BIOGEOCHEMISTRY OF A NEW ENGLAND SPHAGNUM BOG

by

HAROLD FIELD HEMOND

B.S., Worcester Polytechnic Institute
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M.A., Connecticut College
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Signature of Author...
Department of Civil Engineering

Certified by...
Thesis supervisor

Accepted by..
Chairman, Department Committee

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ABSTRACT

Thoreau's Bog in Concord, Massachusetts, is a floating-mat Sphagnum bog developed in a glacial kettle hole. Vegetation of the open mat is dominated by Chamaedaphne calyculata; trees include scattered Picea mariana and Larix laricina. Hydrological investigations show the bog to be entirely rainwater-fed, with annual water input of 1.45 m and annual runoff of .28 m.

Concentrations of K and Mg in the Sphagnum mat are vertically distributed in accord with the inhomogeneous ion-exchange chemistry of peat, while lead concentrations are distributed in accord with historical trends in atmospheric lead fallout. Annual storage rates of K, Mg, and Pb in peat amount to 20, 40, and 97% of the annual inputs respectively.

Bog acidity (pH=3.8) is maintained by organic acids occurring at concentrations of 10^{-3} eq/l. The effect of cation exchange on bog acidity is modest, while the contribution of acid rain is offset by alkalinity increases of the same magnitude resulting from sulfate reduction and nitrate uptake. These latter processes appear to buffer the system strongly against "acid rain" while the accumulation of peat is also a strong buffer against pH change.

"Minus" experiments with Acer rubrum, which consistently fails on the bog, indicate that this species can obtain neither sufficient nitrogen nor sufficient phophorus from bogwater.

^{210}Pb dating and historical records indicate the bog to be relatively young, probably less than 1000 years old. These data suggest the bog is not a relict of colder post-glacial periods; but, instead, must have developed under modern climatic conditions.

Name of Thesis Supervisor:	Francois M. M. Morel
Title of Thesis Supervisor:	Associate Professor of Civil Engineering, M.I.T.

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I. Introduction

> "Consider how remote and novel that swamp. Beneath it is a quaking bed of sphagnum, and in it grow *Andromeda polifolia*, *Kalmia glauca*, *Menyanthes* (or buck bean), *Gaylussacia dumosa*, *Vaccinium oxycoccus*, plants which scarcely a citizen of Concord ever sees. It would be as novel to them to stand there as in a conservatory, or in Greenland--there are square rods in Middlesex County as purely primitive as they were a thousand years ago, which have escaped the plow, the axe, and the scythe and the cranberry rake, little oases of wilderness in the desert of our civilization--."
>
> Henry David Thoreau
> (in Eaton, 1969)

Thoreau did not use the more precise word, "bog", in differentiating this habitat from the shrubby or forested wetlands we now call swamps, but his floristic observations were excellent and his statement on the uniqueness of the *Sphagnum* bog is as valid today as it was a century ago. Widely scattered across central New England, *Sphagnum* bogs are as unusual in their physical structure as they are in their vegetation. Carnivorous plants and stunted trees grow on a mat of living *Sphagnum* moss and peat, which is reinforced with roots and floating in yellow-brown, acidic water. The plants include species typically associated with muskeg and boreal forest regions. Transeau (1903) has written a classical work on the bog plant societies of North America. This bog association, which commonly includes species such as *Drosera sp*. (sundew), *Sarracenia purpurea* (pitcher plant), *Larix laricina* (tamarack), *Vaccinium sp*. (cranberry), *Kalmia polifolia* (bog laurel), *Ledum groenlandicum* (Labrador tea), and *Andromeda glaucophylla* (bog rosemary), is so distinctive as to be part of the modern definition of a bog.

Although central New England bogs are a minor component of the landscape, the floating-mat *Sphagnum* bog is closely related to the vast bogs and mosses of northern Europe and the raised bogs and muskegs of North America. Peat is harvested from bogs as a fuel, as a horticultural medium, and even for physico-chemical water treatment. As an engineering medium, bogs and muskegs present severe challenges in many northern regions. As vast reservoirs of carbon, bogs are of biogeochemical significance on a global scale (see Deevey, 1958). Finally, in increasingly populous areas, such as New England, freshwater wetlands in general are receiving increasing attention for their possible roles in affecting yield and quality of surface and ground waters.

Gorham (1967) has written an excellent review of the literature of peatlands, which includes not only bogs, but a continuum of floristically and hydrologically differing wetland types; a more recent book by Moore and Bellamy (1974) discusses many of the problems in more detail. Both of these works have a European emphasis; the North American bogs receive much less attention. Heinselman (1963, 1970) has written extensively on bog and related areas of the Lake Agassiz region of Minnesota; many of the problems are similar, and the author offers a glossary which assists in the translation of a complex European wetland nomenclature to less-precise American usages.

Bogs have always been of interest to the botanist because of their unique flora and perhaps also because of the zonation often observed in the bog-upland ecotone. Equating zonation in time with zonation in space, bogs have been held out as classical examples of a "bio-automatic" succession, a concept which appears to have been overstated by some workers and has been strongly challenged by Heinselman (1970) and others.

Questions of plant nutrition in bogs have concerned many workers, particularly in Europe where "reclamation" of bogs for cropland and forest is of considerable economic importance (e.g., Puustjarvi, 1955). In a few instances, hydrological investigations have related bog systems to local groundwater supplies. Dating and tracing of local and regional vegetational history through the pollen record in bogs has had success through the efforts of several workers (e.g., Turner, 1964; Niering, 1953).

That these several aspects of bog science are related is perhaps obvious. The actual role of hydrology in bog chemistry and vegetation is generally recognized, yet few attempts have been made to explore the interrelationships of geology, hydrology, peat and water chemistry, plant physiology and nutrition, vegetational succession, plant geography, and fossil records at any single site. The research described here is undertaken in an effort, albeit incomplete, to investigate several of these related phenomena in a New England bog, with the hope of understanding its overall significance as an ecosystem.

Organizationally, this work is presented in four separate but related sections. The first deals with the hydrology of the bog; the second section concerns metal speciation and distribution in the bog and the overall metal budgets. Determination of the rates of peat accumulation is critical to understanding the metal budgets, and has general implications for the developmental history of bogs in New England. A third section addresses the unresolved questions of acidity in the Sphagnum bog, and necessarily involves the role of the bog in the cycling of several nonmetallic elements. The fourth section of this investigation was begun under the hypothesis that the metal chemistry of the bog was an important factor in the control and limitation of the plant community of the bog. This no longer appears to be the case; the study of plant nutrition in the bog is not regarded as complete, and nutrition limitations in the bog now appear to be more closely related to the biogeochemistry of the non-metals than to metal availability and the related phenomena of ion-exchange by _Sphagnum_ and complexation by organic acids. The study area, while of considerable historical interest, was chosen for its accessability and for its physical and vegetational structure, which are fully representative of a floating-mat _Sphagnum_ bog in New England.

2. Descriptive Analysis of Thoreau's Bog

2.1 General

Thoreau's Bog, or Gowings Swamp as it was known to Thoreau himself, is a classical floating mat Sphagnum bog. It is located in the town of Concord, Massachusetts, at latitude 42° 27' 43" North and Longitude 71° 19' 42" West (Figure 1). It is located in the Concord quadrangle (USGS, 1970) north and west of Meriam's corner (the junction of Lexington Road and Old Bedford Road). Elevation of the bog is 130 feet above mean sea level, on the Merrimack River watershed. The bog itself is part of a larger wetland complex, the bulk of which may best be characterized as red maple swamp. Total area of the bog is .38 hectares, while the larger wetland complex has an area of 3.6 hectares. The bog was studied by the naturalist and philosopher, Henry David Thoreau (Thoreau, 1854, 1858, 1860) and is frequently the site of botanical field trips conducted by area universities and clubs. A portion of the bog has been purchased for preservation in its natural state by the Sudbury Valley Trustees.

2.2 Postglacial

The surficial geology of the Concord Quadrangle has been described in detail by Koteff (1964). The bog lies within an area of glaciolacustrine deposits deposited in

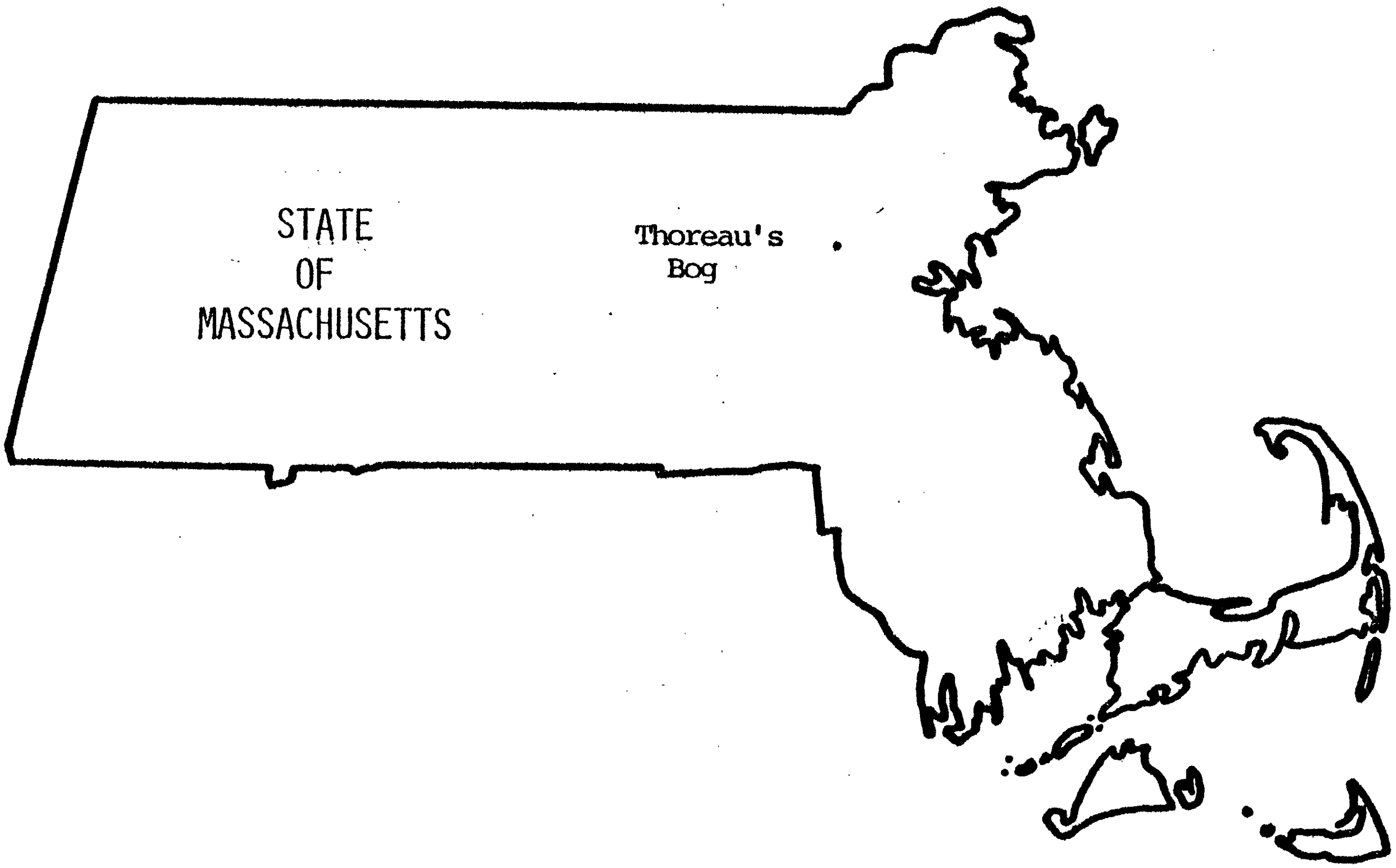


Fig. 1. Location of Thoreau's Bog

glacial Lake Concord, and was formed upon retreat of the ice front by the melting of a large buried ice mass. Revolutionary Ridge, which borders the bog to the south, is a kame delta formation deposited at the high stage of Lake Concord.

The basin in which the wetland complex is formed is partially divided by an ice channel filling which forms a peninsula of mineral soil extending into the wetland from the north. A larger ice channel filling forms the eastern border of the wetland and separates the wetland from a stream and small area of swamp and pond to the east.

Surface drainage from the bog now occurs almost exclusively through a man-made stone French drain at the southeast corner of the wetland (see Figure 2); although, according to a local resident, a previous drainage route had been the now-dry channel about 30 meters to the north. The present drainage channel is dry throughout much of the year, but runs during late winter and spring when bog stage is high. It thus behaves much like a weir. Attempts by man to increase surface runoff from the bog are recorded as early as 1858 (Thoreau, 1858), and a ditch in the peat from the stone drain to the northwest corner of the wetland can be clearly seen on aerial photographs as recent as 1952 (Air Survey Corp., 1960). Remnants of it are still visible in the field. In addition, a man-made pond at one time existed on the north side of the wetland for irrigation purposes;

this pond has since been filled in. A very small amount of surface runoff has been observed through a small channel leading from the northeast portion of the wetland. However, no surface drainages into the bog have been observed.

The entire basin is now essentially filled by swamp and bog deposits. The floating *Sphagnum* mat was probed by Thoreau (1858) and described as "...a crust, about 3 feet thick, of *Sphagnum*, andromeda (*Calyculata* and *Polifolia*), and *Kalmia glauca*, etc., beneath which there is almost clear water, and under that, an exceedingly thin mud." Recent probing with a PVC pipe and hand pump shows that clear water may be pumped from a relatively thin (<½m) stratum of open water in many places, at a depth of about 2 meters. The open water in turn is underlain by further peat deposits to depths as great as 40 feet.

2.3 Vegetation

At least three distinct zones of vegetation may be recognized in the wetland complex containing and surrounding the bog. These include the open, floating mat of *Sphagnum* moss itself, and a transition zone of dense shrubs 2 to 3 meters in height and 5 to 10 meters wide. These first two areas are radially symmetrical about the center of the floating mat, and are surrounded by a red maple tree swamp which extends to the surrounding upland (Figure 2).

The *Sphagnum* mat includes *Sphagnum subsecundum* Nees.

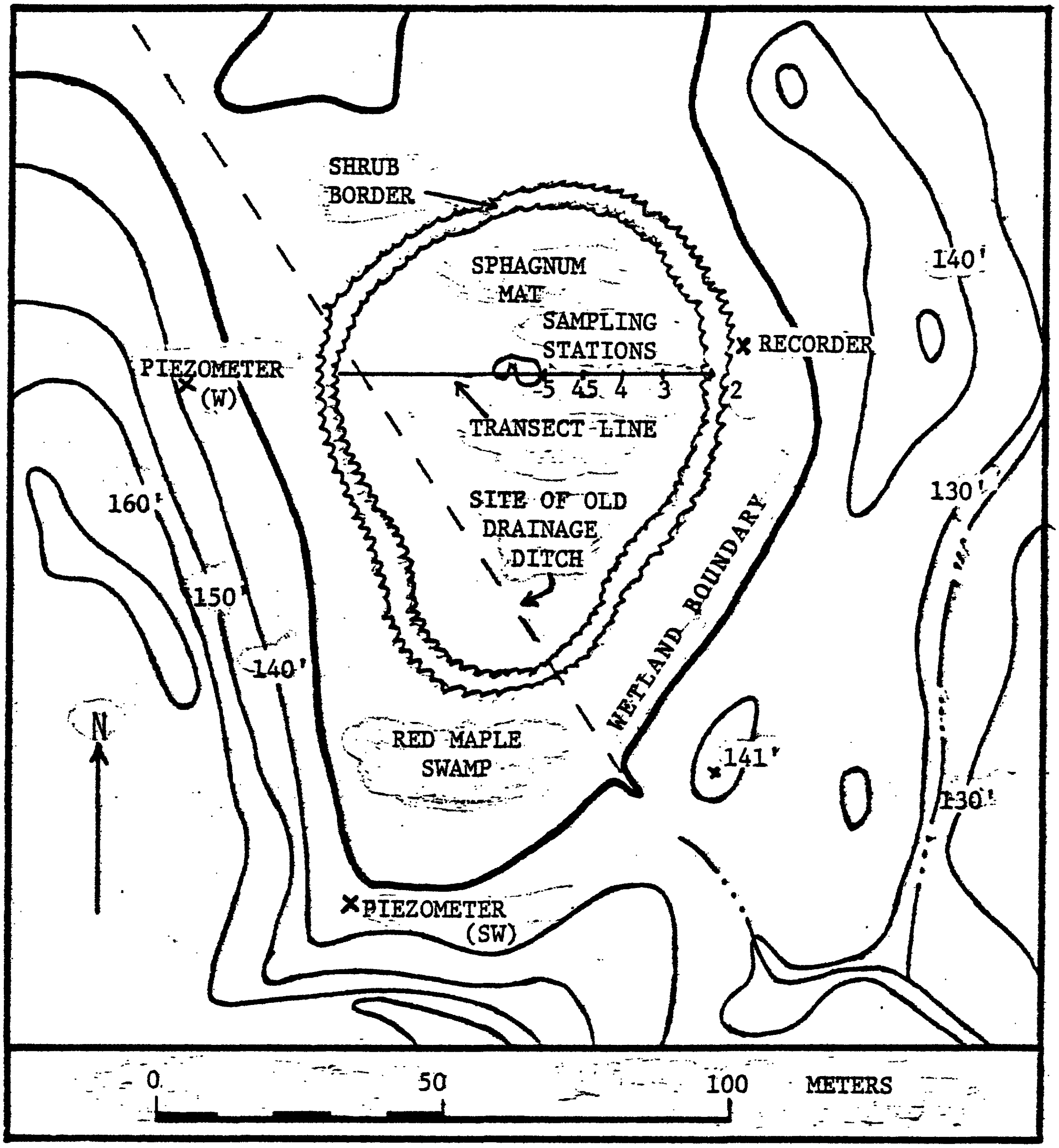


Fig. 2. Map of Thoreau's Bog (adapted from Air Survey Corp. 1960)

and *Sphagnum warnstorfii* Russow, which together form a continuous matrix in which the remainder of the vegetation is anchored. The moss surface is typically ten to twenty centimeters above the water table, although greater depths of *Sphagnum* (hummocks) sometimes form, particularly in association with dense shrub growth or trees. Typical vegetation of the open bog is shown schematically in Figure 3. The dominant shrub is *Chamaedaphne calyculata* (L.) Moench (leatherleaf), which has an average coverage of 25 to 50% on the *Sphagnum* mat (roughly estimated, by eye) and forms nearly pure stands on some hummocks. *Kalmia angustifolia* L. (sheep laurel) is also important on the mat, often occurring in clumps and comprising an estimated 5 to 10% cover. *Andromeda glaucophylla* Link. (bog rosemary) occurs as several rather discrete patches on the *Sphagnum* mat, and comprises significantly less total cover. Two cranberries, *Vaccinium macrocarpon* Ait. and *V. oxycoccos* L., are scattered on the bog surface, often associated with one of the larger shrub species but occasionally occurring in pure stands. Much less abundant is *Kalmia polifolia* Wang. (bog laurel), which is scattered on the bog and comprises considerably less than 1% cover.

Tree species on the bog include *Picea mariana* (Mill.) BSP. (black spruce), *Pinus strobus* L. (white pine), *Larix laricina* (DuRoi) K.Koch (tamarack), and *Acer rubrum*

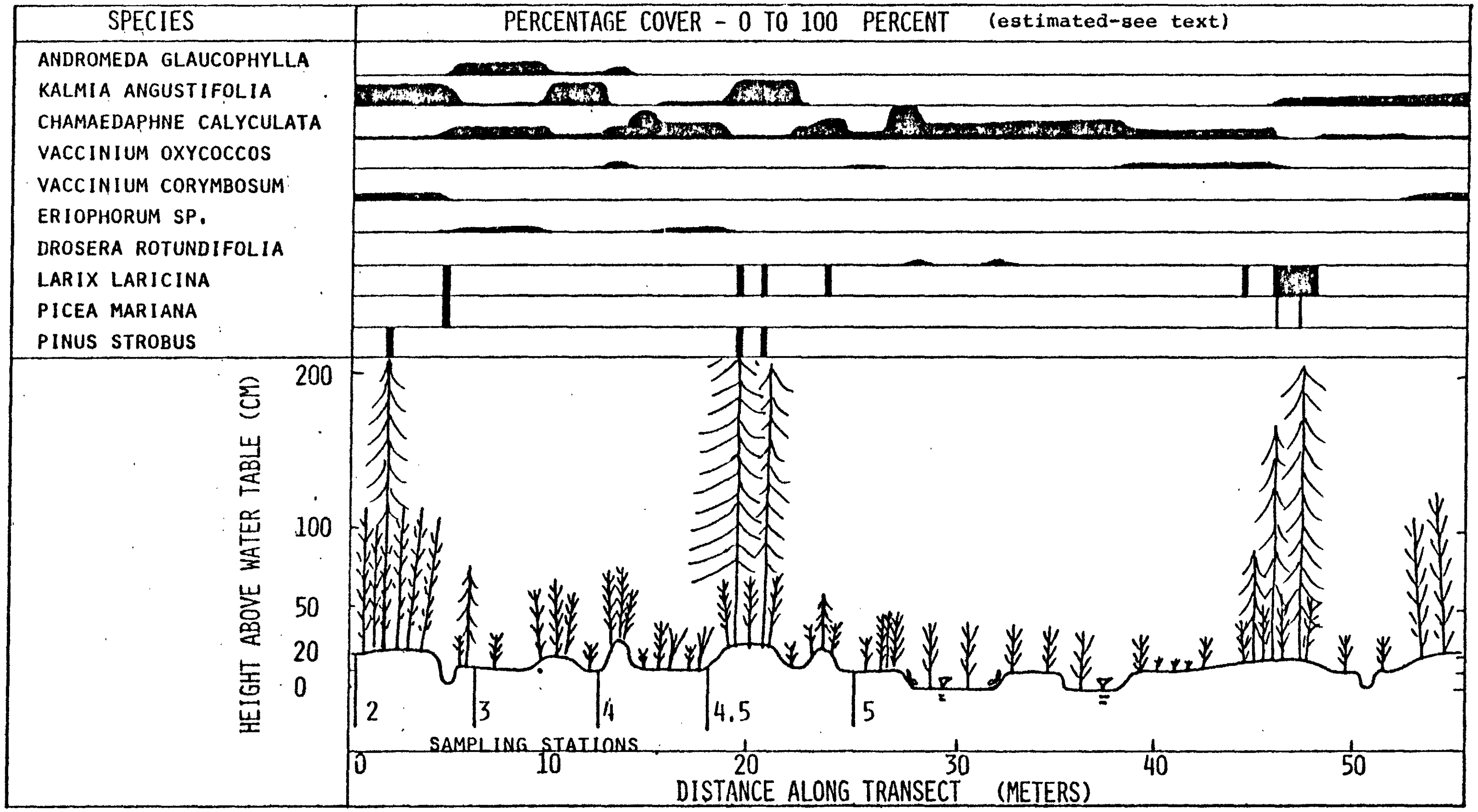


FIG.3. VEGETATION ALONG A TRANSECT THROUGH THE CENTER OF THOREAU'S BOG

L. (red maple). The conifers tend to occur in mixed clumps, and together cover a few percent of the area of the bog. Both tamarack and black spruce are reproducing, and appear to be self-sustaining populations, although their growth forms are often gnarled and their stature seldom exceeds 2 meters. Dead snags are not uncommon, and these too indicate that the trees die long before attaining their potential size. Neither tamarack nor black spruce is observed on the surrounding uplands, further indicating that these species form isolated, self-sustaining populations.

White pine is somewhat of an anomaly in the bog and appears to be present by virtue of a massive seed source represented by mature stands of pine both east and west of the wetland. No seed production has been observed by white pine in the bog, and foliage coloration is distinctly yellow-green.

The red maple population is also sustained by the surrounding seed source. Red maple, however, does not grow beyond a two or four leaf stage, and its foliage color ranges from reddish-green to deep red on the Sphagnum mat. Often the seedings, which may live as long as 3 years (Moizuk and Livingston, 1966), are found nearly engulfed by growing Sphagnum. Herbaceous components of the plant community include Sarracenia purpurea L. (pitcher plant), which occurs scattered throughout the bog, and Eriophorum sp. (cottongrass) which comprises perhaps 1% cover of the bog in mid-to-late summer. *Drosera rotundifolia* L. (broad-leafed sundew) occurs primarily at the center of the bog, bordering a small pool.

The transition zone, or shrub border of the bog begins with dense, exceptionally tall (>1 meter) leatherleaf and sheep laurel. Further toward the upland, *Vaccinium corymbosum* L. (highbush blueberry), typically 2 meters or greater in height, dominates, and *Rhododendron viscosum* (L.) Torr. (swamp azalea) becomes important. White pine occurs and reaches greater stature in this region than on the open *Sphagnum* mat. This transition zone in turn is bordered by a hummocky red maple swamp. Here red maple grows to maturity and the relatively open understory consists largely of highbush blueberry and sheep laurel, with *Clethra alnifolia* (sweet pepperbush) occurring toward the upland. Standing water occurs in this swamp all year, with the exception of late summer and early fall, and much of the vegetation is restricted to the hummocks, most of which are associated with red maple stems. During the dry summer of 1976, considerable red maple reproduction was observed both on and between hummocks.

The upland surrounding the bog is characterized by nearly pure stands of mature white pine on the east and west sides of the bog. *Betula papyrifera* Marsh. (paper birch) and *Quercus sp*. (oaks) are associated with the pine to the west, while the upland to the north is dominated by oaks of mixed age. Occasional *Castanea dentata* Marsh. (American chestnut) sprouts occur to the west and north of the wetland area, and one notable chestnut specimen, which may not be of sprout origin, has attained 7" (18 cm) DBH. Also notable is the frequency of *Cypripedum acaule* Ait. (pink lady slipper orchid) on the forest floor.

The growing season of the bog was observed throughout 1976 and part of 1975 and 1977. Ice-free areas of *Sphagnum* appear in mid-March, and by late March or early April, red maple is in bloom in the swamp areas. Most bog shrubs have leafed out by late April and leatherleaf, bog rosemary and highbush blueberry bloom in late April. Bog laurel blooms in the first week of May, and red maple seeds are shed heavily in mid-May. About this time, red maple seedlings in the bog begin to leaf. The small cranberry blooms in early June as do the first pitcher plants. Sheep laurel blooms over a considerable interval in mid-June, and cottongrass flowers in July. Newly-germinated red maple seeds are found in the *Sphagnum* throughout late spring and early summer. Red maple seedlings in the bog appear to go into dormancy in September, earlier than mature counterparts in the swamp, although it is not until late November that the first hard freezes occur and ice begins to form in the bog.

3 Hydrological Analysis

3.1 Introduction

The role of hydrology as a factor in bog development and bog ecology has been widely recognized in the literature. In the raised bogs common in Europe a convex surface is commonly found, and is an indication that the bog is, at least near the center of the peat dome, ombrotrophic or "nourished by rain". The association between ombrotrophy and the vegetation has been observed repeatedly, and most contemporary discussions of the vegetation and the chemistry of wetlands make reference to the relative influence of mineral soil water in contrast to the influence of water from precipitation. Gorham (1950), Sparling (1966), and Heinselman (1963, 1970) have pointed out that the movement of water, as well as its origin, is in general an important factor in bog ecology. It is evident that in wetland systems, the supply of water-borne nutrients may be a critical factor differentiating very different biological communities and, by so doing, determining the evolution of the organic substrate of the bog. This evolution, including the building, erosion, and decomposition of peat, together with the plant communities of the wetland, in turn may profoundly alter the hydrology of the area. Understanding the nature, function, and development of a wetland, then, is inseparably linked with understanding its hydrology.

Unlike raised bogs or riverine swamps, Thoreau's Bog is not readily characterized hydrologically. Eaton (1969) suggested the bog was spring-fed, and IEP (1975) claims the wetland is a groundwater discharge area. This view was also held by Koteff (personal communication). However, floristically the bog more resembles an ombrogenous raised bog than a swamp or fen. Clearly, some knowledge of the directions of groundwater flow is necessary to resolve this question. The direction of water flow in a phreatic aquifer can be determined by measurement of piezometric head differentials; this can be accomplished by installing piezometers, surveying them for elevation, and comparing water heights. Thoreau's Bog lends itself well to such an investigation, due to the nature of the surficial geology in the area of the bog. The sorted glacial Lake Concord deposits are relatively deep and uniform, and are easily bored with a hand auger. The absence of bedrock outcrops suggests that the association of the wetland with a confined aquifer system is not likely. Finally, the amount of instrumentation required is minimized by the existence of bodies of open water, clearly part of the same groundwater system, to the east and northwest of the bog.

Evapotranspiration rates in wetlands are known to be substantial. McComas et al (1972) suggest that evapotranspiration from Volo Bog in Illinois exceeds evaporation from a nearby lake, while Miller (1965) indicates that Great

Swamp in New Jersey may be a groundwater discharge area due to its considerable evapotranspiration rates. O'Brien (1973) has determined an annual hydrological budget for a red maple swamp in Lincoln, Massachusetts and found evapotranspiration to equal about half of annual precipitation. The Lincoln wetland is only a few miles south of Thoreau's Bog, but has a significantly different vegetation, and lacks the areas of floating Sphagnum mat which present a large moist surface area to the atmosphere.

Evapotranspiration may be calculated from a knowledge of the energy budget of an area, or a knowledge of air movement and the saturated and actual vapor pressures of water in the air. Several of these methods are summarized by Eagleson (1970); however, the data requirements of these methods are substantial. An alternate method is to construct a water balance for the bog, and determine evapotranspiration as a difference between precipitation and runoff. This approach, using a continuous water level recorder, is used in this investigation. Separation of runoff and transpiration is based on the strongly cyclic nature of evapotranspiration, on both a 24-hour and a yearly time period. Daily step-like decreases in stage in a raised bog in Kirkcudbrightshire have been described and attributed to evaporation by Boatman and Tomlinson (1973). The same hydrographs also provided evidence of stage-dependent subsurface runoff which was attributed to a vertical gradient in the permeability of the peat substrate. If runoff from a system is a function of stage only, it should be possible to construct a stage vs. runoff function from the non-cyclic component of a hydrograph. The resulting function may then be applied to subtract runoff from the hydrograph and obtain an evapotranspiration versus time curve.

The floating nature of the Sphagnum mat is a feature of hydrological significance; since, unlike the surface of a raised bog, the surface vegetation of a floating mat will subside and remain water-saturated during dry periods. Buell and Buell (1941) have studied the surface of a Minnesota floating mat bog and found that the center portion of the mat conforms most closely with changes in bog stage, while toward the periphery the surface rises and falls through a lesser range. Presumably, the greater thickness of a mat towards the edges accounts for this phenomenon; the mat may in effect begin to "bottom out" during periods of low water in some bogs. The physical structure of the Sphagnum peat itself is quite complex in its physical properties (Hofstetter, 1965) and conventional measurement of permeability (as by pumping; for example, USDI (1968); Lowe (1969)) may not be entirely reliable. However, the existence of a lens of open water beneath a floating mat should be demonstrable by tapping the lens with a suitable tube and pumping clear water from it.

3.2 Materials and methods

3.2.1 Equipment and instrumentation

Piezometers were obtained from National Plastifab, Inc., and consisted of 120μ porous polyethylene tubes, 2.5 cm in diameter and 15 cm long, sealed at one end and attached to 1.25 cm polyethylene tubing at the other. A 1¼" hand auger from Forestry Suppliers, Inc., was used to drill holes for piezometer installation. A 1¼" schedule 40 PVC water pipe with a handle at one end and teeth filed on the other end was used as a casing where needed to prevent sloughing of soil. A TMK Model TP-5S pocket volt-ohm-milliammeter (VOM) was used in obtaining water depth readings in the piezometers.

Water level, or stage records for the bog were obtained with a Stevens Type F Recorder with an 8-day time base and 1:1 gearing between the float and the rotating drum. The instrument housing was supported by 2 inch iron pipe. Separate stilling and counterweight wells were of 6" and 3" PVC pipe respectively. The stilling well was perforated for most of its length with 5/8" holes.

3.3.3 Measurement of groundwater level

Piezometers were installed along the border of the wetland area at the locations shown in Figures 2 and 7, in holes bored with the hand auger. Where sloughing of the sides of the hole occurred, the casing was worked into the hole, and drilling proceeded by short advances of the auger followed by short advances of the casting. Piezometers were inserted when the depth limit of the auger was reached, or when the auger was below the water and repeated attempts to drill deeper in the vicinity had failed. Each piezometer was backfilled and the tube communicating with the surface was cut off at ground level. The opening was then plugged and camouflaged to discourage vandalism and prevent the entry of soil. The elevation of the piezometers was determined relative to a series of benchmarks by means of a transit. Water levels in each piezometer were measured by lowering a calibrated, insulated copper wire into the tube while measuring total resistance between the wire and a ground rod with the VOM. Contact of the exposed end of the wire with the water surface was indicated by a sharp discontinuity in the resistance reading. Accuracy of this method was verified both by wooden dipstick and by means of a pump and small plastic tube. Groundwater levels were measured at approximately monthly intervals throughout the year. Piezometer elevations were re-checked a year after installation to detect tampering or initial survey error.

3.2.3 Stage recording

3.2.3.1 Recorder operation

The water level recorder was located in the outer extreme of the shrub border surrounding the bog, as shown in Figure 2. The instrument housing was mounted on a section of 2" iron pipe which was driven a depth of fourteen feet to resisting material, presumably mineral soil. The stilling well and counterweight well were first inserted into the peat and removed. The peat cores were driven out and the wells reinstalled in the holes thus created. The recorder was installed with a 3-inch float, and the housing elevation surveyed in. Charts were changed regularly throughout the ice-free portion of the study period. At each chart change, bogwater level, with respect to the housing, was checked with a measuring tape. Housing elevation was re-checked a year after installation to detect any settling, ice damage, or initial survey error. Inasmuch as the recorder was supplied with charts graduated in .01 foot units, and was readable to ±.001 foot, the daily hydrologic budgets were worked out using units of feet. An unnecessary source of roundoff error was thus eliminated by converting only the final results to MKS units.

3.2.3.2 Hydrograph separation

Evapotranspiration was graphically separated from groundwater and surface water runoff following the procedure demonstrated in Figure 4. This method is based on the assumptions that: 1) total runoff is a function of water level only; 2) evapotranspiration may approach zero at

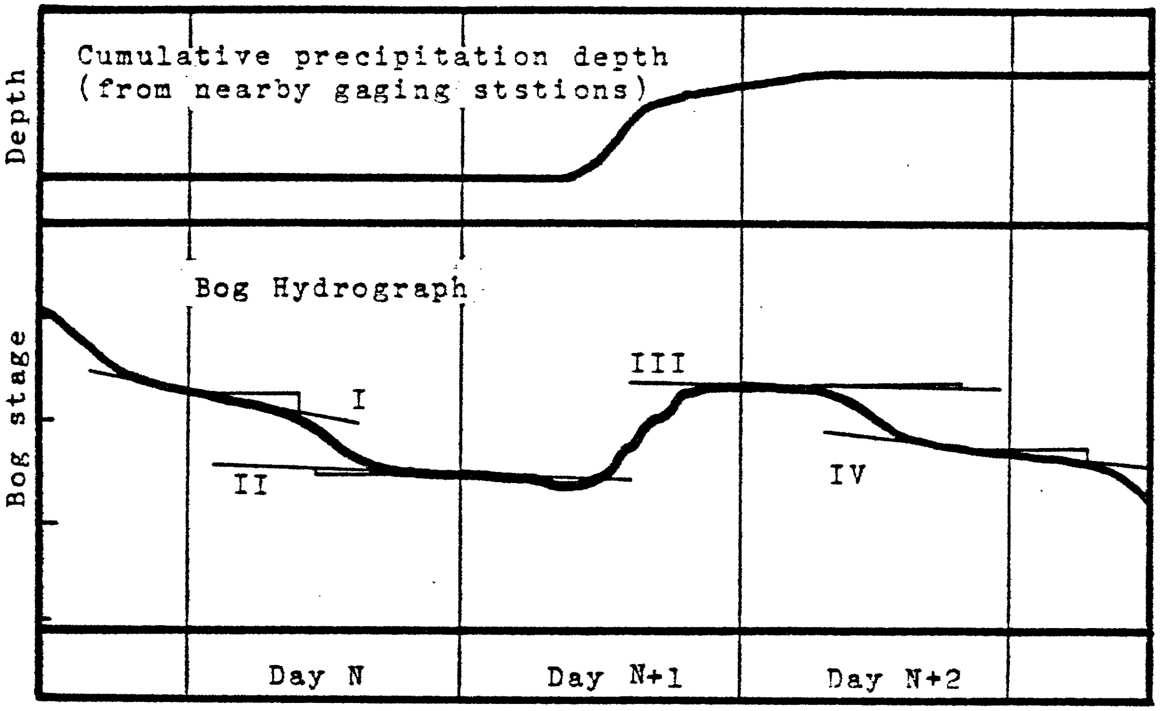


Fig. 4. Hydrograph Separation Procedure

In this four-day interval, bog stage changes by only a few thousandths of a foot, and thus total runoff rate is assumed constant. Tangent lines I, II, III, and IV are drawn to the hydrograph at the regions of lowest slope (generally nighttime) and their slopes compared. In this example, line III is associated with precipitation and is rejected. Lines I and IV both have greater slopes than line II, indicating that evaporation is occurring. Therefore, the slope of line II is taken as the best estimate of runoff rate at this bog stage. The procedure is the same whether or not the surface drainage channel is flowing night; and 3) onset of precipitation in the bog is usually evident either from relatively rapid changes in rate of water level change or from precipitation recordings of West Concord or Bedford. The water level records (bog hydrographs) were scanned for minimum rates of decline over the entire range of observed bog stage. Data points which appeared to be associated with precipitation were rejected, and the remaining points were plotted on a graph of runoff versus water level (Figure 5). A regression line was fitted to the points using a least-squares routine, and was subsequently used to compute daily runoff rates from daily bogwater levels. The remainder of each day's water level decline was attributed to evapotranspiration.

3.2.4 Precipitation gauging

Precipitation data was obtained from three locations in the vicinity of the bog. One station is located in West Concord, at latitude 42° 20' north, longitude 71° 25' west, or about twenty kilometers southwest of the bog. This station is operated by the M.I.T. Meterology Department, and obtains a continuous recording of precipitation on a Friez dual-traverse rain gauge. The second station is located in Bedford, Massachusetts, at latitude 42° 29' north, longitude 71° 17' west, or about four kilometers northeast of the bog. This station is operated by Northeast Weather Service and is part of the National Cooperative

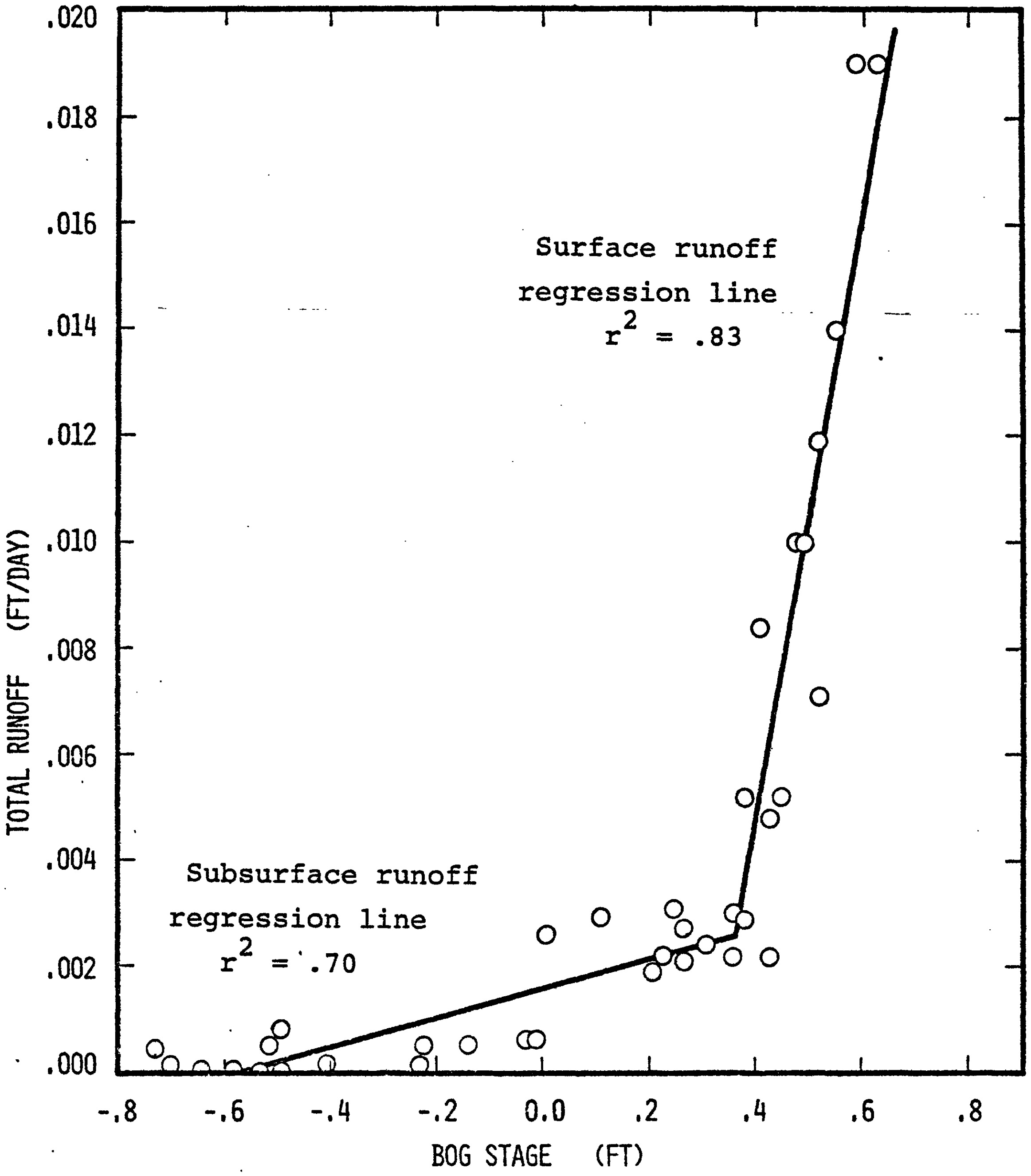


Fig. 5. Stage vs. runoff curve for Thoreau's Bog

Weather Service Network. Precipitation is reported as 24-hour totals, from midnight to midnight. The third station is located on Logan Field in Boston, Massachusetts, at latitude 42° 22' north, longitude 71° 02' west, or 27 kilometers south and east of the bog. This station is operated continuously by the National Weather Service and reports precipitation as daily totals and as hourly totals.

3.3 Results

3.3.1 Groundwater flow

Figure 6 shows the water levels in the bog and in the piezometers over the 15-month interval from March 1976 to July 1977. In every instance, the head differential between the piezometers and the bog is in the direction which would cause water flow, if any, to be out of the bog. Observations of water level in the intermittent pond north and west of the bog and in the stream east of the bog also show that the gradient in piezometric head is consistently away from the wetland. A reversal of the head differential between piezometer N and piezometer SW (Figure 6) indicates that the groundwater system north of the bog is relatively independent of the system to the south of the bog, suggesting that the bog lies on a groundwater divide. This is consistent with the topography of the area (Figure 7). The small pond about ½ Km north of the bog is somewhat lower than the bog (Air Survey Corp.,

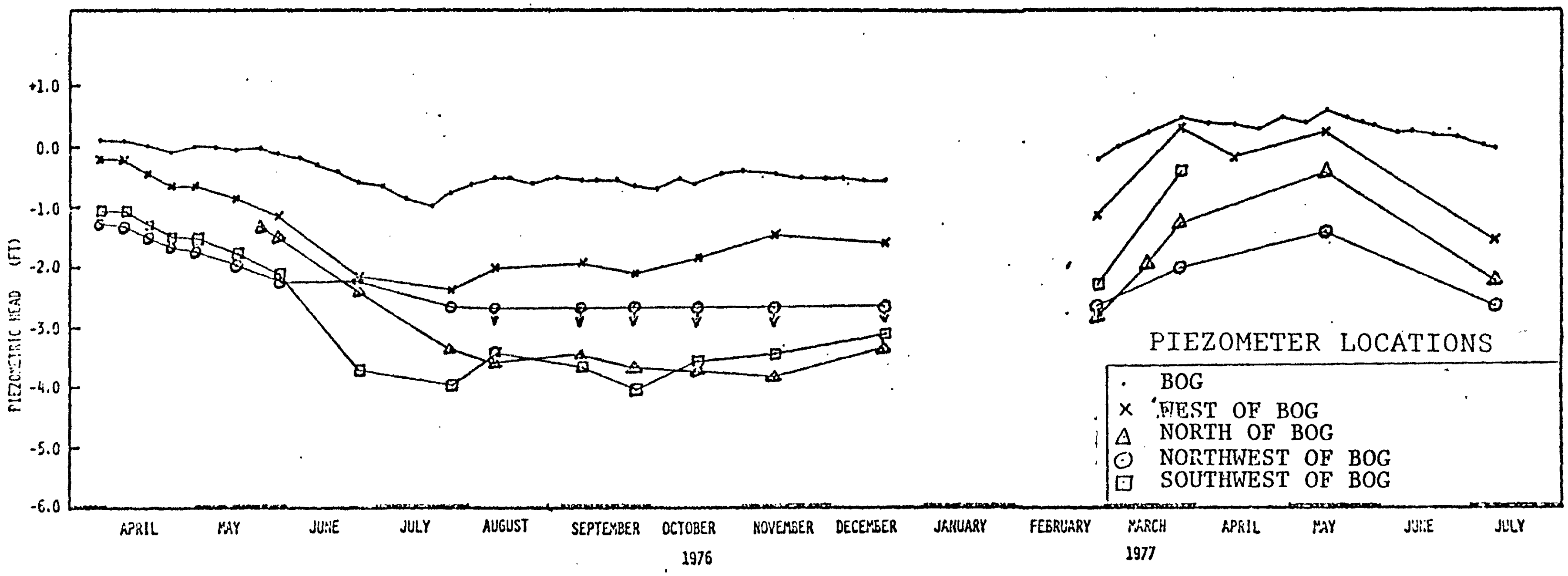


Fig. 6. Piezometric head in Thoreau's Bog and in piezometers located at adjoining upland sites, during the interval from March, 1976 to July, 1977.

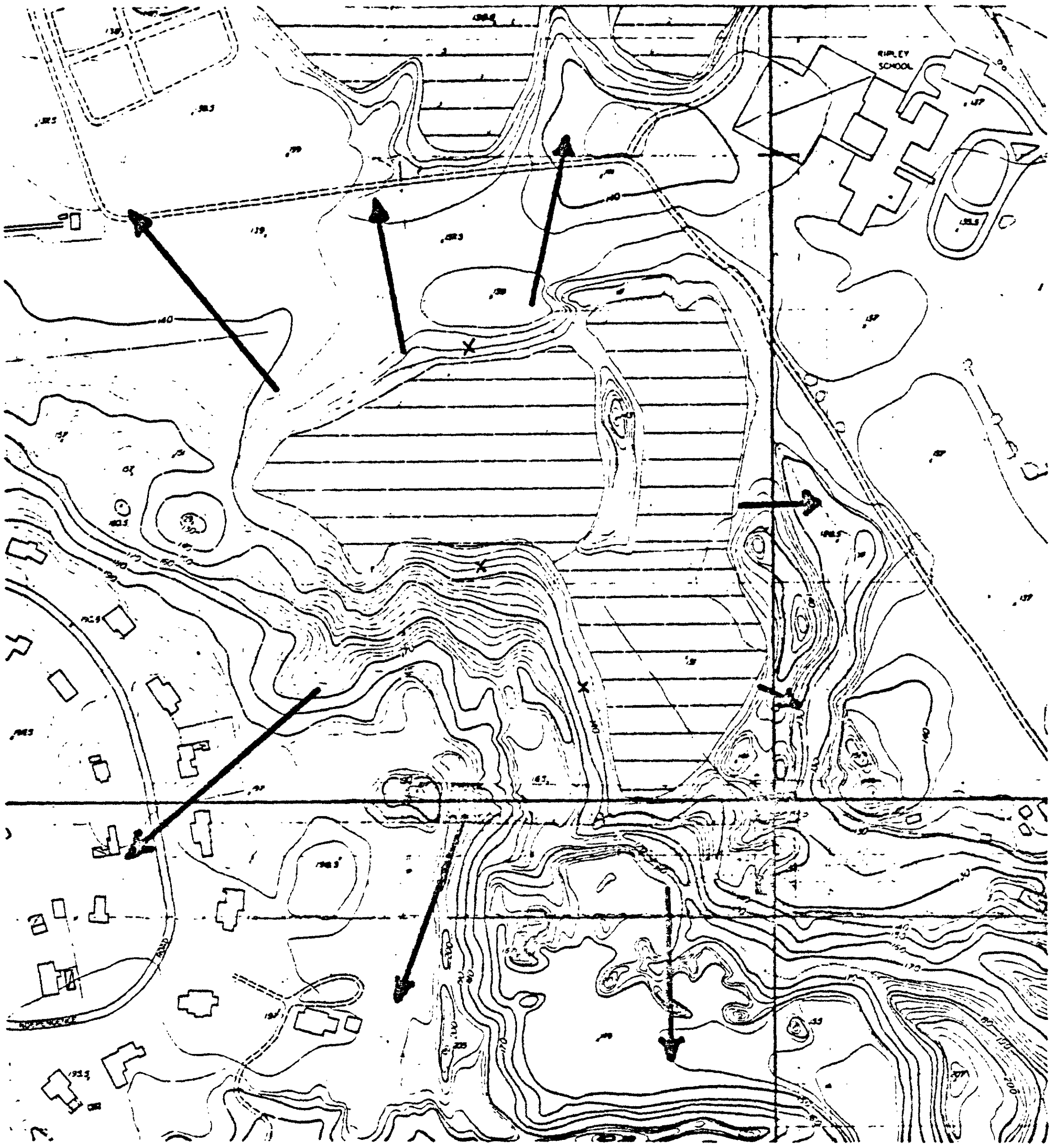


Fig. 7. Thoreau's Bog and vicinity. Heavy arrows indicate inferred directions of groundwater movement. x indicates piezometer location.

1960), and drains directly to the Concord River. Groundwater south of the bog must move toward Mill Brook, which runs along the south side of Revolutionary Ridge and also carries surface runoff from the bog (Figure 7).

Further confirmation of the ombrogenous nature of the wetland is found in the absence of a delayed water level response in the bog following precipitation. Recharge of the bog by a groundwater system would, on the contrary, exhibit measurable inflow after the cessation of precipitation.

3.3.2 Precipitation input

Precipitation on the bog is summarized in Table 1. These figures include a correction for bog runoff during storms; this correction is only significant for storms of considerable duration at bog stages in excess of +.2 feet. (Bog stage is measured with respect to a fixed, but arbitrary datum.) Interpretation of the record requires, furthermore, that the effects of evapotranspiration be considered negligible during a precipitation event.

During the summer of 1976, and particularly during July, it was noted (Table 1) that apparent precipitation in the bog was considerably in excess of precipitation at Bedford. This phenomenon is believed due to runoff from hummocks in the red maple swamp portion of the wetland, and operates for bog stages less than -.2 feet. Evidence

TABLE 1

Monthly hydrologic summary for Thoreau's Bog

Month	Precipitation (ft)	Bog runoff (ft)	Evapotranspiration (ft)	Precip. at Bedford (ft)
April 16-30, 1976	.126	.021	.105	.149
May, 1976	.140	.040	.220	.252
June, 1976	.141	.016	.625	.038
July, 1976	.854	0	.924	.369
August, 1976	.619	0	.499	.540
September, 1976	.281	0	.411	.241
October, 1976	.629	.009	.320	.368
November, 1976	.092	.004	.228	.058
December 1-4, 1976	.001	0	.010	.014
December 5-31, 1976	1.176	.366	0	.271
January, 1977			0	.227
February, 1977			0	.222
March 1-15, 1977			0	.206
March 16-31, 1977	.294	.087	.077	.309
April, 1977	.451	.183	.208	.351
May, 1977	.342	.269	.223	.208
June, 1977	.269	.060	.369	.317

for this interpretation includes: 1) the statistical relationship between the observed ratio of precipitation in the bog to precipitation at the Bedford (and West Concord) rain gauges, and stage, shown in Figure 8; 2) the field observation that hummocks are fully submerged at high water levels, but are prominent above the water table at midsummer water levels; and 3) the existence of a modest but consistent non-diurnal decline in water level during the one-to-two-day interval immediately following major summer storms. This latter observation is believed due to slow water adsorption by newly-submerged hummock volume.

During the period of ice from December 4, 1976 to March 16, 1977, the recorder installation was frozen and precipitation inputs to the bog were inferred from measurements made at the Bedford Weather Station. This station is nearer to the bog than the West Concord Station, and was found to be the best available predictor of precipitation at the bog (r^2 = coefficient of determination = .98) during the interval from March 1977 to the end of June 1977 (Table 2). During this interval, the water levels in the bog were high enough to prevent significant interference from the "hummock runoff" factor.

3.3.3 Surface and Groundwater Runoff

Total runoff from the bog is summarized in Table 1.

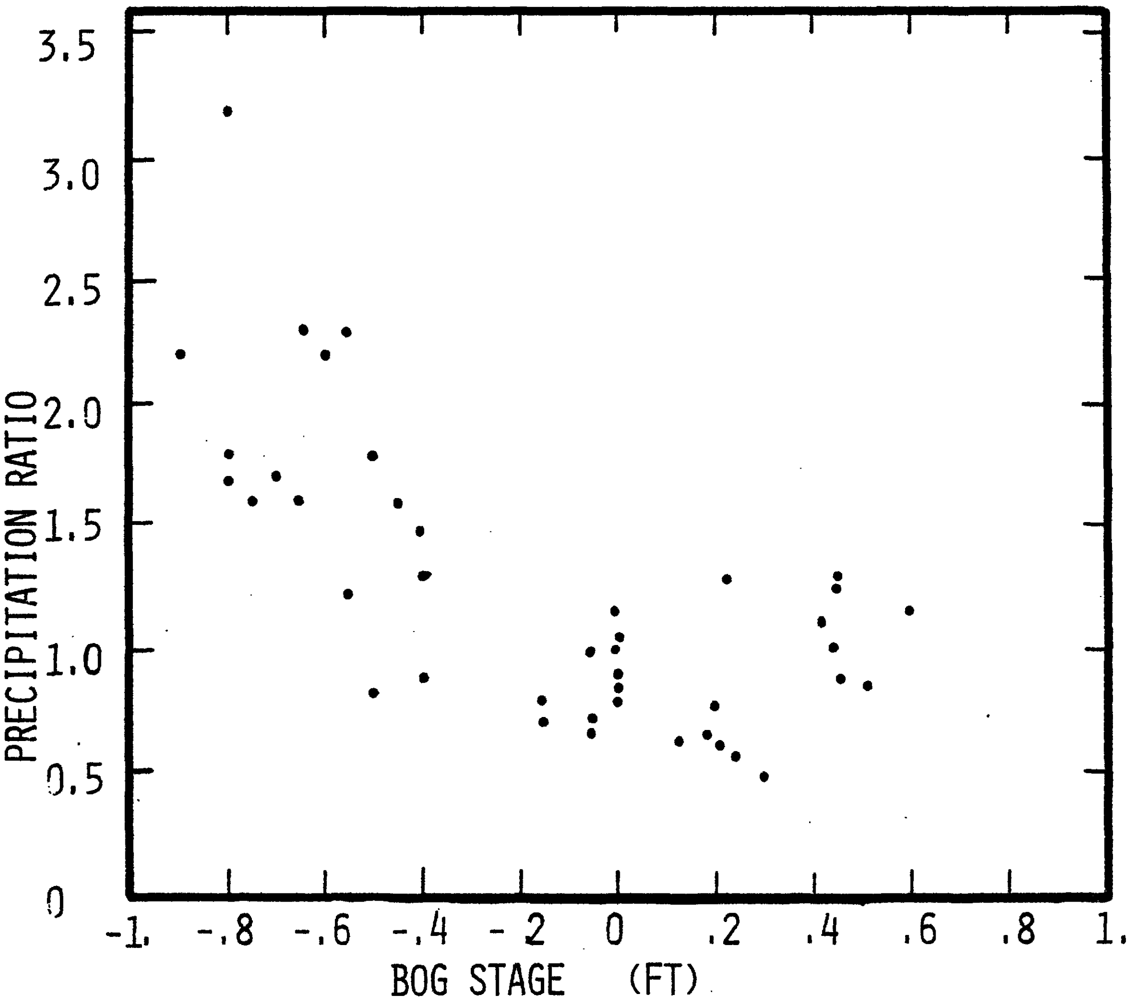


Fig. 8. Ratio of precipitation in Thoreau's Bog to precipitation at the Bedford weather station. Each point represents total precipitation for a single storm.

TABLE 2

Storm depths at bog and nearby weather stations

Storm Dates (1977)	Bog	Depth (ft) West Concord	Bedford
March 18-19	.032	.070	.063
March 22-23	.224	.153	.199
March 28-29	.033	.034	.033
April 2-3	.021	.019	.018
April 4-5	.118	.092	.088
April 8	.008	.008	.009
April 23-25	.301	.258	.236
May 5	.005	.007	.004
May 9-11	.314	>.108	.270
May 18	.023	.035	.027
June 1-2	.009	.010	.018
June 7-8	.024	.034	.042
June 10-11	.146	.068	.114
June 18	.029	.028	.048
June 20-21	.008	.010	.010
June 25-26	.041	.041	.063
June 29	.011	.014	.018

Coefficients of determination:

West Concord as predictor for bog	$r^2 = .92$
Bedford as predictor for bog	$r^2 = .98$
Mean of Bedford and West Concord as predictor for bog	$r^2 = .96$

Total bog runoff was computed, on a daily basis, from bog stage data taken from the bog hydrographs (Figure 9). Runoff rates were determined from stage data using the plot of observed runoff rates versus stage shown in Figure 5.

The plot of runoff versus stage was constructed to reflect the nature of the data, which exhibits a definite break at a bog stage of about +.3 feet (Figure 5). This is interpreted as evidence for two significant flow systems; one represented by the stone drain and surface runoff channel, and the other by a subsurface flow system. This interpretation is consistent with the field observation that surface runoff occurs only at high bog stages. Both the data and the physical structure of the drain suggest a threshold phenomenon for surface drainage. Accordingly, the stage-vs-runoff data was fitted by a pair of regression lines, forming a composite stage-vs-runoff function.

3.3.4 Evapotranspiration

Evapotranspiration is the major mechanism of water loss from the bog (Table 1). Its importance is immediately apparent from inspection of any of the water level records during the growing season (Figure 8). Evapotranspiration is calculated on a daily basis and is equal to decline in bog stage plus precipitation minus runoff. The assumption that evapotranspiration is neglegible during the iced-over period of the year may not be strictly true, but is made out

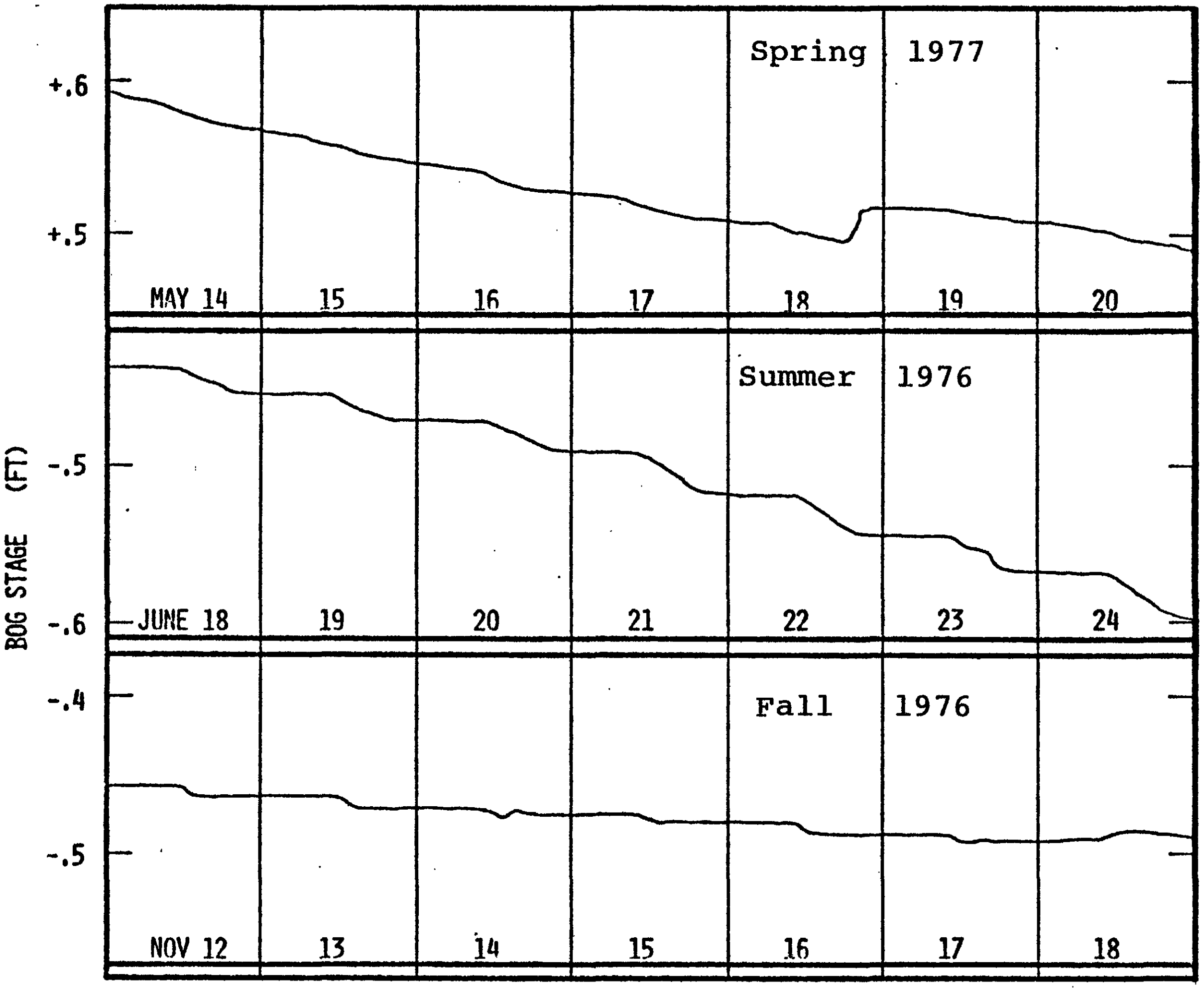


Fig. 9. Representative spring, summer, and fall hydrographs from Thoreau's Bog. Shape of hydrographs is a function of both evapotranspirational rate and bog stage.

of necessity. This approximation is supported by extrapolation of evapotranspiration rates in late fall as freezing approaches, and by the observation that surface runoff is a significant process in mid-to-late winter. This latter process is accompanied by the melting of the ice cover near the drainage channel as early as the month of January.

3.3.5 Annual water budget

The annual water budget is summarized in Table 3. For the months of April, May, and June, average values for 1976 and 1977 are presented. Since water levels in April, May, and June of 1977 are all higher than the corresponding levels in 1976, it is not possible to pick a 1-year interval over which water loss equals water gain in the bog. June of 1976 was extremely droughty, while the spring of 1977 followed a winter of exceptionally heavy snowfall. Thus, in this composite water year, precipitation amounted to 4.75 feet while runoff was .80 feet and evapotranspiration was 3.35 feet. This corresponds to a net storage of water in the bog. The mean annual water budget must, of course, be essentially balanced in a stable system. Since there is no obvious or compelling reason to assign this storage to either runoff or evapotranspiration, it is divided between them such that the ratio of runoff to evapotranspiration is not changed, giving an annual precipitation depth of 4.75

TABLE 3

Hydrologic summary for the period from March 16, 1976 through June 30, 1977

Month	Precipitation (ft)	Runoff (ft)	Evapotranspiration (ft)	Precip. at Bedford (ft)
March 16-31*	.294	.087	.077	.206
April*	.363	.146	.217	.308
May*	.241	.154	.181	.230
June*	.205	.038	.497	.177
July	.854	0	.924	.369
August	.619	0	.499	.540
September	.281	0	.411	.241
October	.629	.009	.320	.368
November	.092	.004	.228	.058
December thru March 15	1.177	.366	0	1.190
TOTAL	4.75	.80	3.35	3.69
ADJUSTED TOTAL	4.75 (1.45 m)	.91 (.28 m)	3.83 (1.17 m)	3.69 (1.12 m)

* Mean of 1976 and 1977 data

feet (1.45 m), annual runoff of .91 feet (.28 m), and annual evapotranspiration of 3.83 feet (1.17 m).

3.4 Discussion of results

The demonstration that this bog is ombrogenous has major implications for the nutrition of plant communities in the bog, as well as for the biogeochemical role of this and similar bogs. With the atmosphere as the sole transporter of nutrients to the floating mat, it is to be expected that a highly oligotrophic situation will exist, and that the biological community will reflect that situation. Assuming that the plant communities defining a bog are in fact the product of a rain-nourished environment, and will not persist under appreciable groundwater influence, then the geographical range of bogs such as the study area may well be limited by the necessity of adequate precipitation and meteorologic conditions which do not promote excessive evapotranspirational losses. In particular, the runoff term of the annual hydrologic budget is very sensitive to changes in either precipitation input or evapotranspirational water loss, since it is a small difference between these relatively large quantities. The bog appears to lack mechanisms to control evapotranspirational losses, particularly inasmuch as the Sphagnum mat is floating, and thus tends to maintain a moist surface even during low bog stage. Yet, an annual excess of precipitation over evapotranspiration, resulting in runoff, may be of considerable biogeochemical and ecological importance, since runoff is the only significant export mechanism for many chemical species. It may be suspected, then, that basin characteristics and meteorological conditions are of critical importance in the establishment of floating-mat Sphagnum bogs, and that relatively modest but long-term variations in climate may substantially alter such wetlands.

Given the chemistry of rainfall, it becomes possible to examine the chemical budgets for the entire bog system (Chapters 4 and 5). Relating such a budget to the nutritional requirements of bog and non-bog plants should give insight into the developmental processes of bogs and their characteristic flora and chemical conditions.

The numerical results presented here must, of course, be interpreted recognizing that they are based on 15 months of data, while the study area is the product of hundreds, if not thousands of years of development. Long-term data, over intervals of tens of years, is necessary to provide a more precise hydrologic budget. At increased levels of precision, errors which are neglected in this analysis will become important. In particular, direct calculation of evapotranspiration from micrometeorological data will be necessary, both during the ice season and to compensate for differential evapotranspiration rates which may exit between the bog and the hydrologically coupled swamp area during the growing season.

4 Mass Balance of Metals

4.1 Introduction

The demonstration that Thoreau's Bog is hydrologically isolated from the local groundwater regime and therefore receives its input of minerals solely from the atmosphere associates this wetland closely with the ombrogenous "raised bogs" or "blanket bogs" of the European continent and more northerly North American regions. Floristically it more resembles a raised bog than it does a fen, and the observed low pH of the wetland also associates it with the poorer, more acidic, generally ombrogenous raised bog situations.

The biogeochemistry of the bog is thus critically dependent on the chemistry of bulk precipitation and on the influence of bog vegetation and its remains. Comparisons of rainwater chemistry with elemental analyses of bogwater show that, in general, a simple hydrologic model of evaporative concentration is not adequate to explain the mass balances of raised bogs, and that biological influences are of major importance for many elements. (See data of Yefimov and Yefimova, 1973; Gorham, 1967.) As a minimum, it is also necessary to consider the effects of Sphagnum and peat, and the role of organic acids in the water of the bog.

The chemistry of bulk precipitation in New England has been investigated most notably at the Hubbard Brook Experimental Watershed in central New Hampshire, and elevenyear average concentrations of all major cations and anions have been published (Likens et al., 1977). The data on major ions in bulk precipitation published by Pearson and Fisher (1971) is more extensive in area, but covers no more than a single year at any New England station. Lazrus et al. (1970) have investigated the trace metal content of bulk precipitation throughout the U.S., but their New England data consists of only 6 months of data at one station.

The chemistry of precipitation is variable in both time and space; this is evident not only in the above work, but also in the extensive records compiled by the pan-Scandinavian air and precipitation network (Egner and Eriksson, 1955; Barrett and Brodin, 1955; Brodin, 1955). Inasmuch as the nearest sampling station of Pearson and Fisher (1971) is sixty-five kilometers south of the bog, and Hubbard Brook is two hundred kilometers to the north, some local bulk precipitation analysis is clearly desirable, and is undertaken as part of this investigation.

The ability of the sphagna to exchange cations has been known since the early 1900's (Devaux, 1916), and a possible role of cation exchange in the bog environment was proposed by Baas-Becking and Nikolai (1934), primarily in the context of a mechanism for producing acidity. The cation exchange capacity of live Sphagnum has since been determined to be from .7 to 1.7 meq/gram (Anschutz and Gebner, 1954;

Puustjarvi, 1959; Craigie and Maass, 1966) and relative affinities for various cations have been determined (Bell, 1959; Anschutz and Gebner, 1954; Andre, 1976). Not surprisingly, sodium and potassium have the lowest affinities, while divalent cations (Ca^{++}, Mg^{++}) are more strongly bound and the trivalent cation, La^{+++}, is still more strongly bound by Sphagnum. Theander (1954) found Sphagnum to contain complex polysaccharides which included uronic acids, and Clymo (1963) found excellent correlation between the polyuronic acid content of different species of Sphagnum and their cation exchange capacity. Schwarzmaier and Brehm (1974) identified polygalacturonic acid in the cellulose matrix of the cell wall as the ion exchanger in Sphagnum magellanicum. Andre (1976), however, interprets the pH titation of unidentified Sphagnum species as showing the presence of phenolic groups (not present in uronic acids), and indicates that a portion of the exchange capacity is soluble in alkaline solution. No mathematical model yet appears to adequately describe the aqueous chemistry of Sphagnum in general. Furthermore, most treatments ignore the metabolic activity of the moss which was emphasized by Ramaut (1955) in his studies on bog acidification. Anschutz and Gebner (1954) noted an expectedly high ability of S. acutifolium and S. cuspidation to take up potassium ion while Puustjarvi (1959) observed high concentrations (5 to 20X) of potassium in living moss relative to concentrations in the adjacent peat.

The role of peat in the bog is closely related to that of the living *Sphagnum*, and new peat is continuously formed by the death and humification of the lower end of moss stems. The cation exchange capacity of peat is comparable to that of live *Sphagnum*, although compaction and loss of mass accompanies humification, and the exchange capacity must become increasingly due to humic substances. Peat is generally a slightly weaker binder of cations than is the corresponding moss (Puustjarvi, 1958), although Rathsack and Jungk (1964) observed selectivities in peat ($Na^+ < NH_4^+$, $K^+ < Mg^{++} < Ca^{++}$) similar to those observed in *Sphagnum* mosses. Gore and Allen (1956) found that most or all of the metal bound to peat samples was exchangeable by a $BaCl_2$-triethanolamine extraction procedure. Thus, the roles of the living *Sphagnum* appear to be similar to those of peat, but with enough differences to require the investigation of both components in the bog system.

Organic complexing agents in the bog may act to shift the equilibrium between dissolved and exchanger-bound metal in favor of the dissolved state. The acids of bogs are not well characterized, although humic and "humolimnic" (after Shapiro, 1957) acids in general appear to be important in natural water chemistry. Shapiro (1957) demonstrated yellow organic acids in Connecticut lake water to be capable of complexing Fe^{+++} at pH as high as 9.5.

Barsdate and Matson (unpublished) found that colored organic materials in Smith Lake in Alaska were important in trace metal speciation, and Wilson and Kinney (1977), working with organic material from the same lake and from seawater, found the material to have considerable complexing ability for Pb, Cu, and Zn. Koenings (1976) found organic acids in a Michigan bog lake, at pH 4-5, to complex both Fe^{+++} and Fe^{++}. The yellow organic material present in bogwater, then, may be suspected as playing a significant role in metal speciation within the bog.

The quantity which is of most direct relevance to the biogeochemistry of a bog system is the extent to which inputs of ions are retained by the bog system. In a hydrologically defined system, this becomes a question of partition between the immobile phases of the bog (i.e., peat, Sphagnum, and higher plants) and the mobile phase (water and colloids) which may seep or flow out of the bog. The relevant chemical parameter in the case of a metal may be defined as:

$$K''_M = \frac{[M^{+Z}]_T}{[M^{+Z}]}$$

where:

K''_M = partition coefficient for metal M

$[M^{+Z}]_T$ = total concentration of metal ion M^{+Z} in solution

$[\overline{M^{+Z}}]$ = concentration of metal ion M^{+Z} in peat (dry weight basis)

The exchange properties of peat and Sphagnum are, in general, complex functions of pH, ionic strength, and other competing cations, and are only poorly known empirically. However, three assumptions may be made which greatly simplify the representation of ion-exchange equilibria. These are:

1) constant ionic strength of electrolyte
2) constant pH
3) exchanger essentially in H^+ form, major metals present in trace quantities.

Under these conditions, metal concentration in the exchanger phase may be related to metal activity in the aqueous phase by a single coefficient, namely:

$$\overline{K'}_M = \frac{\{M^{+Z}\}}{[\overline{M^{+Z}}]} \qquad (2)$$

Under the same set of assumptions, and given that the total concentration of an organic ligand is constant (and greatly in excess of total metal concentration), then the complexation of M^{+Z} by a generalized organic ligand, -R, may be described similarly:

$$K'_M = \frac{\{M^{+Z}\}}{[M - R]} \qquad (3)$$

The partition of metal between fixed and mobile phases then becomes:

$$K''_M = \frac{[M^{+Z}]_T}{\overline{[M^{+Z}]}} = \frac{[M - R] + [M^{+Z}]}{\overline{[M^{+Z}]}}$$

$$= \frac{\{M^{+Z}\}\ (1/K'_M + 1/\gamma_M)}{\{M^{+Z}\}\ (1/\overline{K'}_M)} = \frac{\overline{K'}_M(K'_M + \gamma_M)}{\gamma_M\ K'_M} \qquad (4)$$

where γ_M = activity coefficient for M^{+Z}

The partition coefficient is thus independent of metal concentrations under the conditions postulated.

The rate of peat accumulation is clearly of utmost importance in the mass balance of a bog; if concentrations of metals in the peat remain constant from year to year, the storage of metal is directly proportional to growth rate. Active growth of the bog is believed to be occurring, inasmuch as the Sphagnum mat is floating and is therefore not, at this time, subject to the drying out that may occur on a raised bog. Current rates of peat accumulation for bogs in New England are not known; ^{14}C dating yields usable ages only for samples older than, perhaps, 500 years; this interval is certainly long enough to cast doubt on the then-necessary assumption that the accumulation rate has been constant for 500 years. Indeed, many floating-mat bogs may not be that old. Swan and Gill (1970) have estimated the advancement rate of the Harvard Pond bog at 6.3 cm/year, at which rate a Sphagnum mat, halfway to the center of Thoreau's Bog, could be as young as 250 years old. Thoreau (1860), mapped the center of the bog as an ellipse 20 x 25 paces wide, although in 1854, he estimated the open pool in the center to be 20 to 30 feet in diameter. The central area of open water is now essentially bisected by an advancing tongue of Sphagnum mat, whose rate of advancement, based on these measurements, must have been between 2½ and 10 cm/year.

Estimates of growth rates in European bogs have been made, and are summarized by Clymo (1964). Apart from the questions of applicability, these data show a wide range of growth rates, from 1 to 12 metric tons/hectare-year.

Two dating techniques, however, do have applicability on a time scale of decades, and appear useful in determining the ages of recent peat deposits. The deposition rate of atmospheric lead is associated with industrialization and, in particular, has been found to be correlated with regional consumption of leaded gasoline (Lazrus et al , 1970). If Sphagnum and peat have sufficiently high affinities for this lead, then the beginning of leaded gasoline use could be expected to be recorded as an increase in lead concentration at some point in the peat profile. Such a point of increase would correspond to a date after the introduction of leaded gasoline in 1927.

A second dating technique is based on the fallout of radioactive ^{210}Pb in precipitation. This flux originates as a decay product of naturally occurring radon and is believed to be independent of industrialization and nuclear testing, (Koide et al , 1976). The half-life of ^{210}Pb (22.26 years) (McCaffrey and Thomson, 1973), is convenient for dating on the time scale of decades. No assumption of constant net deposition rate is required, as long as total ^{210}Pb activity can be integrated from the surface of the sediment down to the depth whose age is to be determined (see Crozaz et al , 1964). This technique has been applied to marine sediments (Farrington et al , 1977) and to a Connecticut salt marsh (McCaffrey and Thomson, 1973), and involves fewer of the uncertainties that are involved in interpreting a total lead profile. Because of the importance of accurate dating, however, both techniques have been adopted for use in this investigation. Since both methods depend on a mimimal degree of mixing of lead in the bog system, particular attention was paid to the partitioning of lead between the fixed and mobile phases.

Knowledge of the hydrological regime, the partition of metals between the mobile and immobile phases of the bog, the chemistry of precipitation, and the accumulation rate of exchange capacity in the bog should be sufficient to construct for any "conservative" element a complete mass balance of the bog ecosystem, of the form:

input = storage + output

or

$$C_i^{\circ} Q^{\circ} = \Delta(N\, C_{P_i}) + C_i\, Q_r$$

where

C_i° = concentration of element i (mg/l) in bulk precipitation

Q° = annual precipitation (l /m^2-yr = depth in meters x 10^3)

N = total mass of peat in bog, per unit area (Kg/m^2)

C_{P_i} = mean concentration of element i in peat (PPM = mg/Kg)

C_i = concentration of element i in bog water (mg/l)

Q_r = annual runoff (l/m^2 - yr)

The above expression may be simplified if the distribution of element i is known. For example, if the concentration of element i is known to be constant throughout the peat, then:

$$\Delta\ (N\, C_{P_i}) = \dot{N}\, C_{P_i}$$

where $\dot{N}$ = net rate of peat accumulation (Kg/m^2-yr). This equation holds in a nonhomogeneous system as well, if C_{P_i} is understood to represent the concentration of element i in the <u>effective</u> annual increment of peat accumulation. The effective annual increment of peat is not, in general, the current year's growth of bog vegetation, inasmuch as a continuous process of humification and possible redistribution of metals is also occurring.

Finally, it should be noted that although this treatment is primarily addressed to metals, it is applicable to anions although the low ion-exchange capacity by Sphagnum (Clymo, 1963) means the storage term may be negligible for anions of low relative biological activity (e.g., chloride). Significant departures from a balanced budget may be taken as evidence that a given element is nonconservative with respect to the hydrological system and may enter or leave the bog by way of another mechanism, such as in gaseous form.

4.2 Materials and Methods

4.2.1 Equipment and instrumentation

pH titrations were performed using an Orion model 801 digital pH meter, and an Orion glass electrode and single-junction reference electrode. Titrant additions were made with a 5.0 ml manual burette, and progress of each titration was recorded on an 11 inch Honeywell recorder. A CO_2 - free atmosphere was provided by N_2 passed through an Ascarite-filled drying tube, bubbled through carbonate-free distilled water, and maintained over the solution at a pressure of .5 cm H_2O by a trap in the vent line. A double-walled beaker and circulator maintained solutions at 25.0°C, and a magnetic stirrer was employed for mixing.

Peat corings were obtained with a Russian-type peat corer (West, 1968) built entirely of stainless steel and aluminum. The device is designed to cut a hemicylindrical core of peat 4.3 cm in diameter, 50 cm long, and bisected by a longitudinal fin. A few earlier samples were obtained with a 1¼ inch PVC pipe and a close-fitting steel auger.

Apparatus for peat digestions consisted of 500 ml round-bottom Pyrex flasks, each fitted with a 470 mm Vigreaux distilling column and heated by a 270 watt electric mantle.

Sampling wells for the collection of bogwater were constructed of 1/2 inch PVC water pipe, plugged at the bottom and perforated by shallow transverse saw cuts along the lower 25 cm of length. One micron 47 mm Nucleopore filter disks were used to filter the bogwater samples.

Precipitation collectors were made from 250 ml polypropylene beakers mounted atop wooden 2" x 2" stakes.

A Perkin-Elmer model 360 atomic adsorption spectrophotometer, equipped with a 4-inch single slot burner, or a Perkin-Elmer model 403 was used for magnesium and potassium analyses.

4.2.2 Reagents

A 1000 ppm magnesium standard was prepared by dissolving 1000 g of magnesium metal in 25 ml of 6N distilled

HCl and making up to a volume of 1 liter with distilled, deionized water. A 1000 ppm potassium standard was prepared by dissolving 1.598 grams of oven-dried $Pb(NO_3)_2$ in 1% distilled HNO_3 and making up to a total volume of 1 liter with 1% distilled HNO_3. Standard base was made up in CO_2 - free water and titrated against oven-dried potassium acid phthalate. Sulfuric acid used for peat digestion was of "suitable for Mercury determination" grade, manufactured by Baker Chemical Co. Distilled HCl and HNO_3 were prepared from reagent-grade acid in a 1-liter Vycor glass still. All other chemicals and acids used were of analytical reagent grade.

4.2.3 Exchange capacity of _Sphagnum_

Samples of _Sphagnum_ were added to a 100 ml Pyrex or Teflon beaker, and 50 ml of distilled, deionized water were added. The contents of the beaker were made 10^{-2} molar in NaCl by the addition of .5 ml of 1 N NaCl, and the solution was acidified with 6N HCl to pH 2.5. Additions of standardized NaOH were then made, the titration continuing until pH 11. Exchange capacity of a sample of _Sphagnum_, was taken as the number of equivalents of base required to produce the pH change from pH 2.5 to pH 11, minus the number of equivalents of base required to produce the same change in a distilled water sample. Theoretical blank values were used in titrations with a manual burette; these theoretical values were later compared favorably with the results of pH titrations by automatic equipment (see Chapter 5).

4.2.4 Coring and analysis of peat

Peat and Sphagnum samples were collected at the depths and locations indicated in Appendix C. The corer was rinsed with bogwater between samples. The two halves of each sample were immediately removed from the corer and transferred to separate 4½" by 12" Whirlpak sampling bags. Upon return to the laboratory, one half was frozen and stored as a backup, while the other half was transferred to an acid-washed 600 ml Pyrex beaker and dried at 80°C for at least 24 hours. After cooling, each beaker was weighed with its contents, and the sample was transferred to an acid washed digestion flask. The beakers were then re-weighed and the mass of dry sample determined by difference.

Two-hundred (200) ml of concentrated nitric acid and 50 ml of concentrated sulfuric acid were added to the sample in each digestion flask, and heat was applied. After refluxing for approximately two hours, the digestate was cooled, quantitatively transferred to a 250 ml acid-washed volumetric flask, and made up to 250 ml with distilled water. Samples were then transferred to acid-washed polyethylene bottles for storage. Combined standards of appropriate concentrations for the preparation of calibration curves were made by pipetting 1000 ppm standards, or dilutions of them, into digestion flasks and carrying the material through the same digestion procedure used for peat and Sphagnum.

Analysis of the digested samples was performed using an air-acetylene flame. Analytical lines used were 285.2 nm, 766.5 nm, and 283.3 nm for Mg, K, and Pb respectively. Potassium was measured by flame emission, while magnesium and lead were measured by absorbance. Blanks were subtracted from all absorbances or emission measurements to ensure a calibration curve which passed through the origin, and a best-fit calibration curve of the form concentration = a (emission or absorbance)^b was fitted to the standards data by the power curve fit routine supplied with a Hewlett-Packard HP-25 calculator. In a few instances, this procedure was scaled down to accommodate smaller peat samples, and digestions were carried out on a micro-Kjeldahl apparatus. In all cases, standards were also carried through the scaled-down digestion procedure.

One set of three peat samples was combined and mixed, then divided three ways and analyzed. Differences between the results were taken as measure of error in the digestion and metal analysis procedure. Maximum deviations from the mean were 3%, 4%, and 9% for potassium, magnesium, and lead, respectively.

4.2.5 Collection and analysis of bogwater

Bogwater was collected at the locations and depths indicated in Table 4. Each sampling well was washed, rinsed in distilled, deionized water, soaked at least 8 hours in 2N HCl along the perforated region, and given a final rinse in distilled, deionized water prior to installation in the bog. Prior to collection of samples, each well was pumped out and allowed to refill. Water samples of approximately 250 ml were drawn into acid-washed polypropylene bottles by means of a hand-operated vacuum pump. Each sample was subsequently filtered through a 1 μ Nucleopore filter and returned to its original bottle. 1 ml of distilled 6N HCl was added per 100 ml of sample, and the samples then refrigerated at -2 °C until analysis.

Combined AA standards for water analysis were prepared by serial dilution of 1000 ppm stock solutions with distilled, deionized, glass-distilled water using acid-washed glassware. 1 ml of distilled 6N HCl was added per 100 ml of standard solution. Analysis of samples for Mg and K was performed as described for the analysis of peat digestate. Analysis for lead was carried out at 283.3 nm with the graphite furnace, using a 50 μl sample injection, a drying at 125 °C for 40 seconds, and an atomization at 2000 °C for 15 seconds. Inner furnace purge gas flow was interrupted during atomization, and readings were integrated over 3 seconds.

Inasmuch as analyses for potassium and magnesium in bogwater were carried out in the same manner as were the analyses for potassium and magnesium in peat digestate, the values of error of measurement obtained for peat analysis (3 to 4%) are believed to be reasonable estimates of the error of measurement of these elements in water.

Lead analyses of bogwater, however, were often made out near the reliable limits of detection of the instrument, and roundoff error of the digital readout alone was typically of the order of 10%. In 3 series of 4 determination on the same sample, the standard deviation was 30% of the mean in the worst case, and zero in the best case. A possible error of ±30% is therefore considered reasonable for lead analysis of bogwater samples of low lead concentration.

4.2.6 Precipitation analysis

Precipitation was collected from the precipitation collectors at intervals averaging from 7 to 21 days during the period of December 4, 1976 to March 26, 1977. Collections were timed such that collectors contained adequate water for analysis but did not overflow. No correction was made for evaporation; however, since most of the water was collected as snow and ice, evaporative errors were not believed to be severe. Water samples which could not be analyzed soon upon return to the laboratory were transferred to 125 ml acid-washed polyethylene bottles and acidified with 1% 6N distilled HCl. Analysis of rainwater was carried out using the same procedures described for metal analysis of bogwater. The errors of analysis are believed comparable, except in the case of lead, where the substantially higher concentrations present in rainwater improved the precision of analysis appreciably. In a representative series of determinations of six samples, with replicate measurements of each sample, no two replicates differed by more than 10%.

4.2.7 Lead - 210 analysis

Sequential cores, 4.0 cm in diameter by 12 cm long, were taken from the bog about 4 meters south of, and equidistant from, stations 3 and 4, using a section of sharpened steel tubing and a close-fitting piston to assist in retaining the core. Cores were oven-dried at 105°C to constant weight, homogenized in a Waring blender, and subsampled to obtain an estimated total ^{210}Pb activity per sample of about 5 d.p.m. (.3 to 3 grams, depending on depth - estimates were based on an annual deposition rate of 1 dpm/cm^2-year and dates determined from the total lead profile). The samples were spiked with 20 d.p.m. of ^{208}Po and digested with concentrated nitric acid, finishing with hydrofluoric acid and finally perchloric acid. Fuming with $HClO_4$ was continued until samples were colorless, or nearly so (approximately 8 hours total digestion time). Reagent blanks were run to ascertain the absence of contamination.

The digestate was quantitatively transferred with 50 ml of 2N HCl, and the polonium plated onto silver discs by the procedure of Flynn (1968); however, plating time was increased to 4 hours. Counting of the ^{208}Po and ^{210}Po activity was carried out as described by Bacon (1975).

4.3 Results

4.3.1 Analysis of peat, *Sphagnum*, and water

4.3.1.1 Exchange capacity of *Sphagnum*

Figure 10 shows the extent to which live *Sphagnum* exchanges H^+ for Na^+ as a function of pH. The curve is a composite of two titrations (to minimize dilution effects) performed in an initial background of $10^{-2}M$ sodium chloride. Minimum ion exchange capacity, based on the extent of exchange occurring as pH is raised from pH 2.5 to pH 9, is 1.1 meq/gram. Above pH 9, a break occurs in the curve, suggesting that another mechanism or set of exchange sites may operate at these high values of pH. A reversible color change, from the characteristic reddish color of leaves near the growing tips of the moss to a black color, occurs at high pH values. As noted by Clymo (1964), the kinetics of ion exchange by *Sphagnum* are quite slow, particularly

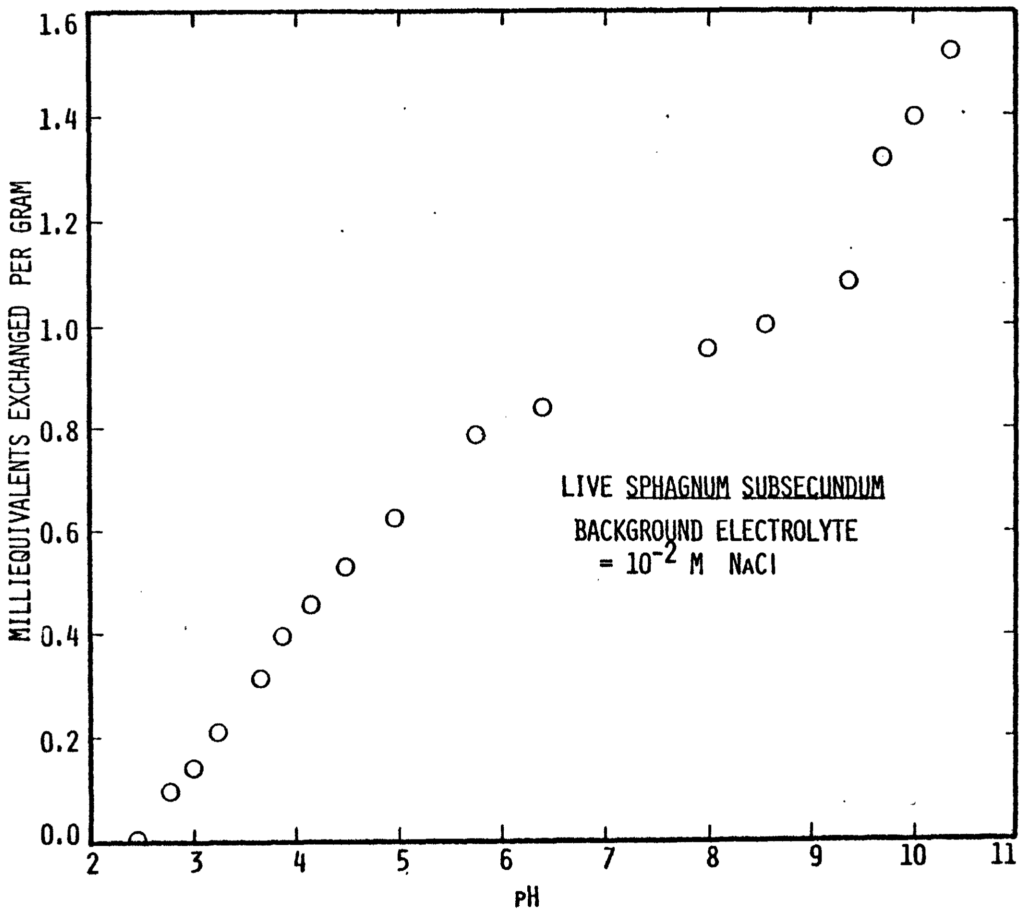


Fig. 10. Exchange of H^+ for Na^+ by live _Sphagnum_ as a function of pH. Background electrolyte is 10^{-2} M NaCl.

above pH 5.

Assuming a value of 1.1 meq/gram ion exchange capacity of live Sphagnum, it is found that, using typical concentrations found in Sphagnum, the mole fraction of magnesium (the most abundant metal in peat) in exchange sites is about 3%.

The results of pH titrations of bogwater are summarized in Chapter 5, and show bogwater to have an exchange capacity of about 1 meq/l.

4.3.1.2 Partition coefficients

Preliminary experiments conducted in vitro with live Sphagnum, steam-killed Sphagnum, and Sphagnum peat revealed that steam-killed Sphagnum exhibits a lesser affinity for most metals, and an order of magnitude lower affinity for potassium, than does live Sphagnum. The experiments suggested, furthermore, that the affinity of Sphagnum peat for metals may be lower still. However, the mechanical difficulties involved in eluting metals from this crumbly, partially-decomposed material resulted in the abandonment of further in vitro work in favor of the determination of overall partition coefficients by analysis of corresponding peat or Sphagnum and water fractions taken from the bog.

Partition coefficients for magnesium are shown in Figure 11. Although considerable scatter is evident, a clear ($r=.56$, $P<.01$) correlation between K''_{Mg} and depth

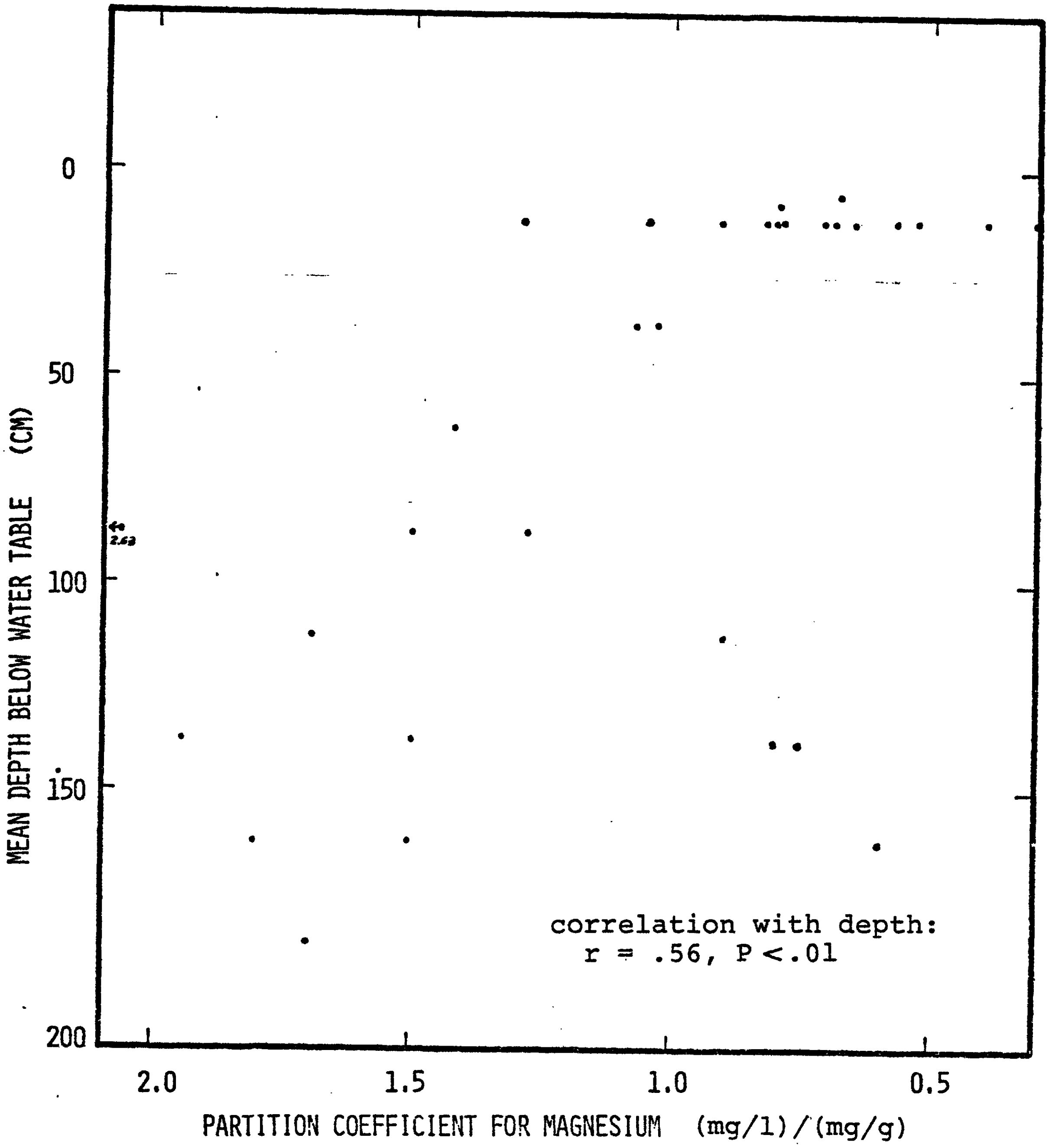


Fig. 11. The partition coefficient for magnesium (K''_{Mg}) as a function of depth in the bog. Each point represents one determination (see also Appendix B)

exists. Partition coefficient data for potassium (Figure 12) exhibit a marginally significant ($r=.38$, $P<.05$) correlation. Lead (Figure 13) likewise, exhibits a marginally significant ($r=.39$, $P<.05$) correlation with depth.

Of considerable significance are the absolute values of the partition coefficient which range from the neighborhood of 1 to 5 for potassium, to values about three times lower for magnesium, and finally to values of around .01 to .07 for lead. The affinity of peat for lead is thus at least an order of magnitude higher than it is for magnesium and perhaps 1½ orders of magnitude greater than it is for potassium.

4.3.1.3 Distribution of metals in peat and Sphagnum

Figures 14, 15, and 16 show the horizontal distribution of magnesium, potassium, and lead, respectively, in peat at a depth of 0-25 cm along the transect line from the edge of the bog to its center. No significant trends appear in this data and the correlations of each metal concentration with distance from the bog center are very small and statistically insignificant. (see Appendix D) Standard deviations of metal concentrations are 35%, 17%, and 75% of the mean for K, Mg, and Pb, respectively. The latter value is reduced to 37% by the omission of a single datum which exceeds the mean of the others by over 300%.

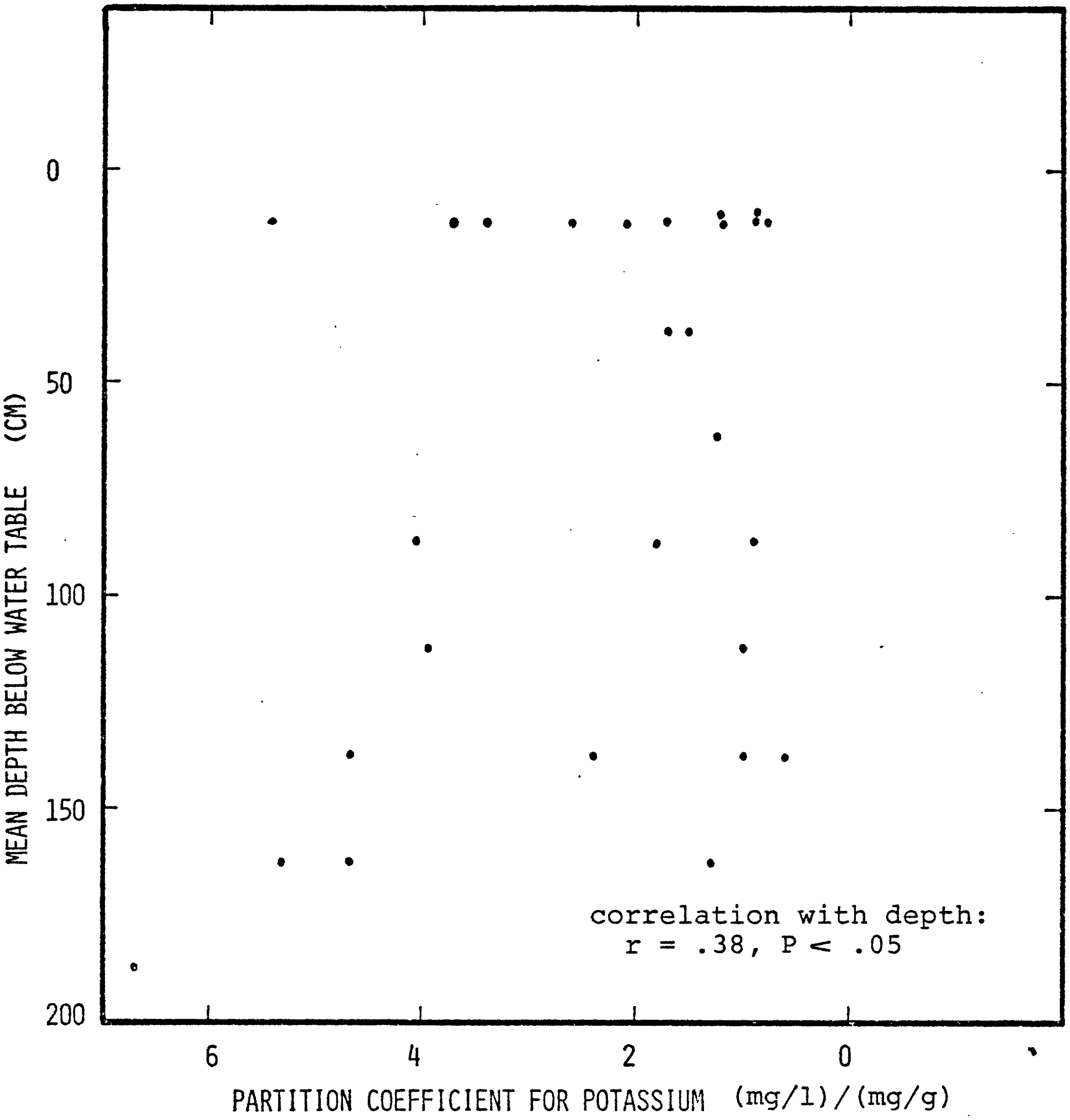
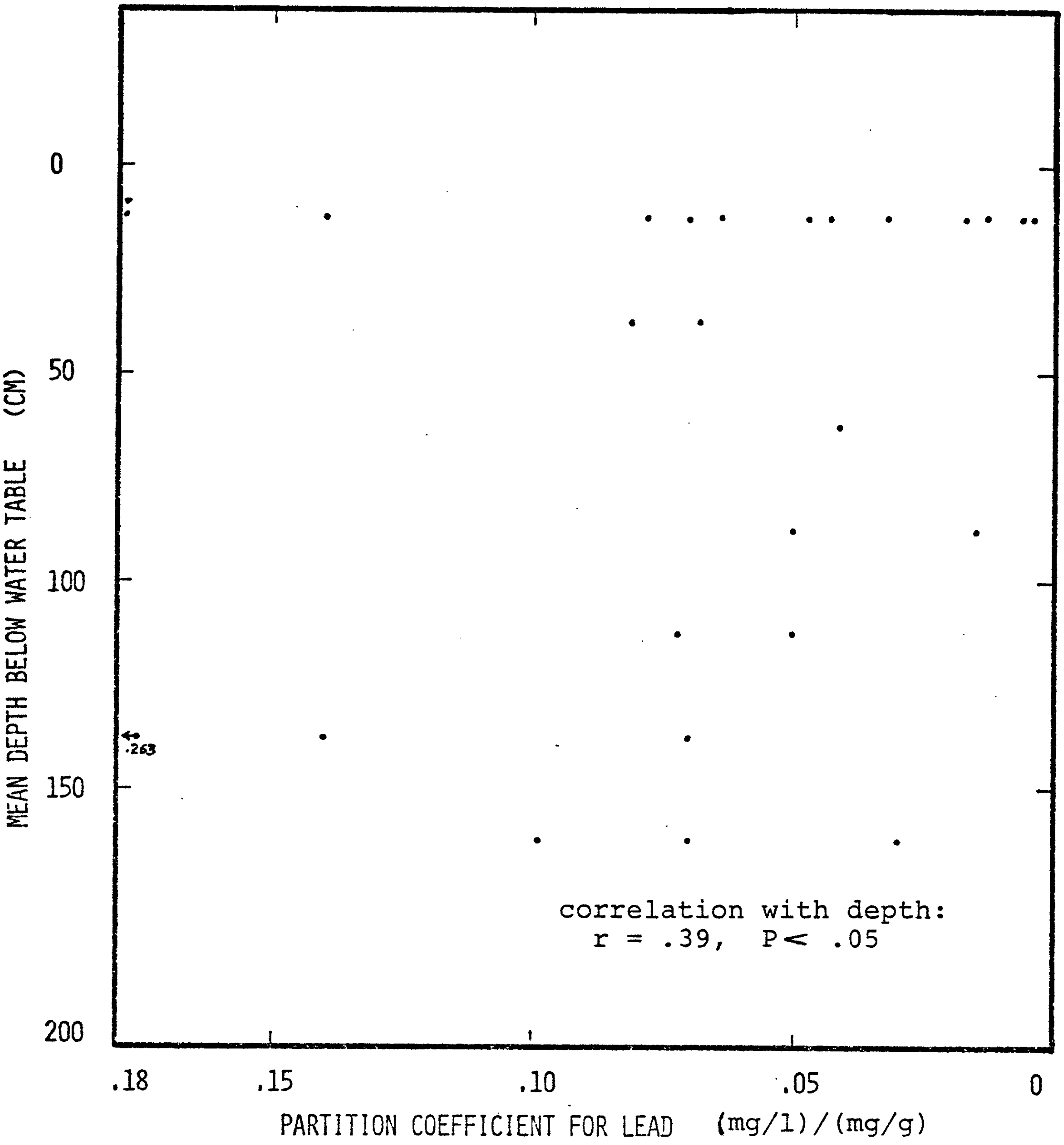


Fig 12. Partition coefficient for potassium (K''_K) as a function of depth in the bog. Each point represents one determination (see also Appendix B)



correlation with depth:
$r = .39$, $P < .05$

Fig. 13. The partition coefficient for lead (K''_{Pb}) as a function of depth in the bog. Each point represents one determination. (see also appendix B)

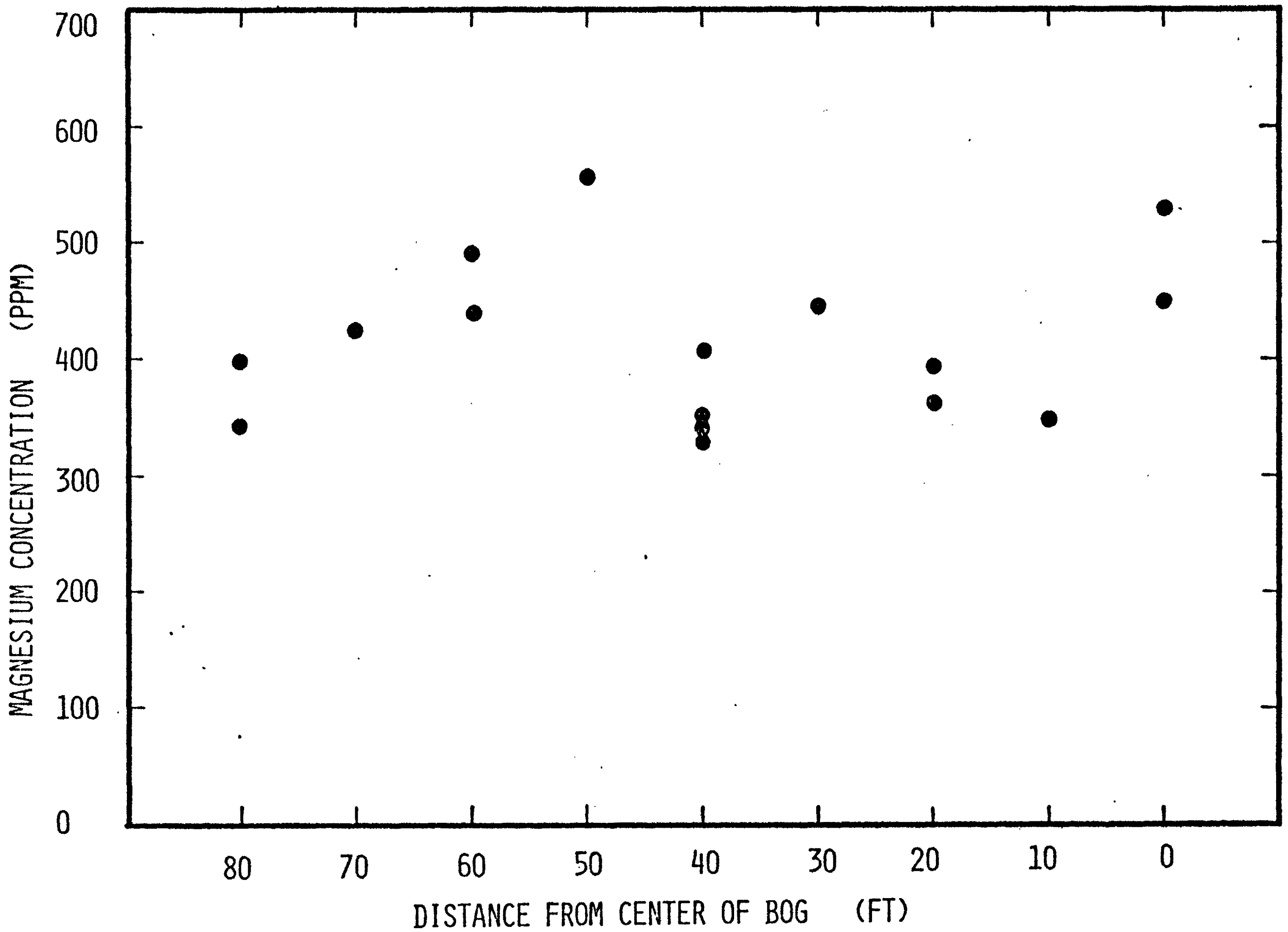


FIG. 14. MAGNESIUM CONCENTRATION IN 0-25 CM PEAT CORES AS A FUNCTION OF LOCATION IN BOG

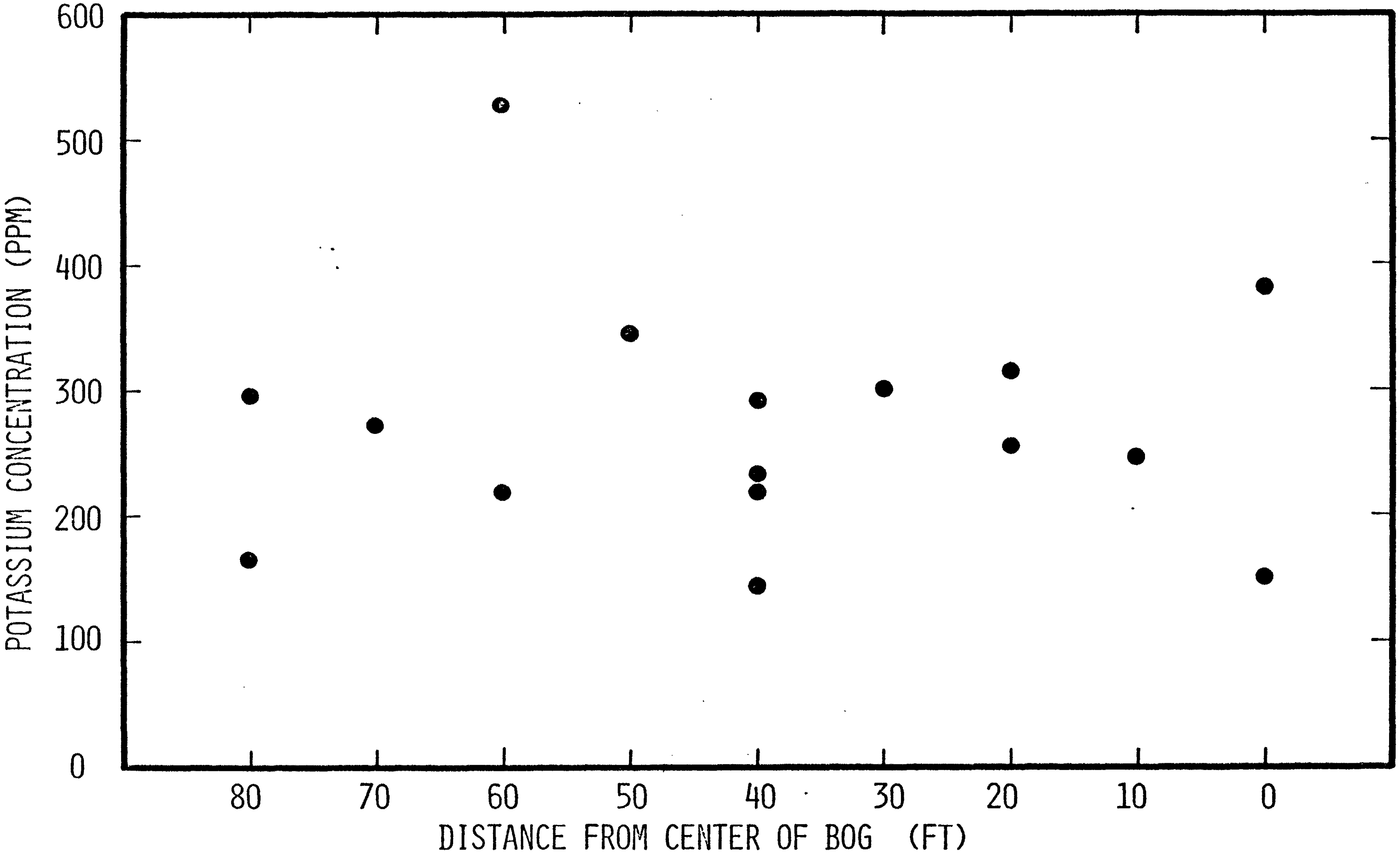


FIG. 15. POTASSIUM CONCENTRATION IN 0-25 CM PEAT CORES AS A FUNCTION OF LOCATION IN BOG

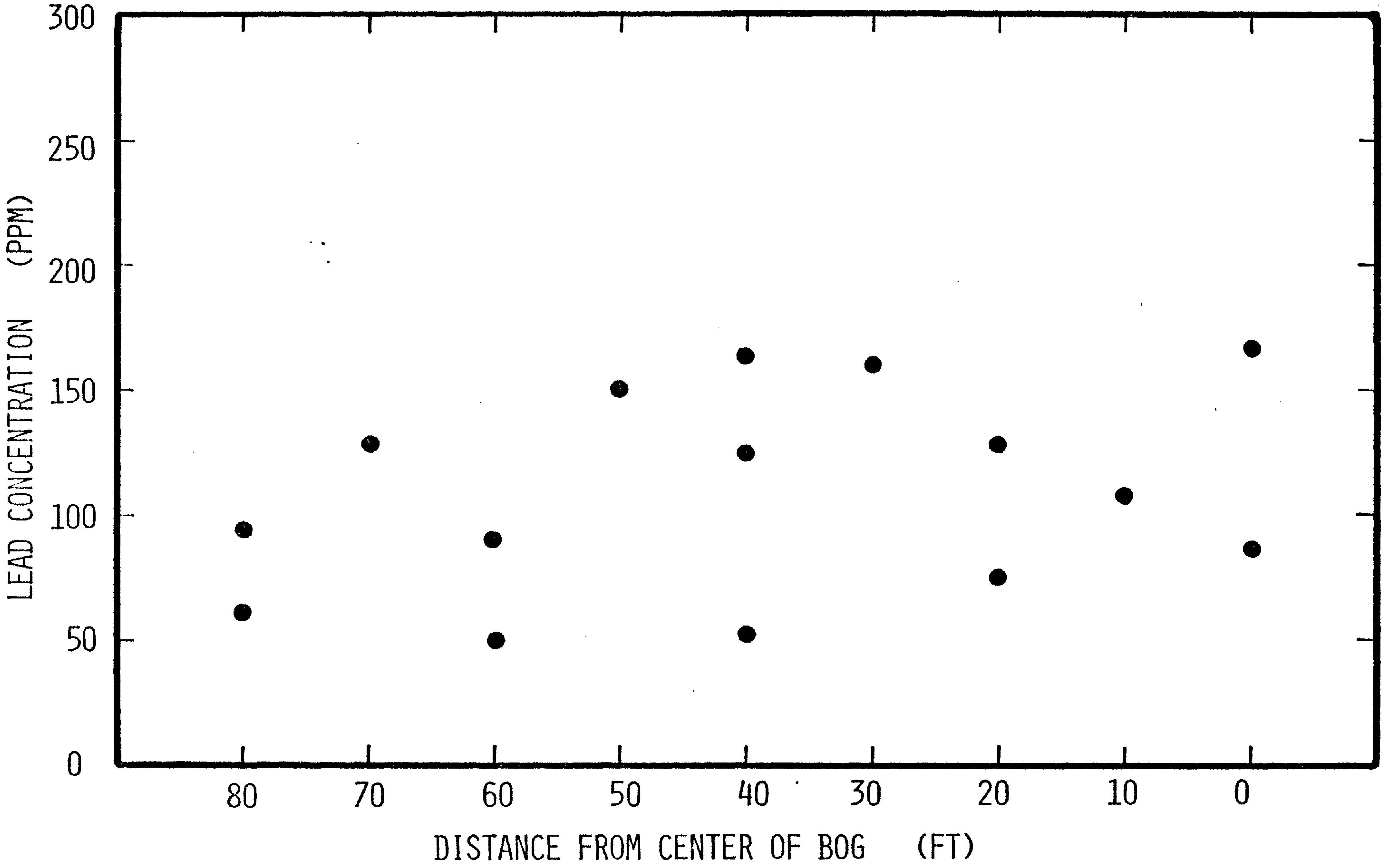


FIG. 16. LEAD CONCENTRATION IN 0-25 CM PEAT CORES AS A FUNCTION OF LOCATION IN BOG

The distribution of magnesium in the vertical dimension (Figure 17) shows a decrease in magnesium concentration with depth, with a range from over 600 ppm at the surface to values less than 200 ppm at 80 cm and below. The negative correlation between magnesium concentration and depth is highly significant ($P<.001$), and the length of this region suggests that active uptake is not a major factor in magnesium distribution, inasmuch as living Sphagnum has not been observed to extend more than about 10 cm below the bog surface. Alteration of the exchange properties of peat as compaction and decomposition proceeds appears to be responsible for this trend, inasmuch as the affinity of peat for magnesium is also observed to decline with depth (Figure 11), and exhibits a similar range of about four to one from maximum to minimum affinity.

The distribution of potassium in the vertical dimension (Figure 18) shows a remarkable peak in the upper 5 to 10 cm of peat. This peak corresponds with the region of living Sphagnum and is predicted on the basis of the high potassium uptake of live Sphagnum in vitro. Below this layer, the correlation between potassium concentration and depth is very small, and is statistically insignificant.

The distribution of lead with depth (Figure 19) shows a peak located approximately 20 cm below the water table. Based upon the location of the peak, and the assumption that lead fallout increased rapidly in the 1930's due to

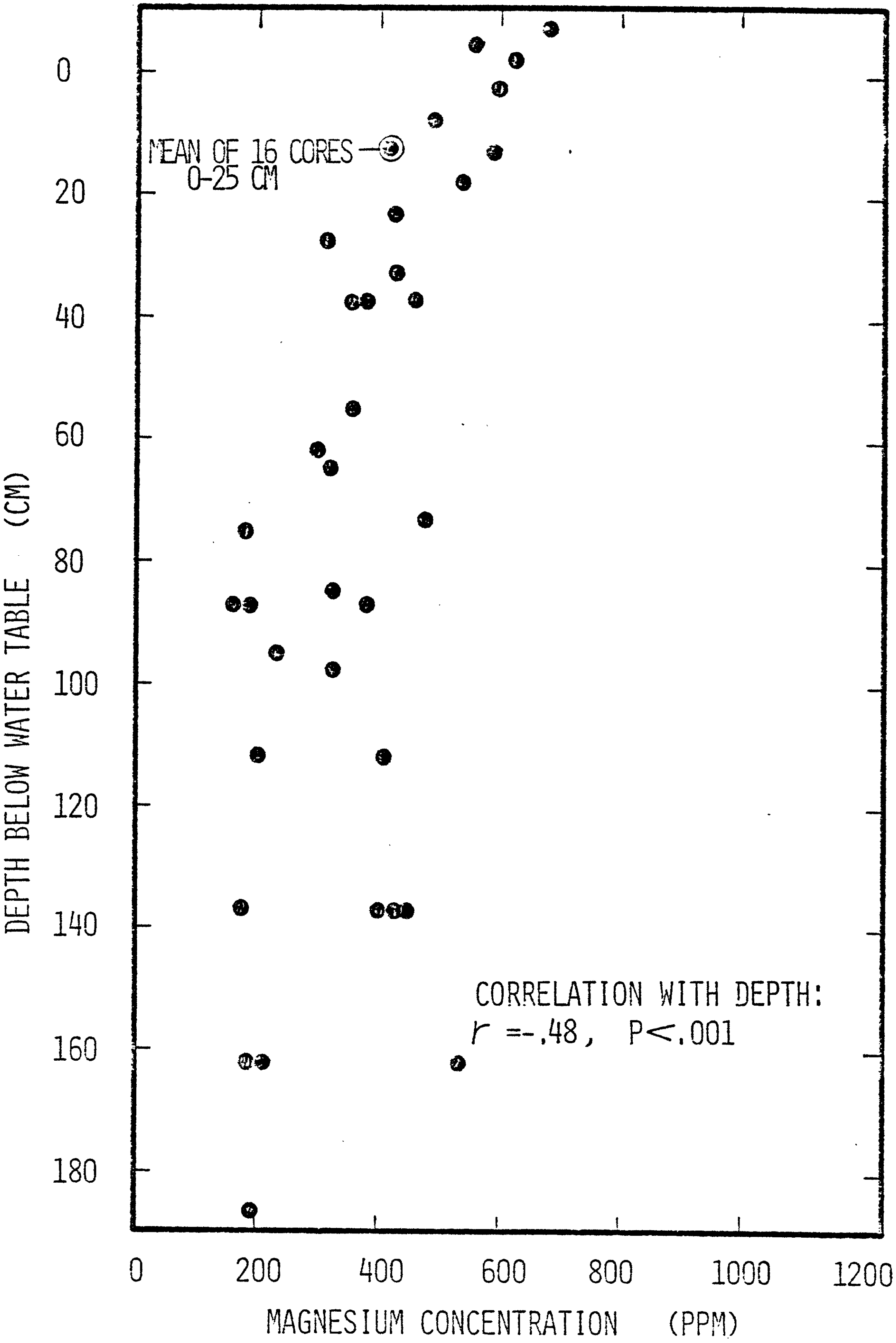


FIG 17 MAGNESIUM CONCENTRATION IN PEAT AS A FUNCTION OF DEPTH

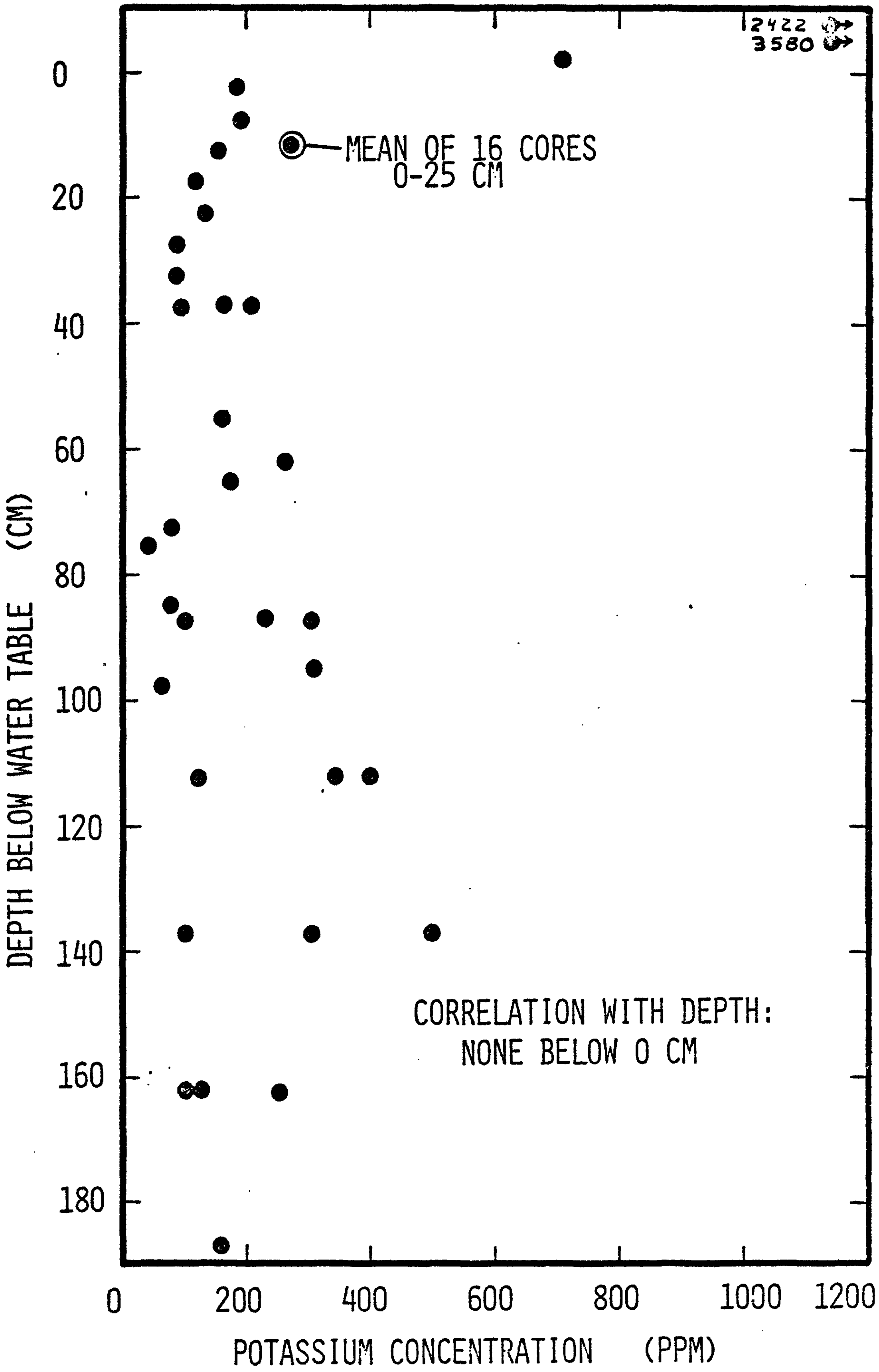


FIG 18 POTASSIUM CONCENTRATIONS IN PEAT AS A FUNCTION OF DEPTH

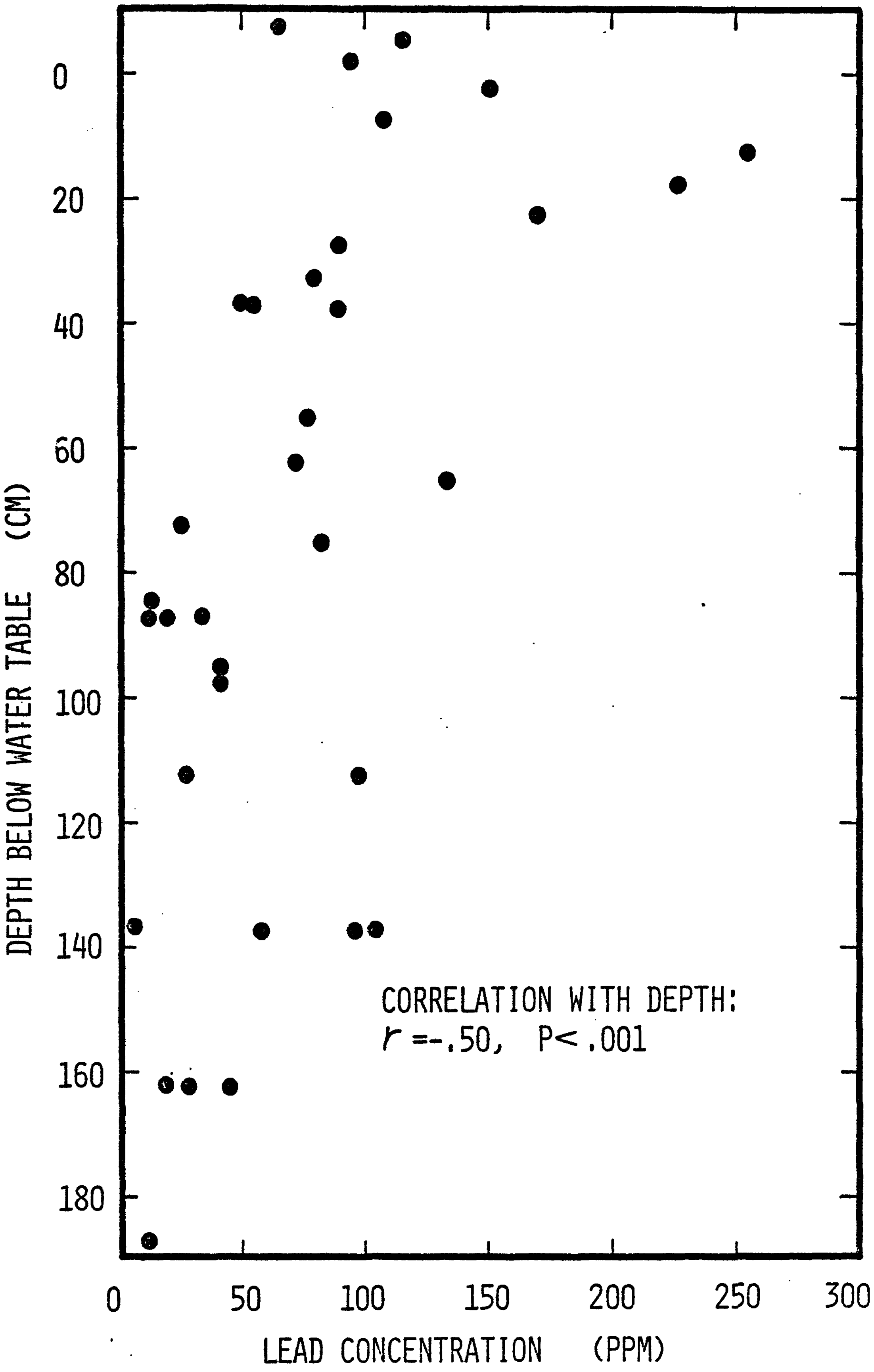


FIG 19 LEAD CONCENTRATIONS IN PEAT AS A FUNCTION OF DEPTH

the adoption of leaded gasoline, the lead profile is useful in estimating the net rate of peat accumulation (see 4.3.3.). On the larger scale, lead concentration is significantly correlated ($r = -.5$, $p<.001$) with depth over the entire profile.

4.3.1.4 Distribution of metals in bogwater

Magnesium in bogwater exhibits a statistically insignificant correlation ($P>.1$) with depth, supporting the notion that the moderate increase of magnesium with elevation in the upper peat profile is a function of peat chemistry only. Any slight concentration gradient of mobile magnesium which may exist is upwards, from a lower region of lesser immobile magnesium concentration to an upper region of higher concentration.

The distribution of metals in the mobile phase is shown in Table 4. Potassium concentrations in bogwater exhibit a slight, statistically insignificant ($P>.1$) correlation with depth, confirming that the concentration of potassium in living *Sphagnum* is a function only of the biological and chemical properties of the moss.

From inspection of Table 4, mobile lead, which exists at very low concentrations due to the high affinity of peat for this element, appears to be present in higher concentrations in the upper portion of the bog, where immobile lead is concentrated. The correlation, however, is signif-

TABLE 4

Metal concentrations in bogwater as a function of depth in Thoreau's Bog

Sampling Station	Date	Mean depth (cm)	PPM Mg	PPM K	PPM Pb
3	7/5/77	12	.258	.375	ND
4.5	7/5/77	12	.222	.170	ND
2	6/27/77	12	.28	.20	.013
3	6/27/77	12	.57	.47	.007
4	6/27/77	12	.24	.46	.007
4.5	6/27/77	12	.38	.24	.006
5	6/27/77	12	.24	.26	.003
3	6/11/77	12	.53	.63	ND
4	6/11/77	12	.18	.46	ND
2	5/13/77	12	.12	.35	---
3	5/13/77	12	.39	.58	.0032
4	5/13/77	12	.14	.49	.0025
4	5/13/77	12	.22	1.11	.0016
4	5/13/77	12	.34	.79	.0009
4.5	5/13/77	12	.36	.31	.0013
5	5/13/77	12	.21	.33	.0005
N	3/16/77	12	.20	.70	ND
3	3/26/77	12	.03	.39	ND
5	3/26/77	12	.07	.05	ND
5	4/4/77	12	.13	.12	ND
4	11/11/77	12	.38	.32	.012
4	6/29/76	12	.35	.61	ND
3	3/29/76	12	.45	.38	ND
5	3/29/76	12	.20	.38	ND
3	6/27/77	62	.46	.36	.004
4.5	6/27/77	62	.43	.33	.003
4	5/13/77	62	.51	.46	.0004
3 *	12/4/76	88	.28	.69	.001
3	6/27/77	112	.38	.57	.002
4.5	6/27/77	112	.35	.49	.002
4	5/13/77	112	.33	.52	.0006
4.5 *	12/4/76	112	.39	.46	.005
3 *	12/4/76	137	.66	.75	.015
4 *	12/4/76	137	.31	.33	.004
4.5 *	12/4/76	137	.35	.35	.007
3 *	12/4/76	162	.31	.69	.001
4 *	12/4/76	162	.31	.33	.003
3	6/27/77	162	.17	.36	.003
4.5	6/27/77	162	.35	.49	.002
4	5/13/77	162	.32	.69	.0003
4.5 **	11/11/77	188	.34	1.07	---
4.5 **	11/11/77	188	.34	.35	.002
3 *	12/4/76	188	.34	.38	.001

(continued on next page)

TABLE 4 (continued)

Sampling Station	Date	Mean depth (cm)	PPM Mg	PPM K	PPM Pb
4	12/4/76	200	.20	.49	.0005
4.5 *	11/11/76	237	.36	.36	---
3 *	11/11/76	237	.30	.37	---
Mean			.30	.46	.0036
Standard deviation			.13	.21	.0038
Correlation with depth			.186	.158	-.296
Confidence limit			N/S	N/S	P≈ .07

* offset 6 meters north

** offset 6 meters south

icant only at $p = .07$. If, indeed a lead flux exists from the upper to the lower strata, its magnitude is limited, not only by hydrological factors, but by the low value of K''_{Pb}.

4.3.2 Metal content of precipitation

The influx of K, Mg, and Pb to the bog during the interval from December 4, 1976 to March 26, 1977 is summarized in Table 5. Weighted means are considered more representative for the purpose of computing annual metal fluxes, and are computed by the formula:

$$\text{weighted mean} = \frac{\Sigma \overset{\circ}{C}_i\, d_i}{\Sigma d_i}$$

where $\overset{\circ}{C}_i$ = concentration of metal in precipitation sample, and d_i = depth of precipitation sample. Each sample value, in turn, is a mean of values from each of three identical precipitation collectors.

Magnesium concentration of bulk precipitation during this interval was .091 ppm, which lies between the values of Pearson and Fisher (1971) and Likens et al (1976) (Table 6). The potassium concentration was .061 ppm, a value which is higher than the values of Likens et al (1976) but significantly below those of Pearson and Fisher (1971). Lead concentrations are in accord with those found by Lazrus (1970) (Table 6).

TABLE 5

Concentrations of Mg, K, and Pb in precipitation at Thoreau's Bog

12/4/76 through 3/26/77

Time interval	Precip. depth (1/1000 ft)	PPM K	Depth-conc. K	PPM Mg	Depth-conc. Mg	PPM Pb	Depth-conc. Pb
12/4-12/11	100.	.111	11.1	.300	30.	.013	1.3
12/11-12/18	35.	.300	10.5	N/D	---	.032	1.1
12/18-1/5	175.	.038	6.7	.057	10.	.076	13.3
1/5-1/15	400.	.043	17.2	.041	16.	.026	10.4
1/15-2/5	90.	.111	10.0	.173	16.	.050	4.5
2/5-2/26	190.	.063	12.0	.083	20.	.030	5.7
2/26-3/5	80.	.062	5.0	.103	8.	.036	2.9
3/5-3/16	158.	.042	6.6	.054	9.	N/D	---
3/16-3/26	264.	.045	11.9	.091	24.	N/D	---

Element	K	Mg	Pb
Total precip. depth sampled	1.49 ft	1.46 ft	1.07 ft
Total depth-conc. product	91. PPM-ft	133. PPM-ft	39.2 PPM-ft
Weighted mean concentration	.061 PPM	.091 PPM	.037 PPM

TABLE 6

Metal contents of New England precipitation

Source or authority	Location of study	Metal concentrations (ppm) Mg	 K	 Pb	Remarks
Thoreau's Bog data		.091	.061	.037	Data for 4 months Dec. thru March
Pearson & Fisher (1971)	Northeast U.S.	.15	.107	N/D	Up to 3 yrs. data
	Taunton, Mass.	.19	.18	N/D	1 year data
Likens et al (1976)	Hubbard Bk., N.H.	.074	.045	N/D	Data for 12 years
Lazrus et al (1970)	Average for U.S.	N/D	N/D	.034	Data for 5 months, Sept. thru Jan.
	3 New England locations	N/D	N/D	.05 to .09	Data for 6 months, Sept. to March

4.3.3 Age and rate of deposition of the peat profile

Total activity of 210_{Po} in each 12 cm section of peat is shown in Figure 20. The general similarity to the total lead profile (Figure 19) is immediately apparent, although the mechanism responsible for the decrease with depth is anthropogenic in one case and a consequence of radioactive decay in the other. The total activity of the core is 330 DPM, which corresponds to an annual deposition rate of .8 dpm/year-cm^2. The calculated ages of the peat core at each of five depths are shown in Figure 21. The relatively recent date at the bottom of the first increment undoubtedly reflects the lack of compaction in this upper region, which includes about 5 cm of living moss. The density of this increment is about half that of the lower increments. The effect of compaction and decomposition at greater depths can be seen in successively lower increments. While the top 12 cm represents only 6 years growth, the second 12 cm represents 25 years growth and the third represents 28 years growth. The fourth and fifth combined represent over 35 years per 12 cm. The annual gross production of *Sphagnum* is thus about 2 cm/year, or 460 g/m^2-year. Annual net production, which takes into account decomposition and compaction, is between .48 and .32 cm/year, depending on the increments used to calculate the value. The probable errors due to incomplete humification in upper increments must be

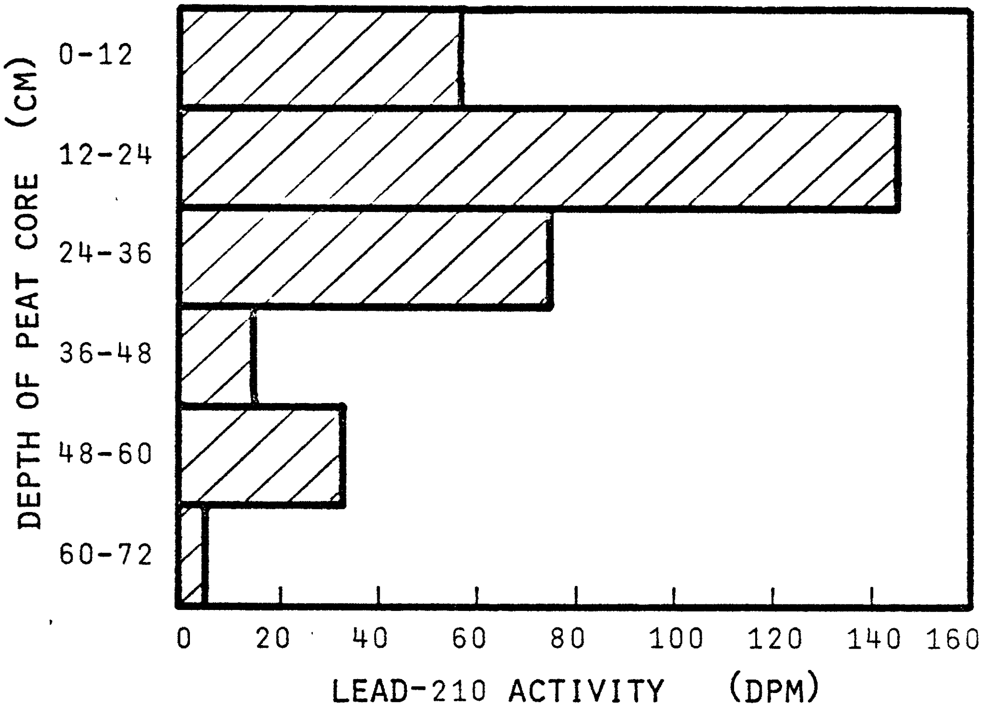


Fig 20. Unsupported ^{210}Pb activity in each of six segments of a continuous peat core.

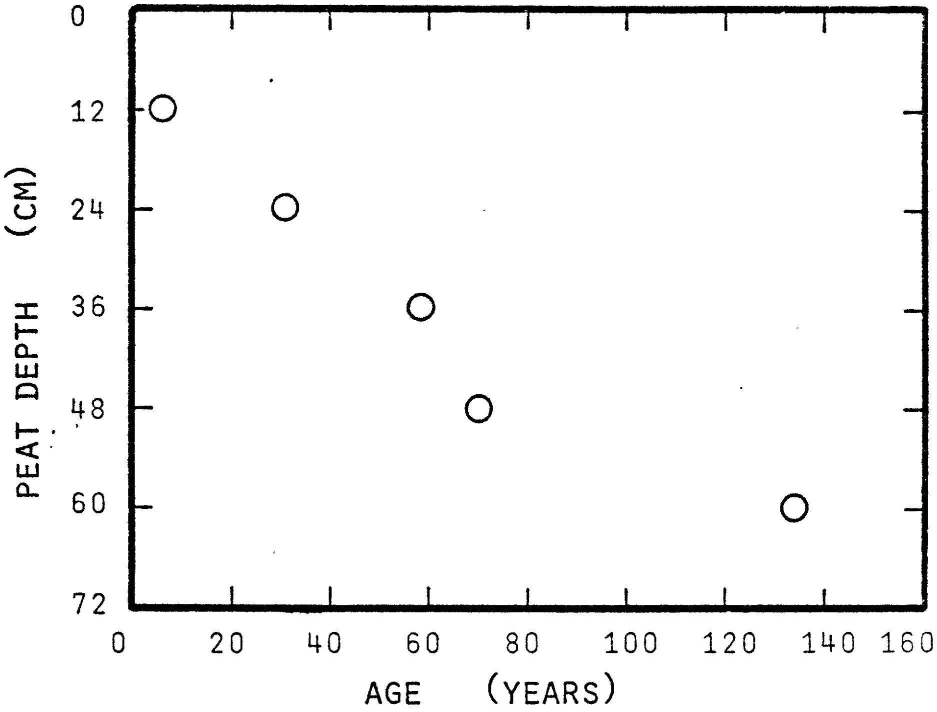


Fig. 21. Ages of the peat profile calculated from ^{210}Pb activity.

balanced against the greater uncertainty associated with dating the deeper profiles. If the 24-36 cm increment is chosen, net Sphagnum accumulation is determined to be .43 cm/year, or 180 g/m^2-year (note the dependency of this latter value on both ^{210}Pb-determined age and density of the core).

4.3.4 Mass balance of metals

The mass-balance for K and Mg, shown in Table 7, is based upon the composite water year of Table 3, the metal contents of rainwater in Table 5, a value of 180 g/m^2-year net peat accumulation, and metal concentrations in the peat profiles of Figures 17 and 18. The lead balance (Table 7) uses gross peat accumulation rate (460 g/m^2-yr) and the average concentration of lead in the upper 12 cm of the bog, thus reflecting the effects of historical increase in lead fallout. Potassium and magnesium show important variations with depth, and average metal concentrations for the purpose of mass balance calculations are taken from below the regions of significantly elevated metal concentration. Since the evidence indicates that the decreases in metal concentrations with depth are due to changes in the chemistry of the Sphagnum and peat, it is expected that the observed metal concentration profiles will, in effect, move upward at a rate equal to net annual peat accumulation, and that the effective contribution to

TABLE 7

Annual balance of K, Mg, and Pb in Thoreau's Bog

Element	Conc. in rain mg/l	Precip. depth l/m^2	Annual input mg/m^2	Conc. in bog water mg/l	Volume of runoff l/m^2	Annual output mg/m^2	Conc. in peat (ppm)	Net peat accum. g/m^2	Annual storage mg/m^2
K	.061	1,450	89	.45	280	134	200	180	36
Mg	.091	1,450	130	.30	280	84	300*	180	54
Pb	.037	1,450	54	.0045	280	1.2	100**	460**	46

* peat in lower portion of profile (below 100 cm), most representative of effective annual increment

** based on data from upper 12 cm of bog, which shows effect of increased lead fallout metal storage in the bog is best determined using the concentration of metal in peat below the region of elevated metal concentration.

In the case of lead, however, the assumption of constant deposition rate is not valid, and the higher concentrations of lead in the upper strata of peat are more representative of current storage rates. Thus, the lead storage term is based on these higher concentrations.

4.4 Discussion of results

4.4.1 Homogeneity of peat and water

It is immediately apparent that the variance observed in the measurement of partition coefficients is considerably greater than the variance which could be accounted for by measurement errors alone, even when the measurement error allowance is doubled to account for the fact that each K" determination is a quotient of two metal concentrations. Thus, inhomogeneity, even on a short distance scale, appears to be a real characteristic of the bog system. Several factors may contribute to this inhomogeneity:

1) The spatial variability of the peat-forming vegetation, which includes two species of Sphagnum. The roots, stems, and leaf litter of several other plants is also incorporated into peat on a spatially irregular fashion.

2) The assumptions discussed in 4.1 regarding the ion-exchange chemistry are not strictly true in the bog system. Although variations in ionic strength effects are probably not significant in the bog, due to the low ionic strength of bogwater, both pH variations and metal concentrations higher than "trace" levels may compromise the invariance of K". The mean pH of the surface waters of the bog, measured over a 2-year period, is 3.8. The standard deviation of H^+ concentration is 9×10^{-5} moles/l, corresponding to +.4, -.2 pH units, with fluctuations occurring over both time and distance. Furthermore, peat analyses indicate that up to several per cent of the ion exchange capacity of the peat and Sphagnum may be occupied by metals; thus, the exchange isotherms are probably not strictly linear at the levels of metal concentration encountered in the bog.

3) The constancy of K" also depends on a constant organic ligand concentration. The process of production of organic acids in the bog is not understood, and its distribution in space and over time may not, in general, be uniform.

The above list may not be inclusive, but only points out a few of the possible sources of scatter in the K" data. The question of scatter of the metal concentration data, in both bogwater and peat, is addressed similarly.

4.4.2 Metal distribution in peat

Despite the variability of the data, the concentrations in peat of each metal investigated demonstrate a statistically strong relationship with depth in the bog. In general, the functional relationship between depth and metal concentrations must be the result of many factors including transport and reaction kinetics, peat accumulation and decomposition rates, and the possibility of a time-varying input. However, given the density and age of the peat along a vertical profile, it is possible to construct a theoretical metal profile for two special cases.

The first case is the case where K" is large, and thus the metal is relatively mobile in the bog and is essentially in equilibrium with the entire profile. The second case is the case where K" is very small, and thus only a very small portion of the metal (in the limit, none of the metal) can move. In the former case, the metal will be distributed along the vertical profile with concentrations proportional to 1/K". In the latter case, the concentrations of metal along a vertical profile will be influenced only by growth and decomposition rates, and will retain a record of a time-varying input. (It is assumed that as decomposition occurs, metal originally present in the peat will remain absorbed on the solid decomposition product.)

Magnesium, which is much more mobile in the bog than lead, appears to approximate the first case, and the decline of magnesium concentration with depth parallels the increase of K''_{Mg} with depth. Active uptake by living moss, which is clearly the dominant factor in potassium distribution, does not appear to be of comparable importance in magnesium distribution, since the region of elevated magnesium concentrations is much deeper than is the region of live moss.

In the case of lead, K" is quite small, and the ratio of mobile to fixed lead is approximately equal to:

$$\frac{\text{mobile Pb}}{\text{fixed Pb}} = \frac{\text{Pb conc. in water mg/l}}{\text{Pb conc. in water (mg/l)}} \quad \text{X}$$

$$\frac{1}{[K''\ (\text{mg/l})/(\text{mg/g})]^{-1}[\text{density of peat (g/l)}]}$$

$$= \frac{1}{(20)\ (40)} = \frac{1}{800}$$

Lead thus approximates the second case. The lead flux in precipitation is known to have been influenced in recent times by industrialization; however, a theoretical curve assuming a constant input can be constructed from available age and density data and compared with the observed lead profile.

Theoretical concentrations of lead, assuming $K''_{Pb} \to 0$ and assuming a constant rate of lead input to the bog, are calculated from ^{210}Pb dates and sample densities and shown in Table 8. (The ages of increments 4 and 5 are averaged for curve smoothing purposes only.) It is significant that such a curve exhibits a strong decrease in metal concentration near the top of the peat profile, and becomes essentially constant with depth about a half-meter below the bog surface. (The exact trend depends on assumptions about the rate of continuing decomposition in the lower portion of the bog. Certainly, it is much slower in the deeper, more humified material.)

The second column of Table 9 shows hypothetical lead concentrations determined on the assumption that lead concentrations below 60 cm are a good indicator of the pre-industrial lead flux into the bog. Actual observed lead concentrations in each 12-cm-thick layer of the bog are compared with these hypothetical concentrations, and the difference attributed to post-industrial alteration of the lead flux. This augmentation of the natural lead flux (column 6) shows a striking increase in the period from 1920 to 1948 and is thus consistent with the known association between lead fallout and industrialization. It is

TABLE 8

Theoretical lead concentration profile in peat, assuming constant lead input rate

Increment no.	density (g/cm^3)	age at bottom (yrs)	years accumulation	mass of increment (g)	relative Pb concentration	absolute Pb concentration (ppm)*
1	.024	6	6	3.62	1.9	17.
2	.050	30	24	7.62	3.1	28.
3	.043	58	28	6.52	4.3	38.
4	.040	71	37	6.05	6.1	54.
5	.044	132	37 avg.	6.63	5.6	50.

* based on observed lead profile, which shows lead concentration of 50 ppm in deep peat

TABLE 9

Historical increase in lead fallout in precipitation at Thoreau's Bog *

Increment no.	mass of increment (g)	theoretical Pb. conc. (ppm) **	actual Pb conc. (ppm)	"extra" Pb (ug/incr)	"extra" Pb year (ug/cm^2) ***	dates of increment
1	3.62	17	103	311.	3.6	1971-1977
2	7.62	28	176	1127	3.7	1948-1971
3	6.52	38	178	913	2.6	1920-1948
4	6.05	54	86	193	0.4	1881-1920
5	6.63	50	84	225	0.5	1844-1881

*baseline (pre-1880) lead fallout 0.7 ug cm^2-yr

**see table 8

***increase over baseline rate

also consistent with the assumption that lead is relatively immobile in the peat, an assumption which is essential to the validity of ^{210}Pb dating.

In summary, observed metal distributions in bogwater support the assumption that the major cations are essentially in equilibrium throughout the bog, while the variation of the overall partition coefficients with depth indicates that the death and humification of Sphagnum do change its ion-exchange properties. The most radical change occurs with the death of the moss and its order-of-magnitude decrease in affinity for potassium. The process of humification per se appears to effect a significant decrease in the affinity of peat for magnesium. In the case of lead, distribution is controlled by the low value of K''_{Pb} and the historical changes in lead input. No evidence of chromatographic effects in the bog system is noted, and indeed the annual precipitation falling directly on the mat and thus representing downward water flow is closely balanced by an upward evapotranspiration term. Radial inflow from hummock runoff is of similar magnitude to annual runoff; thus, essentially invariant metal concentrations along a radius of the bog are, in retrospect, not surprising.

4.4.3 Mass balance of metals

The magnesium budget (Table 7) shows remarkable agreement between the observed rate of magnesium input to the bog and its disposition as either storage or runoff. The input term is also reasonable when compared with other workers' data (see Table 6). The budget is consistent with the assumption that both growth rates of Sphagnum and the rate of magnesium fallout in precipitation have been relatively constant during the past few hundred years. Both hydrological and ion-exchange factors play a major role in determining the magnesium balance of the bog.

The potassium budget, based on the precipitation data obtained at the bog, shows a net export of potassium, which could result either from a major recent fluctuation in the potassium content of rain or from an underestimate of the actual long-term potassium fallout. The latter explanation seems the most likely, especially since precipitation sampling at the bog was done for only part of a year and would thus fail to show any annual cycle in potassium concentration. If anything, summer levels of potassium might be expected to be higher, since potassium is readily leached from plant leaves and could become airborne through wind action on foliage. A value of .12 ppm of potassium in bulk precipitation would result in a balanced potassium budget in Table 7, and such a value is well within the range of reported concentrations.

The lead budget shows good agreement between the input term and the storage term, and shows that nearly all lead coming into the bog is retained by the peat and Sphagnum moss. The lead budget is thus dominated by the ion exchange chemistry of the bog, and is little influenced by the hydrology. Total lead input to the bog is also reasonable when compared with the data of Lazrus (1970) (Table 6).

4.4.4 Peat accumulation rates and bog ecology

The growth rate of Sphagnum and the size of the resultant storage terms are somewhat surprising, and indicate that the present bog system is comparatively young and has developed within the last several hundred years. The calculated growth rate of Sphagnum of 460 g/m^2-yr is comparable to representative growth rates in European bogs as summarized by Clymo (1964), and even a net accumulation rate of 1/3 cm/yr, as determined from core increments 4 and 5, would allow a 2-meter thick mat to be built in only 600 years. At a constant rate of mat advance, this age is consistent with Thoreau's measurements of the central area of open water.

The apparent youth of the bog also has implications for the plant community, which must then have immigrated during recent times across appreciable distances of inhospitable terrain from rather small and scattered bog habitats. It suggests that bog development is a modern, ongoing process rather than a relic of the last glacial retreat. It also addresses the question of bog persistence, for the bog must either raise its own water level over time by impeding drainage with peat deposits or it must eventually "bottom out" as the mat thickens, and thus, become susceptible to surface drying.

5 Mechanisms of pH Control

5.1 Introduction

The low pH of Sphagnum bogs is such an intrinsic feature of this wetland type that, along with a characteristic, mostly ericaceous flora, it is generally considered part of the definition of a bog. The pH of Thoreau's Bog, for example, averages about 3.8 at the surface. Yet, the mechanisms whereby the low pH is established and maintained have been the subject of considerable controversy. Bass-Becking (1934, 1960) attributed the acidity to ion exchange by Sphagnum; this view has been strongly championed by Clymo (1963, 1964). However, Ramaut (1954, 1955) attributes the acidity to organic acids released by Sphagnum, and demonstrates the metabolic role of the moss in the acidification process. Still other workers (Gorham, 1957) attribute the low pH to the presence of strong acids. Evidence has been presented on all sides of this question.

Ramaut (1955) has demonstrated a strong stimulatory effect of glucose on the acidification of media by S. recurvum. He has also shown that the ability of killed Sphagnum to acidify media may be reduced by prior solvent extraction (Ramaut, 1954), and that acidic substances can be found in the extract (Ramaut, 1955). Clymo (1963), on the other hand, claims that, even if the mechanism of acidification were the secretion of a simple organic acid, Sphagnum could not contain enough acid to account for the observed values of pH in bogs. Supporting the ion-exchange theory are data of Williams and Thompson (1936), who report that while dried Sphagnum has a significant effect on the pH of salt solutions, it has no effect on distilled water. Growth rates of Sphagnum are adequate, according to Clymo (1964), to maintain a typical bog at pH 4 entirely by ion exchange mechanisms. Gorham (1957) recognizes the presence of organic acid in bogs but claims they are essentially undissociated in the presence of strong mineral acid. The major mineral acid, according to Gorham (1967), is sulfuric acid, derived either from industrial pollution or the oxidation of organic sulfur compounds in peat. Gorham (1956), however, notes that water analyses of bogwaters from British bogs have shown an apparent excess of anions over cations, suggesting that dissociated organic acids are present. Gies and Lotschert (1972) indicate that Sphagnum mosses do take up cations and thus permanently lower the pH of water, while Yefimov and Yefimova (1973) attribute the low pH of highmoor bogs to organic acids.

There is, of course, a very real possibility that several mechanisms operate to determine the pH of a bog, and that these mechanisms may differ in importance from bog to bog.

Analysis of the individual bogwaters is necessary to resolve the question, and at least three bases exist for differentiation between mineral acids and weak organic acids in a water sample.

First, a charge balance analysis for inorganic ions should reveal the presence of organic acids by showing an excess of cations over inorganic anions.

Secondly, the presence of weak organic acids should be manifest as a rise in pH upon subjecting the system to sufficiently oxidizing conditions. The use of ultraviolet light to oxidize organic material in natural waters is described by Armstrong et al (1966), who report essentially complete oxidation of "humic acids" by this procedure. The complete elimination of all organic materials is apparently not assured, however, since certain species (notably urea) appear to oxidize very slowly under UV irradiation.

Thirdly, the pH buffer capacity of bogwater may be compared with the buffer capacity of a strong acid solution. Since organic acids are invariably weak acids, their presence will reveal itself through the comparison of pH titration curves of bogwater and strong acid solutions of equal pH. By beginning the pH titration at a sufficiently low pH to insure that all organic acids are initially undissociated, a curve of dissociation vs. pH may be prepared and the relative importance of organic acids determined by comparing the initial H^+ concentration of the sample with the concentration of H^+ released by the sample at the original pH. Low pH as a result of ion exchange will, of course, be indistinguishable from low pH due to the addition of mineral acid, once the exchanger phase is removed.

A combination of these techniques is employed in this study. First, bogwater is filtered to remove solids, and its pH is determined. A complete change balance analysis of this filtered bogwater is greatly complicated by its color, making a direct charge balance analysis difficult. Colorimetry involves corrections which take on the character of unproven assumptions when the color of the water has an absorbance as great as or greater than the colored complex being measured. Furthermore, organic acids, if present, may interfere directly with analyses by complexation. This is reported (Gorham, 1956) in the analysis of sulfate by precipitation with barium. Furthermore, interference by organic acids can be suspected in the titration of chloride with silver ion. Therefore, the remaining analyses (except for NH_4^+ by electrode, which is done before and after irradiation), are preceded by irradiation of the sample with ultraviolet light. This oxidation destroys the interfering color and, as demonstrated by copper titration, destroys most or all of the complexing ability of the water. A complete charge balance analysis subsequent to oxidation by ultraviolet light becomes feasible. The change in H^+ concentration accompanying the oxidation may then be attributed to organic acids.

Secondly, bogwater, filtered to remove solids, is titrated with strong base. On the basis of preliminary titrations, pH=3 is considered sufficiently low that all organic acids are undissociated and do not contribute to buffering of the solution. This also appears to be the case with titrations of humic acids by Wilson and Kinney (1977). Complete exclusion of CO_2 is, of course, necessary to avoid confusing the results with the kinetics of CO_2 dissolution. The resulting curve of acid dissociation versus pH may then be compared with the mineral acidity of the sample to determine the relative influence of weak and strong acids in the bogwater.

Determination of the presence of organic acids in bogwater does not, of course, establish the origin of the acids, which could be secretion by live *Sphagnum* or the humification of dead *Sphagnum* and plant remains. Neither does the presence of mineral acidity by itself indicate the mechanisms by which mineral acidity arises in the bog. A general scheme for the major processes of bog acidity is proposed in Figure 22. The mass balances of water, as well as of the major metals and anions, are needed to estimate the relative magnitude of each process. Much of the necessary information is available from Chapters 3 (hydrology) and 4 (mass balances of metals). Information on anion inputs is taken both from the literature and from analyses of precipitation at the bog.

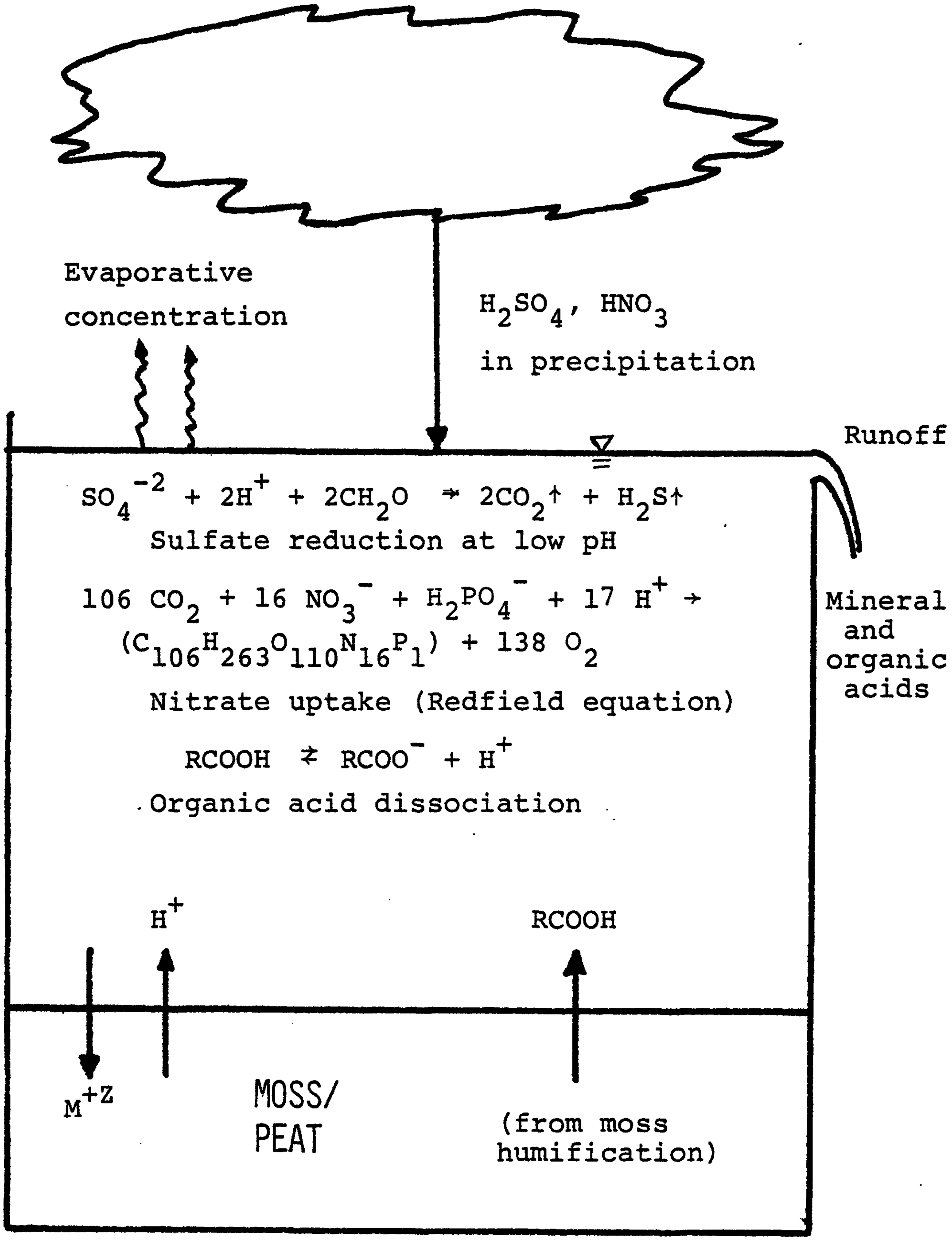


Fig. 22. Processes influencing pH of the bog.

5.2 Materials and methods

5.2.1 Equipment and instrumentation

pH measurements were made with an Orion model 601 pH meter, and an Orion glass electrode and single-junction reference electrode. pH titrations were carried out with a Mettler DV 10 digital burette drive operated by a pulse counting automatic controller built by the author, and fitted with a Mettler DV 202 1.0 ml burette. Temperature was regulated by a constant-temperature circulator with a 250 ml double-jacketed beaker, and CO_2 was excluded by maintaining the solution under N_2 which had passed through an Ascarite-filled drying tube. A Honeywell recorder, modified to function as a stepping-motor-recorder, was used to record titrations and to judge equilibrium when specific ion electrodes were used. A Radiometer Selectrode with the silver coating was used to indicate the status of chloride titrations, and an Orion ammonia gas electrode was used in determinations of ammonia ion. An Orion liquid-ion-exchanger nitrate electrode was used in the determination of high ($>10^{-5}$M) nitrate levels. A Perkin-Elmer Model 360 atomic absorption spectrophotometer was used to determine metals, and a Beckman model 25 spectrophotometer was used in all measurements of absorbance or turbidity in the liquid phase. Ultraviolet irradiations of all samples were carried out with Ultraviolet Products, Inc., model PCQ ultraviolet lamps. Precipitation sampling apparatus is described in Chapter 4.

5.2.2 Reagents

Standard 1000 or 500 PPM solutions of sodium, potassium, calcium, and magnesium were prepared according to Perkin-Elmer (1976); sodium and potassium standards were prepared from the oven-dry chlorides, calcium standard was prepared from primary standard $CaCO_3$, and magnesium standard was prepared from magnesium ribbon. 2×10^{-3}M silver nitrate standard was calibrated against the above potassium chloride and sodium chloride solutions. 1000 PPM sulfate standard was prepared from the dry disodium salt, and was checked against the silver nitrate standard. Nitrate standards were prepared from the potassium salt. In all instances, necessary dilutions were made immediately before use in acid-washed volumetric flasks with acid-washed volumetric pipets and distilled, deionized water. Standard acid and base were prepared from Fisher Acculite solutions; all base was diluted with boiled, distilled, deionized water and was stored in containers fitted with Ascarite CO_2 traps. 20-30 mesh $BaCl_2$ for sulfate analysis was sieved from the stock chemical. All reagents, unless otherwise noted, were prepared from analytical reagent grade materials in acid-washed glassware.

5.2.3 Oxidation of humic acids

Approximately 350 ml of water from the bog, filtered through a .45μ filter, was added to a 500 or 1000 ml Erlenmeyer flask. The flask was then equipped with either a magnetic stirrer or a fritted glass air bubbler to provide agitation and aeration of the sample. An ultraviolet lamp was inserted into the flask, and the entire assembly was wrapped with alumnium foil to protect laboratory workers from UV radiation. Lamps were then allowed to operate from 36 to 40 hours, at the end of which time, the water samples were stored for chemical analysis.

5.2.4 Charge balance analysis

5.2.4.1 Metal analysis

Metals in the filtered, irradiated water were determined in a lean acetylene-air flame, in atomic absorption made for calcium and magnesium, and in flame emission mode for sodium and potassium. Fresh combined aqueous standards, covering a 4:1 concentration range in 5 increments, were used for calibration. Distilled deionized water was used as a blank. The calibration points were fitted, after subtraction of any blank, with a curve of the form $Y=a\ X^b$, using the "Power Curve Fit" routine on an HP-25 calculator. This same calculator routine was then used to convert sample absorbances into concentrations.

5.2.4.2 Sulfate analysis

Sulfate content of the filtered, irradiated water was determined by the turbidimetric method of Taras et al (1971). All volumes were halved for the analysis, and a MacDonald's spoon was found to be ideal for the prescribed addition of $BaCl_2$ to the sample. Turbidity measurements were corrected by subtracting the absorbance of the sample only at 420 nm. A calibration curve was obtained from turbidity measurements as described above in 5.2.4.1.

5.2.4.3 Nitrate analysis

Nitrate in both irradiated bogwater and precipitation was determined by measuring absorbance at 220 nm, as described by Taras et al (1971). When nitrate concentrations in bogwater by this method exceeded 2×10^{-5} molar, measurements were confirmed by use of the nitrate electrode. The nitrate electrode was used in conjunction with a magnetic stirrer, a constant-temperature bath, and an Orion single-junction reference electrode filled with a .8N NaCl filling solution saturated with AgCl. Voltages were measured on the Orion model 601 and equilibrium was determined from a record on the Honeywell recorder. A calibration curve was obtained before and after sample measurement by consecutive additions of 10^{-2}M $NaNO_3$ to 50.0 ml of distilled, deionized water. No ionic strength adjustment was used.

Sample concentrations of nitrate were determined from a calibration curve prepared on semi-logarithmic graph paper.

5.2.4.4 Ammonium analysis

Ammonium ion was determined in both irradiated and unirradiated, filtered samples using the Orion ammonia electrode. The electrode was used in conjunction with a magnetic stirrer and double-jacketed beaker with constant temperature bath, and voltages were measured on the Orion model 601. The Honeywell strip chart recorder was used to determine electrode equilibrium. A 50.0 ml sample was used, and .5 ml of 10N NaOH was added prior to measurement. Calibration curves were determined before and after all measurements by consecutive additions of 1.0×10^{-2}M NH_4 Cl standard to a distilled, deionized water blank. Sample concentrations of ammonium were determined directly from a calibration curve prepared on semi-logarithmic graph paper.

Measurements of ammonium determined by the ammonia gas electrode were confirmed by the analysis of replicate samples using the Phenate method described by Taras et al (1971). This method was also used to determine ammonium concentrations in precipitation. Calibration curves were fitted to the data as described above in 5.2.4.1.

5.2.4.5 Chloride analysis

Chloride analysis of irradiated bogwater samples was performed by titration with silver and determination of equivalence point by Gran plot, as described by Orion Research (1975). However, all volumes were halved, and the Selectrode was used to follow the progress of the titration. Titrant was added in 0.50 ml aliquots by the DV-10 digital burette drive and DV-210 10 ml burette, and electrode voltages were measured on the Orion model 601. The Honeywell recorder was used to determine equilibrium. Equivalence points were determined from plots of each titration on Orion 10% volume-corrected graph paper.

5.2.5 pH titrations

50.0 ml of bogwater, filtered through a .45 filter, was added to a 100 ml beaker, and .5 ml of 1M NaCl added for ionic strength adjustment. 100 μl of 1.00 N HCl was added to bring initial pH below 3.0, and the solution was isolated from the atmosphere by an N_2 blanket. The burette control was set to add .0128 ml aliquots of base every 2 minutes, and the titrations begun. Titration was allowed to continue until pH exceeded 11.

The extent of dissociation of organic acids was determined at each pH by comparison of the volume of base added with the corresponding volume required to titrate a distilled water blank to the same pH. Dissociation was considered to be negligible at a pH of 3.0.

5.3 Results

Charge balance analyses of four samples of bogwater, subjected to oxidation by ultraviolet radiation, are shown in Table 10. Cation and anion sums, after irradiation, are not significantly different for these samples ($P \approx .1$, student's t). However, cation sums before irradiation are approximately twice the anion sums, reflecting the much higher H^+ concentration (.08 to .30 meq/l versus .001 to .02 meq/l) of unirradiated bogwater. Ammonium concentrations were essentially unchanged by the irradiation, and the other species present in Table 10 are not known to be altered by ultraviolet radiation. Thus, by inference, the charge balance of unirradiated bogwater is made up by organic acid anions. The magnitude of organic anion concentration indicates that organic acids are the major source of bog acidity.

Similarly, titration of bogwater shows the presence of weak acids at a concentration of about 1 meq/l. It is apparent from the shape of the titration curve (Figure 23) that the apparent pKa of these acids varies with pH, as is typical of humic acids.

That the dissociation of these weak acids is adequate to account for the observed pH of the bog is demonstrated quantitatively by these data. For example, the bogwater

TABLE 10

Charge balance analysis of bogwater

	Water sample number			
	Station 3 6/11/77 0-25 cm	Station 4 6/11/77 0-25 cm	Station 3 7/5/77 0-25 cm	Station 4.5 7/5/77 0-25 cm
CATIONS	equivalents/liter x 10^{-5}			
H^{+} *	21.9	29.5	11.5	16.6
H^{+}	2.6	0.1	3.2	3.2
NH_4^{+}	8.0	3.5	11.4	8.7
Ca^{+2}	1.2	0.5	1.1	1.0
Mg^{+2}	3.5	1.5	2.1	1.8
Na^{+}	4.8	4.4	4.0	3.9
K^{+}	1.4	1.2	1.0	0.4
TOTAL	21.5	11.2	22.8	19.0
ANIONS				
Cl^{-}	7.5	4.4	7.6	6.1
SO_4^{-2}	8.8	5.8	9.1	9.2
NO_3^{-}	1.7	1.5	8.5	6.5
TOTAL	18.0	11.7	25.2	21.8
INFERRED ORGANIC ANIONS **	19.3	29.4	8.3	13.4

Average total cations after irradiation = 18.6

Average total anions after irradiation = 19.1

Paired t statistic = .38 (cation and anion means not statistically different)

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* determined before oxidation by ultraviolet light (all other determinations made after oxidation, except for NH_4^{+}, which was determined both before and after)

** inferred for unoxidized bogwater, from shift in charge balance of inorganic species (decrease in H^{+}) resulting from oxidation of organic species under ultraviolet irradiation.

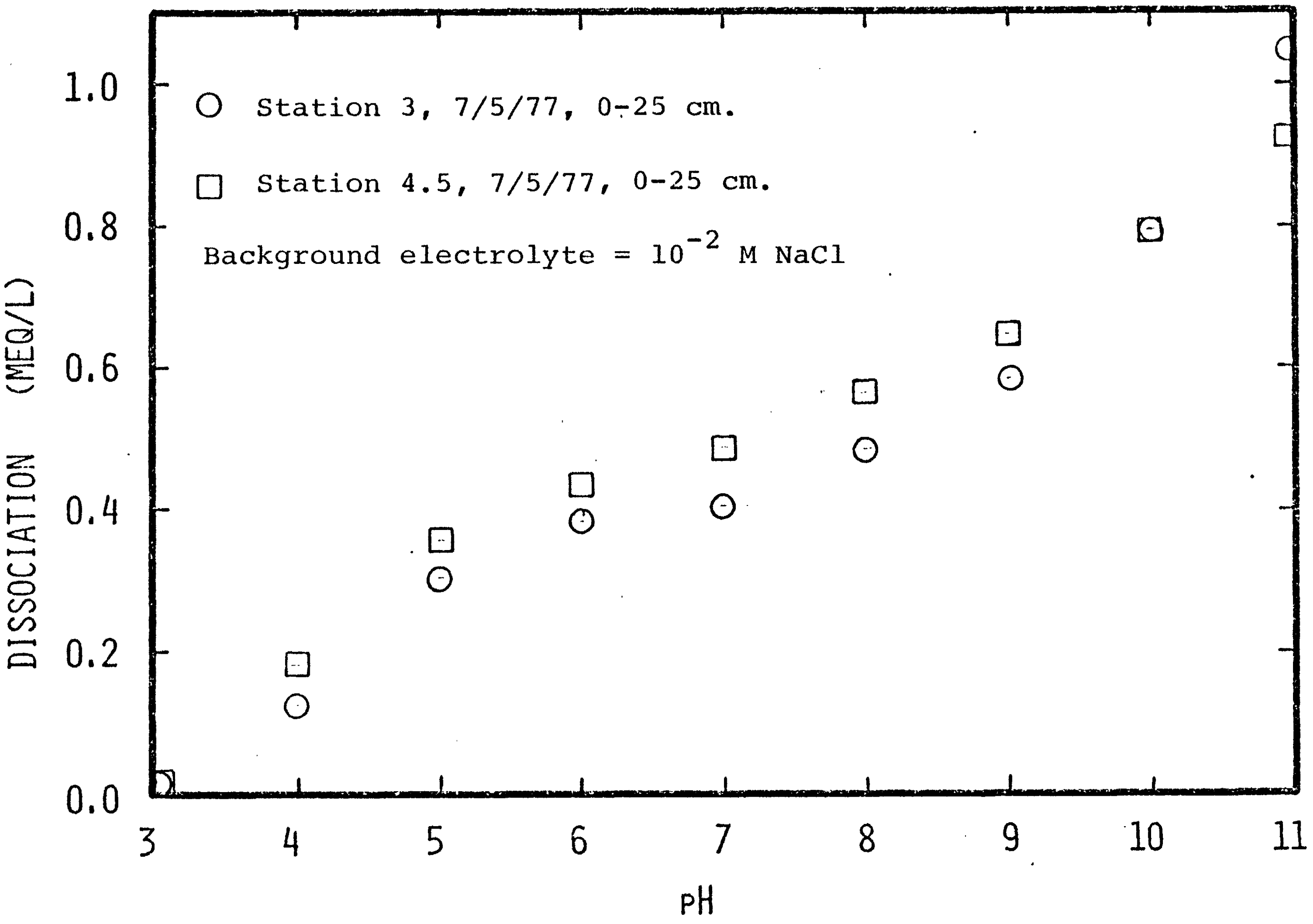

Fig. 23. Dissociation of bog acids as a function of pH.

sample of Station 4.5, collected on July 6, 1977, had a mineral acidity, determined from pH after irradiation, of .032 meq/l. From the dissociation curve, by trial and error, it is found that the weak acids dissociate to the extent of .15 meq/l at a pH of 3.75, and resulting total H^+ concentration is (.15 + .03) meq/l, corresponding to a pH of 3.75. This compares well with the initial pH of this sample, which was 3.78. (This treatment ignores the activity correction for H^+, which is calculated to be about .98 in bogwater.) This not only indicates the importance of organic acids, but quantitatively indicates their importance relative to mineral acidity as a mechanism of bog acidity.

Weighted means of nitrate and ammonia concentration in precipitation at the bog, measured over a 3-month interval, are presented along with data from Likens et al (1976) and Pearson and Fisher (1971), in Table 11 below.

Table 11

Anion Concentrations in Precipitation
(eq/l x 10^{-5})

Species	Weighted Mean: Thoreau's Bog	Liken *et al*., Hubbard Brook	Pearson & Fisher, Northeast U.S.
NH_4^+	1.1	1.3	1.2
NO_3^-	4.3	2.3	.6
$SO_4^=$	N/D	6.0	8.6
CI^-	N/D	1.4	1.2 to 5.9

The NH_4^+ and NO_3^- data are not inconsistent with the data of Likens et al (1977), which because of their completeness are adopted for the mass balance of major anions presented in Table 12. These data indicate that the bulk of the sulfate input to the bog is transformed, presumably to H_2S, and over half of the nitrate input to the bog is transformed, presumably by biological uptake.

5.4 Discussion of results

The above data may be interpreted in the context of the generalized bog system of Figure 22. The initial assumption is made that all inputs to the system are constant over time, and that the chemistry of the bogwater (which is a consequence of these inputs) is also constant. The volume of the system, under these assumptions, may be arbitrary; however, discussion is simplified if we assume a volume such that the mean residence time of organic acids in the bog is one year. It is helpful, also, to consider at first the system containing only the current year's effective accumulation of peat. Since the water chemistry is assumed constant, there will be no net interaction with the remainder of the peat in this model, and the remainder of the peat may be removed, conceptually at least, from the system. Mass balances of mineral acidity and organic acids may then be constructed.

TABLE 12

Approximate mass balances of major anions in Thoreau's Bog

Species	Concentration in precipitation (x 10^{-5} eq/l)	Annual input* to bog (meq/m^2)	Concentration in bogwater (x 10^{-5} eq/l)	Annual export* from bog (meq/m^2)	Net trans- formation in bog (meq/m^2-yr)
NO_3^-	2.3	33.	4.5	13.	-20.
NH_4^+	1.3	19.	9.0	25.	+6.
SO_4^{-2}	6.0	87.	8.2	23.	-64.
Cl^-	1.4	20.	6.4	18.	-2.

* based on an annual precipitation depth of 1.45 m and an annual runoff of 0.28 m.

A mass balance of mineral acidity may take the form:

Input = storage + output

In Thoreau's Bog, the input is rainwater, which in New England has received considerable attention due to its appreciable mineral acidity. A pH of 4.3 is not unreasonable to assume for the purposes of discussion.

The adsorption of cations (other than H^+) by peat is effectively a storage of negative mineral acidity, and can be quantified from knowledge of the total equivalents of metals in the effective annual increment of peat.

The biologically- mediated processes of sulfate reduction and nitrate uptake effectively represent outputs of mineral acidity from the system. The magnitude of these processes can be determined from the mass balances of sulfate and nitrogen in the bog.

The export of chemical species in bog runoff represents another output term. This term may be expressed as bog mineral acidity times annual runoff depth; thus, knowledge of all other terms in the mass balance enables a solution for bog mineral acidity. It should be noted that the effects of evaporative concentration are implicit and are reflected in the difference between precipitation depth and runoff depth.

Superposed on the mineral acidity of the system is the effect of weak organic acids. These weak organic acids are the result of biological activity, and under steady input and steady peat accumulation rate assumptions, the rate of organic acid production should be constant. Given the weak acid concentration, this rate may be determined from purely hydrological considerations.

The mass balance of mineral acidity may thus be formulated as:

$$Q^\circ A^\circ = -\dot{N} \Sigma M_i + Q_{SO_4^=} + Q_{NO_3^-} + Q_r A \qquad (5.1)$$

where:

Q° = annual precipitation (l/m^2)
A° = mineral acidity of rain (eq/l)
$\dot{N}$ = net peat accumulation rate (g/m^2)
M_i = concentration of cation i in annual effective peat increment (eq/g)
$Q_{SO_4^=}$ = annual sulfate reduction (eq/m^2)
$Q_{NO_3^-}$ = annual nitrate uptake (eq/m^2)
Q_r = annual runoff (l/m^2)
A = mineral acidity of bogwater

The expression for mineral acidity of the water in the system is thus:

$$A = \frac{Q^\circ A^\circ + \dot{N}\Sigma M_i - Q_{SO_4^=} - Q_{NO_3^-}}{Q_r} \qquad (5.2)$$

Chloride does not appear in this expression since it is relatively inactive biologically and is present in the bog in amounts expected on purely hydrological grounds (evaporative concentration only). Curiously, ammonium concentrations in the bog are also approximately as would be expected of an inert species. It is not possible to tell from these data whether ammonium is in fact inert in the bog, or whether this result is a balance between competing processes of ammonification, ammonium uptake, and loss of ammonia gas. This distinction is critical from the biological standpoint, but does not greatly alter the conclusions of the mass balance of mineral acidity.

The entries on the right side of equation 5.2 are thus known at least as to order of magnitude. $\dot{N}\Sigma M_i$ is calculated from the storage terms of K^+ and Mg^{+2} in Table 7 (Chapter 4) and from storage terms for Na^+ and Ca^{+2} based on an annual peat accumulation rate of 180 g/m^2 and metal concentrations determined on about one third of the samples of Appendix C. A hypothetical acid rain of pH 4.3 is assumed, and $Q_{SO_4^=}$ and $Q_{NO_3^-}$ are taken from Table 12. Equation 5.2 then becomes.

$$A = \{(1450\ \mathrm{l/m^2})(.05\ \mathrm{meq/l}) + (180\ \mathrm{g/m^2})(.06\ \mathrm{meq/g}) - 20\ \mathrm{meq/m^2} - 64\ \mathrm{meq/m^2}\}\ /280\ \mathrm{l/m^2} \qquad (5.3)$$

or:

$$A \approx \left(\frac{75 + 11 - 20 - 64}{280}\right)\frac{\mathrm{meq}}{\mathrm{l}} \qquad (5.4)$$

or:

$$A \approx .01\ \mathrm{meq/l}$$

It should be emphasized that this mineral acidity balance is approximate; its important features are the relatively modest size of the cation exchange term (the second term of equation 5.4) and the fact that mineral acidity is a relatively small difference between the larger terms representing acid precipitation (the first term) and biological processes (the third and fourth terms). Mineral acidity may thus be expected to undergo substantial fluctuations with changes in rain content or biological activity (the latter is certainly seasonal). Actual mineral acidities of bogwater, as determined from the pH of irradiated samples, have been observed as high as .03 meq/l and as low as -.002 (net alkalinity).

The mass balance of organic acids, given that all acids originate as a result of biological activity in the bog, is straightforward. The total concentration of weak acid in bogwater is approximately 1 meq/l; net weak acid production in the bog must equal wash out if bog chemistry is to be constant over time. Thus, the mass balance equation is:

Net organic acid production = (runoff rate)(concentration of organic acid) or:

$$\text{Net organic acid production/m}^2 = (280\ \text{l/m}^2)(1\ \text{meq/l})$$

Net annual organic acid production in the bog must, therefore, be about 300 meq/m^2, a value which is surprisingly close to the estimated decomposition rate of Sphagnum.

This latter value is simply the Sphagnum growth rate minus the net peat accumulation rate, expressed in equivalents of exchange capacity, and is about (460-180) g/m^2-yr x 1 meq/g ≈ 300 meq/m^2-yr. This suggests that much of the organic acid originates from the humification of Sphagnum moss, and that exchange capacity is little altered by the process.

The buffering of this theoretical bog system, containing only one year's production of peat and organic acids, is in some sense dominated by the acids. The resistance by the peat system to a lowering of pH is limited to the amount of metal that can be exchanged for H^+, or about 10 meq/m^2; while about 10% of 300 meq/m^2, or 30 meq/m^2 of re-association of organic acid may occur. The actual equilibrium established after an addition of titrant to the system is, of course, highly dependent on the metal make up of the system due to the selectivity of the peat.

In the actual bog, however, the theoretical system described here is in equilibrium with several hundred years' accumulation of peat, while acids are constantly being washed out. The resistance to pH change of this system following an addition of acid or base is a complex result of ion-exchange, weak acid dissociation or reassociation, and, on a longer time scale, biological activity. pH buffer capacity due to the weak acid system may be estimated from the slope of the dissociation curve (Figure

23). At a pH of 3.8, this slope gives a pH buffer capacity, β_H, of .15 (meq/l)/pH unit. At this same pH, the pH buffering capacity of the water alone is about .3 (meq/l)/pH unit.

The contribution of the peat to the pH buffering of the bog depends on the displacement of a complex, nonlinear system of equilibria between all cation species in the peat and cations in the aqueous phase. The buffering by the peat is also a function of the amount of peat present, which is approximately 50 grams per liter of bogwater. The pH buffering of this system may be roughly estimated from the Na^+ - H^+ exchange relationship discussed in Chapter 4 (Figure 10). From the slope of this curve, which is about .27 (meq/g)/pH unit at a pH of 3.8, the contribution of peat to the buffering of the bog system is of the order of .27 (meq/g)/pH unit x 50 g/l, or about 15 (meq/l)/pH unit. This is about two orders of magnitude greater than the buffer capacity of the weak acids alone.

The bog appears to be buffered by the biological system as well. This follows from the comparable magnitudes of the terms of equation 5.4 and inferences that may be made concerning the historical increase in the acidity of precipitation. For example, the bulk of the present annual input of sulfate to the bog is reduced biologically. Given substantially lower (perhaps order of magnitude lower) sulfate inputs, which must have occurred in pre-acid-rain times, it is clear from mass-balance considerations that annual sulfate reduction in the bog was once much lower than it is now. Thus, the bog has apparently reacted to the increased input of sulfuric acid by reducing much of the additional sulfate.

A similar argument can be made regarding nitrate. Although both nitrate and sulfate concentrations in precipitation are believed to have increased markedly as a result of industrialization, it appears that most of their influence, as acid rain on the bog, has been countered by corresponding increases in their biological transformation by the bog system.

In conclusion, it can be said that organic acids are responsible for maintaining the pH of the bog around 3.8, on a steady state basis. The peat provides the major buffering mechanism against a hypothetical addition of strong base or acid, although homeostatic biological processes have actually maintained the low mineral acidity of the bog in the face of an historical increase in strong acid inputs.

6 Mineral Nutrition of *Acer rubrum*

6.1 Introduction

The red maple (*Acer rubrum*) is the characteristic wetland tree of New England. Although it possesses an exceptional ecological amplitude, and may commonly be found on the upland, it is almost invariably a component of wetland vegetation and is frequently the dominant aboreal species in swamps and lowlands. It is considered particularly significant, therefore, that despite abundant germination of this species in Thoreau's Bog, red maple is not observed to grow beyond the seedling stage on the *Sphagnum* mat. It seems likely that the physiological and/or nutritional factors which inhibit red maple will be found to be the factors responsible for the sharp differentiation between bog vegetation and the vegetation of other lowlands.

The bog environment is unquestionably an oligotrophic environment, but it provides an adequate substrate for a number of plant species. It is unlikely that non-bog wetland species are excluded by a deficiency of all plant nutrients. Rather, one or a few necessary nutrients are likely to be deficient.

Classically, North American bogs are considered nitrogen-deficient. Small (1972a) has shown that the foliage of bog plants is generally lower in nitrogen and phosphorus than is the foliage of non-bog species, and has demonstrated (Small 1972b) that bog species, especially bog evergreens, are able to manufacture significantly more photosynthate per unit of acquired nitrogen or phosphorous than are the non-bog species tested. Watt and Heinselman (1965) have found good correlation between site index for black spruce and foliar nitrogen content in a Minnesota spruce bog, while finding no relationship between site quality and Mg, Cu, B, Zn, Mo, Al, or Na.

On the other hand, Goodman and Perkins (1968) found that additions of potassium had a greater effect on the growth of Eriophorum vaginatum on a lowland community than did either added nitrogen or phosphate.

The possibility exists, of course, that toxicity, perhaps of hydrogen ion, prevents the establishment of red maple on the bog surface. Stone (1944), however, found no correlation between soil pH and red maple distribution over the pH range of 3.5 to 6.9 on a variety of sites. The possibility of other toxicity phenomena in the bog has apparently not been investigated.

Mozuk and Livingstone (1966) have investigated the phenomenon of red maple exclusion from a central Massachusetts bog, and concluded that the mechanism of exclusion is nutritional. In a series of minus experiments on red maple seedlings grown in live Sphagnum and watered with -N, -K, -P, or complete Hoagland's solution, they found that comparable growth was achieved in the -K and complete series, while growth failure occurred in both the -P and the -N series.

None of the experiments to date has shown a relationship between the oligotrophic nature of the *Sphagnum* environment and the presence of *Sphagnum* per se. However, Heilman (1966) has described the deterioration of black spruce sites with the invasion of *Sphagnum* on the north slope of Alaska. This process of paludification is accompanied by a decrease in foliar nitrogen in the black spruce, and the ultimate conversion of the site to muskeg. While Heilman hypothesises that the thermal effects of *Sphagnum* reduce rates of mineralization and thus effect a nitrogen deficiency, it is also true that the water chemistry must be altered by the ion-exchange properties of *Sphagnum*. Possible nutritions deficiencies resulting from the exchange of trace metals for hydrogen ion have not been investigated.

In this investigation the question of limiting nutrients is addressed through a series of "minus" experiments, with red maple transplants growing in bogwater to which salts of all except one of the essential plant nutrients are added. Lack of growth in any series is evidence that the omitted element is deficient in the bog. Of course, interactions between nutrients exist both within the plant and the medium, and it is desirable to confirm the results of a "minus" experiment by obtaining growth of plants in the natural substrate with the addition of _only_ the limiting nutrient(s). This is done in a series of "plus" experiments in which only the elements found to be limiting in the "minus" experiment are added. A series of foliar spray applications is also made, although the foliar uptake of all plant nutrients is not established. Foliar spray applications of certain trace elements is, however, an established horticultural practice. Finally, since red maple has not been reported to have been grown in vitro at controlled low values of pH, an experiment is conducted to verify that pH per se is not limiting the growth of red maple under the acidic conditions of the _Sphagnum_ bog.

6.2 Materials and Methods

6.2.1 Equipment and Instrumentation

All plant material grown in the laboratory was maintained at ambient room temperature (about 20°C) under a combination of natural and artificial lighting. Artificial light was provided by a fixture, built by the author, which holds sixteen forty-watt fluorescent tubes about forty centimeters above an eight foot bench. An electromechanical timer provided the desired ON-OFF cycle. A moderate level of natural daylight was available through laboratory windows.

Seedlings were grown in new 250 ml polypropylene beakers, which were unpacked from their sealed container immediately prior to use. Each container was given a coat of flat black paint to exclude light. Plant holders were cut from 1/16" posterboard, slotted and punched to receive the stems of maple seedlings. pH adjustments were monitored with an Orion 407A pH meter and combination electrode.

6.2.2 Reagents

Media were based on the standard Long Ashton medium (Hewitt, 1975) and were prepared from analytical reagent grade chemicals. Certain stock solutions (tables 613 and 614) were prepared containing only one salt each, to facilitate the omission of any single element. Purified nitrate and phosphate stocks were prepared by stirring 100ml of 1.4M $NaNO_3$ solution or .16M NaH_2PO_4 solution with 1 g of washed 100 mesh Chelex ion-exchange resin (in the sodium form) and filtering through S&S #595 filter paper.

Foliar sprays were prepared as shown in tables 13 and 14.

Bogwater was collected in one batch from station 3 on August 8, 1976.

6.2.3 Plant Material

Red maple seedling transplants were pulled from the bog in June and in early August of 1976. Plastic gloves

TABLE 13

Major element stocks and solutions used in mineral nutrition experiments

	Major Elements (Molarity)								
Solution	KNO_3	$NaH_2PO_4 .H_2O$	$C{=}NO_3 .4H_2O$	$MgSO_4 .7H_2O$	$NaNO_3$	KCl	$CaCl_2 .2H_2O$	$MgCl_2$- $6H_2O$	Na_2SO_4
Long Ashton medium	10^{-3}	$1.2x10^{-3}$	$5.4x10^{-3}$	$1.5x10^{-3}$					
P only foliar spray		0.05							
N only foliar spray					1.0				
Nitrate stock					2.4				
Potassium stock						0.8			
Calcium stock							0.8		
Magnesium stock								0.19	
Sulfate stock									0.18
Phosphate stock		0.16							

TABLE 14

Trace element solutions used in mineral nutrition experiment

	Chemical (Molarity)						
Solution	H_3 BO_4	$CuSO_4$	NH_3MoO_4	$FeCl_3$	Na-cit.	$MnSO_4$	$ZnSO_4$
Boron stock	0.05M						
Copper stock		0.001M					
Molybdenum stock			0.0005M				
Iron stock				0.02M	0.02M		
Manganese stock						0.01M	
Zinc stock							0.001M
Cu foliar spray		0.0001M					
Cu + Zn foliar spray		0.0001M					0.0003M
Complete trace metal foliar spray	0.005M	0.0001M	0.00005M	0.002M	0.002M	0.001M	0.001M
Trace element component of Long Ashton medium	$5x10^{-5}M$	$10^{-6}M$	$5x10^{-7}M$	$10^{-4}M$	$10^{-4}M$	$10^{-5}M$	$10^{-6}M$

were worn to minimize contamination of the plants, which were stored in polyethylene bags partially filled with bogwater prior to use. For each experiment, plants were selected with respect to height and number of leaves to obtain a more uniform experimental population.

6.2.4 "Minus" Experiments

New polypropylene beakers were each filled with 250 ml of bogwater, and nutrient stocks were added as shown in Table 15. One element was omitted from each beaker, except for a series of "complete" controls and a series of "bogwater only" controls. Two concentrations were used, the "high" concentrations approximating Long Ashton medium and the "low" concentration approximating a 10 to 1 dilution of Long Ashton medium. Replicates were run for each concentration and each missing element. Transplant seedlings were then placed in the beakers and grown on a 16-8 light-dark cycle. Growth was measured in terms of height, number of new leaves, and color of leaves.

6.2.5 pH Tolerance

Two groups of five red maple transplant seedings were grown, one group in 1 liter of complete Long Ashton medium titrated to pH 3.6 with dilute HCl and the other in similar medium titrated to pH 4.2 with dilute HCl. Plants were grown in 16:8 light-dark cycle, and growth

TABLE 15

Nutrient additions to bogwater for each "minus" treatment
(high/low)

Treatment	NO_3 (mM)	K (mM)	Ca (mM)	Mg (mM)	SO_4 (mM)	PO_4 (mM)	F (uM)	Mn (uM)	Zn (uM)	Cu (uM)	B (uM)	Mo (uM)
Complete												
high	9.6	3.2	3.2	0.76	0.76	0.64	80	40	4.0	4.0	200	2.0
low	0.96	0.32	0.32	0.076	0.076	0.064	8	4	0.4	0.4	20	0.2
-N high	0.0	3.2	3.2	0.76	0.76	0.64	80	40	4.0	4.0	200	2.0
low	0.0	0.32	0.32	0.076	0.076	0.064	8	4	0.4	0.4	20	0.2
-K high	9.6	0.0	3.2	0.76	0.76	0.64	80	40	4.0	4.0	200	2.0
low	0.96	0.0	0.32	0.076	0.076	0.064	8	4	0.4	0.4	20	0.2
-Ca high	9.6	3.2	0.0	0.76	0.76	0.64	80	40	4.0	4.0	200	2.0
low	0.96	0.32	0.0	0.076	0.076	0.064	8	4	0.4	0.4	20	0.2
-Mg high	9.6	3.2	3.2	0.0	0.76	0.64	80	40	4.0	4.0	200	2.0
low	0.96	0.32	0.32	0.0	0.076	0.064	8	4	0.4	0.4	20	0.2
$-SO_4$ high	9.6	3.2	3.2	0.76	0.0	0.64	80	40	4.0	4.0	200	2.0
low	0.96	0.32	0.32	0.076	0.0	0.064	8	4	0.4	0.4	20	0.2
$-PO_4$ high	9.6	3.2	3.2	0.76	0.76	0.0	80	40	4.0	4.0	200	2.0
low	0.96	0.32	0.32	0.076	0.076	0.0	8	4	0.4	0.4	20	0.2
-Fe high	9.6	3.2	3.2	0.76	0.76	0.64	0	40	4.0	4.0	200	2.0
low	0.96	0.32	0.32	0.076	0.076	0.064	0	4	0.4	0.4	20	0.2
-Mn high	9.6	3.2	3.2	0.76	0.76	0.64	80	0	4.0	4.0	200	2.0
low	0.96	0.32	0.32	0.076	0.076	0.064	8	0	0.4	0.4	20	0.2
-Zn high	9.6	3.2	3.2	0.76	0.76	0.64	80	40	0.0	4.0	200	2.0
low	0.96	0.32	0.32	0.076	0.076	0.064	8	4	0.0	0.4	20	0.2
-Cu high	9.6	3.2	3.2	0.76	0.76	0.64	80	40	4.0	0.0	200	2.0
low	0.96	0.32	0.32	0.076	0.076	0.064	8	4	0.4	0.0	20	0.2
-B high	9.6	3.2	3.2	0.76	0.76	0.64	80	40	4.0	4.0	0	2.0
low	0.96	0.32	0.32	0.076	0.076	0.064	8	4	0.4	0.4	0	0.2
-Mo high	9.6	3.2	3.2	0.76	0.76	0.64	80	40	4.0	4.0	200	0.0
low	0.96	0.32	0.32	0.076	0.076	0.064	8	4	0.4	0.4	20	0.0
no additions	0	0	0	0	0	0	0	0	0	0	0	0

was measured by height, number of new leaves, color of leaves, and root system development.

6.2.6 "Plus" Experiments

"Plus" experiments were conducted in the same manner as "minus" experiments, except that two transplant seedlings were placed in each beaker, and the bogwater medium was modified only with purified nitrate stock, purified phosphate stock, or both. The +P treatments contained a .64mM concentration of added phosphate while the +N treatments contained a 9.6mM concentration of added nitrate.

6.2.7 Foliar Spray Experiments

Seven 1 x 1 meter quadrats were marked off near the center of the bog, using string and wooden stakes. Once a week, beginning on May 28, 1976, each red maple in each quadrat was sprayed with one or more foliar sprays according to the schedule in table 16. Each quadrat was observed throughout the summer for any indication of new growth or greener coloration on any of the red maple seedlings.

6.3 Results

The results of the foliar spray experiments failed to show any stimulation of red maple growth. The Sphagnum appeared to be burned in quadrats receiving the N treatment

TABLE 16

Foliar spray treatments applied to bog quadrats during Summer, 1976

Quadrat	Foliar spray				
	Cu	Cu+Zn	all trace metals	N only	P only
1	X				
2		X			
3			X		
4				X	
5					X
6				X	X
7			X	X	X

after several weeks of spraying, suggesting that Sphagnum is intolerant of even modest applications of fairly concentrated nitrate solutions. No stimulatory effects were noted on any plants in any of the treated areas.

All plants in the pH tolerance experiments grew well, and developed substantial root systems and new green foliage at both pH values. No significant differences were noted between the two groups.

The results of the "minus" experiments are summarized in table 17. The results indicate that both nitrate and phosphate must be added to the bogwater medium in order to obtain significant growth of A. rubrum seedlings under these experimental conditions. Plant growth under the -K treatment was poorer than under all but -P and -N treatments, and -K plants all developed a leaf fungus disease. However, the growth of plants under the -K treatment was much better than under the bogwater only treatment, indicating that potassium is not a limiting nutrient under these experimental conditions. As a rule, plants under the -trace element treatments grew well; the only possible deficiency symptom noted was in one of the -B high level treatments. This one plant developed abundant new foliage, but the leaves had a warped, twisted appearance. This symptom has not been observed in the field, however, and

Table 17

Results of "minus" experiments

<u>Acer</u> <u>rubrum</u> in supplemented bogwater media

Treatment	Height increase (cm)**	Pairs of new leaves **	Appearance of plants	
			(replicate 1)	(replicate 2)
-N high	0	0	-	-
-N low	0	0	-	-
-K high	0	0.5	-	++
-K low	0	1	+	+
-Ca high	5	2.5	++	++
-Ca low	1	2	+R	+R
-Mg high	5	3.5	++	++
-Mg low	1	2.5	++	++
-SO_4 high	3	3.5	++R	++R
-SO_4 low	3	2	++R	++R
-PO_4 high	0	0.5	+	-
-PO_4 low	0	0	-	-
-Fe high	15	5	+++	+++
-Fe low	2	1.5	++	+
-Mn high	2	1.5	++	-
-Mn low	2	3	++R	++R
-Zn high	18	5	+++	+++
-Zn low	3	1.5	++	+
-Cu high	16	5	+++	+++
-Cu low	4	2	++	++
-B high	5	4	++	+*
-B low	5	3	++R	++
-Mo high	2	3	++	-
-Mo low	3	3	++R	+
high	5	5	+++	-
low	2	2	++	++
control	0	0	-	-
control	0	0	-	-

+++ vigorous growth ++ moderate growth + slight growth

- no sign of growth R red foliage *see text

**mean for 2 plants

boron is not considered to be a limiting nutrient on the basis of these experiments. It is also noted that the high-level treatments, in general, produce more growth than do the low-level treatments, although plant vigor under the latter conditions is dramatically greater than is observed in the field.

Results of the "plus" experiments were less clear-cut. None of the +P only or +N only plants showed any signs of growth, and leaves retained the reddish color of plants receiving no nutrient treatment at all. Plants receiving the N+P treatment had green leaves, and one of the six plants grew a new pair of leaves. Results of this experiment are not conclusive, possibly because the experiment was conducted with transplant seedlings which had been maintained indoors in bogwater for four weeks before the experiment was begun. Furthermore, on the date on which the experiments were begun, _A_. _rubrum_ seedlings in the bog had already begun to enter dormancy. Thus, loss of vigor due to prolonged storage, or possible dormancy effects, may have reduced the ability of _A_. _rubrum_ to respond to any nutritional treatment.

6.4. Discussion of Results

The results of this limited investigation of red maple nutrition are not considered conclusive, although they strongly support the view that neither nitrogen nor phosphorous are adequately available to red maple in the bog environment. The possibility that one or more elements present as a trace contaminant in the chemicals used could play a significant role still exists. More conclusive results of the "plus" experiments, which employed purified chemcials, would have minimized this possibility, and the plus experiments are thus being repeated. Failure of +N and +P foliar sprays to stimulate the growth of red maple in situ are not conclusive due to the uncertainty regarding foliar applications of nitrate or phosphate and their availability to red maple.

The finding that ammonium ion is present in the bog at relatively high levels (in comparison with other elements) adds another dimension to the question, inasmuch as most higher plants are able to utilize ammonium nitrogen. The possibility exists that red maple is simply unable to take up ammonium ion from the bog substate, particularly in the presence of a high hydrogen ion concentration. It may be that the bog processes of ammonification and acidification taken together may be of major significance in excluding many swamp species. Phosphorous deficiency in the bog may be in part related to nitrogen deficiency, since an adequate level of either of these elements is known to facilitate uptake of the other (Salisbury and

Ross, 1969). Knowledge of the nutritional requirements of red maple is essential to address these questions. In particular, nitrogen uptake as a function of form of nitrogen, concentration of nitrogen, pH, and phosphate concentration of the medium must be investigated.

7. Conclusions: Directions for Further Research

The results of these investigations shed some light on the nature and role of the Sphagnum bog as a feature of the central and southern New England landscape. Hydrologically, Thoreau's Bog and, by implication, similar bogs in this region appear to be rather unique. Due to the very high rates of evapotranspiration from the bog surface, annual water loss per unit bog area by this mechanism approaches the depth of annual precipitation. Thoreau's Bog appears to owe its existence to a surprisingly tight basin which restricts runoff and seepage, and a hummocky border area which augments the annual rainfall with a small amount of runoff. Much increase in water loss could destroy the bog. On the other hand, augmentation of water input through runoff could threaten the oligotrophic nature of the bog and lead to the invasion of swamp vegetation. These factors may combine to restrict bogs to special basin situations in southern and central New England. To the north, a decrease in annual evapotranspiration may be responsible for the appearance of raised bogs, while in warmer, more southern locations floating-mat bogs essentially disappear. This hypothesis concerning the hydrological restrictions of raised and floating mat Sphagnum bogs is subject to testing and warrants further area-extensive investigation of Sphagnum bogs and their water budgets.

Within the established floating-mat bog, the major biogeochemical role of Sphagnum appears to be the retention of metallic cations. The exchange properties of moss and peat vary widely from metal to metal, and control of metal movement through the bog system may be dominated by either hydrological or chemical considerations. Lead (and apparently many other divalent or trivalent transition elements) is bound so strongly to both live Sphagnum and peat that its mobility in the bog is nearly nil, and almost all of it is retained. Magnesium is intermediate in that about 50% of the annual input to the bog is retained. Potassium, at the other extreme, is relatively weakly held and its concentration in the bog appears to be determined more by hydrological considerations.

Potassium, however, is concentrated in the small layer of living mass at the bog surface, while other elements are not so concentrated by the metabolic activity of moss. Thus the actual distribution of potassium in the bog is significantly affected by biological activity. Other elements, such as magnesium, are vertically distributed in apparent accord with the gradually changing cation exchange chemistry of peat as it undergoes humification. In the case of lead, mobility in the bog is so slight that the vertical concentration profile reflects the history of lead deposition in the bog.

This immobility of lead provides a basis for accurately dating the peat accumulation, which appears to be exceptionally rapid. Not only does this rapid accumulation form the basis of a large metal storage term in the metal budget; it also has implications for the development of the bog under present climatic conditions in New England. The rapid rate of peat accumulation is entirely incompatible with the traditional view that the bog is a relic of the last glacial period, its vegetation having become established during the cold climatic conditions prevailing behind the retreating glaciers. Thoreau's Bog is apparently less than a thousand years old, and its plant community must have become established under climatic conditions similar to those prevailing today. Thus, significant migration of the bog flora must have occurred in the recent past, and may be continuing today. As a modern process, bog formation is not generally recognized in central New England; yet, the evidence suggests that under the right conditions a <u>Sphagnum</u> mat can form and the members of the bog association can immigrate from tiny islands dozens of miles away or from larger areas hundreds of miles to the north. Research, from the viewpoint of plant geography, is needed to support this hypothesis. Datings from other bogs, and corroborating evidence from peat profiles, is also needed.

The low pH of the bog is largely the result of organic acids whose origin is not clear, although direct release from *Sphagnum* or release during the humification of *Sphagnum* must be involved. The rate of release is substantial and is comparable to annual rates of peat accumulations when expressed on an equivalent basis. The organic acids are also a significant factor in metal speciation in the bog. Other mechanisms which are significant, but not dominant in determining bog pH are cation exchange, uptake or reduction of anionic species, and acid rain.

Within the bog, the exact nature of plant competition is still not clear, although it is apparent that nutrients are the most limiting resource. Certainly the well-defined group of plants which comprise the bog association will be found to have special adaptations to the bog substrate, while other wetland plants do not. The general view that nitrogen and phosphorous are critical limiting elements seems to be substantiated, although much more work is needed to ascertain the mechanisms involved. As yet, neither organic acids nor ion exchange appear to play a direct role in nutritional deficiency in the bog. However, evidence that most of the nitrogen is present as ammonium may prove to be significant at the low pH of the bog.

BIBLIOGRAPHY

Air Survey Corp. 1960. Photogrammetry of the town of Concord, Massachusetts. On file with the Department of Public Works, Concord, Massachusetts.

André, J.P. 1976. Les propriétés d' échangeur cationique de la tourbe de sphaignes: échanges bicationiques entre le proton et un cation métallique. Ann. Agron. 27(1): 17-31.

Anschütz, I., and F. Gebner. 1954. Der Ionenaustauch bei Torfmoosen (*Sphagnum*). Flora (Jena) 141: 178-236.

Armstrong, F.A.J., P.M. Williams, and J.D.H. Strickland. 1966. Photo-oxidation of organic matter in sea water by ultra-violet radiation, analytical and other applications. Nature 211: 481-483.

Baas-Becking, L.G.M., and E. Nicolai. 1934. The ecology of a *Sphagnum* bog. Blumea 1: 10-44.

Baas-Becking, L.G.M., I.R. Kaplan, and D. Moore. 1960. Limits of the natural environment in terms of pH and oxidation-reduction potentials. J. Geol. 68: 243-284.

Bacon, M. 1975. Ph.D. thesis, Joint MIT-Woods Hole Oceanographic Institution Program in Oceanography.

Barrett, E., and G. Brodin. 1955. The acidity of Scandinavian precipitation. Tellus 7: 251-257.

Barsdate, R.J., and W.R. Matson. Trace metals in arctic and sub-arctic lakes with reference to the organic complexes of metals. Unpublished.

Bell, P.R. 1959. The ability of Sphagnum to adsorb cations preferentially from dilute solutions resembling natural waters. J. Ecol. 47: 351.

Boatman, D.J., and R.W. Tomlinson. 1973. The Silver Flowe. I. Some structural and hydrological features of Brishie Bog and their bearing on pool formation. J. Ecol. 61: 653-666.

Boelter, D.H. 1964. Hydraulic conductivity of peats. Soil Sci. 100(4): 227-231.

Brehm, K. 1975. Mineralstoffernahrung und Kationenaustausch auf Hochmooren. Biol. Unserer Zeit. 5(3): 85-91.

Brodin, G. 1955. Current data on the chemical composition of Air and precipitation III. Tellus 7(3): 395-400.

Buell, F., and H. Buell. 1941. Surface level fluctuation in Cedar Creek bog, Minnesota. Ecology 22: 317-321.

Coupal, B., and J. Lalancette. The treatment of waste waters with peat moss. Université de Sherbrooke. Unpublished.

Craigie, J.S. and W.S.G. Maass. 1966. The cation-exchanger in Sphagnum spp. Ann. Bot. (N.S.) 30: 153-154.

Crozaz, G., E. Picciotto, and W. DeBrueck. 1964. Antarctic snow chronology with Pb^{210}. J. G.R. 69(12): 2597-2604.

Clymo, R.S. 1963. Ion exchange in Sphagnum and its relation to bog ecology. Ann. Bot. N.S. 27(106): 309-323.

Clymo, R.S. 1964. The origin of acidity in Sphagnum bogs. The Bryologist 67: 427-431.

Dachnowski, A.P. 1924. The stratigraphic study of peat deposits. Soil. Sci. 17: 107-133.

Dansereau, P., and F. Segadas-Vianna. 1952. Ecological study of the peat bogs of eastern North America. I. Structure and evolution of vegetation. Can. J. Bot. 30: 490-520.

Deevey, E.S., Jr. 1958. Bogs. Sci. Am. 199(4): 114-122.

Devaux, H. 1916. Action rapide des solutions salines sur les plantes vivantes: déplacement réversible d'une partie des substances basiques contenues dans la plante. Comptes Rendus 162: 561-563.

Downie, N.M., and R.W. Heath. 1965. Basic statistical methods. 2nd ed. Harper and Row, New York.

Eagleson, P. 1970. Dynamic Hydrology. McGraw-Hill, New York.

Eaton, R. 1969. Gowings Swamp. Conn. Conservationist: June, 1969.

Egner, H., and E. Eriksson. 1955. Current data on the chemical composition of air and precipitation. Tellus 7: 134-138.

Farrington, J.W., S.M. Henrichs, and R. Anderson. 1977. Fatty acids and Pb-210 geochronology of a sediment core from Buzzards Bay, Massachusetts. Geochim. Cosmochim. Acta 41: 289-296.

Flynn, W.W. 1968. The determination of low levels of Polonium-210 in environmental materials. Anal. Chim. Acta 43: 221-227.

Gambell, A.W., and D.W. Fisher. 1964. Occurrence of sulfate and nitrate in rainfall. J.G.R. 69(20): 4203-4210.

Gates, F.C. 1942. The bogs of northern Lower Michigan. Ecol. Monogr. 12: 213-254.

Gies, T., and W. Lötschert. 1973. Investigations on the cation-content in a bog. II. Seasonal changes and influence of the *Sphagnum* vegetation. Flora 162: 244-268.

Goodman, G.T., and D.F. Perkins. 1968. The role of mineral nutrients in *Eriophorum* communities. III. Growth response to added inorganic elements in two *E. vaginatum* communities. J. Ecol. 56(3): 667-683.

Gore, A.J.P., and S.E. Allen. 1956. Measurement of exchangable and total cation content for H^+, Na^+, K^+, Mg^{++}, Ca^{++}, and iron, in high level blanket peat. Oikos 7: 48-55.

Gorham, E. 1950. Variation in some chemical conditions along the borders of a Carex lasiocarpa fen community. Oikos 2(2): 217-240.

Gorham, E. 1955. On the acidity and salinity of rain. Geochim & Cosmochim Acta 7: 231-239.

Gorham, E. 1956. On the chemical composition of some waters from the Moor House Nature Reserve. Jour. Ecol. 44: 375-382.

Gorham, E. 1957. The development of peatlands. Quart. Rev. Biol. 32: 145-166.

Gorham, E. 1967. Some chemical aspects of wetland ecology. 12th Ann. Muskeg. Res. Conf. Proc. Tech. Mem. 90, N.R.C. Assoc. Comm. on Geotechnical Res. pp. 20-38.

Heilman, P.E. 1966. Change in distribution and availability of nitrogen with forest succession on north slopes in interior Alaska. Ecology 47: 825-831.

Heinselman, M.L. 1963. Forest sites, bog processes, and peatland types in the Glacial Lake Agassiz region, Minnesota. Ecol. Monog. 33(4): 327-374.

Heinselman, M.J. 1970. Landscape evolution, peatland types, and the environment in the Lake Agassiz Peatlands Natural Area, Minnesota. Ecol. Mon. 40: 235-261.

Helfferich, F. 1962. Ion Exchange. McGraw-Hill, New York.

Hewitt, E.J., and T.A. Smith. 1964. Plant Mineral Nutrition. John Wiley and Sons, New York.

Hofstetter, R.H. 1963. Some observations on the permeability properties of peat. Proc. 9th Musk. Res. Conf. Tech. Mem. No. 81. pp. 195-204.

Interdisciplinary Environmental Planning. 1976. Concord Wetland Survey. On file with the town of Concord, Massachusetts.

Koenings, J.P. 1976. In situ experiments on the dissolved and colloidal state of iron in an acid bog lake. L.O. 21(5): 674-683.

Koide, M., A. Soutar, and E.D. Goldberg. 1972. Marine Geochronology with ^{210}Pb. Earth Plan. Sci. Letters 14: 442-446.

Koteff, C. 1964. Surficial geology of the Concord quadrangle, Massachusetts. U.S. Geological Survey, Washington.

Lazrus, A.L., E. Lorange, and J.P. Lodge, Jr.. 1970. Lead and other metal ions in United States precipitation. Env. Sci. & Tech. 4(1): 55-58.

Likens, G.E., N.M. Johnson, J.N. Galloway, and F.H. Bormann. Acid precipitation: strong and weak acids. Science 194: 643-645.

Lotschert, W., and T. Gies. 1973. Untersuchungen über den Kationengehalt im Hochmoor. I. Abstufungen in den Vegetations Komplexen. Flora 162: 215-243.

Lowe, J., III. 1969. Embankment dams. In Handbook of Applied Hydraulics. C.V. Davis and K.E. Sorensoen, eds. McGraw-Hill, New York.

McCaffrey, R.J., and J. Thomson. A record of trace metal fluxes to a Connecticut salt marsh as determined by Pb^{210} dating. Unpublished.

McComas, M.R., J.P. Kempton, and K.C. Hinkley. 1972. Geology, soils, and hydrogeology of Volo Bog and vicinity, Lake County, Illinois. Illinois State Geological Survey, Urbana, Illinois.

Miller, E.G. 1965. Effect of Great Swamp, New Jersey, on streamflow during base-flow periods. U.S. Geol. Survey Prof. Paper 525-B, pp. B177-B179.

Moizuk, G.A., and R.B. Livingston. 1966. Ecology of red maple (Acer rubrum L.) in a Massachusetts upland bog. Ecology 47: 942-950.

Moore, P.D., and D.J. Bellamy. 1974. Peatlands. Springer-Verlag, New York.

Niering, W.A. 1953. The past and present vegetation of High Point State Park, New Jersey. Ecol. Monog. 23: 127-148.

O'Brien, A. 1973. Hydrological investigations of two wetlands in Lincoln, Massachusetts. Ph.D. thesis. Boston University, Department of Geology.

Orion Research. 1975. Analytical methods guide. Orion Research, Inc., Cambridge, Massachusetts.

Pearson, F.J., Jr., and D.W. Fisher. 1971. Chemical composition of atmospheric precipitation in the northeastern United States. USGS Water Supply Paper 1535-P.

Puustjärvi, V. 1955. On the factors resulting in uneven growth on reclaimed treeless fen soil. Acta. Agric. Scandinavica 6: 45-63.

Puustjärvi, V. 1959. On the cation uptake mechanism of Sphagnum mosses. J. Sci. Agric. Soc. Finland 31: 103-109.

Ramaut, J. 1954. Modification de pH apportées par la tourbe et le Sphagnum sec aux solutions salines et á l'eau bidistillée. Acad. Roy. Belg. Bull. Sci. Sér. 5, 40: 305-319.

Ramaut, J. 1955. Extraction et purification de l'un des produits responsables de l'acidite des eaux des Hautes tourbieres et sécreté par Sphagnum. Ebenda 5: 41, 1168-1199.

Ramaut, J. 1955. Etude de l'origine de l'acidité naturelle des tourbiéres acide de la Baraque Michel. Ebenda 5: 41, 1037-1052.

Rathsack, K., und A. Jungk. 1964. Über die Puffering und Kationensorption von Torf. Z.f. Pflanzenernähr., Dung., Bodenk. 104: 194-205.

Rigg, G.B. 1940. The development of *Sphagnum* bogs in North America. Botan. Rev. 6: 666-693.

Salisbury, F.B., and C. Ross. 1969. Plant Physiology. Wadsworth Publ. Co., Belmont, California.

Schwarzmaier, U., and K. Brehm. 1974. Detailed characterization of the cation exchanger in *Sphagnum magellanicum* Brid. Z. Pflanzenphysiol. 75: 250-255.

Shapiro, J. 1957. Chemical and biological studies on the yellow organic acids of lake water. L.O. 2: 161-179.

Small, E. 1972a. Ecological significance of four critical elements in plants of raised *Sphagnum* peat bogs. Ecology 53: 498-503.

Small, E. 1972b. Photosynthetic rates in relation to nitrogen recycling as an adaptation to nutrient deficiency in peat bogs. Can. J. Bot. 50: 2227-2233.

Small, E. 1972c. Water relations of plants in raised *Sphagnum* peat bogs. Ecology 53: 726-728.

Stanek, W., J.K. Jeglum, and L. Orloci. 1977. Comparisons of peatland types using macro-nutrient contents of peat. Vegetatio 33: 163-173.

Stone, M.H. 1944. Soil reaction in relation to distribution of natural plant species. Ecology 25: 379-386.

Sparling, J.H. 1966. Studies on the relationship between water movement and water chemistry in mires. Can. J. Bot. 44: 747-758.

Swan, J.M.A., and A.M. Grill. 1970. The origins, spread, and consolidation of a floating bog in Harvard Pond, Petersham, Massachusetts. Ecology 51: 829-840.

Taras, M.J., A.E. Greenberg, R.D. Hoak, and M.C. Rand, eds. 1971. Standard methods for the examination of water and wastewater. 13th ed. American Public Health Association, Washington, D.C.

Theander, O. 1954. Studies on Sphagnum peat III. A quantitative study of the carbohydrate constituents of Sphagnum mosses and Sphagnum peat. Acta Chim. Scand. 8: 989-1000.

Thoreau, H.D. 1854. Journal VI. In: The Writings of Henry David Thoreau; Journal, Bradford Torrey ed. Houghton Mifflin and Co., Boston, 1906.

Thoreau, H.D. 1858. Journal X. In: The Writings of Henry David Thoreau; Journal, Bradford Torrey ed. Houghton Mifflin and Co., Boston, 1906.

Thoreau, H.D. 1860. Journal XIII. In: The Writings of Henry David Thoreau; Journal, Bradford Torrey ed. Houghton Mifflin and Co., Boston, 1906.

Transeau, E.N. 1903. On the geographic distribution and ecological relations of the bog plant societies of northern North America. Bog. Gaz. 36: 401-420.

Turner, J. 1964. The anthropogenic factor in vegetational history. I. Tregaron and Whixall mosses. New Phytol. 63: 63-73.

U.S. Department of the Interior, Bureau of Reclamation. 1968. Earth Manual. USGPO, Washington.

USGS. 1970. Concord quadrangle, 7.5 minute series. U.S. Geological Survey, Washington.

Watt, R.F., and M.L. Heinselman. 1965. Foliar nitrogen and phosphorus level related to site quality in a northern Minnesota spruce bog. Ecology 46: 357-361.

West, R. 1968. Pleistocene biology and geology. Wiley, New York.

Williams, K.T., and T.G. Thompson. 1936. Experiments on the effect of *Sphagnum* on the pH of salt solutions. Int. Revue. Hydrobiol. und Hydrographie 33: 271-275.

Wilson, D.E., and P. Kinney. 1977. Effects of polymeric charge variations on the proton-metal ion equilibria of humic materials. L.O. 22(2): 281-289.

Yefimov, V.N., and Z.S. Yefimova. 1973. Chemical composition of bogwater in the northwestern part of the European USSR. Pochvovedeniye 11: 27-36. (Translation)

Appendix A *

Daily Hydrologic Budget

April 1976

Date	Stage	Runoff	Precipitation	Net Change
16				
17	-.01	.002	0	-.072
18	-.03	.002	0	-.072
19	-.04	.001	0	-.072
20	-.05	.001	0	-.072
21	-.07	.001	0	-.072
22	-.08	.001	.017	+.017
23	-.07	.001	0	-.004
24	-.08	.001	0	-.007
25	-.05	.001	.057	+.055
26	+.02	.002	.037	+.034
27	+.02	.002	.010	-.003
28	+.01	.002	.005	-.007
29	+.01	.002	0	-.013
30	-.01	.002	0	-.012
TOTAL	0	.021	.126	
EVAPOTRANSPIRATION =				.105

* all data in feet

Daily Hydrologic Budget

May 1976

Date	Stage	Runoff	Precipitation	Net Change
1	-.02	.002	.023	+.020
2	+.03	.002	.023	+.021
3	+.02	.002	0	-.005
4	+.01	.002	0	-.013
5	.00	.002	0	-.012
6	-.01	.002	0	-.013
7	-.04	.001	0	-.009
8	-.02	.002	0	-.002
9	-.03	.002	0	-.009
10	-.04	.001	0	-.012
11	-.05	.001	0	-.013
12	-.04	.001	.034	+.033
13	-.04	.001	0	-.012
14	-.05	.001	0	-.017
15	-.05	.001	0	-.008
16	-.07	.001	0	-.015
17	-.07	.001	.015	+.015
18	-.06	.001	.001	0
19	-.06	.001	0	-.002
20	-.06	.001	0	-.002
21	-.05	.001	.044	+.035
22	-.03	.002	0	-.007
23	-.04	.001	0	-.005
24	-.06	.001	0	-.012
25	-.07	.001	0	-.013
26	-.08	.001	0	-.009
27	-.09	.001	0	-.013
28	-.11	.001	0	-.021
29	-.12	.001	0	-.011
30	-.13	.001	0	-.007
31	-.14	.001	0	-.014
TOTAL	-.12	.040	.140	
EVAPOTRANSPIRATION=				.220

Daily Hydrologic Budget

June 1976

Date	Stage	Runoff	Precipitation	Net Change
1	-.15	.001	.014	0
2	-.15	.001	.004	-.006
3	-.16	.001	0	-.017
4	-.18	.001	0	-.026
5	-.21	.001	0	-.013
6	-.22	.001	0	-.007
7	-.23	.001	0	-.006
8	-.24	.001	0	-.017
9	-.25	.001	0	-.029
10	-.28	.001	0	-.020
11	-.30	.001	0	-.007
12	-.32	.001	0	-.034
13	-.34	.001	0	-.017
14	-.36	.001	0	-.017
15	-.38	.001	0	-.020
16	-.40	.001	0	-.025
17	-.42	0	.001	-.014
18	-.44	0	0	-.017
19	-.46	0	0	-.017
20	-.48	0	0	-.020
21	-.50	0	0	-.028
22	-.53	0	0	-.027
23	-.56	0	0	-.024
24	-.58	0	0	-.024
25	-.61	0	.004	-.023
26	-.64	0	0	-.029
27	-.66	0	0	-.011
28	-.68	0	0	-.028
29	-.69	0	.009	-.007
30	-.65	0	.109	+.109
TOTAL	-.50	.016	.141	
EVAPOTRANSPIRATION=				.625

Daily Hydrologic Budget

July 1976

Date	Stage	Runoff	Precipitation	Net Change
1	-.60	0	0	-.019
2	-.62	0	0	-.035
3	-.66	0	0	-.025
4	-.68	0	0	-.023
5	-.71	0	0	-.027
6	-.74	0	0	-.023
7	-.76	0	0	-.018
8	-.78	0	0	-.022
9	-.80	0	0	-.025
10	-.81	0	0	-.025
11	-.88	0	.032	+.004
12	-.80	0	.139	+.118
13	-.77	0	0	-.043
14	-.80	0	.007	-.015
15	-.83	0	0	-.030
16	-.86	0	0	-.031
17	-.88	0	.012	-.024
18	-.92	0	0	-.035
19	-.96	0	0	-.035
20	-.99	0	0	-.031
21	-.92	0	.202	+.197
22	-.83	0	0	-.059
23	-.88	0	.006	-.035
24	-.78	0	.212	+.170
25	-.76	0	0	-.043
26	-.79	0	0	-.041
27	-.82	0	0	-.025
28	-.85	0	0	-.033
29	-.88	0	.046	+.028
30	-.78	0	.198	+.195
31	-.67	0	0	-.019
TOTAL	-.07	0	.854	
EVAPOTRANSPIRATION=				.924

Daily Hydrologic Budget

August 1976

Date	Stage	Runoff	Precipitation	Net Change
1	-.64	0	.073	+.068
2	-.63	0	0	-.042
3	-.67	0	0	-.035
4	-.70	0	0	-.027
5	-.73	0	0	-.025
6	-.75	0	.026	+.011
7	-.69	0	.088	+.085
8	-.65	0	.087	+.084
9	-.53	0	.080	+.070
10		0	.009	0
11		0	0	0
12		0	0	0
13		0	.013	0
14	-.50	0	0	-.022
15	-.43	0	.093	+.073
16	-.45	0	0	-.028
17	-.48	0	0	-.031
18	-.50	0	0	-.029
19	-.53	0	0	-.024
20	-.55	0	0	-.018
21	-.57	0	0	-.022
22		0	│	│
23		0	│	│
24		0	│	│
25		0	│	│
26		0	.150	+.072
27		0	│	│
28		0	│	│
29		0	│	│
30	-.51	0	│	│
31	-.52	0	0	-.022
TOTAL	+.12	0	.619	
EVAPOTRANSPIRATION=				.499

Daily Hydrologic Budget

September 1976

Date	Stage	Runoff	Precipitation	Net Change
1	-.55	0	0	-.028
2	-.55	0	.070	+.070
3	-.50	0	0	-.010
4	-.51	0	0	-.016
5	-.51	0	.014	+.009
6	-.53	0	0	-.023
7	-.54	0	0	-.014
8	-.55	0	0	-.015
9	-.56	0	0	-.017
10	-.57	0	.088	+.087
11	-.50	0	.003	-.025
12	-.53	0	0	-.045
13	-.55	0	0	-.016
14	-.57	0	0	-.011
15	-.58	0	0	.012
16	-.60	0	0	-.012
17	-.59	0	.026	+.026
18	-.57	0	.047	+.036
19	-.57	0	0	-.020
20	-.57	0	.001	-.011
21	-.57	0	.002	-.002
22	-.58	0	0	-.024
23	-.61	0	0	-.023
24	-.63	0	0	-.020
25	-.65	0	0	-.022
26	-.67	0	.007	-.001
27	-.66	0	.020	+.016
28	-.66	0	.003	-.015
29	-.67	0	0	-.011
30	-.68	0	0	-.014
TOTAL	-.130	0	.281	
EVAPOTRANSPIRATION=				.411

Daily Hydrologic Budget

October 1976

Date	Stage	Runoff	Precipitation	Net Change
1	-.70	0	0	-.007
2	-.70	0	0	-.003
3	-.70	0	0	-.015
4	-.72	0	0	-.017
5	-.73	0	0	-.002
6	-.73	0	0	-.002
7	-.74	0	0	-.011
8	-.75	0	0	-.004
9	-.60	0	.265	+.256
10	-.50	0	0	-.035
11		0	0	-.080
12		0	0	-.080
13		0	0	-.080
14		0	.010	-.080
15		0	0	-.080
16	-.60	0	0	-.080
17	-.61	0	0	-.008
18	-.62	0	0	-.011
19	-.63	0	0	-.009
20	-.50	0	.132	+.126
21	-.39	.001	.132	+.121
22	-.40	.001	0	-.016
23	-.42	0	0	-.018
24	-.44	0	.024	-.002
25	-.41	.001	.009	+.008
26	-.38	.001	.043	+.040
27	-.38	.001	0	-.012
28	-.39	.001	0	-.007
29	-.39	.001	0	-.007
30	-.40	.001	0	-.007
31	-.40	.001	.014	+.014
TOTAL	+.30	.009	.629	
EVAPOTRANSPIRATION=				.320

Daily Hydrologic Budget

November 1976

Date	Stage	Runoff	Precipitation	Net Change
1	-.39	.001	0	-.011
2	-.40	.001	0	-.011
3	-.41	.001	0	-.007
4	-.41	.001	0	-.003
5	-.42	0	0	-.003
6	-.43	0	.001	-.008
7	-.43	0	0	-.006
8	-.44	0	0	-.005
9	-.44	0	0	+.011
10	-.45	0	.034	+.011
11	-.45	0	0	-.006
12	-.46	0	.001	-.006
13	-.47	0	.001	-.008
14	-.47	0	.004	-.004
15	-.48	0	0	-.005
16	-.48	0	.001	-.007
17	-.49	0	.001	-.004
18	-.49	0	.006	+.003
19	-.49	0	.003	-.004
20	-.50	0	0	-.006
21	-.51	0	0	-.007
22	-.52	0	0	-.017
23	-.53	0	0	-.006
24	-.53	0	0	-.006
25	-.54	0	0	-.008
26	-.54	0	.006	+.001
27	-.54	0	.006	+.005
28	-.54	0	0	-.003
29	-.51	0	.027	+.023
30	-.52	0	.001	-.005
TOTAL	-.130	.004	.092	
EVAPOTRANSPIRATION=				.218

Daily Hydrologic Budget

December 1976

Date	Stage	Runoff	Precipitation	Net Change
1	-.52	0	.001	0
2	-.53	0	0	-.004
3	-.53	0	0	0
4	-.53	0	0	0
TOTAL	-.010	0	.001	
EVAPOTRANSPIRATION=				.010

Daily Hydrologic Budget

March 1977

Date	Stage	Runoff	Precipitation	Net Change
16	+.28	.002	0	-.007
17	+.27	.002	0	-.013
18	+.26	.002	.016	+.016
19	+.28	.002	.016	+.016
20	+.29	.002	.002	+.002
21	+.29	.002	.002	+.002
22	+.32	.002	.187	+.183
23	+.50	.011	.037	+.029
24	+.49	.010	0	-.011
25	+.48	.009	0	-.033
26	+.46	.008	0	-.033
27	+.45	.008	0	-.011
28	+.43	.007	.014	0
29	+.45	.008	.019	+.007
30	+.44	.007	0	-.015
31	+.41	.005	.001	-.017
TOTAL	+.13	+.087	.294	
EVAPOTRANSPIRATION=				.077

Daily Hydrologic Budget

April 1977

Date	Stage	Runoff	Precipitation	Net Change
1	+.41	.005	0	-.018
2	+.40	.005	.016	+.002
3	+.41	.005	.005	-.012
4	+.39	.004	0	-.012
5	+.46	.008	.118	+.102
6	+.48	.009	.001	-.017
7	+.47	.009	.002	-.014
8	+.46	.008	.008	-.010
9	+.44	.007	0	-.012
10	+.43	.007	0	-.013
11	+.42	.006	0	-.014
12	+.41	.005	0	-.015
13	+.39	.004	0	-.009
14	+.38	.004	0	-.017
15	+.37	.003	0	-.013
16	+.35	.002	0	-.012
17	+.33	.002	0	-.017
18	+.32	.002	0	-.009
19	+.31	.002	0	-.006
20	+.30	.002	0	-.020
21	+.28	.002	0	-.010
22	+.27	.002	0	-.008
23	+.33	.002	.129	+.127
24	+.46	.008	.166	+.158
25	+.55	.013	.006	-.007
26	+.54	.013	0	-.016
27	+.53	.012	0	-.012
28	+.52	.012	0	-.019
29	+.50	.011	0	-.021
30	+.47	.009	0	-.016
TOTAL	+.06	.183	.451	
EVAPOTRANSPIRATION=				.208

Daily Hydrologic Budget

May 1977

Date	Stage	Runoff	Precipitation	Net Change
1	+.46	.009	0	-.015
2	+.45	.009	0	-.008
3	+.43	.007	-	-.017
4	+.42	.006	-	-.012
5	+.41	.005	.005	0
6	+.41	.005	0	-.007
7	+.39	.004	0	-.016
8	+.38	.004	0	-.013
9	+.46	.008	.149	+.140
10	+.60	.016	.150	+.131
11	+.64	.018	.015	+.001
12	+.63	.018	0	-.020
13	+.61	.017	0	-.025
14	+.58	.015	0	-.023
15	+.56	.014	0	-.020
16	+.54	.013	0	-.019
17	+.52	.012	0	-.018
18	+.51	.011	.023	+.009
19	+.51	.011	0	-.009
20	+.50	.011	0	-.018
21	+.49	.010	0	-.013
22	+.47	.009	0	-.017
23	+.45	.008	0	-.018
24	+.44	.007	0	-.013
25	+.42	.006	0	-.016
26	+.40	.005	0	-.021
27	+.38	.004	0	-.018
28	+.36	.003	0	-.024
29	+.33	.002	0	-.020
20	+.32	.002	0	-.017
31	+.31	.002	0	-.015
TOTAL	-.15	.269	.342	
EVAPOTRANSPIRATION =				.223

Daily Hydrologic Budget

June 1977

Date	Stage	Runoff	Precipitation	Net Change
1	+.30	.002	+.006	-.009
2	+.30	.002	+.003	0
3	+.29	.002	0	-.018
4	+.27	.002	0	-.017
5	+.26	.002	0	-.013
6	+.24	.002	0	-.017
7	+.24	.002	+.019	+.019
8	+.25	.002	+.005	-.006
9	+.24	.002	0	-.010
10	+.23	.002	+.027	+.020
11	+.25	.002	+.119	+.117
12	+.30	.002	0	-.011
13	+.28	.002	0	-.016
14	+.27	.002	0	-.014
15	+.25	.002	0	-.017
16	+.23	.002	0	-.021
17	+.22	.002	0	-.011
18	+.21	.002	+.029	+.014
19	+.22	.002	+.001	-.012
20	+.20	.002	+.008	-.009
21	+.20	.002	0	-.013
22	+.18	.002	0	-.019
23	+.17	.002	0	-.014
24	+.15	.002	0	-.013
25	+.14	.002	+.007	-.002
26	+.18	.002	.034	+.010
27	+.16	.002	0	+.010
28	+.15	.002	0	-.015
29	+.14	.002	.011	+.008
30	+.14	.002	0	-.021
TOTAL	-.16	.060	.269	
EVAPOTRANSPIRATION =				.369

Appendix B

Partition coefficients, K", at several depths below the water table

Sampling Station	Date	Mean depth (cm)	K''_{Mg}	K''_{K}	K''_{Pb}
4.5	6/27/77	-5	.10	.68	.057
2	6/27/77	12.5	1.20	.82	.14
3	6/27/77	12.5	.90	1.29	.078
4	6/27/77	12.5	2.09	.71	.043
4.5	6/27/77	12.5	.76	1.05	.047
5	6/27/77	12.5	1.72	.53	.018
2	5/13/77	12.5	1.20	.30	---
3	5/13/77	12.5	2.6	.80	.064
4	5/13/77	12.5	3.4	.69	.013
4	5/13/77	12.5	5.4	.57	.032
4	5/13/77	12.5	3.7	.65	.004
4.5	5/13/77	12.5	1.2	.91	.017
5	5/13/77	12.5	.86	.40	.006
4.5	6/27/77	37.5	1.73	1.07	.081
4	5/13/77	37.5	1.5	1.03	.068
4.5	6/27/77	62.5	1.24	1.42	.041
4.5	6/27/77	88.5	4.06	2.38	.187
4	5/13/77	88.5	1.8	1.27	.015
3 *	12/4/76	88.5	.9	1.5	.05
4.5	6/27/77	112.5	3.92	1.69	.072
4.5 *	12/4/76	112.5	1.	.9	.05
4.5	6/27/77	137.5	4.67	1.94	.263
4.5 *	12/4/76	137.5	1.	.8	.07
4 *	12/4/76	137.5	.6	.75	.07
3 *	12/4/76	137.5	2.4	1.5	.14
4.5	6/27/77	162.5	4.67	1.80	.098
3 *	12/4/76	162.5	5.3	1.5	.03
4 *	12/4/76	162.5	1.3	.6	.07
4.5 **	11/11/76	188.5	6.7	1.7	---

<u>Statistics</u>:

Mean	2.3	1.1	.068
Standard deviation	1.7	.5	.058
Mean, 0-25 cm	2.1	.7	.053
Std. deviation, 0-25 cm	1.4	.3	.047
Mean >100 cm	3.1	1.3	.096
Std. deviation, >100 cm	2.2	.5	.070

(continued on next page)

	K''_{Mg}	K''_{K}	K''_{Pb}
Statistics (continued):			
Correlation with depth	r=.38	r=.56	r=.39
Confidence limits	$P<.05$	$P<.01$	$P<.05$

* offset 6 meters north of transect
** offset 6 meters south of transect

Appendix C

Variation of metal concentration in peat as a function of depth below water table

Sampling Station	Date	Mean sample depth (cm)	Metal Concentrations		
			K	Mg	Pb (ppm)
3	5/21/77	-7.5	3550	686	65
3	5/21/77	-5	2422	558	114
3	5/21/77	-2.5	704	625	95
3	5/21/77	2.5	187	596	151
3	5/21/77	7.5	195	492	108
2	6/27/77	12.5	166	343	92
2	5/13/77	12.5	296	399	60
2-3	6/27/77	12.5	272	425	127
3	6/27/77	12.5	524	441	90
3	5/13/77	12.5	219	487	50
3-4	6/27/77	12.5	346	556	150
4	6/27/77	12.5	220	340	162
4	5/13/77	12.5	234	331	126
4	5/13/77	12.5	146	406	53
4	5/13/77	12.5	291	351	480
4-4.5	6/27/77	12.5	302	447	159
4.5	6/27/77	12.5	316	362	127
4.5	5/13/77	12.5	255	394	74
4.5-5	6/27/77	12.5	247	348	107
5	6/27/77	12.5	151	452	166
5	5/13/77	12.5	382	528	86
3	5/21/77	12.5	159	589	254
3	5/21/77	17.5	121	539	229
3	5/21/77	22.5	135	428	170
3	5/21/77	27.5	90	315	90
3	5/21/77	32.5	87	430	79
3	5/21/77	37.5	97	363	89
4.5	6/27/77	37.5	165	380	55.6
4	5/13/77	37.5	213	458	51
3	5/29/77	55	106	356	77
4.5	6/27/77	62.5	266	303	73.7
3	5/29/77	65	176	321	134
3	5/21/77	72.5	82	482	28
3	5/29/77	75	49	183	83
3	5/29/77	85	82	328	15
4.5	6/27/77	88.5	101	164	13.4
3 *	12/4/77	88.5	306	188	19.4
4	5/13/77	88.5	233	386	34
3	5/29/77	95	314	235	42
3	5/23/77	97.5	66	325	43
4.5	6/27/77	112.5	125	207	27.9

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Appendix C (continued)

Sampling			Mean sample	Metal Concentrations		
Station		Date	depth (cm)	K	Mg	Pb (ppm)
4.5	*	12/4/76	112.5	404	416	96
4.5		6/27/77	137.5	105	180	7.6
4.5	*	12/4/76	137.5	350	450	97
3	*	12/4/76	137.5	307	447	104
4	*	12/4/76	137.5	500	412	57
4.5		6/27/77	162.5	105	194	20
4	*	12/4/76	162.5	253	541	43
3	*	12/4/76	162.5	129	212	29
4.5	**	11/11/76	188.5	160	196	13
Correlation with depth				r=-.061	r=-.48	r=-.50
Confidence limit				N.S.	P<.001	P<.001

* offset 6 meters north of transect

** offset 6 meters south of transect

Appendix D

Metal contents of peat at 0-25 cm depth below water table, as function of radius from center of bog

Sample Station	Date	Dist. from center	PPM Mg	PPM K	PPM Pb
2	6/27/77	80'	343	166	92
2	5/13/77	80'	399	296	60
2-3	6/27/77	70'	425	272	127
3	6/27/77	61'	441	524	90
3	5/13/77	61'	487	219	50
3-4	6/27/77	51'	556	346	150
4	6/27/77	41'	340	220	162
4I	5/13/77	41'	331	234	126
4II	5/13/77	41'	406	146	53
4III	5/13/77	41'	351	291	480
4-4.5	6/27/77	31'	447	302	159
4.5	6/27/77	21'	362	316	127
4.5	5/13/77	21'	394	255	74
4.5-5	6/27/77	10'	348	247	107
5	6/27/77	0	452	151	166
5	5/13/77	0	528	382	86
Mean			413	273	108
Standard deviation			69	95	40
Correlation with distance (r)			-.10	-.05	-.12
Confidence limit			N/S	N/S	N/S