

data presented in Tables I, II, and III. Although the results in Table IV do not show a soil effect, in a duplicate of the same experiment with two high pH soils, 100 pounds of phosphorus pentoxide as monocalcium phosphate supplied 17 times as much available phosphorus as an equivalent amount of fused rock phosphate. This is in contrast to the 1 to 1 ratio shown in Table IV.

Plant species may also affect the availability of the fertilizer. In a study of the feeding power of plants for rock phosphate, Fried (3) showed that the percentage of phosphorus derived from the fertilizer is a function of plant species when one of the sources of phosphorus is rock phosphate. The quantitative evaluation of factors affecting fertilizer

evaluation such as soil, plant species, and others is a further extension of the proposed technique.

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## TRACE ELEMENTS

# Progress Report on Research with Particular Reference to New Jersey Soils

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For the past 14 years the New Jersey Agricultural Experiment Station's department of soils has been studying trace-element relationships in soils and plants. These studies involved laboratory, greenhouse, cylinder, and field work with boron, molybdenum, iron, manganese, zinc, copper, cobalt, iodine, fluorine, and bromine. Soils were examined for their total and available contents of these elements. Efforts were made to determine optimum levels of these elements in crop plants and to diagnose deficiency and toxicity symptoms. Finally, some conclusions were arrived at, and suggestions made concerning use of these elements in crop production, with particular reference to New Jersey.

**B**ORON, MOLYBDENUM, IRON, MANGANESE, ZINC, AND COPPER, belong to a group called minor or trace elements, among the 15 elements that are known to be required by plants. Soil supplies of nitrogen and of the major and secondary mineral nutrients, including phosphorus, potassium, calcium, magnesium, and sulfur, are regularly renewed by use of fertilizers and liming materials. But the soil itself is usually depended on to supply the necessary amounts of trace elements. Applications of manure and compost aid in maintaining adequate quantities of these elements in usable form. Deep-rooted plants, such as sweet clover, alfalfa, and ragweed, absorb trace elements from lower soil horizons and elevate them to the surface. Additional supplies are made available by growing green manures and plowing them under (7).

The standard fertilizer and liming materials contribute small quantities as impurities. But there are many condi-

tions under which it becomes necessary to supply additional amounts of one or another or of several of these elements for plant use. As crop yields are stepped up to ever higher levels, likelihood of trace-element deficiency is increased.

Trace-element requirements of animals are somewhat similar to those of plants, but there are important differences. Animals require iron, manganese, copper, and zinc but, so far as is known, they have little if any direct need for boron or molybdenum. Deficiencies of these elements in soils, however, may result in the production of low-quality crops, thus indirectly affecting the animals that consume them. Animals also require cobalt, fluorine, and iodine, trace elements that are normally contained in but have no known value to crop plants. Because most crop plants are grown primarily for food or feed, it is important to consider trace elements in soils in relation to the needs of both plants and animals.

#### Experimental Program

The soils department of the New Jersey Agricultural Experiment Station has studied soil-plant relationships of every one of these trace elements, and some additional ones, in considerable detail during the past 14 years. A large amount of analytical work, involving spectrographic as well as chemical procedures, has been and is being done on soils and plants. Tests of trace-element salts on plants have been carried out in the greenhouse with solution cultures and soil, in outdoor cylinders of soil, and in fields on the Station Farm and at widely separated locations about the state.

Early in these studies 20 of the most important agricultural soils of New Jersey were selected for special examination. Representative virgin areas of these soils were located, from which supplies could be obtained as required. The names of these soils and their content of nine trace elements are given in Table I.

Because an acre of soil to plow depth of 7 inches weighs approximately 2,000,000 pounds, the value shown can be calculated to pounds per acre by multiplying by 2. Thus the plow depth of 1 acre of Norton silt loam contains over 10,000 pounds of total manganese but less than 5 pounds of total molybdenum.

The quantities of trace elements in whole plants and in their several parts vary between wide extremes. They differ greatly even among plants of the same species and variety, depending on the nature of the soil on which the plants were grown and the weather that prevailed. They vary also from species to species of plants so grown (Table II). Kentucky bluegrass, spinach, and ragweed were notably high in most of the trace elements reported on.

Analyses were also made of plant samples that were systematically collected from widely separated parts of the state, primarily from areas of the 20 important soil types previously referred to. High and low values are given in Table III. Special attention is called to the number of weeds listed in the column of plants containing the highest quantities of these elements.

Assuming 10,000 pounds dry weight of plant material, a yield that is readily produced annually by 1 acre of good land, the content of zinc varied between 0.06 pound in red clover and 2.8 pounds in lamb's-quarters. Similarly, the molybdenum content of that weight of produce varied between 0.001 pound in cauliflower and 0.12 pound in ladino clover.

The availability to plants of the soil's mineral supplies of trace elements is greatly influenced by its reaction. Most of these elements have higher availabilities at low than at high pH values (Table IV). But, contrary to previous findings, the availability of copper was not reduced (73) as soil pH values were raised, and the availability of molybdenum (9) was greatly increased. These statements apply to the Sassafras sandy loam, both as it came from the field and after it had received liberal additions of trace-element salts, and they appear to be applicable to other soils.

The atmosphere is a possible source of trace elements, especially at points in close proximity to industrial centers, such as New Brunswick, N. J., where precipitation was collected and analyzed for five of these elements (Table V). The quantities found were large enough to be significant in agricultural practice.

Analyses for trace elements were made of 223 samples of edible portions of six crops that were carefully chosen from 18 states (2). Wide variations were found in the trace-element content of each species (Table VI). In alfalfa, obtained under instructions from California, Utah, Colorado, Oklahoma, Kansas, Nebraska, Minnesota, Wisconsin, Michigan, New York, and New Jersey, the lowest boron

value, 18 p.p.m. of dry matter, was obtained in Michigan, the lowest iron and molybdenum values, 110 and 0.1 p.p.m., respectively, in Wisconsin, the lowest manganese value, 10 p.p.m., in Colorado, the lowest copper and cobalt values, 13 and 0.04 p.p.m., respectively, in Kansas, and the lowest zinc value, 13 p.p.m. in Utah (3).

Trace-element values for cabbage, lettuce, snap beans, spinach, and tomatoes, collected in South Carolina, Virginia, Maryland, New Jersey, New York (Long Island), Ohio, Indiana, Illinois, and Colorado, tended to increase from east to west, except for manganese, of which the reverse was true. Cabbage had a molybdenum range between 0.0 and 24 p.p.m. Lettuce had a manganese range between 1 and 169 p.p.m. and a copper range between 3 and 60 p.p.m. Snap beans had a cobalt range between 0.00 and 0.26 p.p.m., spinach a boron range between 12 and 88 p.p.m., and tomatoes an iron range between 1 and 1938 p.p.m.

A factorial cylinder experiment was set up in which copper, zinc, manganese, molybdenum, and cobalt were applied singly and in combinations of two, three, four, and five of these elements to a Sassafras sandy loam. Standard amounts of a complete fertilizer containing boron and magnesium were applied to all the cylinders. The pH values were made to vary between 4.6 and 8 by applications of calcium carbonate, where required, at the start of the test, and soybeans, wheat, and alfalfa were grown in succession over a 4-year period. The five trace elements were added to the soil in equivalent and relatively large amounts. Data on alfalfa yields during the last 2 years of the test are shown in Table VII. At pH values of 4.6 the alfalfa was a complete failure. At pH 6 the alfalfa grew well, but negative effects resulted from the heavy applications of trace elements. The same applied to pH 7, but all yields were much higher. At pH 8 marked yield increases over the checks were obtained from all trace elements except cobalt, but most notably from applications of manganese.

A similar experiment was conducted with soils of six other series, most of which had much higher cation exchange capacities than the Sassafras sandy loam. For the heavier soils, the quantities of trace-element salts applied were not so excessive and marked yield increases were obtained from one or several of those applied (Table VIII). As total applications increased, with inclusion of three or more salts, yields tended to drop off on all soils, but most notably on Lakewood sand.

### Practical Considerations

From a study of these and many additional data obtained from a large number

of tests, together with observations on a great variety of plants grown in the greenhouse, in outdoor cylinders, and under field conditions, certain conclusions have been reached and practical suggestions have been developed for application to crop production in New Jersey.

**Boron** The boron content of New Jersey soils (78) ranges between 18 and 110 p.p.m., only a very small percentage of which is readily available for crop use. The test for availability is solubility in hot water. A value of 0.35 p.p.m. of soluble boron was set as the passing point for medium-textured soils at pH values between 6.0 and 6.5. Smaller amounts may suffice for such crops as potatoes and sweet potatoes that are grown at low pH values on the lighter types of soil. Larger amounts may be required on heavier soils, on soils at high pH values, and for crops that have high boron requirements, such as alfalfa, cauliflower, celery, and beets. At least 12% of the cropped land in New Jersey is in need of boron for optimum yields of the crops being grown.

The boron content of whole plants ranges between about 5 and 100 p.p.m. based on dry weight of material, but these values can readily be stepped up to much higher levels by applying borax. At these higher levels toxicity symptoms, which are indicated by yellowish brown spots of dead tissue around the edges of leaves, may appear. In severe cases entire leaves and plants may die.

Boron-deficiency symptoms include yellowing and reddening of tip leaves of alfalfa, cracked stems of celery, accordion-like rings on leafstalks of pumpkins, brownish water-soaked areas in turnips, black areas in stem centers of cabbage and other crucifers and on surfaces of root crops, internal corking of apples, with dieback of twigs and rosetting of the leaves of the trees, and discoloration and death of terminal buds of sunflowers and many other plants.

The standard remedy for boron deficiency is to apply, with the fertilizer, from 10 to 25 pounds of borax, containing 11.34% boron, an acre, the smaller quantity on the sandier soils and for the more sensitive crops and the larger quantity on the heavier soils and for the less sensitive crops. For some crops, notably cauliflower, applications of 50 pounds of borax may be required, especially on overlimed heavy soils. Fertilizer companies are asked to add 5 pounds of borax to each ton of fertilizer sold in New Jersey, and it is common practice to raise this to 100 pounds a ton in fertilizer that is to be used for top-dressing alfalfa. Because borax is readily leached out of the soil, some consideration has been given to a less soluble form of boron such as colemanite.

Sassafras soils are notably deficient in available boron. Alfalfa yields were

**Table I. Trace Elements in A Horizons of 20 Important Agricultural Soils of New Jersey<sup>a</sup>**

Soil Type	(in parts per million, on dry-weight basis)									
	Mn	Zn	Cu	Co	Ni	Mo	B	I	F	
Norton silt loam	5200	225	39	30.8	40	2.2	110	12.1	220	
Lawrenceville silt loam	1850	45	16	6.1	12	2.1	75	8.2	161	
Rockaway stony loam	1300	132	24	9.8	19	1.8	20	4.6	156	
Annandale loam	1250	94	60	18.2	19	2.3	27	1.8	110	
Washington loam	1120	156	22	8.6	17	..	..	8.0	..	
Rockport shale loam	960	105	37	11.6	24	..	..	4.5	..	
Palmyra gravelly loam	950	89	12	4.7	14	2.3	25	3.9	249	
Bermudian silt loam	900	95	40	11.5	32	2.1	70	4.9	166	
Hazen stony loam	600	101	25	8.2	19	2.0	40	1.2	409	
Squires loam	580	25	18	4.3	16	2.3	30	0.0	220	
Dutchess shale loam	570	77	14	6.6	15	3.3	50	6.2	370	
Hoosic gravelly loam	330	92	16	6.3	23	1.9	55	2.4	285	
Matapeake loam	210	70	12	3.2	12	2.2	55	1.6	111	
Sassafras gravelly loam	200	16	2	0.6	3	..	..	4.0	..	
Whippany silty clay loam	160	67	8	4.3	11	1.5	30	2.3	201	
Colts Neck sandy loam	160	43	7	1.9	0	1.6	50	4.7	105	
Collington loam	160	69	11	2.5	8	1.8	65	2.8	107	
Woodstown silty clay loam	150	32	6	1.9	10	..	..	3.6	..	
Lakewood sand	120	10	2	0.2	2	0.8	18	0.0	29	
Evesboro loamy sand	90	50	19	2.8	14	1.2	30	1.5	105	

<sup>a</sup> Fe content of these soils would be expected to range between 1 and 6%.

increased as much as 1 ton dry weight an acre on such soils by applications of 20 pounds of borax. Hay from boron-treated soil contained boron equivalent to about 2 pounds of borax a ton.

The heavier soil types have considerable capacity to fix water-soluble boron. Yet nearly 75% of a 20-pound application of borax an acre was leached from such soils by water equivalent to one fourth the annual rainfall of New Jersey. The amount of water-soluble boron in a soil is materially increased by use of green manures, but such increases are not sufficient to meet the entire boron needs of crops growing on boron-deficient soils.

**Molybdenum** The molybdenum content of New Jersey soils (5) ranges between 0.8 and 3.3 p.p.m. The test for availability is solubility in a/N solution of ammonium acetate adjusted to pH 9 with ammonium hydroxide. The solubility of soil molybdenum increases markedly with rise in pH value. The good effects that sometimes result from very heavy applications of liming materials to acid soils in preparation for such crops as alfalfa and cauliflower may be due in large part to the resulting increase in the amount of molybdenum at their disposal. In nutrient-solution cultures 1 part of molybdenum in 1 billion parts of solution is sufficient to meet alfalfa requirements (8).

Except for those of the Dutchess series, New Jersey soils, notably those of limestone origin, are characteristically low in molybdenum. Their molybdenum is largely associated with the clay fraction. The water-soluble molybdenum that is added to soils in fertilizers and liming materials is too small in amount to meet requirements on molybdenum-deficient soils.

The molybdenum content of New Jersey plants normally ranges between

about 0.3 and 5 p.p.m. dry weight of material (7). These levels can readily be increased to 100 p.p.m. or more by applications of soluble forms of the element. These high values do not appear to be injurious to plants, but they may be highly toxic to animals with resulting development of "teart" disease, the first symptom of which is very serious diarrhea. With continued consumption of feed containing large amounts of molybdenum animals become badly emaciated, and they may die. Toxicity is known to be greatly reduced if the feed is also high in copper or if a copper salt has been made available to the animals.

The best-known symptom of molybdenum deficiency in plants is "whiptail" in cauliflower. As the word indicates, the older leaves become long and slender, consisting mostly of the midrib, with relatively small amounts of ruffled leaf tissue. The younger terminal leaves tend to curl counterclockwise. Salable heads are not formed, and the small ones that develop have leaves scattered through the curd. In one field of 75 acres of New Jersey cauliflower, about 45 acres was unmarketable because of molybdenum deficiency. Alfalfa and tomatoes were the only other crops on which molybdenum-deficiency symptoms were noted. The symptoms on alfalfa included yellowing of the leaves and serious retardation of growth (8). Molybdenum deficiency on tomatoes was characterized by interveinal chlorosis and cupping of the older leaves.

The remedy for molybdenum deficiency is some available form of the element, such as molybdc oxide or sodium or ammonium molybdate, dusted over the seed, applied with the fertilizer, or used in spray form. The suggested rate of application in dry form is not over 8 ounces of molybdc oxide, or

its equivalent in sodium molybdate, an acre on acid soils, and half that quantity on soils having pH values above 6. Significant yield increases in alfalfa were obtained in four of six New Jersey fields to which 1 pound of sodium molybdate an acre was applied (5), the average yield increase for all tests being 13.2%. Molybdenum applied to alfalfa seed was more effective than that applied broadcast. The average molybdenum content of the untreated alfalfa was 0.82 p.p.m. and that of the alfalfa receiving the molybdate was 3.84 p.p.m. Whiptail was cured by applying 1 pound of sodium molybdate in 100 gallons of water an acre in spray form.

Because potatoes are grown at low pH values in humid regions to avoid scab, it was thought they might respond to applications of molybdenum. A 26% increase in top growth and an 87% increase in tubers resulted under greenhouse conditions during the winter months, after potato seed pieces had been dipped into a 0.05% solution of sodium molybdate. Similar effects were noted following applications of sodium molybdate as a spray to potato foliage in the field in early spring, but no significant yield increase resulted.

**Iron** The iron content of New Jersey soils ranges between about 1 and 6%. The solubility of this iron increases markedly with lowering of pH values, and is further increased when the element is changed to the reduced form, as by the action of microorganisms effecting decomposition of soil organic matter. In poorly drained soils, indicated by bluish green, gray, and mottled shades, ferrous iron accumulates in soluble form to the extent that it may be toxic to plants.

The iron content of New Jersey plants ranges normally between about 100 and 1000 p.p.m. dry weight of material.

Less than these amounts may be found in grains, tubers, and other high-carbohydrate parts of plants. Much higher values are occasionally found, owing to precipitation and accumulation within the plant or to contamination of the sample with soil.

Iron deficiency, characterized by golden yellow foliage, notably on trees, is widespread in irrigated arid regions. Relatively little attention has been paid to this element in the humid acid-soil regions of the United States, it having been assumed that adequate amounts of iron would be available for plant use if the soil contained reasonable amounts of decomposing organic matter. Considerable doubt has arisen as to validity of this concept. Increasing difficulty from iron deficiency has been experienced in fruit production on coastal plain soils. The standard remedy has been to spray the trees with a 1% solution of iron sulfate or to apply this salt under the spread of the branches at rates up to 30 pounds a tree.

Much smaller quantities of iron will suffice for use by way of the soil if it is supplied in chelated form (15). The commonly used chelate is an iron compound of ethylenediaminetetraacetic acid. This product is relatively resistant to decomposition by soil microorganisms and it does not ionize, the iron thus remaining in solution when applied to the soil. One gram of iron in this form can replace as much as 1 pound of iron sulfate in overcoming a deficiency in the plant by way of the soil.

Application has been made of this principle in New Jersey in connection with the growing of azaleas, *Quercus palustris*, *Pieris japonica*, and *Ilex glabra*. Marked improvement in color of foliage and rate of growth of plants has resulted from the use of a commercial form of chelated iron at the rate of 30 pounds an acre. Iron deficiency may be widespread in plants growing on the sandy coastal plain soils of New Jersey. Chelated forms of iron, and of other trace elements as well, are being tested on a variety of plants under such soil conditions.

**Manganese** The manganese content of New Jersey soils (22) ranges between about 100 and 5000 p.p.m. These quantities are relatively very large in comparison with those of the other trace elements. But most of this manganese is unavailable to plants. Tests of availability involve determinations of that present in exchangeable and easily reducible forms. The usual testing procedure is to extract the soil with 1 *N* neutral solution of ammonium acetate. As with most of the other trace elements, the lower the pH value of the soil the greater the degree of availability of its manganese. This is notably true for the heavier soil types. Decomposing organic matter materially in-

creases availability of soil manganese, but the effects are largely limited to the period of decomposition (4). Manganese availability to plants is reduced by increasing the water content of soils to high levels. Most of the manganese deficiency observed in New Jersey has been in connection with the use of excessive amounts of liming materials, especially where soil pH values have been raised to 7 or higher (6).

The manganese content of plants normally ranges between 10 and 100 p.p.m. dry weight of material, but manganese values may be much higher if the soil pH value is permitted to drop below 5. Thus the manganese content of soybean plants growing on Sassafras sandy loam was 189 p.p.m. at pH 4.5, in comparison with 109 p.p.m. at pH 8. Soybeans had a greater capacity to absorb manganese from this soil than did alfalfa. Marked increases in alfalfa yields were obtained at pH 8 by use of liberal amounts of manganese sulfate. At low pH values marked manganese toxicity was noted. The problem involved is that of maintaining the level of available manganese in the soil at a point that is safely below toxicity levels and yet high enough to avoid deficiency.

Manganese-deficiency symptoms are often similar to those of magnesium, except that manganese deficiency is first noted on the newer top leaves whereas that of magnesium occurs on the older lower leaves. The affected leaves have dark green veins, with chlorotic tissue in between. Leaves of small grains

show gray areas about half way between base and tip, from which has come the name "gray-speck" disease. Visual symptoms of manganese deficiency occur at values of 50 p.p.m. dry weight of plant or less, but usually are at values below 20 p.p.m. Crop yields may fall off before deficiency symptoms are noted.

The manganese content of soybean plants grown on 20 New Jersey soils ranged between 20 and 265 p.p.m. dry weight of material on Lakewood sand and Norton silt loam, respectively. The lower value was probably a deficiency level and the higher value one of toxicity.

Manganese deficiency from overliming can be overcome by applying manganese sulfate at rates of 50 to 100 pounds an acre. This practice is widespread in Bergen county, New Jersey, where soil pH values on many farms are above 7 as a result of excessive use of liming materials. Manganese sulfate has also been used successfully in spray form at concentrations of 0.2 to 0.5%. Acid-forming agents, such as sulfur, aluminum sulfate, or ammonium sulfate, can be applied instead for the purpose of lowering pH values to 6.5 or less, and thus increasing the availability of the manganese that is naturally present in the soil.

**Zinc** The zinc content of New Jersey soils (23) ranges between 10 and 225 p.p.m. The best known test for available zinc in soils involves extracting them with an 0.05*M* potassium chloride solution, adjusted to pH 3.2 with glacial acetic acid. Deficiencies of this element occur most frequently in trees and vines,

**Table II. Trace Elements in 20 Plant Species Grown in Field Under Identical Conditions on Sassafras Loam**

Plants	(In parts per million, on dry-weight basis)						
	Mo	Fe	Mn	Zn	Cu	Ni	Co
Legume Hays							
Alfalfa, 1st cutting	0.9	261	27	27	8.3	1.15	0.14
Alfalfa, 2nd cutting	0.7	214	38	..	8.1	1.01	0.16
Ladino, 1st cutting	1.8	340	52	37	11.8	1.80	0.17
Red clover, 1st cutting	1.7	143	46	34	13.7	1.47	0.13
Soybean forage	1.6	212	53	31	11.2	0.91	0.12
Grasses							
Kentucky bluegrass	2.8	503	40	43	10.4	2.38	0.20
Orchard grass	4.8	231	77	29	8.2	1.58	0.09
Sudan grass	1.0	135	22	32	7.0	0.66	0.05
Timothy	2.7	144	34	36	6.9	1.10	0.06
Grains							
Corn	0.5	64	4	..	1.8	0.34	0.01
Oats	3.2	178	38	37	6.8	0.91	0.02
Soybeans	5.1	108	32	42	16.0	1.40	0.20
Sweet corn	0.5	38	3	..	3.2	0.40	0.01
Vegetables							
Beet	0.3	108	22	..	12.0	0.43	0.08
Lettuce	0.4	136	36	45	13.1	1.50	0.07
Potato	0.6	35	10	..	11.7	0.20	0.06
Spinach	0.3	540	69	122	12.0	2.15	0.27
Weeds							
Lamb's-quarters	0.9	94	52	29	7.6	0.51	0.08
Pigweed	1.8	308	65	33	8.0	0.85	0.20
Purslane	1.0	264	38	..	19.0	2.08	0.32
Ragweed	1.3	426	53	60	13.5	1.35	0.20

the indications being that the availability of the zinc in the lower horizons of the soil profile is less than that in the plow depth of soil. This suggests that decomposing organic matter must either supply appreciable amounts of zinc or contribute to the solution of that contained in the soil in mineral form.

The most important factor in determining whether adequate amounts of zinc will be available for crop use is the pH value of the soil. Zinc deficiency is most common on highly calcareous and alkaline soils. The zinc content of plants, including their several parts, was reduced to about one half by raising pH values of the culture solutions in which they were grown, from 4.5 to 7.5. Zinc availability to plants was not lowered by increasing the phosphate content of culture solutions, but marked reduction in availability of zinc occurs in high-phosphate soils or following heavy applications of superphosphate.

The zinc content of plants normally ranges between 25 and 100 p.p.m. dry weight of material. That of oats decreased from 19.5 p.p.m., when grown on

soil having a pH value of 4.5, to 5.9 p.p.m., when the pH value was raised by liming to 6.5. When zinc falls below 25 p.p.m., deficiency may develop in crop plants.

The most common symptom of zinc deficiency in plants is an interveinal chlorosis of the leaves. In apples, the terminal growth is long and slender with few lateral buds. Terminal rosettes are formed. The most spectacular form of zinc deficiency is that shown by corn, the central bud and leaves of which turn white, the common name for this being "white bud." Symptoms of zinc deficiency are seldom seen in New Jersey, although there are occasional signs of it in apple orchards and in corn fields.

The standard remedy for zinc deficiency is to apply zinc sulfate in salt form to the soil under the spread of the branches of trees, or as a spray on the foliage. At high pH values zinc deficiency is likely to prevent production of optimum yields, even though no symptoms of deficiency may have been noted. Some of the good effects of zinc-containing fungicides have been credited to nutri-

tional value of the zinc contained in them. Marked increases in yield of alfalfa were produced in three of six soils tested in 1951-52, following use of 144 pounds of zinc sulfate an acre in 1949 and half that quantity in 1950 (Table VIII). In 36 tests of a solution containing 2 pounds of zinc sulfate in 100 gallons of water applied in spray form to alfalfa, corn, and lettuce in farmers' fields in seven New Jersey counties no visual evidence of benefit was noted.

**Copper** The copper content of New Jersey soils (73) ranges between about 2 and 60 p.p.m. Copper sprays and dusts have been widely used for fungicidal purposes on potatoes, tomatoes, apples, and celery, and soils of such fields contained as much as 70 p.p.m. more copper than nearby virgin soils. No very definite relationship exists between pH values of soils and the copper content of crops grown on them. Heavy applications of copper sulfate had toxic effects on plants, notably at low pH values. This did not necessarily result in increased plant uptake of copper, the effect being primarily on the roots, which were badly stunted.

The copper content of leaves of trees growing on virgin areas of 20 New Jersey soils varied between 4.1 p.p.m. dry weight in wild cherry on Gloucester stony loam to 18.6 p.p.m. in beech on Colts Neck sandy loam.

Lakewood, Sassafras, Woodstown, Colts Neck, and Whippany soils have a low content of total copper, and crops growing on them are likely to develop copper deficiency under intensive systems of farming. The copper content of the A horizon of soils was usually higher than that of the B horizon. Use of Bordeaux sprays on potatoes and other crops tends to result in accumulation of copper in the plow depth of soils.

The copper contents of several samples of alfalfa were so low, falling to levels of less than 5 p.p.m. dry weight, as to make it doubtful whether the amounts were sufficient to meet the requirements of animals to which they might be fed. Purslane (*Portulaca oleracea*) contained 19 p.p.m. of copper on a dry-weight basis, more than any other of the 25 plants grown under identical conditions on Sassafras loam.

The copper content of plants ordinarily ranges between 2 and 20 p.p.m. dry weight of material. Plants that have been sprayed or dusted with copper fungicides may show larger amounts of copper because of surface contamination. Some of the highest copper values are found in weeds, indicating that such plants may have copper-accumulating capacity, possibly by tapping copper resources in the lower soil horizons.

The most common symptom of copper deficiency is a stunting and dying of the growth tips, followed by initiation of

**Table III. Extremes in Trace Element Content of Plants**

(From survey of New Jersey field vegetation<sup>a</sup>. Pounds in 10,000 pounds dry weight of produce)

	Lowest	Highest
B	Wheat straw 0.07	Peach tree leaves 1.23
Mo	Cauliflower plants 0.001	Ladino clover plants 0.12
Fe	Onion bulbs 0.29	Rye forage 6.63
Mn	Sweet corn seed 0.03	Pokeberry plants <sup>b</sup> 6.72
Zn	Red clover plants 0.06	Lamb's-quarters plants <sup>b</sup> 2.81
Cu	Field corn seed 0.018	Pepper plants 0.196
Ni	Potato tubers 0.002	Ragweed plants <sup>b</sup> 0.078
Co	Field corn seed 0.0001	Rye forage 0.007
I	Wild carrot plants 0.001	Wild carrot plants <sup>b</sup> 0.052
F	Buckwheat plants 0.09	Tomato leaves 0.76

<sup>a</sup> Approximate weight of total annual produce of 1 acre of good crop land.

<sup>b</sup> *Phytolacca decandra*, *Chenopodium album*, *Ambrosia artemisiifolia*, and *Daucus carota*, respectively.

**Table IV. Relation Between Soil pH and Trace Element Content of Soybean Plants Grown in Outdoor Cylinders of Sassafras Sandy Loam**

Soil pH Value	(In parts per million, on dry-weight basis)			
	4.6	6.0	7.0	8.0
	No trace elements applied to soil			
Mo	0.27	0.48	0.63	1.2
Mn	189	143	135	109
Zn	332	256	228	205
Cu	8.6	10.6	11.3	11.7
Co <sup>a</sup>	0.08	0.05	0.06	0.05
	Trace elements applied in liberal quantities <sup>b</sup>			
Mo	49	107	109	106
Mn	399	260	191	149
Zn	775	349	212	196
Cu	14.4	12.6	12.4	13.0
Co <sup>a</sup>	3.8	1.14	0.38	0.35

<sup>a</sup> Co determinations on wheat heads rather than soybean plants.

<sup>b</sup> Mo applied as sodium molybdate, other elements as sulfates, salt rates being 40, 224, 144, 125, and 70 pounds an acre for Mo, Mn, Zn, Cu, and Co, respectively, in 1949, and half these quantities in 1950. No further applications were made. The purpose of these high rates of equivalent quantities of trace elements was to magnify any effects they might have on soils and plants. A 10-10-10 fertilizer, made from c.p. materials and carrying 40 pounds of MgO and 10 pounds of borax, was applied at rate of 1000 pounds an acre at seeding time. Subsequent top dressings, as needed, were at rate of 1000 pounds 0-10-10 containing 10 pounds of borax. Soybeans were grown in 1949, the first year, wheat in 1950, and alfalfa in 1951 and 1952.

growth from new points, which also die. The terms "dieback" and "wither-tip" are commonly employed in describing this symptom. Copper-deficient oat plants in culture solutions turned light green, tillering was reduced, and leaves were short and narrow. Finally the leaves withered and died from the tips downward. New leaves developed, but these also died. The optimum content of copper in the nutrient solution was between 0.01 and 0.05 p.p.m. Toxicity developed at 1 p.p.m., and roots stopped growing and became thick and stubby.

The only serious need for copper that has developed in New Jersey has been in connection with crops growing on newly drained peat. The standard remedy is the use of copper sulfate, applied at the rate of 50 pounds an acre once in 5 years. The copper content of wheat when grown on peat was 6.6 p.p.m., in comparison with 11.1 p.p.m. when grown on Norton silt loam. Copper applications appeared to increase yields of red clover on Lakewood, Colts Neck, and Hoosic soils, all inorganic types, under greenhouse conditions, but the increases were not significant. The total copper in these soils was very low, 2 to 16 p.p.m., in comparison with 60 p.p.m. in Annandale soil, the one that was highest in this element.

#### Cobalt, Iodine, And Fluorine

Cobalt, iodine, and fluorine are of interest primarily in relation to the well-being of animals and man. The question that arises is as to whether, in case of deficiency, it is desirable to add salts of these elements to the soil to increase their content in crop plants, or whether equally satisfactory results can be obtained by feeding the salts directly to animals or supplying them in the drinking water (27).

Studies of the quantities of these elements in New Jersey soils and plants show a high degree of variation. Lakewood, Sassafras, Colts Neck, Collington, and Evesboro soils contain less than 3 p.p.m. of cobalt, in comparison with 18 p.p.m. in Annandale, and 30 p.p.m. in Norton soils. Squires, Hazen, Evesboro, and Annandale soils contain less than 2 p.p.m. of iodine in comparison with 8 p.p.m. in Lawrenceville and 12 p.p.m. in Norton soils (17). Lakewood soil contained less than 30 p.p.m. of fluorine in comparison with over 400 p.p.m. in Hazen soil.

The cobalt content of hay collected from over the state ranged between 0.015 p.p.m. dry matter in timothy growing on Lakewood sand to 0.31 p.p.m. in red clover on Colts Neck sandy loam (10). Kentucky bluegrass was relatively high in cobalt. The cobalt content of alfalfa was markedly reduced by liming the soil on which it was grown, decreasing from 0.12 to 0.05 p.p.m. when grown on Sassafras loam as its pH value was raised from 5.8 to 7.6.

**Table V. Content of Water-Soluble Trace Elements in Rain Water Collected at New Brunswick, N. J., 1949-52**

Collection Period	(In pounds an acre for 3-month and yearly periods)				
	Co	Cu	Mn	Mo	Zn
August-October, 1949	Trace	0.08	...	...	...
November-January, 1950	0.00210	2.70	...	...	...
February-April, 1950	0.00067	0.35	...	...	...
May-July, 1950	0.00047	0.14	...	...	...
Total for year	0.00324	3.27			
August-October, 1950	...	0.02	0.04	0.02	0.39
November-January, 1951	...	0.09	0.13	0.02	0.38
February-April, 1951	...	0.06	0.19	0.01	0.23
May-July, 1951	...	0.04	0.10	0.01	0.24
Total for year		0.21	0.46	0.06	1.24
August-October, 1951	...	...	0.11	0.02	0.30
November-January, 1952	...	...	0.14	0.02	0.35
February-April, 1952	...	...	0.30	0.15	0.10
May-July, 1952	...	...	0.13	0.04	0.23
Total for year			0.68	0.23	0.98

Cobalt is a constituent of vitamin B<sub>12</sub>, which is essential in animal nutrition. This vitamin can be produced by the microorganisms in the rumen of cattle and other ruminants from inorganic forms of cobalt. Only traces of B<sub>12</sub> are found in plants. Forage containing between 0.04 and 0.07 p.p.m. of cobalt is considered adequate. All the alfalfa growing on Lakewood and Dover soils had cobalt values between these levels, and over 50% of that from Collington, Gloucester, and Washington soils was within this range. In proportion as the hay or forage was made up of hay grasses, the cobalt values were reduced to lower levels.

Cobalt sulfate is now being added to many thousands of tons of dairy cattle feed at the rate of about 2 grams for each ton of feed. Potassium iodide is being added to salt for human and animal consumption at the rate of 1 part in 5000. The fluorine content of drinking water is being standardized at 1 p.p.m. in some localities.

#### Supplemental Research Findings

Boron deficiency in plants is characterized by increase in the number and size of cells and decrease in differentiation in the meristematic regions. It occurs well in advance of any apparent deficiency symptoms.

Symptoms of boron deficiency and boron toxicity become more pronounced with increasing supplies of available potassium (19). Calcium applications have much the same effect as those of potassium in increasing boron-deficiency symptoms, but quite opposite effects on boron-toxicity symptoms. Plants growing on an acid soil that has been limed benefit much more from boron applications than those growing on unlimed soil. Both calcium and boron must be present throughout the feeding zone of plant roots for satisfactory continued growth of the roots.

The first damage from molybdenum deficiency is found in palisade tissue just beneath the upper epidermis, which is the cause of the characteristic cupping of leaves of molybdenum-deficient plants.

Molybdenum is essential for nitrogen fixation by legumes and for utilization of nitrate nitrogen. Molybdenum-deficient legumes are relatively low in total nitrogen, and they tend to accumulate nitrate nitrogen.

Molybdenum applications did not reduce the severity of tobacco and tomato mosaic virus, as has been suggested.

Molybdenum uptake by plants was related to the cation exchange capacity of their roots.

Molybdenum applications to 15 vegetables did not materially increase yields but did increase the ascorbic acid content of the produce.

Succinic dehydrogenase activity of molybdenum-deficient plants was much less than that of normal plants.

The iron-manganese ratio in plant sap should be about 2 to 1. Otherwise the enzymes catalase, peroxidase, and cytochrome do not function properly.

Symptoms of iron deficiency are similar to those of manganese toxicity, but distinctive symptoms of deficiency for each of these elements can be developed.

Use of radioactive manganese-54 revealed (20) that when manganese sulfate was applied at the rate of 100 pounds an acre to Norton silt loam having a pH value of 7, alfalfa growing on that soil obtained 12% of its manganese from that applied and 88% from the natural supply in the soil. For Sassafras loam these percentages were 55 and 45, respectively. About 38% of the applied manganese had been changed to the higher oxides in the Norton soil at the end of 145 days. For the Sassafras loam this percentage was 62.

Autoradiographs showed numerous small "islands" of manganese-54 in the interveinal tissue of mature soybean and

**Table VI. Trace Elements in Edible Portions of Six Crops from Analyses of 223 Samples from 18 States**  
(In parts per million, on dry-weight basis)

	B	Mo	Fe	Mn	Zn	Cu	Co
Alfalfa							
Highest	68	4.6	675	48	58	61	0.24
Lowest	18	0.1	110	10	13	13	0.04
Cabbage							
Highest	42	24.1	94	13	..	48	0.15
Lowest	7	0.0	20	2	..	0	0.00
Lettuce							
Highest	37	4.5	516	169	..	60	0.19
Lowest	6	0.0	9	1	..	3	0.00
Snap beans							
Highest	73	8.1	227	60	..	69	0.26
Lowest	10	0.1	10	2	..	3	0.00
Spinach							
Highest	88	5.6	1584	117	..	32	0.25
Lowest	12	0.0	19	1	..	0	0.20
Tomatoes							
Highest	36	1.3	1938	68	..	53	0.63
Lowest	5	0.0	1	1	..	0	0.00

tomato leaves. Painted on leaves the manganese-54 moved upward and downward to regions of active growth. Use of iron-59 under identical conditions failed to result in any appreciable movement within the plant after absorption. Addition of cobalt to nutrient solutions reduced manganese-54 uptake.

Use of radioactive zinc-65 showed that zinc concentration was very high in the inflorescence of plants, which is of possible interest in associating zinc with auxin. Zinc-65 concentration was high also in the pulvini of plant leaves in contrast to the almost complete absence of calcium in these zones.

Zinc deficiency is known to be most severe under conditions of high light intensity. Corn growing on a zinc-deficient soil in the greenhouse showed typical zinc-deficiency symptoms in late summer, but recovered its normal dark green with shorter days and decreased light intensity in the fall.

Copper-toxicity symptoms were developed on wheat growing on Sassafras sandy loam with a pH value of 5 by application of 125 pounds of copper sulfate per acre. This toxicity was accentuated by application of zinc, reduced by application of molybdenum, and eliminated by liming to pH 6. At pH 7, the plants were benefited by the copper application. Copper toxicity, seldom experienced in field crops, is common around buildings, where water from copper spouting is permitted to flow over the soil.

Essentiality of cobalt to plants was not demonstrated. By careful purification of water, nutrient salts, containers, and air, the cobalt content of nutrient solutions was reduced to an estimated 0.006

part per billion. Let plants grown from second-generation seed in these solutions still contained 0.004 to 0.008 p.p.m. of cobalt. Additions of cobalt to these nutrient solutions did not increase yields.

The cobalt content of plants was reduced by increasing the amounts of manganese or iron in the nutrient solution, the effect of manganese being much more marked than that of iron. As the manganese content of the solution was raised from 0 to 1 p.p.m., the activity of leaves that were being supplied with cobalt-60 was reduced from 420 to 160 disintegrations per minute per gram of oven-dried tissue.

No evidence of essentiality of iodine to plants was found (72). Plants grew equally well in the presence or absence of small amounts of potassium iodide in the nutrient solution. Most crop plants contained less than 1 p.p.m. of iodine on a dry-weight basis, but concentrations of 2000 p.p.m. were developed in plants growing in nutrient solutions. The range in iodine content of New Jersey crop plants was between about 0.1 and 5 p.p.m. Contrary to what was expected, the iodine content of the soil and of vegetation did not increase from the interior of the state seaward.

No evidence of essentiality of bromine to plants was found (72). None of the forage plants examined contained over 7 p.p.m. of bromine. Tomatoes supplied with potassium bromide accumulated 2800 p.p.m. of bromine in leaflets, 6300 p.p.m. in stems, and 2100 p.p.m. in roots, without evidence of injury.

The fluorine content of New Jersey soils ranges between 29 and 409 p.p.m. It tends to increase with depth, and to be higher in fertilized than in virgin soils. A considerable part of the fluorine

in soils of industrial areas in New Jersey may have been brought to the earth in rainfall. In some parts of the state extensive damage to crops has resulted, both by direct action of fluorine fumes and through its absorption by plants by way of the soil. The availability to plants of soluble soil fluorine is readily reduced below the toxic limit by liming to pH 6.5.

No evidence was found that fluorine is required by plants (17). The fluorine content of New Jersey plants normally ranges between 15 and 20 p.p.m. on a dry-weight basis. Extreme values for field vegetation in the state were 9 and 76 p.p.m. Certain trees and bushes, notably mulberry, willow, and camellia, accumulated fluorine. Plant uptake of fluorine has little relationship to total fluorine content of soil on which it was grown. Among the plants most sensitive to fluorine toxicity are sweet potato, white pine, day lily, and gladiolus. Ragweed is highly resistant to fluorine, showing little evidence of injury at high atmospheric concentrations.

New Jersey soils contain between 2 and 40 p.p.m. of nickel (14). The nickel content of B horizon soil is higher than that of the A horizon. Soils of serpentine origin may contain as much as 800 p.p.m. of nickel, and this, rather than their high magnesium content, was believed to be a cause of their lack of productivity. An unproductive Conowingo silt loam from Harford County, Maryland, or serpentine origin, contained 140 p.p.m. of nickel and had a natural pH value of 4.2. The nickel content of oats grown on this soil was about 10 p.p.m. on a dry-weight basis. Liming the soil to pH 6.5 reduced the nickel content to less than 5 p.p.m. Crop yields were normal following use of lime and complete fertilizer, indications being that the toxic factor was the soil's high content of available manganese.

The nickel content of New Jersey plants normally ranged between about 0.50 and 2.50 p.p.m., on a dry-weight basis. Ragweeds were notably high in nickel, containing up to 7.8 p.p.m. of the element. Soybeans growing on Colts Neck soil contained 6.6 p.p.m. of nickel, in comparison with only 1.6 p.p.m. in those growing on Palmyra soil.

Nickel toxicity of tomatoes was induced in sand cultures at 0.5 p.p.m. of nickel in the nutrient solution. Plants showing toxicity symptoms contained over 40 p.p.m. of nickel. Nickel-induced chlorosis of plants was similar to that resulting from manganese deficiency. The nickel content of plants was reduced by adding copper, zinc, manganese, or iron to the nutrient solutions. No deficiency symptoms appeared and growth was normal when the nickel content of wheat was reduced to 0.19 p.p.m. and that of tomatoes to 0.25 p.p.m.

## Some Current Research

The laboratory data contained in this paper have been obtained largely by the usual quantitative chemical procedures. Detailed methods for the separation and determination of each trace element have been developed (16). Search for more rapid methods of analysis finally led to the purchase of a fully automatic large stigmatic grating Jarrell-Ash spectrograph, with the necessary accessories. As a result of more than a year's intensive study of spectrographic techniques, the conclusion has been reached that they can be applied to the analyses of biological materials with as much accuracy as chemical procedures. Procedures have been developed for ashing and solubilizing such materials and for extracting and concentrating the trace elements. The spectrograph permits very rapid determinations of trace elements on a qualitative and semiquantitative basis and has the advantage that those not under study are also revealed, including major and secondary nutrient elements in plant and animal tissues, as well as those that are present only in traces. But quantitative data on trace elements of a high degree of precision can also be obtained in biological materials by carefully controlled spectrographic procedures such as have been developed in this laboratory. This also applies to major and secondary elements.

Although primary objective of this work is that of determining to what extent trace-element deficiencies occur in New Jersey soils and plants and the means by which such deficiencies can be avoided or overcome, there remains the much larger problem of investigating the functions of these elements in plants and animals. This phase of the problem is also under study in a major research project involving cooperation among agricultural biochemistry, plant physiology, and soils staffs. This work is being largely financed by Herman Frasch Foundation funds. It has for its purpose the determination of the influence of partial deficiencies of trace elements on the vitamin content of plants, the amino acid composition of plant proteins, and the activities of plant enzymes. In addition, a study is being made of the effect of such deficiencies on growth-promoting value of proteins of seeds harvested from mature plants.

The laboratory is also cooperating with the Sloan-Kettering Institute for Cancer Research by examining normal and diseased tissues of human beings for their trace-element contents.

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**Table VII. Total Dry Weight of Alfalfa Grown on Sassafras Sandy Loam at Three pH Levels<sup>a</sup> with Various Trace-Element Treatments<sup>b</sup>**

(Total yields in grams dry weight on outdoor cylinder, 1951 and 1952)

Trace Elements	pH 6	pH 7	pH 8
None	488	640	406
Cu	446	571	541
Zn	390	510	478
Mn	356	545	613
Mn, Zn	345	520	457
Zn, Cu	315	505	550
Mn, Cu	309	513	544
Mn, Zn, Cu	265	461	499
Mn, Zn, Cu, Mo	426	506	544
Mn, Zn, Cu, Mo, Co	251	464	492

<sup>a</sup> pH values were established in 1949, and average values had dropped from 6 to about 5.5, from 7 to about 6, and from 8 to about 7, respectively, by end of 1952 crop year.

<sup>b</sup> See Table IV for rates of application of trace elements and supplemental fertilizers.

**Table VIII. Total Dry Weight of Alfalfa Grown on Soils<sup>a</sup> of Six Series with and without Various Trace Elements<sup>b</sup>**

(Total yield in grams dry weight on outdoor cylinder, 1951 and 1952)

Trace Elements	Annandale	Collington	Dover	Lakewood	Norton	Peat
None	418	437	399	194	316	366
Zn	572	510	365	281	239	304
Zn, Mo	548	571	278	262	359	311
Mn, Mo	522	523	460	257	354	409
Zn, Mn, Mo	579	516	320	215	277	323
Zn, Mn, Mo, Cu	529	486	298	150	290	411
Zn, Mn, Mo, Cu, Co	445	442	163	36	293	298

<sup>a</sup> See Table IV for rates of application of trace elements, and of supplemental fertilizers.

<sup>b</sup> pH values of these soils were raised to 7 at start of test, but permitted to drop without correction during 4 years of experiment, over last 2 years of which alfalfa was grown.