BNL--30369

DE82 006254

58--1

MASTER

GENERATION OF DOSE-RESPONSE RELATIONSHIPS TO ASSESS THE EFFECTS OF ACIDITY IN PRECIPITATION ON GROWTH AND PRODUCTIVITY OF VEGETATION

Lance S. Evans

Laboratory of Plant Morphogenesis
Manhattan College
The Bronx, New York 10471

and

Land and Freshwater Environmental Sciences Group
Department of Energy and Environment
Brookhaven National Laboratory
Upton, New York 11973

Prepared for presentation at
The Second Annual Meeting of
The Society of Environmental Toxicology and Chemistry
Arlington, Virginia
November 22-24, 1981

This research was performed under the auspices of the United States Department of Energy under Contract No. DE-AC02-76CH00016.

ABSTRACT

Experiments have been performed with several plant species in natural environments as well in a greenhouse and/or tissue culture facilities to establish dose-response functions of plant responses to simulated acidic rain. These results are necessary to determine environmental risk assessments to ambient levels of acidic rain. Characteristics of ambient precipitation such as chemistry, frequency, duration, and volume of rainfalls are necessary in order to relate experimental conditions to the ambient environment. Response functions of foliar injury, biomass of leaves and seed of soybean and pinto beans, root yields of radishes and garden beets, as well as reproduction of bracken fern are considered. A dose-response function of soybean seed yields in the field with the hydrogen ion concentration of simulated acidic rainfalls has been determined. This function is expressed by the equation $y = 21.06-1.01 \log x$ where y = seed yield in grams per plant and x = the hydrogen concentration in $\mu\text{eq}\ \ell^{-1}$. The correlation coefficient of this relationship is -0.90. A similar dose-response function was generated for percent fertilization of ferns in a forest understory. When percent fertilization is plotted on logarithmic scale with hydrogen ion concentration of the simulated rain solution, the Y intercept is 51.18, slope -0.041 with a correlation coefficient of -0.98. Other dose-response functions have been generated that assist in a general knowledge as to which plant species and which physiological processes are most impacted by acidic precipitation. Some responses do not produce convenient dose-response relationships. In such cases the responses may be altered by other environmental factors or there may be no differences among treatment means. Dose-response functions may provide a scientific basis for the establishment of a standard for acidic precipitation to protect vegetation.

Acidic precipitation is defined as wet or frozen precipitation (i.e., rain, fog, sleet, and snow) with an H^+ concentration greater than 2.5 μeq ℓ^{-1} (less than pH 5.6) (Evans et al., in press a). Acidic precipitation has the same meaning as the commonly used term "acid rain." Significant interest has been aroused in both legislative and executive branches of the United States Government in determining the severity of problems relating to acidic precipitation. As a result of this interest an air quality standard might be considered which limits the concentrations or even the total deposition of pollutants associated with acidic precipitaition to prevent or ameliorate its impacts.

Establishing an air quality standard for precipitation acidity to protect terrestrial vegetation involves several assumptions. The first of these is that acidity in precipitation causes injury to vegetation. A widely used method to assess injury to vegetation involves establishment of dose-response relationships between pollutant dose and vegetation responses. Such relationships may be used to derive economic assessments when current market values are considered.

Characteristics of dose — In order to develop dose-response relationships, dose must be characterized. With regard to acidic precipitation, dose must entail considerations of chemistry, frequency, duration, and volume of rainfalls that impact on vegetation. Such considerations are necessary in order to relate experimental conditions to ambient environments. In terms of acidic precipitation, dose may be expressed in terms of H^+ concentration or total H^+ deposition during exposures. In our experiments we have expressed dose in terms of H^+ concentration because (1) no data are available that suggest total deposition, independent of duration, is relevant and (2) treatment durations are held constant within an individual experiment.

Acidic precipitation is present in eastern North America. Acidity of precipitation events may be categorized by the percentage of rainfalls within various 0.5 pH unit ranges. Results of rainfalls obtained among various pH levels at MAP3S stations at Ithaca, New York; University Park, Pennsylvania; and Charlottesville, Virginia are shown in Table 1. These stations were chosen as three representative stations within the northeastern U.S. in which data for three years (1976–1979) are available (Benkovitz, personal communication). Most rainfalls had pH levels between pH 3.5 and 4.5. Thirty-two per cent of all rainfall samples had a pH below 4.0. Less than 0.5% of all rainfalls were below pH 3.0 or above 5.5.

For categorization purposes, MAP3S stations pool data on a weekly basis. The chemistry of individual events may show a different pattern of rainfall acidities. Figure 1 shows the acidity of rainfalls at Brookhaven National Laboratory, Upton, NY, U.S.A. taken on an event basis for the crop growing season (12 May through 26 August) (Evans et al., in press b) of 1980. Over 70% of all ambient rainfalls had a pH below 4.5 and all rainfalls had a volume weighted mean H^+ concentration of 86.6 μeq ℓ^{-1} (pH 4.06).

The chemistry of precipitation may be characterized in terms of mean concentrations of constituents throughout the growing season. Data in Table 2 show the mean hydrogen concentration at Brookhaven National Laboratory for the years 1977 through 1979 was 71.74 μeq ℓ^{-1}. In terms of major anion components of acidic precipitation sulfate, nitrate, and chloride predominate. The elevated concentration of chloride of samples at Brookhaven National

Laboratory is not typical of more inland areas. In general, sulfate and nitrate are the major anions present in rainfalls of eastern North America. It is noteworthy that significant concentrations (above 3 μeq ℓ^{-1}) or iron, zinc, copper, and lead occurred.

During the growing season (12 May through 26 August) of 1980 at Brookhaven National Laboratory, crops were exposed to 55 showers which encompassed 108.1 hr. These showers were of short duration and of low precipitation rate. Fifty percent of all events had durations less than two hours and over 25% had durations shorter than one hour (Fig. 2). Rainfall rates were low. A majority of events had rates less than 1.5 mm hr^{-1} and only 12.5% of all events had rates greater than 3.5 mm hr^{-1}. Data in Figure 3 show 9 of 28 (32%) of all ambient rainfalls during the summer period had volumes below 1 mm and 5 of 29 (18%) had volumes below 0.5 mm. In this way, experiments to determine dose-response functions should have rainfalls that are frequent, of short duration, and of small volume. Simulated rainfalls with such characteristics would most approximate ambient rainfalls during the growing season.

Although weighted mean concentrations of constituents of rainfalls or frequency distributions of such parameters of rainfall duration or volume may be determined, one or two rainfalls of high acidity may have a greater impact than a larger number of low acidity rainfalls. For example, three rainfall events of low volume, short duration with a pH of about 3.88 during a 2-day period were responsible for visible foliar injury to field-grown garden beets at Brookhaven National Laboratory during the summer of 1980 (Evans et al., in press c). In this manner, the characteristics of a few rainfalls may have greater impacts to vegetation than all other rainfalls throughout the growing season.

Characteristics of Response -- Establishing a standard for precipitation acidity to protect terrestrial vegetation involves several assumptions. The first of these is that acidity in precipitation causes injury to vegetation. Injury can be defined as: a) loss of crop yield and/or quality, b) visible injury which would reduce the market value of a crop, c) loss of forest yield or long-term growth of trees, d) visible injury to ornamental plants that would reduce their aesthetic value, and e) substantial alterations of plant community composition leading to ecosystem simplification. There is also an assumption that controlling the acidity of precipitation by establishing a standard which is not allowed to be exceeded will prevent or ameliorate known or highly probable injuries.

Experimental exposures of plants to simulated acidic precipitation over days, weeks, or a growing season are conducted to evaluate relationships between treatment H^+ concentrations and plant responses. In evaluating experimental results, it is important to distinguish between effects observed at H^+ concentrations which are much above the volume-weighted mean H^+ concentration of ambient precipitation, near ambient H^+ levels, and so-called "control" H^+ levels which are much below ambient levels (e.g., pH ≥ 5.6). Both extremes, unusually high and unusually low H^+ concentrations, represent conditions that do not occur in the northeastern United States. However, when a large range of H^+ concentrations are tested, linear or curvilinear functions, with known confidence limits, of plant responses versus H^+ concentration will provide information to estimate plant responses to ambient or anticipated levels of acidity.

Experimental designs must be used that are able to establish dose-response relationships that detect statistically significant differences among treatment means that differ from each other by less than 10%. Such responses are necessary to assess economic and/or environmental impacts. To accomplish these aims a large number of randomized treatment replicates coupled with standard statistical analyses are required to avoid natural variations that occur in agricultural fields and natural vegetation stands. Only the impacts of acidic precipitation on foliage of vegetation will be considered. It is generally accepted that managed soils are not susceptible to acidic precipitation (McFee, 1979). Although natural soils may be influenced (Voigt, 1980; Alexander, 1980) the buffering capacity of soils would probably minimize effects.

In order to standardize experimental results, a uniform expression of data should be utilized. To date, the most meaningful relationships between rainfall acidity and plant responses have been obtained when responses are plotted as a function of the hydrogen ion concentration of the simulated rainfalls. This expression or some other more meaningful expression should be used so data can be compared with ambient precipitation acidities.

Visible foliar injury — Simulated acidic rainfalls (Evans et al., 1977, 1978; Evans and Curry, 1979; Evans, 1980) and ambient rainfalls of low pH (3.88) (Evans et al., in press c) produce visible foliar injury. A significant percentage of leaf area may exhibit lesions. For example, about 0.5%, 2-3%, 5-10%, and 10-15% of the leaf area of pinto beans is injured after 1-4 exposures to simulated acidic rain at pH levels of 3.0, 2.7, 2.5, and 2.4, respectively (Evans et al., 1977). In this way the area showing injury increases with an increase in rainfall acidity.

Experiments were performed to rank species sensitivities to simulated acidic rain. Based upon visible effects of foliage present evidence shows that sensitivity ranks from high to low in the following order: herbaceous, dicots, woody dicots, monocots, and conifers (Evans and Curry, 1979; Evans, 1980). Within each species, the amount of visible leaf injury appears to relate linearly to the hydrogen ion concentration of the simulated rain solution (Fig. 4).

Plant biomass experiments -- Experiments with potted plants were performed to determine dose-response relationships between plant biomass and hydrogen ion concentrations of simulated rainfalls (Evans and Lewin, 1981). When pinto beans were exposed to simulated rains of 794 μeq ℓ^{-1} H^+ or above, dry mass per plant of above-ground vegetation was lower than for plants exposed to rains of 2 μeq ℓ^{-1} H^+ (Fig. 5). Mean values of plants exposed to 794, 1259, 1995, and 3162 μeq ℓ^{-1} H^+ were between 79 and 84% of values of plants exposed to rains of 2 μeq ℓ^{-1} H^+.

Concomitant with this decrease in dry mass of leaves and stems at high acidity, was a decrease in dry mass of seeds. Dry mass of seeds per plant was significantly lower ($p > 0.05$) at both 1995 and 1259 than at 2 μeq ℓ^{-1} H^+. This decrease in seed mass with an increase in rain acidity was also reflected by a lower number of seeds per plant. No differences in mean dry mass of individual seeds occurred among experimental treatments. As a result, the decrease in mean seed number per plant may be attributed to both a decrease in number of seeds per pod and a decrease in number of pods per plant.

Mass of leaves abscised before harvest was significantly ($p > 0.05$) lower for plants exposed to rainfalls of either 2 or 794 μeq ℓ^{-1} H^+ compared with plants exposed to either 1995 or 1259 μeq ℓ^{-1} H^+ (Fig. 4). In pinto beans mass of leaves abscised before harvest was a substantial portion of the entire plant biomass produced. At acidity levels of 2, 794, 1259 and 1995 μeq ℓ^{-1} H^+ about 11, 14, 18 and 16%, respectively, of the entire above-ground plant biomass abscised before harvest. Calculations of mean ratios of seed mass over mass of stems and leaves for individual plants revealed that greater rainfall acidity levels gave higher ratios than rainfalls of 2 μeq ℓ^{-1} H^+.

When soybean plants were exposed to simulated rainfalls of 794 and 3162 μeq ℓ^{-1} H^+ dry mass of stems decreased 15 and 29%, respectively, compared with plants exposed to rains of 2 μeq ℓ^{-1} H^+ (Fig. 6). In a similar manner, dry mass of leaves decreased 5 and 14% in plants exposed to rainfalls of 794 and 3162, respectively, below plants exposed to 2 μeq ℓ^{-1} H^+.

In contrast to the decrease in leaf and stem biomass, mass of seeds per plant increased 11% in plants exposed to 794 compared with plants exposed to 2 μeq ℓ^{-1} H^+. Plants exposed to 3162 μeq ℓ^{-1} H^+ had an 11% decrease in seed mass compared with plants exposed to 2 μeq ℓ^{-1} H^+. Mean number of seeds per plant at rainfall acidities of 2, 794, and 3162 μeq ℓ^{-1} H^+ was 192, 179 and 169, respectively. Mean mass of seeds from plants exposed to rains of 794 μeq ℓ^{-1} H^+ was greater (0.12 g seed^{-1}) than that of plants exposed to rains of either 2 or 3162 μeq ℓ^{-1} H^+ (0.11 g seed^{-1}). The larger seed yield of plants exposed to 794 μeq ℓ^{-1} H^+ was attributed to this greater mass per seed since number of seeds per plant decreased significantly as rainfall acidity increased.

Number of pods per soybean plant decreased as simulated rain acidity increased. Plants exposed to simulated rain of 794 and 3162 μeq ℓ^{-1} H^+ had 9 and 12 fewer pods per plants, respectively, of plants exposed to 2 μeq ℓ^{-1}

H^+ rain. All plants had an average of 2.1 seeds per pod irrespective of rainfall acidity.

In soybeans, plant biomass abscised before harvest was small compared with total biomass produced. Specifically, dry mass of leaves abscised before harvest comprised only 3.3, 3.8 and 2.0% of the entire biomass produced at simulated rain of 2, 794 and 3162 μeq ℓ^{-1} H^+, respectively. A significantly ($p < 0.05$) lower mass of leaves was abscised from plants exposed to rainfalls of 3162 μeq ℓ^{-1} H^+ than from plants exposed to either 2 or 794 μeq ℓ^{-1} H^+.

Mean ratios of seed mass over mass of both stems and leaves for individual plants were significantly ($p < 0.05$) different among experimental treatments. Mean ratios for plants exposed to 794 μeq ℓ^{-1} H^+ were highest followed by ratios of 3162 μeq ℓ^{-1} H^+. Lowest ratios were obtained in plants exposed to 2 μeq ℓ^{-1} H^+. All mean ratios for soybeans were between 0.30 and 0.40. These values were much lower than the ratios of 1.5 to 2.6 obtained for pinto beans.

Experimental results demonstrate that linear relationships occur between several plant parameters with the hydrogen ion concentrations of the simulated rainfalls applied. In experiments with pinto beans, dry mass of above-ground biomass and dry mass of seeds decreased by the same percentages as the hydrogen ion concentration of the solution increased. In general, the decrease in plant biomass was reflected in smaller leaflet surface area that occurred after exposure to rainfalls of higher hydrogen ion concentrations. It is not known if decreases in biomass resulted directly from decreases in leaf area.

The high correlation between seed yield with leaf surface area and total plant biomass in pinto beans was not demonstrated in soybeans. An overall decrease in above-ground biomass with an increase in hydrogen ion concentration of the rainfalls was present in both species. Concomitant with these decreases in total biomass with an increase in hydrogen ion concentration were decreases in both pod and seed quantities. However, total seed mass did not follow this pattern in soybeans. In some way, soybean plants overcame the stress of simulated rainfalls of 794 μeq ℓ^{-1} H^+ to produce a greater seed yield than plants exposed to 2 μeq ℓ^{-1} H^+. The reason(s) for this compensatory response in soybeans is (are) unknown.

Field-grown crops — Several field crop experiments have been performed. In one set of experiments, field-grown soybeans were exposed to short-duration, simulated rainfalls of pH 4.0, 3.1, 2.7, and 2.3, which were applied to foliage three times weekly throughout the growing season. One treatment consisted of plants not exposed to any simulated rainfalls. All plants received ambient rainfalls (Evans <u>et al</u>., in press b). Fig. 7 shows a dose-response function for seed mass. Seed mass plant^{-1} decreased with an increase in hydrogen ion concentration of rainfalls applied. Applications of rainfalls of 100, 794, 1995, and 5012 μeq ℓ^{-1} (pH 4.0, 3.1, 2.7, and 2.3, respectively) decreased seed yields 2.6, 6.5, 11.4, and 8.5%, respectively. A treatment response function was determined for the relationship between the hydrogen ion concentration of the treatments and seed yield (Fig. 7). This function, expressed by the equation $y = 21.06 - 1.01 \log x$, has a correlation coefficient of -0.90 and its slope is significantly different from zero ($F - 13.55$, $P < 0.05$). Decreases in seed mass plant^{-1} with an increase in rainfall acidity resulted from decreases in number of pods plant^{-1} (Table 3) since the number of seeds pod^{-1} (2.6) and the mass of individual seeds (0.21 g) did not vary significantly among experimental treatments.

Some crop responses do not seem to provide convenient dose-response functions. The responses of garden beets to simulated acidic rain do not show a response H^+ concentration similar to soybeans (Evans _et al._, in press c). Plants exposed to simulated rainfalls of pH 5.7 in addition to ambient rainfalls had significantly higher values of fresh mass of tops, fresh mass of roots, dry mass of tops, dry mass of roots per plot than any other treatment (Table 4). With respect to fresh mass of marketable roots per plot, dry mass of roots per plot, and fresh mass of tops of marketable roots per plot values of plants exposed to ambient rainfalls were only significantly greater than for values of plants exposed to ambient rainfalls with simulated rainfalls of either pH 4.0, 3.1, or 2.7. No significant differences were observed among values obtained for simulated acidic rainfall treatments (pH 4.0, 3.1, and 2.7) at all parameters measured. After 3 sprays, foliar injury was observed on some garden beet plants. Plants exposed to ambient rainfalls only and plants exposed to ambient rainfalls plus simulated rainfalls of pH 5.7 exhibited no injury and pH 4.0-treated beets had a moderate amount of injury. A large portion of the leaf surface area of plants exposed to simulated rain at pH 3.1 and 2.7 showed injury, with greatest injury occurring on pH 2.7-treated plants. The lower the pH of the simulated rainfall treatment, the greater degree of foliar injury. Injury was greater for both number of lesions per unit area and total amount of leaf area injured. Lesions appeared as small areas of necrosis similar to the description of leaf injury given by Evans and Curry (1979).

Shortly after visible injury was observed, beets were exposed to several ambient rainfalls of 4 hours total duration which had a mean weighted pH of 3.88. Several days after these ambient rainfalls, injury was observed on beets of all treatments. However, the relationship between pH of treatment or H^+ concentration and quantity of foliar injury which existed prior to these ambient rainfalls was maintained. Garden beets exposed to ambient rainfalls only and plants exposed to ambient rainfalls in addition to simulated rainfalls of pH 4.0, 3.1, and 2.7 exhibited decreased root yields of 24, 35, 23, and 27%, respectively, of plants exposed to simulated rainfalls of pH 5.7 in addition to ambient rainfalls. This decrease in root yield of garden beet was coincident with visible foliar injury. This is the first experiment to demonstrate visible foliar injury due to both ambient rainfalls and simulated rainfalls above pH 3.1 under agronomic conditions. Although beet yields were decreased by exposure to simulated acidic rainfalls, no dose-response functions could be readily applied to the data.

In contrast with garden beets no significant differences were obtained when radishes were exposed to simulated acidic rain (Table 5). As a result no dose-response relationships may be applied to the data.

Fern Reproduction -- For several years we studied the effects of buffered solutions on sperm motility and reproduction of bracken fern (Evans, 1979; Evans and Conway, 1980). These buffered solutions were used to simulate exposure to acidic precipitation. Gametophytes of bracken fern (Pteridium aquilinum L.) in culture dishes were exposed to buffered solutions at a developmental stage for maximum fertilization.

Experiments were performed to determine the relationship between percent fertilization and percent sperm motility with final H^+ concentration of the buffers (Fig. 8). Both percent fertilization and percent motility with H^+ concentration resemble hyperbolic functions. At high H^+ concentrations, motility and fertilization levels are low. High motility and high fertilization were present at low H^+ concentrations. Experimental results show similar responses of spermatozoid motility and fertilization with H^+ concentrations of final pH values.

In an effort to understand effects of acidity on fertilization and spermatozoid motility, data of Fig. 8 were plotted in semi-logarithm form (Fig. 9). When plotted in this form, linear functions were obtained with linear correlation coefficients of -0.99 and -0.98 for log of motility and log of fertilization with H^+ concentration, respectively. These semi-logarithm plots of dose-response functions are very similar to dose-response functions of survival curves of single cells exposed to high doses of ionizing radiation (Elkind and Sutton, 1960; Sinclair, 1965).

Research results are presented in order to explore procedures to establish dose-response relationships of the effects of acidic precipitation on vegetation. From available data responses are most conveniently related to H^+ concentrations of simulated rainfalls. However, in all cases rainfall durations remain constant within an experiment. Dose-response relationships in which H^+ concentration is used to establish dose apply when statistically significant differences among treatments occur and when the only experimental variable is the acidity of the simulated rainfalls, independent of other environmental variables.

References

Alexander, M. 1980. Effects of acid precipitation on biochemical activities in soil. pp. 47-52. In Ecological Impact of Acid Precipitation (D. Drabløs and A. Tollan, Ed.). SNSF Project, Ås, Norway.

Elkind, M.M., and H. Sutton. 1960. Radiation response of mammalian cells grown in culture. 1. Repair of X-ray damage in surviving Chinese hamster cells. Rad. Res. 13: 556-593.

Evans, L.S. 1979. A plant developmental system to measure the impact of pollutants in rain water. J. Air Pollut. Control Assoc. 29, 1145-1148.

Evans, L.S. 1980. Foliar responses that may determine plant injury by simulated acid rain. Pp. 239-257. In Polluted Rain (Ed. T.Y. Toribara, M.W. Miller, and P.E. Morrow), Twelfth Annual Rochester International Conference on Environmental Toxicity, Plenum Publish. Co., New York, NY.

Evans, L.S. and C.A. Conway. 1980. Effects of acidic solutions on sexual reproduction of *Pteridium aquilinum*. Amer. J. Bot. 67: 866-875.

Evans, L.S. and T.M. Curry. 1979. Differential responses of plant foliage to simulated acid rain. Amer. J. Bot. 66: 953-962.

Evans, L.S., N.F. Gmur, and F. Da Costa. 1977. Leaf surface and histological perturbations of leaves of *Phaseolus vulgaris* and *Helianthus annuus* after exposure to simulated acid rain. Amer. J. Bot. 64: 903-913.

Evans, L.S., N.F. Gmur, and F. Da Costa. 1978. Foliar response of six clones of hybrid poplar to simulated acid rain. Phytopathology 68: 847-856.

Evans, L.S., G.R. Hendrey, G.J. Stensland, D. Johnson, and A.J. Francis. In press a. Acidic Precipitation: Considerations of an air quality standard. Water, Air, and Soil Pollution.

Evans, L.S. and K.F. Lewin. 1981. Growth, development, and yield responses of pinto beans and soybeans to hydrogen ion concentrations of simulated acidic rain. Environ. and Exper. Bot. 21: 103-113.

Evans, L.S., K.F. Lewin, C.A. Conway, and M.J. Patti. In press b. Seed yields (quantity and quality) of field-grown soybeans exposed to simulated acidic rain. The New Phytologist.

Evans, L.S., K.F. Lewin, and E.A. Cunningham. in press c. Effects of simulated acidic rain on yields of field-grown radishes and garden beets. Agriculture and Environment.

McFee, W.W. 1979. Effects of acid precipitation and atmospheric deposition on soils. In: A National Program for Assessing the Problem of Atmospheric Deposition (Acid Rain). A Report to the Council on Environmental Quality. National Atmospheric Deposition Program, pp. 64-82.

Sinclair, W.K. 1965. Survival and recovery after x-radiation of synthronized Chinese hamster cells in culture. Jap. J. Genetics (Supplement) 40: 141-161.

Steel, R.G. and J.H. Torrie. 1960. Principles and Procedures of Statistics. McGraw-Hill, New York.

Voigt, G.K. 1980. Acid precipitation and soil buffering capacity. pp. 53-57. In Ecological Impact of Acid Precipitation (D. Drabløs and A. Tollan, Ed.) SNSF Project, Ås, Norway.

Table 1. Percentage Distribution of Rainfall Events in the Northeastern U.S. by pH (Benkovitz, personal communication).

Percentage of all events	pH interval
0.9	3.00-3.49
31.4	3.50-3.99
56.4	4.00-4.49
10.5	4.50-4.99
0.6	5.00-5.49
0.2	5.50-5.99

Mean pH of all samples was 4.12.

Table 2. Mean Concentrations of Selected Ions in Rain.

Cation	$\mu eq\ \ell^{-1}$	Anion	$\mu eq\ \ell^{-1}$
NH_4^+	27.96[a]	$SO_4^=$	96.93[a]
Na^+	45.63[a]	NO_3^-	49.06[a]
Ca^{++}	8.3[b]	Cl^-	51.80[a]
Mg^{++}	11.4[b]	F^-	5.26[c]
K^+	10.0[b]		
Fe^{+++}	3.22[c]	TOTAL ANIONS	203.05
Zn^{+++}	3.98[c]		
Ni^{++}	1.70[c]		
Cu^{++}	5.98[c]		
Cd^{++}	0.71[c]		
Pb^{++}	12.35[c]		
H^+	71.74[a]		
Mn^{++}	1.09[c]		
TOTAL CATIONS:	204.06		

---

[a] Data taken from weighted average of rainfalls collected by BNL Sequential Sampler from May through Sept. for the years 1977, 1978 and 1979.

[b] Data from BNL samples taken from May through Sept. 1979 for the MAP3S network.

[c] Data from R. Adamowicz for Atlantic County, N.J., for the years 1972, 1973, and 1974.

Table 3. Seed Yield Characteristics of Field-grown Soybeans Exposed to Simulated Acidic Rain.

Treatment	Pod Number plant^{-1}	Seed number plant^{-1}	Seed number pod^{-1}	Mass seed^{-1}
Rain pH 2.3	32±1[a/]	87±2[b/]	2.7±0.05[c/]	0.21±0.00[d/]
" " 2.7	32	82	2.5	0.21
" " 3.1	34	89	2.6	0.21
" " 4.0	36	89	2.6	0.21
Ambient Rainfall only (AR)	36	91	2.5	0.22

[a/] Mean and standard error of all means, respectively. Probabilities derived from two-tailed T-tests are: AR vs. pH 2.7: p=0.01; AR vs. pH 2.3: p=0.01 (Steel and Torrie, 1960).

[b/] Means and standard error of all means, respectively. An analysis of variance of the means showed no significant differences among the treatment means.

[c/] Mean and standard error of all means, respectively. An analysis of variance of the means gave the probability value of 0.09. Probabilities derived from two-tailed T-tests are: AR vs. pH 2.3: p=0.01; pH 2.7 vs. pH 2.3: p=0.03.

[d/] Mean and standard error of all means, respectively. An analysis of variance of the means showed no significant differences among the treatment means.

Table 4. **Effects of Application of Simulated Rainfalls to Field-Grown Garden Beets Exposed to Ambient Rainfalls.**

	Treatments				
Parameter Measured	AR[1]	5.7	4.0	3.1	2.7
Number of marketable roots per plot	$15^{a,c}$[2]	15^{a}	13^{b}	13^{b}	$13^{b,c}$
Fresh mass (g) of tops of marketable roots per plot	732.7^{b}	809.3^{a}	577.9^{c}	615.3^{c}	633.4^{c}
Fresh mass (g) of marketable roots per plot	413.6^{a}	483.4^{a}	315.1^{c}	$370.1^{b,c}$	350.8^{c}
Dry mass (g) of tops of marketable roots per plot	66.9^{b}	73.4^{a}	55.2^{c}	57.9^{c}	57.6^{c}
Dry mass (g) of marketable roots per plot	50.6^{b}	59.4^{a}	39.1^{c}	44.2^{c}	$44.0^{b,c}$
Fresh mass (g) per marketable root	29.1^{a}	31.1^{a}	25.5^{a}	29.4^{a}	27.6^{a}
Dry mass (g) per marketable root	3.5^{a}	3.8^{a}	3.1^{a}	3.5^{a}	3.4^{a}

---

[1] AR, 5.7, 4.0, 3.1 and 2.7 denote treatments of ambient rainfalls (AR) only, and simulated rainfalls of pH 5.7, 4.0, 3.1, and 2.7 in addition to ambient rainfalls, respectively.

[2] Statistical significance determined by analysis of variance. For each parameter measured, numbers followed by the same letter are not significantly different ($p < 0.05$) according to the Student-Newman-Keuls Multiple Range Test (Steel and Torrie, 1960).

Table 5. Effects of Application of Simulated Rainfalls to Field-Grown Radishes Exposed to Ambient Rainfalls.[a]

Parameter Measured (per plot basis)	Treatments				
	AR[b]	5.7	4.0	3.1	2.7
Number of marketable roots	54	53	54	51	53
Fresh mass (g) of tops of marketable roots	373.5	380.0	379.6	359.6	382.8
Fresh mass (g) of marketable roots	394.8	399.6	407.0	377.1	396.8
Dry mass (g) of tops of marketable roots	25.7	26.5	26.2	24.7	26.6
dry mass (g) of marketable roots	19.3	19.6	19.8	18.9	19.4
Number of cull plants	7	7	7	8	8
Fresh mass (g) of cull plants	21.0	21.1	21.8	24.1	23.0
Dry mass (g) of cull plants	1.6	1.6	1.7	1.8	1.6
Total number of plants	61	60	61	59	61
Total fresh biomass (g)	789.4	800.7	808.4	760.8	802.6
Total dry biomass (g)	46.6	47.6	47.7	45.3	47.6

[a] Mean values are shown. Within each parameter measured there were no significant differences ($p < 0.05$) as determined by the Student-Newman-Keuls Multiple Range Test (Steel and Torrie, 1960).

[b] AR, 5.7, 4.0, 3.1 and 2.7 denote treatments of ambient rainfalls only (AR), and simulated rainfalls of pH 5.7, 4.0, 3.1 and 2.7 in addition to ambient rainfalls, respectively.

Figure 1. Frequency distribution of the pH of ambient rain events during the 1980 growing season. The figures represent the weighted average of hourly samples collected during each event for the period of 12 May through 26 August 1980. Two percent of all samples had an inadequate volume for the pH to be determined. No rainfall samples had a pH below 3.0 or above 6.5. The volume weighted mean H^+ concentration of all rainfalls was 86.6 μeq ℓ^{-1} (pH 4.06).

Fig.2. Frequency distribution of ambient rainfall shower durations from the period of 12 May through 26 August 1980 at Brookhaven National Laboratory, Upton, Long Island, New York. A shower is defined as a precipitation event in which no additional precipitation occurs within 60 minutes after the end of the event. Other rainfall showers of 263, 360, 381, and 697 minutes were not plotted. These higher duration rainfalls accounted for 7.2% of all showers.

Fig. 3. Frequency distribution of ambient rainfall shower volumes from the period of 12 May through 26 August 1980 at Brookhaven National Laboratory, Upton, Long Island, New York. A shower is defined as a precipitation event in which no additional precipitation occurs within 60 minutes after the end of the event. Other rainfall showers of 9.65, 9.91, 10.4, 11.1, 11.7, 13.97, 16.76, 19.8, 21.1 and 21.84 mm were not plotted. These higher rainfall events accounted for 18% of all showers.

Fig. 4. Dose-response functions for leaf area injured by exposure to simulated acid rain at various hydrogen ion concentrations. The values used for this figure were taken from Evans *et al.*, 1977, 1978; Evans and Curry, 1979. Symbols: open triangles - soybeans (*Glycine max*), open circles - bracken fern (*Pteridium aquilinum*), open squares - oak (*Quercus palustrus*), closed squares - poplar (*Populus* species), closed circles - sunflower (*Helianthus annuus*), closed triangles - pinto bean (*Phaseolus vulgaris*). The regression lines shown were drawn from best-fit curves after statistical analyses of the data. All correlation coefficients were between 0.96 and 0.98.

Fig. 5. Rainfall acidity response relationships of (a) seed quantity (open circles), (b) dry mass of total biomass produced above ground (closed circles), (c) pod quantity (open squares), (d) dry mass of seeds (closed triangles), and (e) dry mass of abscised leaves (closed squares) of pinto bean (Phaseolus vulgaris) plants exposed to simulated rainfalls at various hydrogen ion concentrations are shown. The correlation coefficients of linear regression analyses for the relationships are (a) −0.91, (b) −0.91, (c) −0.95, (d) −0.94, (e) +0.66. The straight lines were drawn from regression analyses data. Single-tailed Dunnett's multiple range test in conjunction with analysis of variance shows the following significant ($p < 0.05$) differences; seed quantity: 2 > 1259 μeq ℓ^{-1} H^+, dry mass of total biomass produced above ground no statistical differences; pod quantity: no statistical differences; dry mass of seeds: 2 > 1995 μeq ℓ^{-1} H^+ (Steel and Torrie, 1960). The experiment was performed three times. Results of the typical experiment are shown.

Fig. 6. Rainfall acidity response relationships of (a) seed quantity (open circles), (b) dry mass of total biomass produced above ground taken at harvest (closed circles), (c) pod quantity (open squares), (d) dry mass of seeds (closed triangles), and (e) dry mass of abscised leaves (closed squares) of soybean (*Glycine max*) plants exposed to simulated rainfalls at various hydrogen ion concentrations are shown. The correlation coefficients of linear regression analyses for the relationships are (a) -0.94, (b) -1.00, (c) -0.86, (d) -0.72 and (3) -0.98. The straight lines and high negative correlation coefficients for (a), (b), (c) and (e) indicate the presence of functional relationships. A low correlation coefficient was found in the case of dry mass of seeds versus hydrogen ion concentration because plants exposed to rainfalls of 794 μeq ℓ^{-1} H^+ had high seed yields. The straight lines (except dry mass of seeds) were drawn from regression analysis data. For values of dry mass of seeds, a line connected all points. The Student-Newman-Keuls multiple range test in conjunction with analysis of variance shows the following significant ($p < 0.05$) differences; seed quantity: 2 > 794 > 3162 μeq ℓ^{-1} H^+; dry mass of total biomass produced above ground taken at harvest: 2 > 794 > 3162 μeq ℓ^{-1} H^+; pod quantity: 2 > 794 > 3162 μeq ℓ^{-1} H^+; dry mass of seeds: 794 > 2 > 3162 μeq ℓ^{-1} H^+; dry mass of abscised leaves: 2 = 794 > 3162 μeq ℓ^{-1} H^+ (Steel and Torrie, 1960). The experiment was performed three times. Results of a typical experiment are shown.

Fig. 7. Relationship between soybean seed yield per plant and the hydrogen ion concentration of the treatments. Ambient rainfalls provided an average hydrogen ion concentration of 7.92 μeq ℓ^{-1}. The four simulated acidic rainfall treatments provided hydrogen ion concentrations of 100, 794, 1995, and 5012 μeq ℓ^{-1}.

Fig. 8. Comparison of percent fertilization (cordate gametophytes with sporophytes above the no buffer control [circles]) and perent motile spermatozoids at various hydrogen ion concentrations. The triangles and squares represent motility samples taken 2-4 and 8-10 min, respectively, after initial exposure to buffers. Percent motility values were plotted against initial pH values because the pH did not change during exposure. Percent fertilization values were plotted against the pH value after 3.5 hr of exposure.

Fig. 9. Comparison of percent fertilization (cordate gametophyes with sporophytes above the no buffer control [circles]) and percent spermatozoids (triangles) after a 2-4 min exposure to buffers various H^+ concentrations. Both percent fertilization and percent motility were plotted logarithmically. When plotted in this fashion, motility data gave the following statistics: Y-intercept value: 58.21; slope: -0.045; correlation coefficient: -0.99. When fertilization data were plotted in the same fashion the following statistics were obtained: Y-intercept value = 51.18; slope -0.041; correlation coefficient = -0.98.

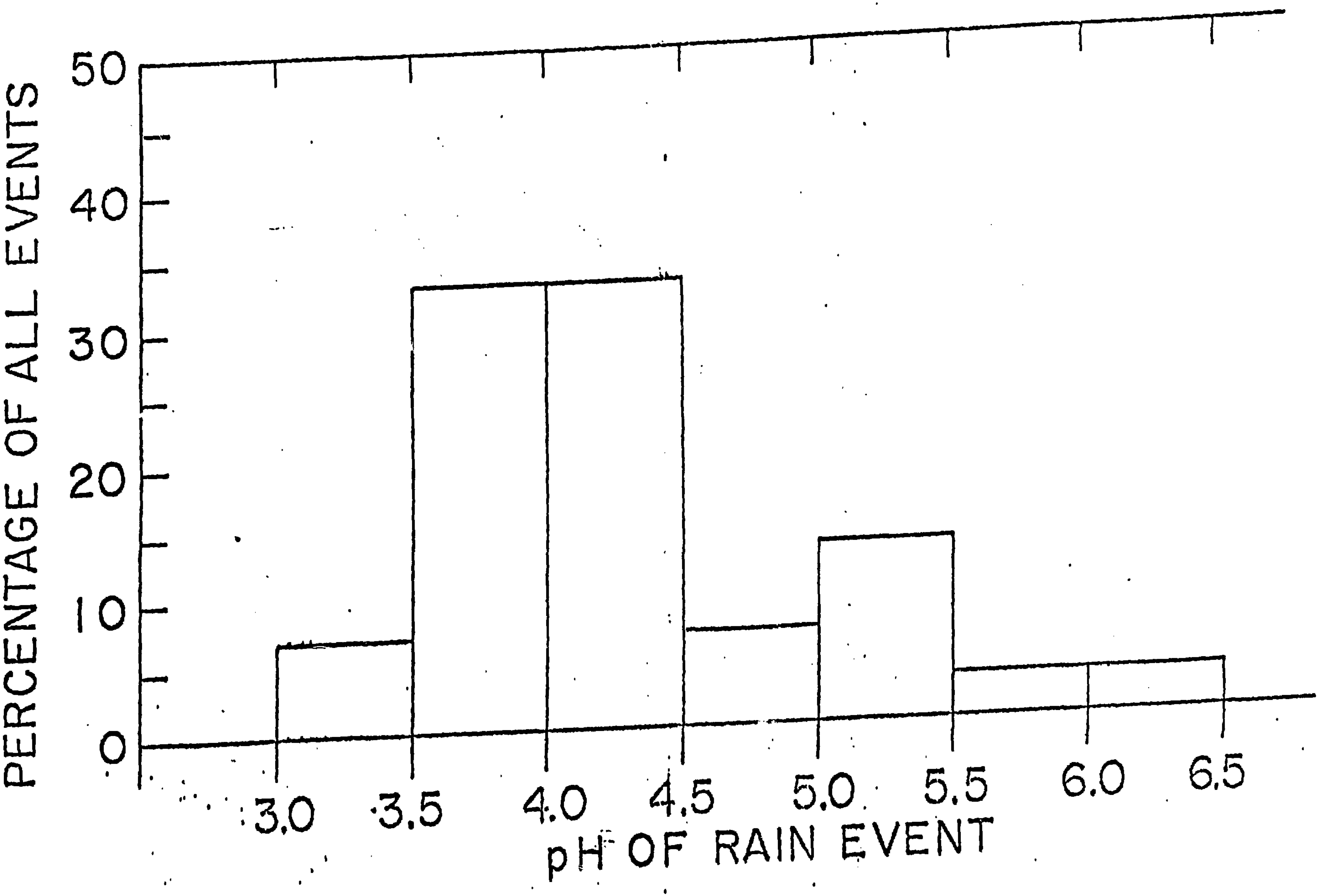

50
40
30
20
10
0
PERCENTAGE OF ALL EVENTS
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
pH OF RAIN EVENT

Figure 1

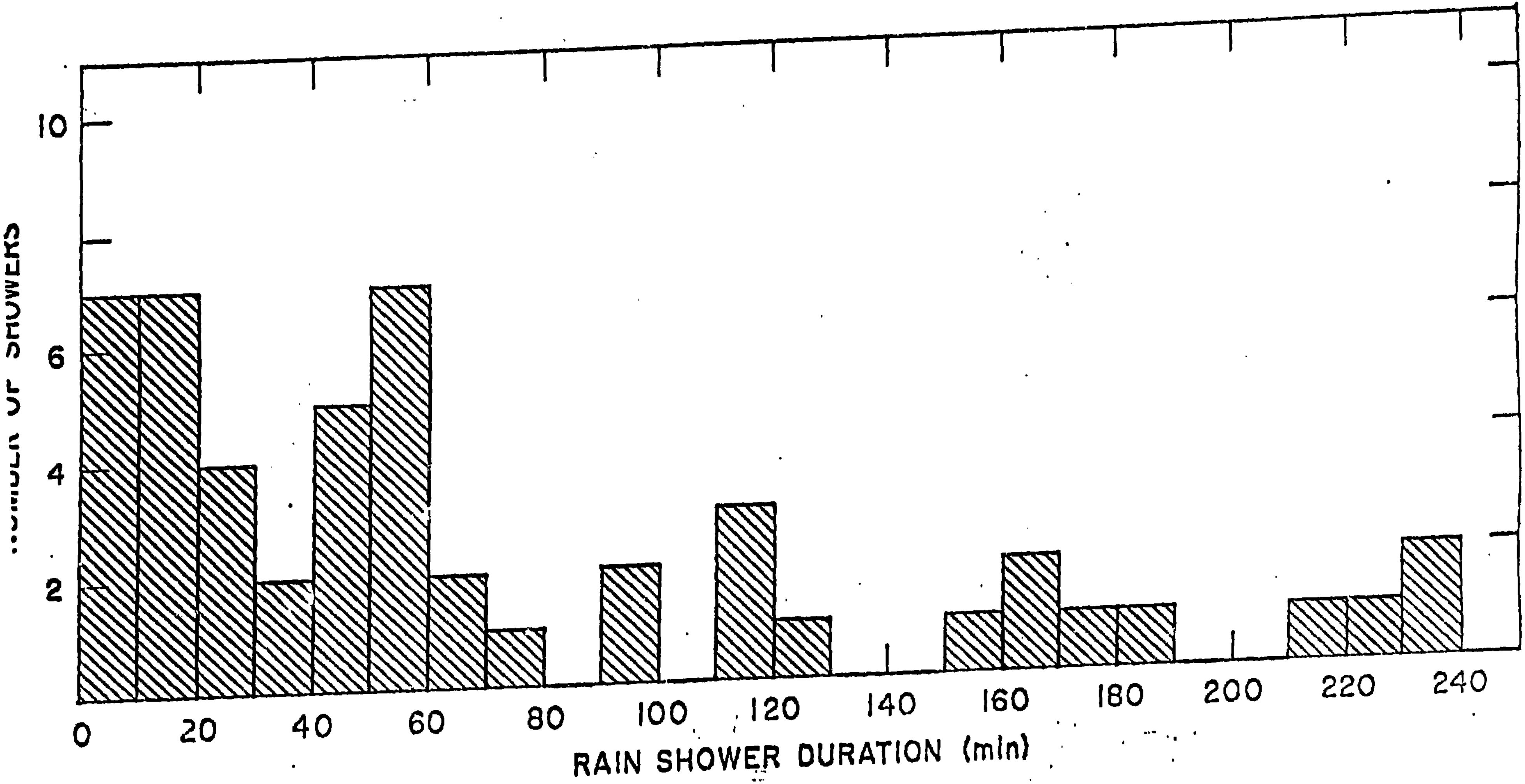

10
6
4
2
0
20
40
60
80
100
120
140
160
180
200
220
240
RAIN SHOWER DURATION (min)
NUMBER OF SHOWERS

Figure 2

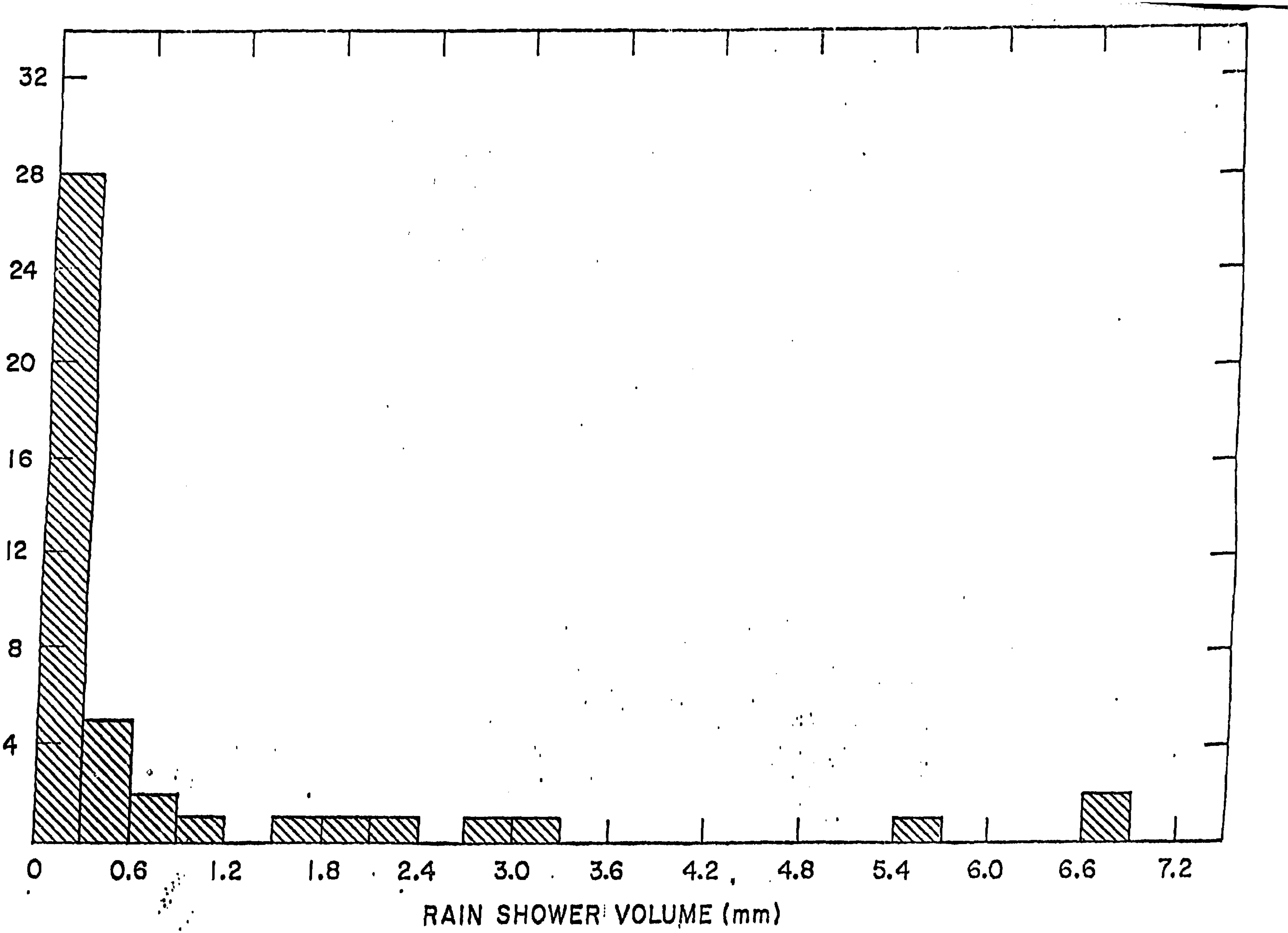

32
28
24
20
16
12
8
4
0
0.6
1.2
1.8
2.4
3.0
3.6
4.2
4.8
5.4
6.0
6.6
7.2
RAIN SHOWER VOLUME (mm)

Figure 3

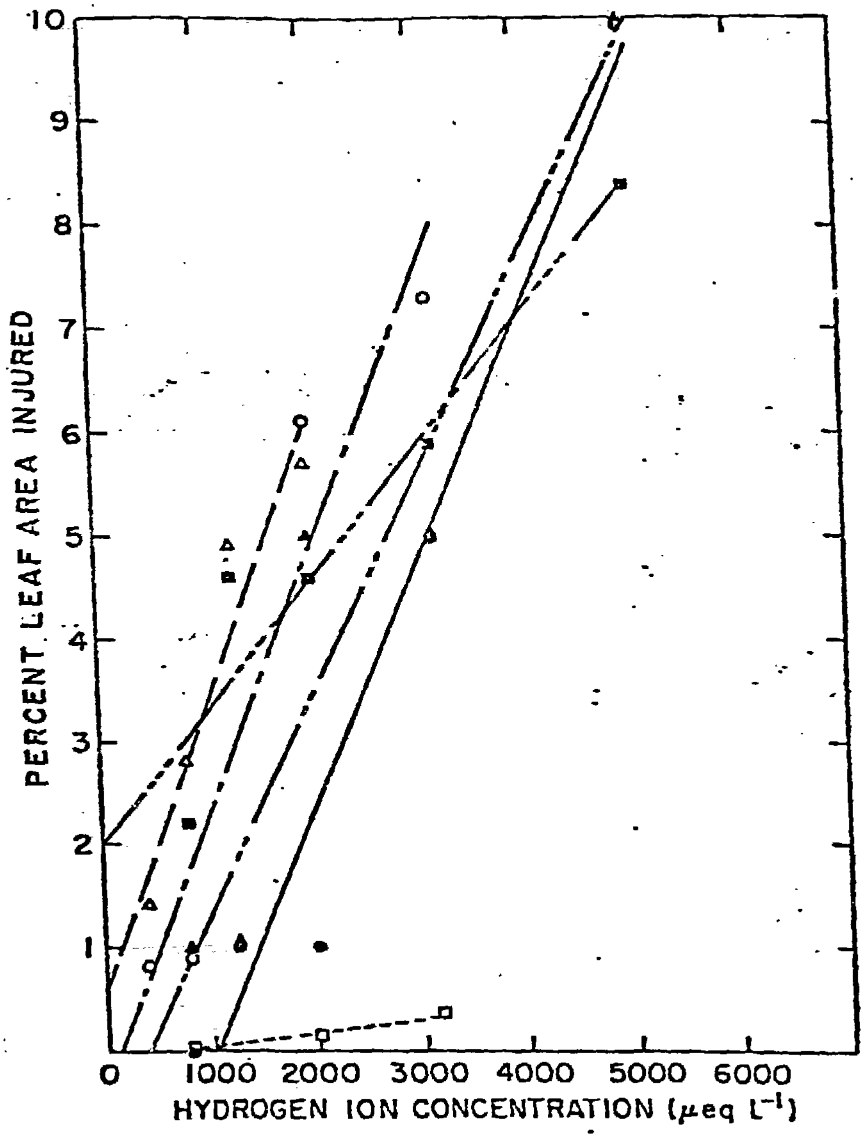

10
9
8
7
6
5
4
3
2
1
PERCENT LEAF AREA INJURED
0
1000
2000
3000
4000
5000
6000
HYDROGEN ION CONCENTRATION (μeq L⁻¹)

Figure 4

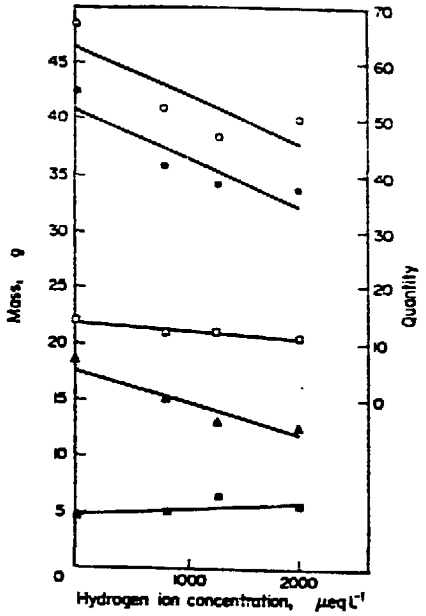
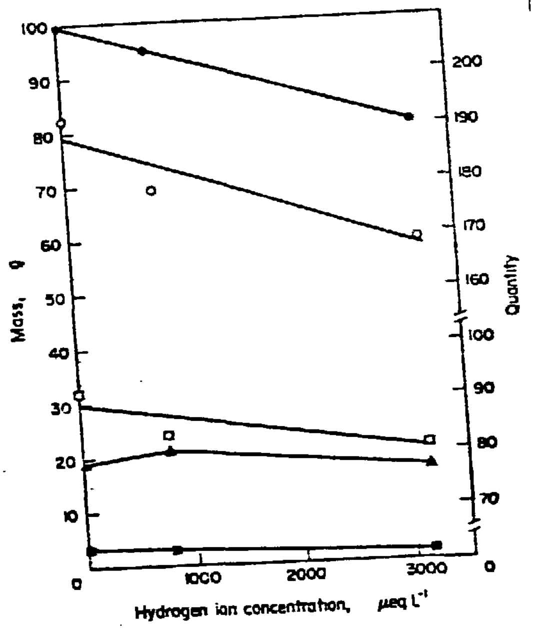

Mass, g
Quantity
0
5
10
15
20
25
30
35
40
45
0
10
20
30
40
50
60
70
1000
2000
Hydrogen ion concentration, μeq L⁻¹

Figure 5



100
90
80
70
60
50
40
30
20
10
0
Mass, g
200
190
180
170
160
100
90
80
70
0
Quantity
1000
2000
3000
Hydrogen ion concentration, μeq L⁻¹

Figure 6

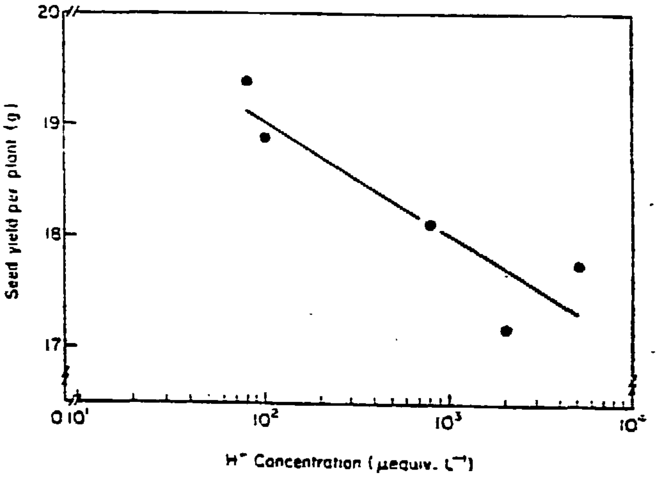

20
19
18
17
Seed yield per plant (g)
0 10¹
10²
10³
10⁴
H⁺ Concentration (μequiv. L⁻¹)

Figure 7

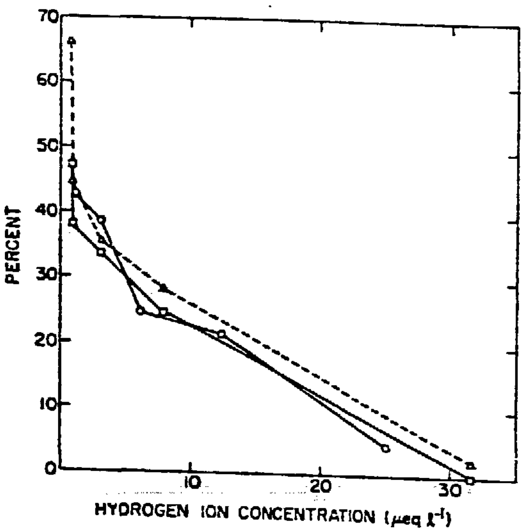

PERCENT
70
60
50
40
30
20
10
0
10
20
30
HYDROGEN ION CONCENTRATION (μeq ℓ^{-1})

Figure 8

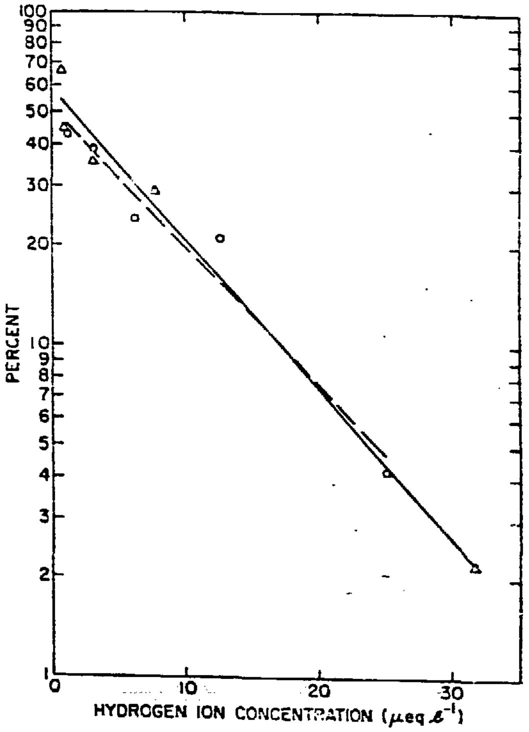

100
90
80
70
60
50
40
30
20
10
9
8
7
6
5
4
3
2
1
PERCENT
0
10
20
30
HYDROGEN ION CONCENTRATION (μeq ℓ^{-1})

Figure 9