acre/day	0.16 lbs P/acre
Summing the total inputs = 4.07 lbs/acre of bog	s = 0.83 + 0.48 + 0.16 + 2 converted to scientific a	2.6 lbs of P units =

EXPORT

PEAK FLOW	MEAN FLOW	BASE FLOW
646,317 gal/day/cfs	646,317 gal/day/cfs	646,317 gal
x 3.45 cfs	x 1.63 cfs	x 0.93 cfs
2,229,794 gal/day	1,053,497 gal/day	601,075 gal
x 3.785 liters/gal	x 3.785 liters/gal	x 3.785 liters
8,439,769 liters	3,987,485 liters	2,275,068
x 0.12 mg/l P	x 0.12 mg/l P	x 0.12 mg
1,012,772 mg of P	478,498 mg of P	273,008 mg
x 0.0022 lbs/gr	x 0.0022 lbs/gr	x 0.0022 lb/gr
2.33 lbs P/acre/day	1.05 lbs P/acre/day	0.60 lbs P

converted to scientific units = 2.33 lbs/2.2 lbs/kg = 1.06 kg x .4047 acres/hectare = 0.43 kg/ha. 1.05 lbs/2.2 lbs/kg = 0.48 kg x 0.4047 acres/hectare = 0.19 kg/ha and 0.60 lbs/2.2 lbs/2.2 lbs/kg = 0.27 kg x 0.4047 acres/hectare = 0.11 kg/ha. These rates of export are also comparable with the unpublished estimates compiled by (Schreiber, 1987) in Wisconsin where the rates of export during the spring and fall from 11 individual bogs ranged between 0.07 and 0.91 kg/ha.

The total available phosphorus loading to the lower bog of 0.75 kg/ha is considered to be a liberal estimate since it assumes no assimilation within the bog and no lose of inflow due to evapotranspiration. A summation of the estimated input flows measured during the 6/2 - 6/3 time period:

1.28 cfs Base flow 0.48 cfs Bennetts Pond discharge <u>1.11</u> cfs Reservoir/Sprinkler 2.87 cfs

Accounts for 83 percent (2.87/3.45) of the measured peak flow indicating that evapotranspiration may not have been a significant factor. The excess is attributed to groundwater discharge to the ditches and sampling error.

The results indicate that between 15 and 57 percent of the phosphorus applied during this period was exported out to the receiving waters. Barry and Simmons (1982) in their study on waterbody nutrient flow in an upland-peatland watershed reported that nutrient export was approximately proportional to the amount of stream flow. Valiela and Costa (1988) report that the Buttermilk Bay watershed is exposed to considerable nutrient loading from different sources. Agricultural sources (primarily cranberry bogs) are estimated to account for 32 percent of the total annual phosphorus loadings and 6.7 percent of the nitrogen to Buttermilk Bay. Concentrations of nutrients tended to range higher in near shore waters. Seasonal variation in nutrient concentrations in the near shore waters were found to be higher and more variable. Seasonal patterns in the ratio of N to P suggest that phytoplankton and benthic algae are less likely to be nitrogen limiting closer to shore and found that nutrients in the near shore are rapidly replaced. Phosphates were reported to decrease during the fall-winter in both the near shore and offshore waters and showed a slight peak in midsummer. Hideaway Village Creek which receives the output from the cranberry bog studied and a housing development located downstream of the bog was reported to have much higher concentrations of N primarily in the form of ammonium ion.

The recovery of glyhosate and its metabolite roughly 3 months after its last reported application is within the range reported by Rao and Davidson (1979) under laboratory conditions.

The recovery of chlorpyrifos in the sediments nearly sixteen months after the last reported application is unexplained. The grower reported two aerial applications in 1985 at the rate of 3 pints/acre, the last occurring on 7/28/85. Hydrolysis in water is reported to increase with increasing pH (personal communication, Matthew Brooks). The sequestering of the pesticide in a low pH environment low may account for its persistence. pH levels in the overlying waters of the discharged ranged between 5.1 and 5.7 during the surveys.

An unpublished study conducted by the State of Wisconsin, Department of Agriculture, Trade & Consumer Protection (personal communication, Ken Schreiber) reported the recovery of 0.407 ppm chlorpyrifos in cranberry bog sediments ampled two days after application. A study of cranberries harvested from areas where glyphosate was used to control weeds found no glyphosate in the berries (Devlin and Deubert, 1987).

Rao and Davidson (1979) in their discussion on the "Estimation of Pesticide Retention and Transformation Parameters..." have cited several "drawbacks in estimating the rate of disappearance of organic solvent-extractable parent compounds. First parent compounds may be degraded to a metabolite and more significantly in the case of this study; both parent and metabolites may so tightly bind to the soil and organic matter that traditional solvent extractions may seriously over estimate the degradation rate and conversely under estimate the residuals. Not withstanding these limitations spike recoveries of parent and metabolites genenerally exceeded 65% (Tables 17-19), in all of the sediment samples, with the exception of the parathion and metabolite paroxon. Rao and Davidson (1979) cite soil organic content and microorganisms as playing important roles.

The total organic carbon content of the respective sample sites B, C, and E ranged from a high of 6.4% at Station B to a low of 0.7% at Station E, the composition of the organic matter differed considerably at each site. Station B organics consisted of a fine brown organic coze with little recognizable material. Station C material was composed of partially decomposed leaf litter small twigs which graded from brown to black with depth indicating a anaerobic decomposition at depth. Station E consisted of a decidedly more granular material which quickly graded from grey green to black with depth, a hydrogen sulfide smell was only slightly apparent.

Table 24 was modified from Rao and Davidson's paper to include data reported by Goring et al., (1975) and this study on the persistence of glyphosate and chlorpyrifos.

#### TABLE 24

### CRANBERRY BOG INFUT STUDY

#### DEGRADATION RATE COEFFICIENTS AND HALF-LIVES OF GLYPHOSATE AND CHLORPYRIFOS

#### UNDER LABORATORY AND FIELD CONDITIONS

PESTICIDE	RATE	COEFFICIENT	(DAY)-1	HALF-LIV	<u>e (Days)</u>	DAYS FROM		
	MEAN		8 CV	MEAN	8 CV	THIS STUDY		
Chlorpyrifos <sup>(3)</sup>				30		471 <sup>(2)</sup>		
Glyphosate <sup>(1)</sup> (1)	lab lab	0.1 0.0086	121.0 93.0	38/08 903	139.5 191.9	104		

(Rao and Davidson, 1979)
Based on personal communications from grower
(Goring et al; 1975)

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#### 7.0 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

The Commonwealth of Massachusetts cranberry production is concentrated in a broad band of glacial outwash deposits located in the low-lying coastal plains bordering Buzzards Bay and Cape Cod Bay. More than 55 percent of the Commonwealth's total 4856 hectares (11,2000 acres), can be found within the Buzzards Bay drainage basin. Cranberry bogs within the Buzzards Bay drainage basin have generally been constructed within existing freshwater wetlands, bogs, and in former wooded and shrub swamps.

Over the decades many of the adjacent water bodies have gradually been dammed, altered, or converted to reservoirs to meet the needs of the growers. During the last thirty-five years reported harvest figures show a substantial increase in the yield per acre. Production levels have increased from 41 barrels/acre in 1950 to an estimated 148.5 in 1984. Conversely, the amount of land under production has declined 25 percent from a high of 6071 ha in 1950 to 4533 ha in 1984 (15000 to 11200 acres). The increased productivity can be attributed to several factors: the increased use of sprinkler systems, a shift to water harvest, improved marketing, use of pesticides controls, and the use of fertilizers.

During the June sampling the flow proportion discharged from the commercial bog was found to contain significantly higher concentrations of total and orthophosphorus when compared to the concentrations found in the discharge of a freshwater wetland. Concentrations of ammonia recovered in the bog discharge were likely the result of residual fertilizer off the planted areas. The concentrations were not significantly different from those observed in the freshwater wetland.

The October sampling of the harvest floodwaters disclosed some sharp differences. The concentrations of ammonia and nitrate were relatively low and uniform at each station. Total and orthophosphorus, however, were significantly greater. Since the fall sampling was conducted a week after the harvest, it is likely that the act of flooding and harvesting released substantial quantities of phosphorus from the sediments, damaged fruit and leaf litter into the overlying waters.

The agricultural management practices observed during these two sampling periods can result in the periodic loading of nutrients in their most active forms. This may have particular significance during the late spring and summer months when the discharges and nutrient concentrations from natural wetlands would be expected to decline in terms of nutrient content and volume.

The cumulative volumes from cranberry bogs may account for a significant percentage of the phosphorus loading to Buttermilk Bay. The impacts on the receiving waters, however, are not tied solely to the industry since the bay receives nutrients from multiple sources i.e., fertilizers from lawns, in street runoff, septic systems and as a component of ground water. Recoveries of the pesticide chlorpyrifos (245 ppb), the herbicide glyphosate (258 ppb) from sediments within the outlet ditch of the bog lend supporting evidence that they are resistent to degradation under certain conditions. The likely factors favoring resistance are the low pH of the soils and overlying waters and the

high organic content of the soils. Analytical precision as evidenced by the good spike recoveries of the parent compounds, methyl parathion ethyl parathion, diazinon and dichlobenil indicate that degradation is nearly complete and that significant amounts of these pesticides are not sequestered within the sediments.

One possible means of quantifying the transport, transformation and fate of pesticides and nutrients in the ecosystem would be with radioactive trancer studies. In the interim it is important for the industry to employ application methods which minimize the introduction of nutrients to the receiving waters. This might be accomplished in several ways: one by maximizing the holding time of nutrient rich waters within the bogs, two by applying fertilizers in amounts which maximize assimilation by the crop and minimize the discharge of residuals, three by putting more study into the use of timed released fertilizers and four by upgrading the water holding facilities within the property.

Downstream segments of the outlet stream physically resembled a first or second order woodland stream. In such streams allochthonous carbon loading in the form of leaf litter usually supports a community of shredders. Isopods which are shredders utilizing coarse particulate organic matter (CPOM) were present in both segments but not in abundance. This was particularly apparent in leaf packs snagged at debris or bends in the stream.

The numbers of macroinvertebrates in the outlet of the cranberry bog channel segment was surprisingly high but not indicative of a particularly diverse community given an anticipated decline due to exposure to pesticides. Scarcity of benthic fauna in downstream sections, while unexpected, can be explained by manipulations in flow due to agricultural practice. Speculations as to influences exerted by transport of pesticides to downstream sites can not be evaluated given the limited amount of data and the aforementioned variability in flow regimes experienced by these benthic populations.

In conclusion, the impact of the cranberry growing industry and its agricultural practices has and will continue to be a cause of concern particularly in light of increasing competition for water and land to support the burgeoning population of the region.

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