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Prepared for:

Agency for International Development

12 April 1971

DISTRIBUTED BY:



Jul 72

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AID/csd-2270-8-1-1

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csd-2270-211d PB 224 367

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Reprinted from

THE AMERICAN MIDLAND NATURALIST

Vol. 88, No. 1, July, 1972, pp. 1-14

University of Notre Dame Press

Notre Dame, Indiana

NATIONAL TECHNICAL INFORMATION SERVICE US Department of Com.. rce Springfield, VA. 22151

Studies of the Biogeochemistry of Boron. I. Concentrations in Surface Waters, Rainfall and Aquatic Plants

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ABSTRACT: Boron concentrations in streams, swamps, ponds and reservoirs of the southeastern United States were usually below 100 ppb. Levels of boron in rainfall varied greatly between different periods of precipitation, but the highest concentrations were observed during winter. However, most rainfall samples contained less than 10 ppb boron. The annual input of boron in rainfall at two Mississippi sites and one station in South Carolina ranged from 62.7 to 74.2 g/ha.

Boron levels in 22 species of aquatic macrophytes from a reservoir ranged from 1.2 to 11.3 ppm dry weight. The plant populations accrued from 0.5 to 6.8 mg boron per m². Boron upta've studies on Typha latifolia populations indicated a maximum rate of uptake during early spring growth. Boron concentrations in T. laifolia and Juneus effusus samples from different sites varied considerably. There was no significant constants to be between concentrations of boron in sails and in plant cant correlation between concentrations of boron in soils and in plant tissues. Standing crops of T, latifolia increased with increasing levels of soil boron.

Introduction

Boron is an essential micronutrient for higher plants. Some fungi, bacteria and algae also require this nutrient (Lewin, 1966; Gerloff, 1968). There is a large body of data on the chemistry of boron in agricultural soils and the influence of this trace element on soil fertility (Gilbert, 1957; Sauchelli, 1969). The role of boron in nonagricultural systems, particularly fresh-water habitats, has not been extensively investigated.

The few available data indicate that boron is usually a minor constituent in fresh-water lakes and streams (Hutchinson, 1957; Livingstone, 1963). Although precipitation is an important source of several nutrients in fresh-water environments (Gorham, 1961), there is a paucity of information on concentrations of boron in rain water (Handa, 1969). Furthermore, data on the accumulation of boron in native aquatic vegetation are scarce (Boyd, 1970a).

The present study includes information on concentrations of boron

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in surface waters and rainfall from the southeastern United States. Data on boron accumulation by vascular aquatic plants are also presented. This information will be useful in considerations of the biogeochemistry of boron in aquatic systems.

MATERIALS AND METHODS

Water samples.—Surface water samples were collected from various areas of South Carolina, Tennessee, Georgia, Alabama, Mississippi, Louisiana and Florida during 1969 and 1970. Of the 199 samples, 173 were taken from small streams (1 to 10 m wide) that had restricted watersheds. Samples were taken at times of medium flow so that surface runoff from the watershed was not an important variable. The remaining samples were taken from swamps (13), ponds (7) and large reservoirs (6). Samples were put in polyethylene bottles and frozen until analyzed for boron.

Rainfall was collected for a 12-month period at Jackson (11 November 1969 - 10 November 1970) and Grenada, Miss. (1 October 1969 - 30 September 1970) and near Aiken, S. Car. (1 January - 31 December 1970). Rainfall was collected in 4-liter polyethylene bottles fitted with large, narrow-necked polyethylene funnels. Recommendations of Allen et al. (1968) were followed to prevent contamination of the samples. Rain water was usually removed following each shower or at 24-lin intervals during extended periods of precipitation. Rainfall was measured at each collection date with a standard rain gage that was positioned near the collecting devices. Rain water samples were poured into polyethylene bottles and frozen until analyzed.

Plant samples.—Three series of aquatic plant samples were obtained. The first represented 22 species from a 1200-ha reservoir (Par Pond) on the AEC Savannah River Plant (SRP) near Aiken, S. Car. All samples were lush, green shoots taken from communities in one fairly small area of the reservoir to insure that the plants were growing under relatively similar environmental conditions and at similar stages of maturity. These specimens were collected and prepared for analysis according to the technique outlined by Boyd (1970b).

The second series consisted of samples of Typha latifolia from 30 sites and Juneus effusus from 15 sites in the southeastern United States. These samples were collected during the period 8-14 June 1969 for previous investigations (Boyd and Hess, 1970; Boyd, 1971a). The T. latifolia sample from Par Pond and an early June sample of this species from both Par Marsh and Pond A (see below) as well as the J. effusus sample from Par Pond were included in this series.

The third group of plant samples were taken at intervals during the 1970 growing season from two *Typha latifolia* populations on the SRP. Descriptions of the sites (Par Marsh and Pond A), harvesting techniques and methods of sample preparation were reported by Boyd (1971b).

Boron analyses.—Rainfall samples in porcelain evaporating dishes were concentrated 5 - 10 times under infrared heat lamps prior to

analysis. It was necessary to concentrate some of the surface water samples, but most were analyzed directly. Samples were filtered before analysis.

Plant samples were ashed at 550 C in a muffle furnace, dissolved in 0.1 N HCl, and filtered (Jackson, 1958). All samples contained sufficient base to present the loss of boron during ignition. Recommendations of Wear (1965) were followed to avoid boron contamination during analysis.

Hot water-soluble boron determinations (Jackson, 1958; Wear, 1965) were made on soil samples from the *Typha latifolia* and *Juneus effusus* stands. Boron-free glassware was used during the hot water extraction procedure. In each case boron in the extracts was measured by the curcumin method (American Public Health Association 1963).

RESULTS AND DISCUSSION

Some of the rainfall and surface water samples contained very small amounts of boron (<1 ppb), and even with concentration we were below optimum levels for analysis. Boron was not detectable in a few samples. However, for most samples the analytical technique was satisfactory. Coefficients of variation for eight replicate analyses of a concentrated sample and eight analyses of an unconcentrated sample were each 10%. No analytical problems were encountered in the plant and soil analyses. All samples had sufficiently large quantities of boron for direct analysis of the extracts without the necessity of concentrating them.

Boron in surface waters. Samples were collected from a fairly large geographic area (Fig. 1). Ten major physiographic regions

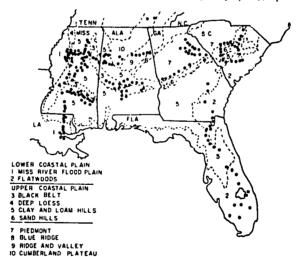


Fig. 1.—Approximate geographic and physiographic locations of sites where surface water samples were collected for boron determinations

(Hodgkins, 1965; Duncan, pers. comm.) were included in the sampling area. Since stream samples were taken at periods of medium flow, most samples were hopefully representative of ground water originating from a particular physiographic area. Stream beds were of rock, clay, silt, sand, or combinations of these substances. A few stream bottoms consisted of highly organic soils. Stream flow characteristics ranged from swift to stagnant waters. Most streams had forested watersheds, but some drainages were almost entirely in agricultural operations.

Results of the boron analyses are presented in a histogram (Fig. 2). Most samples (86.4%) contained less than 100 ppb boron and 50.8% had values less than 20 ppb. Concentrations ranged from less than detectable quantities to 660 ppb. All samples containing above 300 ppb were collected near Lake Pontchartrain, Louisiana, and likely contained salt water intrusion from this brackish bay. The boron content of sea water ranges from 3 to 5 ppm (Igelsrud et al., 1938; Noakes and Hood, 1961), so small additions of sea water would greatly enhance the boron content of inland waters. Some of the high values (100-300 ppb) in agricultural areas may have been due to the use of boron containing fertilizers (Sauchelli, 1969) on crops in the watersheds. Boron compounds have recently been added to fertilizers used in cotton fields in the southeastern United States.

Boron concentrations in waters of certain physiographic regions were higher than those in other regions. Samples from the Cumberland Plateau (mean, 106 ppb) the Mississippi River flood plain (mean, 138 ppb) and the flatwood region (mean, 77 ppb) had the highest levels. All samples from the sand hills and Blue Ridge regions were

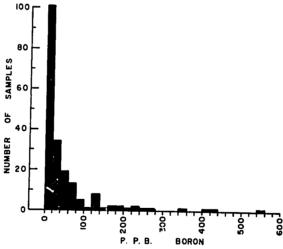


Fig. 2.—Frequency distribution histogram of boron concentrations in surface water samples. Class intervals are given along the base of the histogram

very low in boron (means, 3 and 6 ppb, respectively), while means for other regions were intermediate. There was considerable variation in values of samples within a particular physiographic region. Most regions had surface waters with values lower than 1 ppb and higher than 100 ppb. The average boron content of all samples was 47 ppb. However, in view of the large variation, this value has relatively little meaning as an index of boron levels in surface waters of the southeastern United States. A better assessment of the situation is that surface waters of this geographic region asually have boron concentrations below 100 ppb.

Boron is widely distributed in rocks as aluminosilicates such as tourmaline (Bear, 1964; Wear, 1965). Water soluble boron is generally low in acid soils under high rainfall conditions as a result of leaching. Such is the general situation in the area which we sampled. Hot water-soluble boron in agricultural soils of humid, temperate climates ranges from 0.2 to 1.5 ppm (Bear, 1964). Variations in the amount of previous weathering, the tourmaline content of the soil and underlying geologic strata, patterns of ground water movement and agricultural activity in the watersheds probably account for much of the variation in boron concentrations of stream waters both within and between physiographic regions.

According to Livingstone (1963), the average boron content of the major rivers of USSR was 13 ppb, while several rivers of North America and Norway had a mean of 11.6 ppb. Muto (1956) reported that surface waters in Japan contained from 200-1300 ppb boron. Livingstone (1963) indicated that vulcanism might be responsible for the high values in Japan. Odum and Parrish (1954) found that boron concentrations in 11 lakes and streams in Florida ranged from 12 to 27 ppb (mean, 16 ppb). Many of our values are higher than those reported by Livingstone (1963) and Odum and Parrish (1954). However, their results are for rivers or streams that were much larger than any that we sampled. Large streams consist of flow from many tributaries which will vary in chemical composition depending upon the nature of the rocks in their drainage basins. Therefore, chemical coacentrations in large rivers represent an average of contributions of their tributaries and the concentrations of substances in downstream reaches of rivers tend to resemble one another (Rodhe, 1949; Livingstone, 1963). Boron levels in the small streams that we sampled were more subject to local irregularities in geology than larger streams and rivers. All reservoir and large bayous that we sampled contained less than 25 ppb boron. This finding is probably related to an averaging effect of impounding water from a variety of streams and was expected since most streams have relatively low levels of boron (Fig. 2). Furthermore, all of the higher boron levels, except for the samples from the Lake Pontchartrain area, were obtained for streams at the lower end of the size range of streams that were sampled. The factor involving local geology and watershed size, the apparent salt water intrusion into a few of the streams and the possibinty of fertilizer

pollution probably account for our comparatively high average of 47 ppb when compared to values given by Odum and Parrish (1954) and Livingstene (1963). In arid regions where there has been less leaching of boron from the rocks and soil, concentrations of this nutrient in streams are probably much higher than the values summarized in Figure 1. Lakes with closed basins often contain several hundred ppb boron (Hutchinson, 1957; Livingstone, 1963; Wetzel, 1964). Therefore, data on boron concentrations in waters of other physiographic regions in other parts of the world would be of interest. Intensive sampling of streams in localized areas is also needed to determine the magnitude of variation in boron concentrations within a particular edaphic region. Seasonal differences in boron concentrations should also be investigated.

Boron in rainfall.-Results of rainfall analyses are summarized in Table 1. Values for individual rains ranged from a low of < 1 ppb at all sites to as high as 95 ppb at Jackson, Miss. Boron concentrations in small show is were generally higher than values for heavier rains. Concentrations of many nutrients are high in showers. During the initial phases of heavy rains, nutrient levels are high, but decline with rainfall duration. This is due to the clearing of the atmosphere of dust particles and other substances of terrestrial origin (Eriksson, 1952; Larson and Hettick, 1956). Some of the boron, like much of the chloride in rain water, probably represents cyclic marine salts (Odum and Parrish, 1954). The amount of chloride in rainfall usually decreases with distance from the sea (Eriksson, 1960). A similar situation can probably be expected for boron. The annual mean boron concentration at Grenada, Miss., was lower than the value for Jackson, Miss. Grenada is 385 km and Jackson is 250 km from the Gulf of Mexico, Aiken, S. Car, is only 183 km from the Atlantic Ocean but had an average value similar to the Grenada site. However, much of the rainfall at Aiken is from air masses originating over the Gulf of Mexico which is about 420 km distant. Much more information on boron concentrations in rainfall will be required to determine if its distribution patterns in rainfall are similar to those for chloride.

Variations in boron concentrations of rain water were due to the origin of the air masses producing the rain. There were seasonal variations in levels of boron in rain. The pattern for the Grenada, Miss. station (Fig. 3) is fairly representative of the other two sites, except

TABLE 1.—Summary of data on the boron content of rainfall

Station	ppb Boron			Annual	Annual input
	Min.	Mean	Max.	rainfall (m)	of boron in rainfall (g/ha)
Grenada, Miss. Jackson, Miss. Aiken, S. Car.	<1 <1 <1	5.3 6.7 5.7	37 95 18	1.40 1.25 1.10	74.2 83.7 62.7

that the September increase was not as pronounced at Jackson or Aiken. Concentrations generally increased during the autumn to a peak in February and then declined during the spring, reaching a minimum in the summer.

The total amount of boron delivered in rainfall is fairly large when one considers the small quantities of available boron in soils (Bear, 1964). Thus, the rainfall contribution of boron is likely important to the boron nutrition of some native and crop plants. Odum and Parrish (1954) suggested that much of the boron in inland waters was of atmospheric origin. The mean rainfall values in Table 1 are considerably lower than boron concentrations in most surface water samples. Even when concentration by evaporation is considered, our findings indicate that much of the boron in most surface waters is derived from solution of boron containing minerals in the rocks and soil. The possibility of contamination of some of the streams by fertilizer and sea water was discussed previously.

Muto (1956) reported an average of 98 ppb boron in five samples of rainfall in Japan. Monsoon rains over Calcutta, India, contained from 2 to 65 ppb (mean, 26 ppb) boron (Handa, 1969). Odum and Parrish (1954) found 9 and 15 ppb boron in two samples of rainfall at Gainesville, Fla. It would be interesting to know if the seasonal averages for boron concentrations at these stations are actually higher than those reported in Table 1. The Calcutta, India, Kiriu, Japan and Gainesville, Fla. sites were closer to the ocean than any of our sites. This could account for the values at these sites usually being higher than values for our sites.

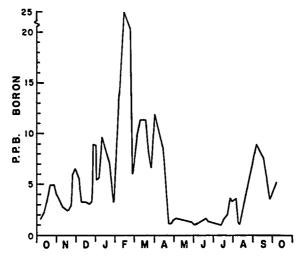


Fig. 3.—Seasonal trends in boron concentrations in rain water at Grenada, Miss. The curve was prepared by calculating three-point moving averages of the data

Boron accumulation by aquatic macrophytes.—Boron analyses of 22 species from Par Pond are reported in Table 2. The values ranged from 1.2 ppm (dry weight basis) in Eleocharis equisetoides to 11.3 ppm in Nymphaea odorata. These results indicate that some species accumulate more boron than others since all plants were growing in the same general area of the lake under fairly similar conditions (transparency, nutrient levels, temperature and substrate characteristics). However, all species do not draw on the same boron supplies. Emergent plants such as Typha, Eleocharis and Scirpus that grow along the shore or in shallow water likely absorb most of their boron from the mud. Floating-leafed species (Nymphaca, Nelumbo and Brasenia) probably absorb a large proportion of their total uptake from the mud, but also absorb boron from the water. Submersed plants with reduced root systems (Potamogeton and Myriophyllum) probably obtain most of their boron from the water. Caution must be used in making conclusions regarding differential uptake of boron by species with different growth habits even when the plants are growing in close proximity to one another. It is interesting to note that four species which either lack or have greatly reduced root systems (Ceratophyllum, Potamogeton, Utricularia and Myriophyllum) were often found in close proximity and had considerably different boron levels. This definitely appears to be a case of interspecific accumulation of boron.

Monocotyledons usually contained less boron than dicotyledons (Table 2). Stiles (1961) reported that grasses absorb less boron than

Table 2.--Boron content of aquatic macrophytes and the accumulation of this element per unit area of plant stand

Species	Boron (ppm dry wt)	Standing crop (g dry wt/m²)	Boron accumulation (mg/m²)
Eleocharis equisetoides	1.2	377	0.5
Glyceria striata	2.0	•••••	• · · · · •
Panicum hemitonium	2.3	1075	2.5
Scirpus americanus	2.7	410	1.1
S. validus	3.2	1381	4.4
Eleocharis quadrangulata	3.7	725	2.7
Ceratophyllum demersion	4.3	*****	•••••
Typha domingensis	4.6	1483	6.8
Hydrochloa carolinensis	4.9	175	0.9
Typha latifolia	5.2	574	3.0
Potamogeton diversifolius	5.3	•••••	•••••
Hydrotrida caroliniana	7.6	304	2.3
Utricularia inflata	7.6	•••••	
Hydrocotyle umbellata	7.7	188	1.4
Pontederia cordata	7.9	716	5.7
Juneus effusus	8.1	•••••	*****
Nuphar advena	8.2	84	0.7
Brasenia schreberi	10.4	105	2.2
Myriophyllum heterophyllum	10.6		
Orontium aquaticum	10.7	244	2.6
Nelumbo lutea	10.9	184	2.0
Nymphaea odorata	11.3	256	2.9

other plants. Monocots also have a lower requirement for boron than dicots (Hewitt, 1963).

Boron levels in Par Pond water measured at several dates averaged 5.2 ppb. Bottom muds in Par Pond are generally very sandy with extremely low levels of boron (< 0.1 ppm). There was a fairly large concentration of boron above environmental levels by the plants. However, as indicated by Odum and Parrish (1954), boron is not concentrated by plants to the extent of phosphorus. Levels of phosphorus in the vascular species of Par Pond ranged from 0.10 to 0.40% of the dry weight (Boyd, 1970b). Phosphorus concentrations in the water of Par Pond during 1970 ranged from 2 to 5 ppb (Tilly, pers. comm.). Thus, we agree with Odum and Parrish (1954) that phosphorus is more likely to be a limiting factor for fresh-water plants than boron. Goldman (1965) reported a slight stimulatory effect of added boron on phytoplankton productivity in Lake Nerka, Alaska. He obtained no response to boron additions in several other lakes.

Polisini and Boyd obtained standing crop data for several species of the Par Pond flora. Although these data will be discussed in detail in another report, we used the values to calculate quantities of boron per unit area of plant stand. Standing quantities of boron ranged from 0.5 to 6.8 mg/m². One m³ of Par Pond water contained about 5.2 mg boron, so populations growing in water 1 m deep would not deplete the dissolved boron supply, even if the lake was considered a static situation. Furthermore, a contribution of boron from the mud either to the plant or to the water and then to the plant probably occurs. It is also interesting to note that the rainfall input of boron (Table 1) is roughly of the same magnitude as the maximum accumulation of boron by a Par Pond plant population. The average concentration of boron in Par Pond water was very similar to mean concentrations in rainfall at Aiken, S. Car. Therefore, the implication that boron in inland waters is derived from atmospheric sources (Odum and Parrish, 1954) is appealing in the case of this reservoir which is located in a very sandy, well-leached watershed.

Several species (Table 2) that had high standing crops of dry matter accrued proportionally much less boron than certain species with lower standing crops. However, when all species were considered, there was a positive correlation between dry matter-standing crop (X-variable) and the mg of boron per m² of stand (Y-variable):

$$Y = 1.105 + 0.003 X (r = 0.75; P < 0.01).$$

Between 23 April and 23 July, the boron content of the two Typha latifolia populations on the SRP decreased from 12.0 to 9.2 ppm and 15.8 to 9.6 ppm, respectively. This decline in boron concentration with age does not fit the general pattern reported for several species. Boron is a relatively immobile nutrient (Hewitt, 1963). It is not translocated readily from old to new growth and tends to concentrate in old leaves. Boron levels increased considerably in the leaves of trees as the growing season progressed (Gulia and Mitchell, 1966). Boyd

(1970a) found that the boron content of two filamentous algae, Chara and Pithophora, increased with age of the thalli.

Seasonal changes in dry matter standing crops at the two *T. latifolia* sites, Pond A and Par Marsh, were given by Boyd (1971b). The percentage of the total boron uptake that was accrued by each successive sampling date is compared with the percentage of the peak standing crop on each date in Table 3. Early in the spring boron uptake was at a proportionally greater rate than net dry matter production. However, as the season progressed, boron uptake decreased to a rate proportionally less than dry matter accrual. Maximum dry matter-standing crop and boron accumulation occurred on the same sampling date for a particular site. The decrease in rate of boron uptake during late spring and early summer accounted for the decline in concentrations of boron in the plants with respect to age. Boyd and Vickers (1971) reported a similar pattern of boron uptake by *Eleocharis quadrangulata*.

Boron levels in *T. latifolia* and *J. effusus* from different sites varied greatly (Fig. 4). Extreme values were 5.2 and 100.0 ppm for *T. latifolia* and 4.6 and 51.0 ppm for *J. effusus*. The majority of samples (63.6 and 75.0% for *Typha* and *Juneus*, respectively) contained less than 20 ppm boron. The magnitude of intraspecific differences (between sites) for each of these two species is about the same as that for interspecific variation in the boron content of the 22 species in Par Pond (Table 2). Similar patterns of variation in concentrations of other nutrients were reported in these species by Boyd (1970b, 1971a) and Boyd and Hess (1970).

Concentrations of hot water-soluble boron in air-dry soils of Typha sites (0.02-9.0 ppm boron) and Juncus sites (0.8-7.4 ppm boron) differed widely. There was no correlation between the amount of boron in soils and the quantities of this element in either species. However, plants from sites low in boron contained less boron than plants from sites high in boron. Factors influencing the degree of accumulation of elements from soils by native vegetation are extremely complex (Shanks and DeSelm, 1963; Boyd and Hess, 1970; Boyd, 1971a). When the different sites were compared, boron was never the only variable. Other nutrients varied greatly between sites and the direction and magnitude of variation were not related to boron levels. Calcium levels are known to influence boron uptake (Hewitt, 1963), and nutrients such as nitrogen and phosphorus have a pronounced

Table 3.—Percentage of total boron accrual and dry matter production by two Typha latifolia populations at intervals during the 1970 growing season

Date	Dry matter	Boron	Dry matter	Boron
23 April	18.7	25.0	22.2	33.3
6 May	39.5	47.1	35.9	35.3
20 May	59.5	63.5	51.3	60.0
	70.1	76.0	75.9	64.7
1 June	92.7	88.4	100.0	100.0
25 June		100.0	100.0	
22 July	100.0	100.0	*****	*****

influence upon plant growth and the uptake of other nutrients. Site variables such as pH, water depth, soil texture and other physical factors probably interact with nutrient levels to influence boron uptake. Therefore, the lack of correlation between internal and external boron concentrations is not surprising.

As pointed out earlier, agricultural soils usually contain less than 1.5 ppm hot water-soluble boron (Bear, 1964). Interestingly, some of the marsh soils in the present study contained considerably larger amounts of boron. A number of these soils contained large percentages of organic matter (20-30% of the dry weight; see Boyd and Hess, 1970). There was a high correlation (r = 0.87; P < 0.01) between soil organic matter (X-variable) and hot water-soluble boron (Y-variable). The regression equation is:

$$Y = 1.348 + 0.183 X.$$

Further studies of boron concentrations in nonagricultural soils appear in order.

Boron concentrations in aquatic plant samples (Table 2, Fig. 4) ranged from 1.2 to 100.0 ppm, although most samples contained below 20 ppm. In an extensive study of the mineral content of native vegetation in Wisconsin, Gerloff *et al.* (1964) reported boron levels of 5.5 to 100 ppm. The majority of their values was above 20 ppm and a

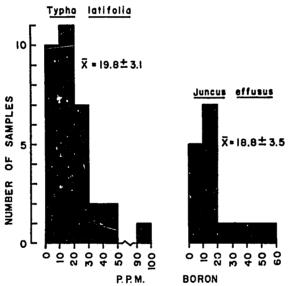


Fig. 4.—Frequency distribution histograms for concentrations of boron (dry weight basis) in samples of $Typha\ latifolia$ and $Juncus\ effusus$ collected from different sites in the southeastern United States. Class intervals are given along the bases of the histograms. Averages \pm one standard error of all samples of each species are also presented

few of these were above 40 ppm. Our data for Typha latifolia and Juneus effusus (Fig. 4) exhibit a range of variation that is very similar to that found by the Wisconsin workers. Boron levels in Par Pond plants are comparatively low. Soils and waters in this reservoir are also low in boron. We suspect that values for any species from Par Pond would be comparatively low if compared with data for that particular species from a large number of sites. This was certainly the case for T. latifolia and J. effusus (Table 2, Fig. 4).

Shoot standing crop data for all samples of T. latifolia in Fig. 4 were reported elsewhere (Boyd and Hess, 1970; Boyd, 1971 b). Boron accrnal calculated for each population ranged from 3 to 157 mg/m² (mean, 20.0). Boron accrual was greatest for populations with highest dry matter-standing crops and lowest for those with the smallest standing crops. However, due to the wide variation in tissue concentrations of boron, this relationship has a low correlation coefficient (r = 0.45; P < 0.05) and is of little predictive value.

Boyd and Hess (1970) reported that shoot standing crops of T. latifolia were correlated with acid-soluble soil phosphorus (r = 0.71; P < 0.01). We regressed shoot standing crops of these same T. latifolia populations against hot water-soluble boron (independent variable). The resulting correlation coefficient (r = 0.48) was significant at the 0.05 level, but, as a simple linear effect, soil boron accounted for only 1/2 as much of the variation in shoot standing crop as phosphorus. Nevertheless, this finding indicates that environmental levels of boron may produce measurable effects on plant growth in nonagricultural systems. Therefore, boron is of ecological interest and further studies of the biogeochemistry and ecological significance of this element should be considered.

Acknowledgments.--This research was supported by Contract AT (38-1)-310 between the U.S. Atomic Energy Commission and the University of Georgia. Manuscript revision was aided by the Department of Fisheries and Allied Aquacultures, Auburn University. The technical assistance of Miss Bonny Didgeon and Beyers Wray is greatly appreciated. Special thanks are extended to O. E. Boyd for collecting rainfall samples at Grenada, Miss. Dan Thompson, C. Phillip Goodyear and Henry Kania kindly collected some of the surface water samples. We are grateful to J. M. Polisini and D. H. Vickers for assistance in harvesting plant samples cited in Table 2. Wendel Marine and T. R. Cummings of the U.S. Geological Survey made helpful suggestions regarding surface water sampling. C. Phillip Goodyear made several helpful suggestions regarding preparation of the manuscript.

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SUBMITTED 12 APRIL 1971

ACCEPTED 18 JUNE 1971

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