Shaughnessy No. 78001

Date Out of EFGWB:

TO: Morrill/Taylor
Product Manager #74
Registration Division (H7505C)

FROM: Henry Nelson, Ph.D., Acting Section Head H Nelson
Surface Water Section
Environmental Fate and Groundwater Branch/EFED (H7507C)

THRU: Hank Jacoby, Chief Hank Jacoby
Environmental Fate and Groundwater Branch
Environmental Fate and Effects Division (H7507C)

Please find attached is the EFGWB review of:

Reg./File #: 000612-4

Chemical Name : Sulfuric acid, monourea adduct

Product Name : Enquik

Type of Product : Herbicide

Company Name : UNOCAL

Purpose : Review of miscellaneous information

Date Received : 11/24/89 Action Code: 311

EFGWB #(s): 90-0082

Total Reviewing Time: 0.5

Deferrals to: ______ Ecological Effects Branch/EFED

______ Science Integration & Policy/EFED

______ Non-Dietary Exposure Branch/HED

______ Dietary Exposure Branch/HED

______ Toxicology Branch I/HED

______ Toxicology Branch II/HED

Excerpts from the following 4 documents or books were submitted to EFGWB for review:

(1) MRID #411914-01. Pages 17-18, 84-89, and 102 of Diagnosis and Improvement of Saline and Alkali Soils. Agricultural Handbook No. 60. Agricultural Research Service, USDA (1984).

(2) MRID #411914-02. Pages 169-171 and pages 181-185 of Soil Fertility and Fertilizers. SL Tisdale and WL Nelson. The Macmillan Company, 2nd Edition.

(3) MRID #411914-03. Pages 269-271 of Western Fertilizer Handbook. Soil Improvement Committee California Fertilizer Association. The Interstate Printers and Publishers, Inc.

(4) MRID #411914-04. Page 5 of Mineral Nutrition of Higher Plants. Horst Marschner. Academic Press (1986).

In their submission, the registrant did not indicate why they were providing the information. S. Morrill of RD/OPP stated that the registrant indicated in a 2/13/91 telephone conversation with him that the information was provided in response to a EFGWB review (see EAB #s 90418-90419 dated 6/2/89-attached). The submitted information on soil analyses, fertilizers, and plant nutrients appears to be only remotely applicable (if at all) to the EFGWB review which discusses the possible effects of the use of Enquik on the pH of treated soil and of surface waters receiving runoff from treated soils. In addition, S. Morrill stated that the registrant indicated that the issues prompting the submission of the information had been resolved. Therefore, EFGWB is returning the above listed submissions (also attached to this review) to RD without further comment.

Shaugnessy Numbers: 078001
6/2/89

TO: Product Manager (25) R. Taylor
Registration Division (TS-767C)

FROM: Thomas Dixon, Chief, Thomas Dixon
Monitoring Coordination Section #6
Exposure Assessment Branch/HED (TS-769C)

THRU: Henry Jacoby, Acting Chief, Thomas Dixon for
Environmental Fate and Groundwater Branch (TS-769C)

Attached, please find the EAB review of:

Reg./File #: 612-4

Chemical Name: Sulphuric Acid Monourea

Type Product: Herbicide

Company Name: Unocal Corp.

Purpose: Review two nonguideline studies:
1. Effect on pH of Simulated ephemeral ponds.
2. Effect on pH of irrigation waters

Date Received: Received in EEB 24 Aug 88 and Deferred to EFGWB

Action Code: 310

Date Completed: 17 May 1989

EAB #(s): 90418-90419

Monitoring Study Requested: No

Total Reviewing Time: 7d

Monitoring Study Volunteered: ______

No Deferrals to any other Branch

DATA EVALUATION RECORD

I. Chemical Description:

Chemical Names: Sulphuric acid monourea
carbamide dihydrogensulfate
monourea sulfuric acid

Common Name: Enquik (formerly N-TAC)

II. Test Materials:

Enquik herbicide -- 81% monocarbamide dihydrogensulfate

III. Study Action Type:

Review simulated ephemeral ponds test at request of Ecological Effects Branch.

IV. Study Citations:

Young, Donald C. 1987. N-TAC: Effect on pH of Simulated Ponds and Irrigation Water. Unocal Science and Technology Division. Laboratory Project I.D. C87-111M.

V. Reviewer:

Robert K. Hitch, Ecologist,
Monitoring Section
Exposure Assessment Branch

Date: 17 May 89

VI. Approval:

Thomas E. Dixon, Chief,
Monitoring Section
Exposure Assessment Branch

Date: 2 June 1989

VII. Conclusions:

This study is judged to be supplemental. EFGWB has no reason to doubt the results of the study. However, we can not project, on the basis of this study, environmental pH values resulting from the use of Enquik. No further information concerning the study is requested at this time, but the registrant shall retain all lab and field notes concerning the study for possible submission to the Agency.

The Ecological Effects Branch has asked us to consider whether a field monitoring study should be required to determine if Enquik might cause deleterious lowerings of pH. Our conclusion is that none should be required.

Our prediction is that Enquik might, in very unusual worst case situations, significantly lower the pH of surface waters. The only example of such a possible event that we have been able to formulate would be a heavy storm wash-off of recently-treated, hilly, impermeable land. We do not believe that it is feasible to monitor in the hopes of capturing a rare storm event.

Spray drift will not be a problem so long as the use patterns are limited to directed sprays from ground equipment (personal communication with R. Holst).

During the process of deciding whether monitoring should be imposed, we have benefited from discussions with a broad spectrum of investigators. The buffering reaction of soil in response to an acid is quite complex, but there is general agreement amongst the soil experts that I have contacted that Enquik use would be very unlikely to cause a sustained pH reduction over a broad geographic area*. Mr. Benjamin Smallwood, a soil scientist of the

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*We might caveat this statement by saying that pH will not remain depressed unless the farmer wants it to be lowered. Dr. Barbarba Goulart, a berry agronomist, notes that blueberry farmers seek pH's well below 5.0 (personal communication attached). On the other hand, Mr. Smallwood of the Soil Conservation Service gives assurance that the United States farmers would find it very feasible to treat with lime (generally a $CaCO_3$ containing material) in order to raise pH. This reaction is:

$$2HX + CaCO_3 = CaX + H_2O + CO_2$$

Farmers are already in the process of protecting their land from leaching losses amounting to 100 to 300 pounds of $CaCO_3$ equivalent per year annually (Bear, 1955).

One might note that each mole of H_2SO_4 provides two equivalents of acid. Each mole of $CaCO_3$ provides two equivalents of base, and therefore one mole of sulphuric acid can be neutralized by one mole of calcium carbonate.

Soil Conservation Service, estimates that within one growing season, agricultural soil pH would have returned to almost or completely ambient conditions after an application of Enquik (personal communication attached). Dr. Willard Lindsay, a soil chemist from Colorado State University is in agreement with Mr. Smallwood.

The concern for the rare rapid wash-off event is exemplified by my discussion with Dr. Robin Church. Dr. Church is investigating the effects of acid deposition including sulphate on surface waters of the United States. He feels that it is conceivable that a large storm runoff event could cause a washoff of surface applied sulphuric acid and that this event could cause a reduction of pH in adjacent waters. This would most likely occur in hilly areas with highly impermeable soils.

It should be noted that we do not believe that significant transport of Enquik is possible by spray drift so long as the use patterns are restricted to directed ground sprays.

VIII. Recommendations.

No field monitoring should be required. The Ecological Effects Branch should, for the environment in general, have a low level of concern with regard to the use of Enquik. We do, however, predict that use patterns involving large areas of hilly terrain, which are subject to quick runoff, could, on rare occasion, cause significant but not permanent decreases in pH of surface waters.

IX. Background

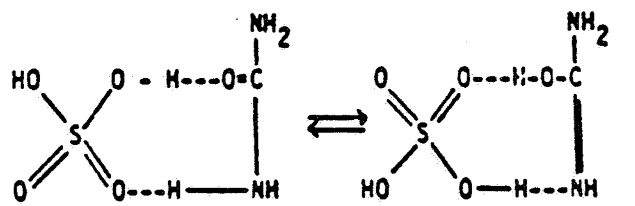
The Environmental Fate and Groundwater Branch (at that time the Exposure Assessment Branch) took the stance several years ago that they would defer requirements for sulphuric acid monourea (personal communication with Robert Taylor).

In personal communication, Mrs. Candy Brassard has told me that EEB's only concern with regard to Enquik is due to possible acidification of the environment.

The question has arisen as to whether sulphuric acid monourea should merely be treated as sulphuric acid for the purposes prediciting its effect on environmental pH. Mr. Harry Day and Dr. James Adams have been consulted in regard to this issue. They agree that the registrant's projected structure for the active in concentrated water water solutions (see below) is reasonable. On the other hand, the registrant's bucket studies show rapid lowering of pH when Enquik is mixed in dilute concentrations with water. Presumably this is due to the dissociation of the sulphuric acid.

Structure of Enquick in Water (from Young, 1987)

The registrant says that he has spectral evidence that Enquik in water exists as resonance forms of $[NHC(OH)NH_2(H_2)(SO_4)]$. The registrant presents the following structures as examples of those resonance forms:



In a meeting of 29 Mar 89, the registrant had a meeting with Agency representatives at Crystal City. During the meeting, a photograph was presented to the Agency showing someone dipping their hand in concentrated Enquik water solution. The implication was that Enquik is safer than sulphuric acid. We note that concentrated sulphuric acid is also dermally benign. Not until sulphuric acid is diluted in water does it become corrosive to the skin.

X. <u>Discussion</u>

In this study the registrant uses five gallon buckets to simulate ephemeral ponds. Various types of soil were put in the bucket and the soils were flooded with distilled water. The water was then sprayed with N-TAC at loadings exceeding application rate. Extremely low pH values were measured in all the buckets.

XI. Completion of One Liner

NA

XI. Confidential Appendix

NA

Reference

Bear, Firman E. 1955. Chemistry of the Soil. Reinhold Publishing Corp. New York. 373 pp.

Record of Personal Communication

Date: 16 May 1989

Benjamin Smallwood, Soil Conservation Service, Soils Division
Washington, D.C.

Phone: (202) 447-6371.

Mr. Smallwood estimates that during the course of a growing season that 185 pounds of sulphuric acid would be largely neutralized in a loam soil and in a sandy soil it would most probably be leached away.

Mr. Smallwood further stated that the, in the United States liming to neutralize 185 pounds of sulphuric acid would be present no problem.

Record of Personal Communication

Date: May 11 89

TO: Dr. Willard Lindsay, Soil Chemist, Colorado State University. Fort Collins.

Phone: 303-491-6552

Dr. Lindsay felt that a maximum application of 185 lbs (see page 9 of Candy Brassard's 21 February 89 Ecological Effects Branch review) Sulphuric acid per year would not be a problem because in areas where they have low exchange capacity agriculturalists have to lime anyway. He did not think that it would be any problem to lime enough to mask the effects of 185 pounds of lime.

Record of Personal Communication

Date: May 12, 89

TO: Dr. Barbara Goulart, Small Fruits Specialist with Penn State University

Phone: 814-863-2303

Dr. Goulart states that for optimal production blueberry cultivators lower their pH to 4.5 to 5.0. This is usually attained by the addition of sulphur. She says that no environmental concern has thus far been raised about this practice.

She expressed interest in a sucker growth control agent for blackberries and raspberries so I gave her Joanne Miller's telephone number.

Record of Personal Communication

Date: 16 May 1989

Dr. Robin Church, USEPA Corvallis, Writing Document on the effects of Sulphate Depostion in the East.

Phone: FTS 420-4666

Dr. Church felt that there was some concern if 185 pounds of sulphuric acid was applied in an area subject to to overland sheet flooding situations. In such a situation there might be movement of the chemical with almost no reaction with the overlying strata. Particularly he had seen the effects of quick overland wash-off movement in apple orchards.

He noted annual Sulphate depositons of 5grm/m_2/yr in NE PA and in the Smoky Mountain area. Levels would be somewhat higher in SW PA (just south of Pennsylvania).

Data Evaluation Record

I. Chemical Description:

Chemical Names: Sulphuric acid monourea
carbamide dihydrogensulfate
monourea sulfuric acid

Common Name: Enquik (formerly N-TAC)

II. Test Materials:

Enquik herbicide -- 81% monocarbamide dihydrogensulfate

III. Study Action Type:

Review simulated irrigation water test at request of Ecological Effects Branch.

IV. Study Citations:

Young, Donald C. 1987. N-TAC: Effect on pH of Simulated Ponds and Irrigation Water. Unocal Science and Technology Division. Laboratory Project I.D. C87-111M.

V. Reviewer:

Robert K. Hitch, Ecologist, Monitoring Section, Exposure Assessment Branch — [signature] Date: 17 May 89

VI. Approval:

Thomas E. Dixon, Chief, Monitoring Section, Exposure Assessment Branch — [signature] Date: 2 June 1989

VII. Conclusions.

This study is judged to be supplemental. EFGWB has no reason to doubt the results of the study. However, we can not project, on the basis of this study, environmental pH values resulting from the use of Enquik.

Refer to the attached review of the ephemeral ponds test concerning EFGWB requirements to support Enquik registrations.

VIII. Recommendations.

Refer to the attached review of the ephemeral ponds study.

IX. Background

Refer to the attached review of the ephemeral ponds study.

X. Discussion

Twelve irrigation water samples were collected from California and Arizona. The amount of Enquik required to lower these water to a pH of 4.5 was measured.

XI. Completion of One Liner

NA

XI. Confidential Appendix

NA

411914-01

STUDY TITLE

Diagnosis and Improvement of
Saline and Alkali Soils

DATA REQUIREMENT

Not Applicable

AUTHOR

United States Salinity Laboratory Staff

STUDY COMPLETED ON

Not Applicable

PERFORMING LABORATORY

Not Applicable

STATEMENT OF NO DATA CONFIDENTIALITY CLAIMS

No claim of confidentiality is made for any information contained in this study on the basis of its falling within the scope of FIFRA Section 10(d)(1)(A),(B), or (C).

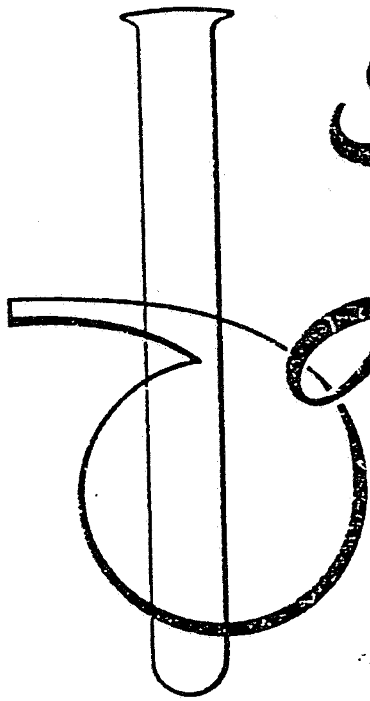
Company: Delta Management Group
1414 Fenwick Lane
Silver Spring, MD 20910

Company Agent: Eliot I. Harrison

Signature: [signature]

Date: August 1, 1989

Diagnosis and Improvement of



Saline and Alkali Soils

United States Salinity Laboratory Staff

Contributing Authors:

L. E. Allison, L. Bernstein, C. A. Bower, J. W. Brown, M. Fireman, J. T. Hatcher, H. E. Hayward, G. A. Pearson, R. C. Reeve, L. A. Richards, L. V. Wilcox

L. A. Richards, Editor

Soil and Water Conservation Research Branch
Agricultural Research Service

Agriculture Handbook No. 60 — Issued February 1954

UNITED STATES DEPARTMENT OF AGRICULTURE

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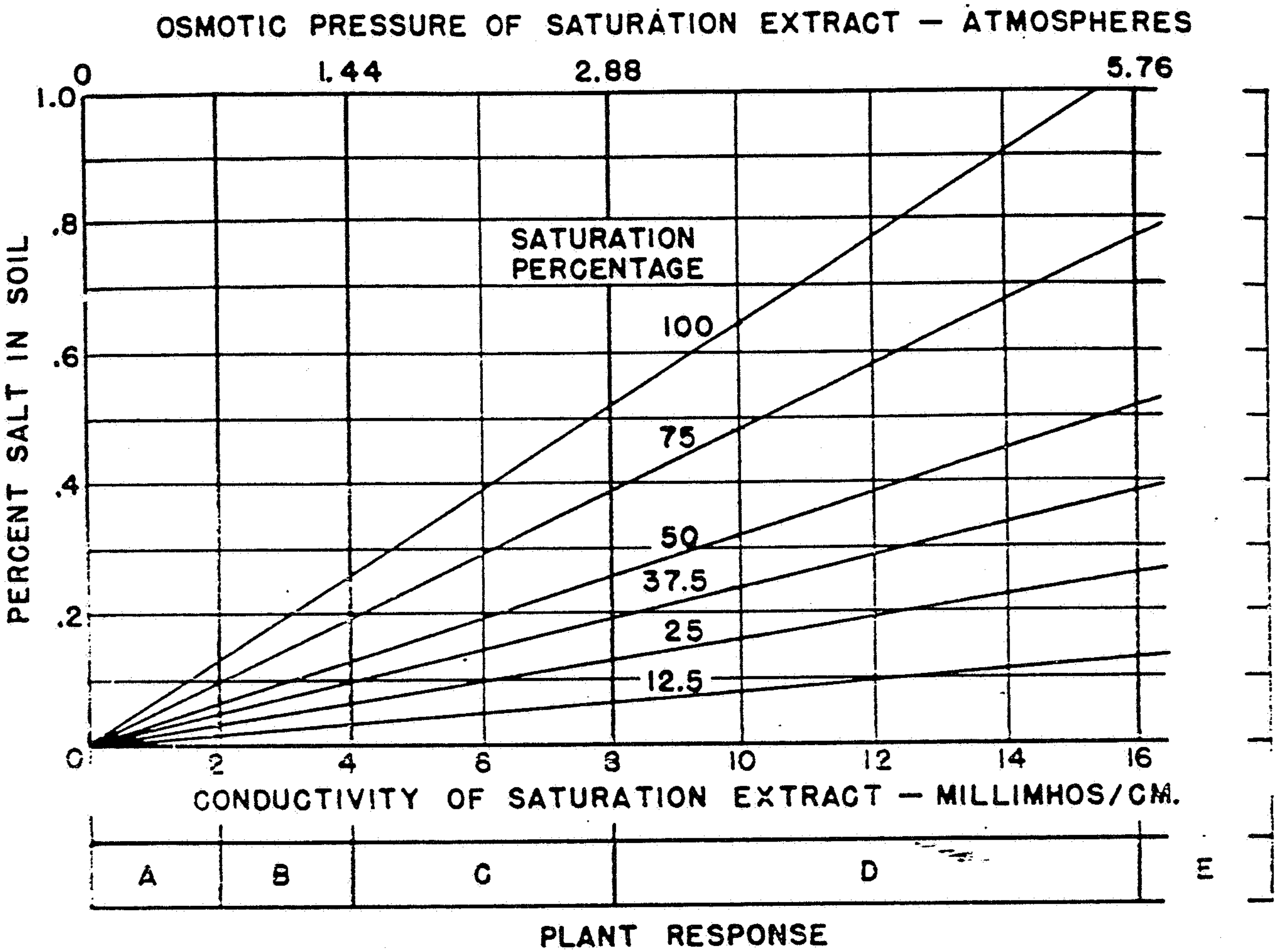

FIGURE 7.—Relation of the percent salt in the soil to the osmotic pressure and electrical conductivity of the saturation extract and to crop response in the conductivity ranges designated by letters. These ranges are related to crop response by the salinity scale on page 9.

$=0.36 \times EC \times 10^3$. P_{sw} = percent salt in water; P_{ss} = percent salt in soil; P_w = percent water in soil; and OP = osmotic pressure in atmospheres. The lower scale gives values for the conductivity of the saturation extract. The top scale shows the osmotic pressure of the saturation extract. The osmotic pressure of the soil solution at the upper limit of the field-moisture range will be approximately double these values.

The diagonal lines help correlate the conductivity of the saturation extract with the percent salt content for various soil textures. For example, at $EC_e \times 10^3 = 4$, nearly all crops make good growth and for a soil with a saturation percentage of 75, as seen in the diagram, this corresponds to a salt content of about 0.2 percent. On the other hand, 0.2 percent salt in a sandy soil for which the saturation percentage is 25 would correspond to $EC_e \times 10^3 = 12$, which is too saline for good growth of most crop plants. Partial lists of crop plants in their order of tolerance to soil salinity are given in chapter 4.

The diagram indicates the growth conditions of crops to be expected for various degrees of salinity in the active root zone of the soil, i. e., the soil volume that is permeated by roots and in which moisture absorption is appreciable. Obviously, the diagram does not apply for soil in which salt has been deposited after the roots have been established and have become nonabsorbing, or to soil adjacent to the plant, either high or low in salt, that has not been permeated by roots. With mature row crops, for example, salt may have accumulated in the ridge to such an extent that the roots no longer function as moisture absorbers and, therefore, the ridge cannot be considered as characteristic of the active plant-root environment.

Chemical Determinations

Soil Reaction—pH

The pH value of an aqueous solution is the negative logarithm of the hydrogen-ion activity. The value may be determined potentiometrically, using various electrodes (Method 21), or colorimetrically, by indicators whose colors vary with the hydrogen-ion activity. There is some question as to the exact property being measured when methods for determining the pH values of solutions are applied to soil-water systems. Apparent pH values are obtained, however, that depend on the characteristics of the soil, the concentration of dissolved carbon dioxide, and the moisture content at which the reading is made. Soil characteristics that are known to influence pH readings include: the composition of the exchangeable cations, the nature of the cation-exchange materials, the composition and concentration of soluble salts, and the presence or absence of gypsum and alkaline-earth carbonates.

A statistical study of the relation of pH readings to the exchangeable-sodium-percentages of soils of arid regions has been made by Fireman and Wadleigh (1951). The effect of various factors such as moisture content, salinity level, and presence or absence of alkaline-earth carbonates and gypsum upon this relationship was also studied. Some of the more pertinent statistical data obtained are presented in table 4. While all the coefficients of correlation given in the table are highly significant, the coefficients of determination show that at best no more than 54 percent of the variance in exchangeable-sodium-percentage is associated with the variance in pH reading. The data on the effect of moisture content indicate that the reliability of prediction of the exchangeable-sodium-percentage from pH readings decreases as the moisture content is increased. Similarly, the data on the effect of salinity indicate that the reliability of prediction is lowest when the salt level is either low or very high. An increase in pH reading of 1.0 or more, as the moisture content is changed from a low to a high value, has been found useful in some areas for detecting saline-alkali soils. However, the reliability of this procedure should be tested before use on any given group of soil samples.

Experience and the statistical study of Fireman and Wadleigh permit the following general statements regarding the interpretation of pH readings of saturated soil paste: (1) pH values of 8.5 or greater almost invariably indicate an exchangeable-sodium-percentage of 15 or more and the presence of alkaline-earth carbonates; (2) the exchangeable-sodium-percentage of soils having pH values of less than 8.5 may or may not exceed 15; (3) soils having pH values of less than 7.5 almost always contain no alkaline-earth carbonates and those having values of less than 7.0 contain significant amounts of exchangeable hydrogen.

Soluble Cations and Anions

Analyses of saline and alkali soils for soluble cations and anions are usually made to determine the composition of the salts present. Complete analyses for soluble ions provide an accurate determination of total salt content. Determinations of soluble cations are used to obtain the relations between total cation concentration and other properties of saline solutions, such as electrical conductivity and osmotic pressure. The relative concentrations of the various cations in soil-water extracts also give information on the composition of the exchangeable cations in the soil.

The soluble cations and anions commonly determined in saline and alkali soils are calcium, magnesium, sodium, potassium, carbonate, bicarbonate, sulfate, and chloride. Occasionally nitrate and soluble silicate also are determined. In making complete analyses, a determination of nitrate is indicated if the sum of cations expressed on an equivalent basis significantly exceeds that of the commonly determined anions. Appreciable amounts of soluble silicate occur only in alkali soils having high pH values. In analyses made by the usual methods, including those recommended in this hand-

TABLE 4.—*Coefficient of correlation* (r)[1] *and coefficient of determination* (r^2) *for the relation of pH reading to exchangeable-sodium-percentage as influenced by moisture content, salinity level, and presence or absence of alkaline-earth carbonates and gypsum*

Moisture content (percent)	Salinity as $EC_e \times 10^3$ at 25° C.	Alkaline-earth carbonates	Gypsum	Samples	r	r^2
				Number		*Percent*
Saturation	Variable	Variable	Variable	868	0.66	44
500	do	do	do	271	.65	43
1,000	do	do	do	289	.53	28
6,000	do	do	do	346	.48	24
Saturation	0–4	do	do	349	.56	31
Do	4–8	do	do	91	.72	52
Do	8–15	do	do	115	.70	49
Do	15–30	do	do	87	.74	54
Do	> 30	do	do	69	.49	24
Do	Variable	Present	Present	237	.72	52
Do	do	do	Absent	452	.56	32
Do	do	Absent	do	154	.41	17

[1] All values are significant at the 1-percent level.

returned to the screened sample if desired. The entire subsample is then placed on a mixing cloth and pulled in such a way as to produce mixing. Some pulling operations will produce segregation instead of mixing, and special care must be exercised to obtain a well-mixed sample. The soil sample is then flattened until the pile is 2 to 4 cm. deep.

For moisture retentivity, hydraulic conductivity, and modulus of rupture tests, 2 to 6 subsamples, each having a fairly definite volume, are required. Use paper cups to hold the individual subsamples. Mark with a pencil line around the inside of the cup the height to which the cup is to be filled to give the correct amount of subsample. Then, using a thin teaspoon or a small scoop, lift small amounts of soil from the pile, placing each in successive cups and progressing around the pile until the cups are filled to the desired level. It is difficult with some soils, especially if they have been passed through a 2-mm. round-hole sieve, to take samples from the pile without allowing the larger particles to roll off the spoon or scoop. This rollback should be avoided because it makes the extracted subsample nonrepresentative. The rollback problem is practically absent from some soils, especially if all the sample has been passed through an 0.5-mm. sieve.

Three data forms, or work sheets, used at the Laboratory are shown herewith. The field data sheet should be at hand during sampling as an aid in recording pertinent information. The other two forms serve as work sheets for recording and calculating laboratory determinations.

(2) Saturated Soil Paste

Apparatus

Container of 250-ml. capacity or greater, such as a cup or moisture box.

Procedure

Prepare the saturated soil paste by adding distilled water to a sample of soil while stirring with a spatula. The soil-water mixture is consolidated from time to time during the stirring process by tapping the container on the workbench. At saturation the soil paste glistens as it reflects light, flows slightly when the container is tipped, and the paste slides freely and cleanly off the spatula for all soils but those with a high clay content. After mixing, the sample should be allowed to stand for an hour or more, and then the criteria for saturation should be rechecked. Free water should not collect on the soil surface nor should the paste stiffen markedly or lose its glistening appearance on standing. If the paste does stiffen or lose its glisten, remix with more water.

Because soils puddle most readily when worked at moisture contents near field capacity, sufficient water should be added immediately to bring the sample nearly to saturation. If the paste is too wet, additional dry soil may be added.

The amount of soil required depends on the measurements to be made, i. e., on the volume of extract desired. A 250-gm. sample is convenient to handle and provides sufficient extract for most purposes. Initially, the sample can be air-dry or at the field-moisture content, but the mixing process is generally easier if the soil is first air-dried and passed through a 2-mm. sieve.

If saturation pastes are to be made from a group of samples of uniform texture, considerable time can be saved by carefully determining the saturation percentage of a representative sample in the usual way. Subsequent samples can be brought to saturation by adding appropriate volumes of water to known weights of soil.

Special precautions must be taken with peat and muck soils and with soils of very fine and very coarse texture.

Peat and muck soils.—Dry peat and muck soils, especially if coarse or woody in texture, require an overnight wetting period to obtain a definite endpoint for the saturated paste. After the first wetting, pastes of these soils usually stiffen and lose the glisten on standing. Adding water and remixing then gives a mixture that usually retains the characteristics of a saturated paste.

Fine-textured soils.—To minimize puddling and thus obtain a more definite endpoint with fine-textured soils, the water should be added to the soils with a minimum of stirring, especially in the earlier stages of wetting.

Coarse-textured soils.—The saturated paste for coarse-textured soils can be prepared in the same manner as for fine-textured soils; however, a different moisture content is recommended for the salinity appraisal of such soils (Method 3b).

Method 27 gives procedures for determining the moisture content of saturated paste, i. e., the saturation percentage.

(3) Soil-Water Extracts

(3a) *Saturation Extract*

Apparatus

Richards or Buechner funnels, filter rack or flask, filter paper, vacuum pump, extract containers such as test tubes or 1-oz. bottles.

Procedure

Transfer the saturated soil paste, Method 2, to the filter funnel with a filter paper in place and apply vacuum. Collect the extract in a bottle or test tube. Pyrex should not be used if boron is to be determined. If the initial filtrate is turbid, it can be refiltered through the soil or discarded. Vacuum extraction should be terminated when air begins to pass through the filter. If carbonate and bicarbonate determinations are to be made on the extract, a solution containing 1,000 p. p. m. of sodium hexametaphosphate should be added at the rate of one drop per 25 ml. of extract prior

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to stoppering and storing. This prevents the precipitation of calcium carbonate on standing.

For appraising soil salinity for most purposes, the extraction can be made a few minutes after preparing the saturated paste. If the soil contains gypsum, the conductivity of the saturation extract can increase as much as 1 or 2 mmhos/cm. upon standing. Therefore, if gypsum is present, allow the saturated paste to stand several hours before extracting the solution.

If the solution is to be analyzed for its chemical constituents, the saturated paste should stand 4 to 16 hours before extraction.

References

Richards (1949a), Reitemeier and Fireman (1944).

(3b) Twice-Saturation Extract for Coarse-Textured Soils (Tentative)

The following procedure gives a moisture content that is approximately 8 times the 15-atmosphere percentage instead of 4 times, which is a usual factor for the saturation percentage of finer textured soils. The conductivity of the "twice-saturation" extract, therefore, is doubled before using the standard saturation-extract scale for salinity evaluation.

Apparatus

Soil container of 10 to 12 cm. diam. (i. e., 1-lb. coffee can) with a loosely fitting basket formed from galvanized screen with openings approximately 6 mm. square.

Pipet, 2-ml. capacity. Other items are the same as for Method 3a.

Procedure

Place the wire basket in the can, fill the basket with soil to a depth of 2 or 3 cm. Level the soil and by use of a pipet add 2 ml. of water dropwise to noncontiguous spots on the soil surface, cover, and allow to stand for 15 min. Gently sift the dry soil through the wire basket and weigh the moist pellets of soil retained thereon. Calculate the moisture content of the pellets as follows:

$$P_w = (2 \times 100)/(\text{wet weight in grams} - 2)$$

Weigh 250 gm. of air-dry soil and add sufficient water to make the moisture content up to 4 times the value found in the pellets. Use a vacuum filter to obtain the soil extract. For salinity appraisal of coarse-textured soil from which this extract was obtained, determine the electrical conductivity of the extract at 25° C. Multiply this conductivity value by 2 before using the standard saturation-extract salinity scale for interpretation (chs. 2 and 4).

(3c) Soil-Water Extracts at 1:1 and 1:5

Apparatus

Filter funnels, fluted filter paper, and bottles for soil suspensions and filtrates.

Procedure

Place a soil sample of convenient size in a bottle, add the required amount of distilled water, stopper, and agitate in a mechanical shaker for 15 min. Allow the contents to stand at least an hour, agitate again for 5 min., and filter. If shaken by hand, invert and shake bottle vigorously for 30 sec. at least 4 times at 30-min. intervals before filtering.

At a 1:1 soil-water ratio, it may be desirable to correct for hygroscopic moisture. Unless high precision is required, this is done by grouping the air-dried and screened soils roughly according to texture, and determining the percent moisture in 2 or 3 samples from each textural group. It is then possible to weigh out soil samples from the various groups and add sufficient water to bring the samples to approximately 100 percent moisture by weight. For example, an air-dry soil containing 3 percent moisture on an oven-dry basis can be brought to a 1:1 soil-water ratio by adding 97 ml. water to 103 gm. of air-dried soil.

At a soil-water ratio of 1:5 or greater, no allowance is ordinarily made for moisture in the air-dried sample.

(3d) Soil Extract in the Field-Moisture Range

A displacement method such as used by White and Ross (1937) does not require complicated apparatus; however, the pressure-membrane method described here can be used for a wider range of soil textures and a wider range of moisture contents.

Apparatus

Pressure-membrane cell with a cylinder 5 or 10 cm. high, tank of commercial water-pumped nitrogen, cans with watertight lids, plain transparent cellophane No. 600.

Procedure

Prior to use, the sheets of No. 600 cellophane are soaked in distilled water with daily changes of water in order to reduce the electrolyte content of the membrane. Electrical conductivity measurements on the water will indicate when the bulk of these impurities has been removed. Since washed and dried membranes may be somewhat brittle, they are stored wet until ready for use. They should be partially dried before mounting in the pressure-membrane apparatus.

The soil should be brought from the field at the moisture condition desired for the extraction and immediately packed in the pressure-membrane apparatus. If the soil has been air-dried, it may be passed through a 6-mm. screen and wetted to the desired water content with a fine spray of distilled water while tumbling in a mixing can or on a waterproofed mixing cloth. This wetted soil is stored in an airtight container, preferably in a constant-temperature room for 2 weeks and is mixed occasionally during this time. The pressure-membrane apparatus is then assembled, using No. 600

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plain transparent cellophane for the membrane. The soil is firmly packed by hand on the membrane in the extraction chamber to a depth of 2 or 4 in., depending upon the height of cylinder available. The chamber is then closed and the extraction process started at 225 lb. per sq. in. (15 atm.) of nitrogen gas.

The extract should be collected in fractions of approximately equal volume. The first fraction is usually discarded to avoid contamination from the membrane. Electrical conductivity measurements can be made on subsequent fractions to determine the degree of uniformity of the extract. The extraction process may require 1 to 4 days.

References

Reitemeier (1946), Reitemeier and Richards (1944), Richards (1947), and White and Ross (1937).

(4) Electrical Conductivity of Solutions

(4a) *Standard Wheatstone Bridge*

Remarks

Electrical conductivity is commonly used for indicating the total concentration of the ionized constituents of solutions. It is closely related to the sum of the cations (or anions) as determined chemically and usually correlates closely with the total dissolved solids. It is a rapid and reasonably precise determination that does not alter or consume any of the sample.

Apparatus

Wheatstone bridge, alternating current, suitable for conductivity measurements. This may be a 1,000-cycle a. c. bridge with telephone receivers, a 60-cycle a. c. bridge with an a. c. galvanometer, or one of the newer bridges employing a cathode ray tube as the null indicator.

Conductivity cell, either pipet or immersion type, with platinized platinum electrodes. The cell constant should be approximately 1.0 reciprocal centimeter. New cells should be cleaned with chromic-sulfuric acid cleaning solution, and the electrodes platinized before use. Subsequently, they should be cleaned and replatinized whenever the readings become erratic or when an inspection shows that any of the platinum black has flaked off. The platinizing solution contains platinum chloride, 1 gm., lead acetate, 0.012 gm., in 100 ml. water. To platinize, immerse the electrodes in the above solution and pass a current from a 1.5-volt dry battery through the cell. The current should be such that only a small quantity of gas is evolved, and the direction of current flow should be reversed occasionally.

A thermostat is required for precise measurements, but for many purposes it is satisfactory to measure the temperature of the solution and make appropriate temperature corrections.

Reagents

Potassium chloride solution, 0.01 N. Dissolve 0.7456 gm. of dry potassium chloride in water and make to 1 liter at 25° C. This is the standard reference solution and at 25° C. has an electrical conductivity of 1411.8 $\times 10^{-6}$ (0.0014118) mhos/cm.

Procedure

Fill the conductivity cell with the reagent, having known conductivity EC_{25}. Most cells carry a mark indicating the level to which they should be filled or immersed. Follow the manufacturers' instructions in balancing the bridge. Read the cell resistance, R_{25} at 25° C. and calculate the cell constant (k), from the relation,

$$k = EC_{25} \times R_{25}$$

The cell constant will change if the platinization fails, but it is determined mainly by the geometry of the cell, and so is substantially independent of temperature.

Rinse the cell with the solution to be measured. The adequacy of rinsing is indicated by the absence of resistance change with successive rinsings. If only a small amount of the sample is available, the cell may be rinsed with acetone and ventilated until it is dry. Record the resistance of the cell (R_t) and the temperature of the solution (t) at which the bridge is balanced. Keep the cell filled with distilled water when not in use.

Calculations

The electrical conductivity (EC_t) of the solution at the temperature of measurement (t) is calculated from the relation

$$EC_t = k/R_t$$

where

$$k = EC_{25} \times R_{25}$$

For soil extracts and solutions, a temperature conversion factor (f_t), obtained from table 15, can be used for converting conductivity values to 25° C. Thus,

$$EC_{25} = EC_t \times f_t = kf_t/R_t$$

References

Campbell and others (1948), National Research Council International Critical Tables (1929).

(4b) *Direct Indicating Bridge*

Apparatus

Conductivity sets are available that have a bridge scale and cell design features suggested by the Laboratory especially for use with saturation extracts (fig. 26). This set is convenient to use and has sufficient accuracy for diagnostic purposes. The conductivity cell supplied with this bridge has a constant of 0.5 cm.$^{-1}$ and a capacity of 2 to 3 ml. of solution. With this cell the

(20b) *Estimation of Exchangeable-Sodium-Percentage and Exchangeable-Potassium-Percentage From Soluble Cations*

Procedure

Prepare a saturation extract of the soil as described under Methods 2 and 3a. Determine the calcium plus magnesium, sodium, and potassium concentrations of the saturation extract, using Methods 7, 10, and 11, respectively.

Calculations

Exchangeable-sodium-percentage

$$=\frac{100\ (-0.0126+0.01475x)}{1+(-0.0126+0.01475x)}$$

where x is equal to the sodium-adsorption-ratio.

Exchangeable-potassium-percentage

$$=\frac{100\ (0.0360+0.1051x)}{1+(0.0360+0.1051x)}$$

where x is equal to the potassium-adsorption-ratio. The sodium-adsorption-ratio and the potassium-adsorption-ratio are calculated as follows:

$$\text{Sodium-adsorption-ratio}=Na^{+}/\sqrt{(Ca^{++}+Mg^{++})/2}$$

and

$$\text{Potassium-adsorption-ratio}=K^{+}/\sqrt{(Ca^{++}+Mg^{++})/2}$$

where Na^{+}, K^{+}, Ca^{++}, and Mg^{++} refer to the concentrations of designated cations expressed in milliequivalents per liter.

A nomogram, which relates soluble sodium and soluble calcium plus magnesium concentrations to the sodium-adsorption-ratio, is given in figure 27. Also included in the nomogram is a scale for estimating the corresponding exchangeable-sodium-percentage, based on the linear equation given in connection with figure 9 (ch. 2). To use this nomogram, lay a straightedge across the figure so that the line coincides with the sodium concentration on scale A and with the calcium plus magnesium concentration on scale B. The sodium-adsorption-ratio and the estimated exchangeable-sodium-percentage are then read on scales C and D, respectively.

Supplementary Measurements

(21) pH Determinations

(21a) *pH Reading of Saturated Soil Paste*

Apparatus

pH meter with glass electrode.

Procedure

Prepare a saturated soil paste with distilled water as directed in Method 2 and allow paste to stand at least 1 hour. Insert the electrodes into the paste and raise and lower repeatedly until a representative pH reading is obtained.

(21b) *pH Reading of Soil Suspension*

Procedure

Prepare a soil suspension, using distilled water, shake intermittently for an hour, and determine pH reading.

(21c) *pH Reading of Waters, Solutions, Soil Extracts*

Procedure

Determine pH reading by means of a glass electrode assembly with the solution in equilibrium with a known CO_2 atmosphere.

Remarks

Opinion varies as to the proper method for making pH readings. It is desirable to select a definite procedure and follow it closely, so that the readings will be consistent and have maximum diagnostic value. The method used should be described accurately so as to aid others in the interpretation of results.

The CO_2 status influences pH readings, and should be controlled or specified. Ordinarily, readings are made at the CO_2 pressure of the atmosphere. A special high-pH glass electrode should be used for pH values appreciably above 9.0.

(22) Gypsum

(22a) *Gypsum by Precipitation With Acetone (Qualitative)*

Reagent

Acetone.

Procedure

Weigh 10 to 20 gm. of air-dried soil into an 8-oz. bottle and add a measured volume of water sufficient to dissolve the gypsum present. Stopper the bottle and shake by hand 6 times at 15-min. intervals or agitate for 15 min. in a mechanical shaker. Filter the extract through paper of medium porosity. Place about 5 ml. of the extract in a test tube, add an approximately equal volume of acetone, and mix. The formation of a precipitate indicates the presence of gypsum in the soil.

Remarks

The soil should not be oven-dried, because heating promotes the conversion of $CaSO_4{\cdot}2H_2O$ to $CaSO_4{\cdot}0.5H_2O$. The latter hydrate has a higher solubility in water for an indefinite period following its solution.

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411914-02

STUDY TITLE

Soil Fertility and Fertilizers

DATA REQUIREMENT

Not Applicable

AUTHOR

Samuel L. Tisdale

STUDY COMPLETED ON

Not Applicable

PERFORMING LABORATORY

Not Applicable

STATEMENT OF NO DATA CONFIDENTIALITY CLAIMS

No claim of confidentiality is made for any information contained in this study on the basis of its falling within the scope of FIFRA Section 10(d)(1)(A),(B), or (C).

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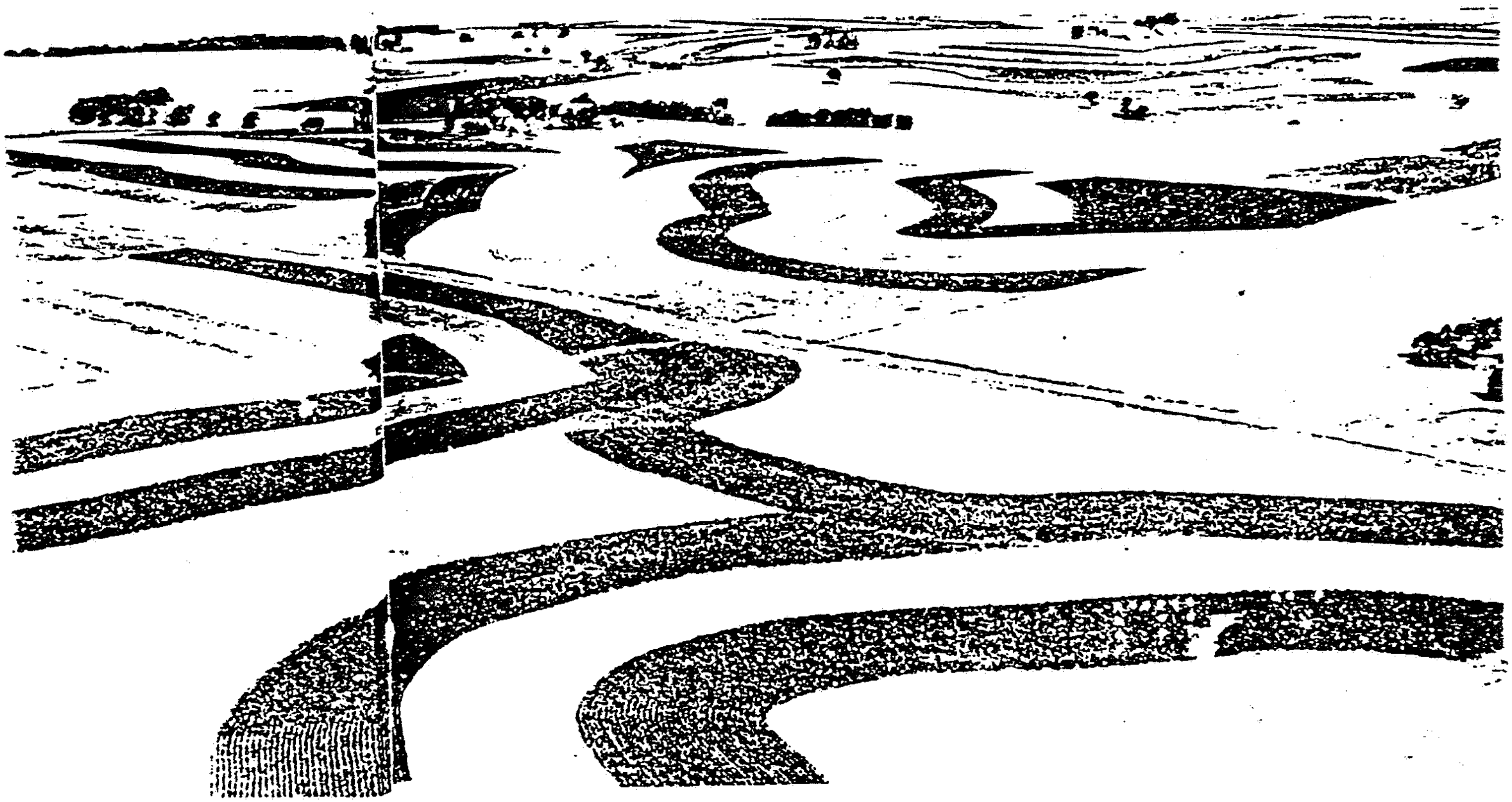
Date: August 1, 1989

SECOND EDITION

SOIL FERTILITY AND FERTILIZERS



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higher rates the ammonium chloride gave poorer results than the sulfate, in part because of the greater injury to the grass when in contact with the leaves. The acceptance of this material by farmers in the United States will undoubtedly depend on any economic advantage it might offer over existing sources of nitrogen.

Urea. Urea [$CO(NH_2)_2$] is produced by reacting ammonia with carbon dioxide under pressure and at an elevated temperature. It contains the highest percentage of nitrogen of any solid material currently available (45%).

Though not an ammonium fertilizer in the form in which it is marketed, it hydrolyzes to ammonium carbonate very quickly when added to the soil, as shown by the following equation:

$$CO(NH_2)_2 + 2H_2O \longrightarrow (NH_4)_2CO_3$$

Ammonium carbonate is an unstable compound and decomposes to ammonia and carbon dioxide. The NH_3 or NH_4^+ so released is adsorbed by the colloidal fraction of the soil and subsequently nitrified. Because of the ammonium ion produced by the hydrolysis of this material, it is somewhat acid in its ultimate reaction with the soil.

The hydrolysis of this material is greatly increased in the presence of the enzyme urease, which is found to varying degrees in soils. In most soils it is present in sufficient concentrations to bring about the rapid conversion of urea to NH_4^+. Once in NH_4^+ form, it behaves like any other ammoniacal source of nitrogen.

Urea is an excellent fertilizer material. However, it possesses several properties which should be understood in order that the greatest benefit may be derived from its use. The first is related to its rapid hydrolysis. If urea is applied to a bare soil surface or to soil in a sod cover, significant quantities of ammonia may be lost by volatilization because of its rapid hydrolysis to ammonium carbonate. Losses of ammonia from urea applied to the soil surface and when mixed with the surface soil to different depths are shown in Figure 5-19. These data were obtained from a laboratory study carried out at 75°F. with a Dickson silt loam to which urea at the rate of 100 lb. N/A. had been applied. The losses were appreciable, enhanced no doubt by the fact that the air was moving through the incubation flasks at a steady rate. However, the effect of mixing the urea with the soil on the reduction of ammonia losses is apparent.

Field studies conducted at the University of Florida have shown that losses of ammonia occur from the bare surface of acid soils. The results of some of this research are given in Table 5-14. It is obvious that losses were greater from some soils than from others and that the losses were greater from pelleted urea than from urea applied in solution. The

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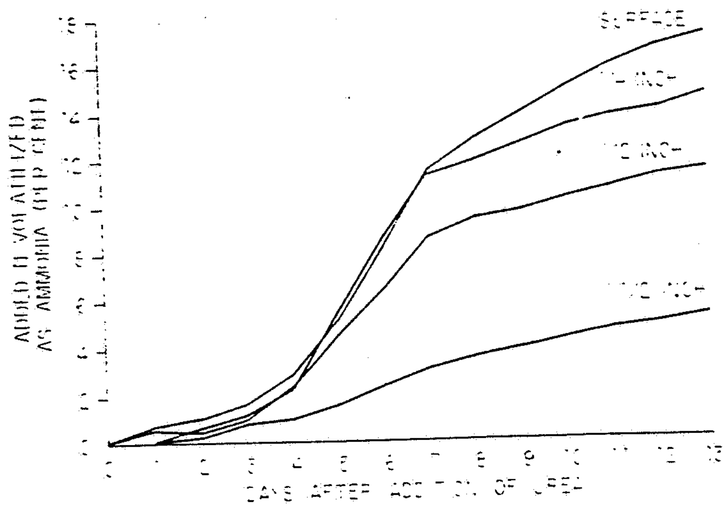

Figure 5–19. Cumulative loss of added nitrogen from urea mixed with surface soil layers of different thickness: 100 lb. urea-N/A. applied to *p*H 6.5 Dickson silt loam and aerated at 75°F. [Ernst et al., *SSSA Proc.*. **24:**87 (1960).]

TABLE 5–14. Gaseous Losses of Ammonia During Seven Days Following Surface Application of 100 lb. of Nitrogen per Acre to Bare, Moist Soils*

				Percentage nitrogen loss from		
Soil type	Soil *p*H	Cation exchange capacity (meq. 100 g.)	Absorption potential (mg. NH_3-N cc. of soil)	Pelleted urea	Ammonium sulfate	Urea-ammonium nitrate solution†
Lakeland fs. I	5.6	1.5	0.38	39.8	0.4	0.6
Lakeland fs. II	6.3	1.6	0.19	59.0	0.9	29.4
Lakeland fs. III	5.4	4.7	1.23	16.8	0.2	1.6
Lakeland fs. IV	6.7	3.5	0.38	48.9	5.5	15.2
Lakeland fs. V	6.3	1.9	0.39	39.4	0.7	4.4
Leon fs. I	4.4	2.8	0.47	26.9	0.1	3.2
Leon fs. II	5.9	5.8	0.75	35.8	1.6	7.5
Red Bay fsl.	5.3	7.2	1.16	19.5	0.2	2.3
Arredondo fsl.	5.8	11.5	1.59	8.6	0.2	0.4
Fellowship fsl.	5.9	23.4	1.93	7.6	0.5	0.1
Brighton peat	5.6	120.0	3.74	3.1	0.2	—
Perrine marl	7.8	7.4	0.31	14.6	36.9	14.4

* Volk, *Agron. J.*. **51:**746 (1959).
† Contained 32% nitrogen—16.5% from urea and 15.5% from ammonium nitrate.

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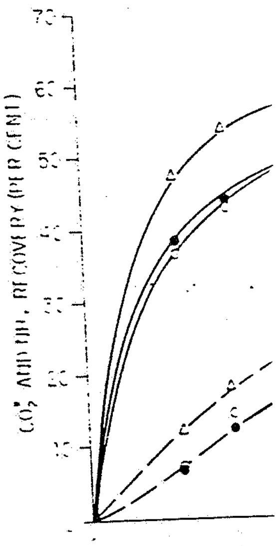

Figure 5–20. The influen
on the amounts of CO_2
SSSA Proc.. **26:**186 (1962

**TABLE 5–15. The Influenc
Bermuda Grass Hay Produ**

Source of Nitrogen (200 lb. A.)
NH_4NO_3
Urea
Urea

* Jackson et al., *Agron. J.*

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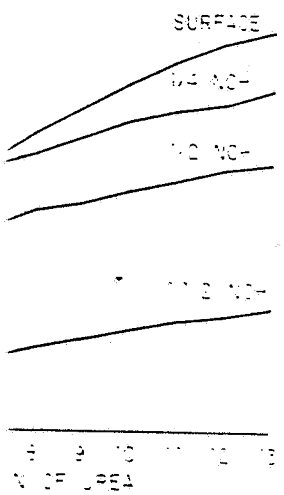

...en from urea mixed with
...rea-N/A. applied to pH 6.5
...et al., *SSSA Proc.*, 24:87

...even Days Following Surface ...e, Moist Soils*

...eted ...ea	Ammonium sulfate	Urea-ammonium nitrate solution†
.8	0.4	0.6
.0	0.9	29.4
.8	0.2	1.6
.9	5.5	15.2
.4	0.7	4.4
.9	0.1	3.2
.8	1.6	7.5
.5	0.2	2.3
6	0.2	0.4
6	0.5	0.1
1	0.2	—
6	36.9	14.4

...ammonium nitrate.

volatilization of ammonia from ammonium sulfate applied to the Lakeland fine sand IV (pH 6.7) and the Perrine marl (pH 7.8) illustrate the losses from ammoniacal sources other than urea which can be expected when such materials are applied to neutral or alkaline soils.

When urea is applied to sod, losses of ammonia can be significant. This is illustrated by the curves in Figure 5-20. The losses were appreciable and tended to level off about six to seven days after application.

Burning as a practical means of controlling ammonia losses from surface applications of urea was suggested by research workers at the Tifton, Georgia, Experiment Station. The results of some of their studies with Coastal Bermuda grass are listed in Table 5-15. Burning the sod before

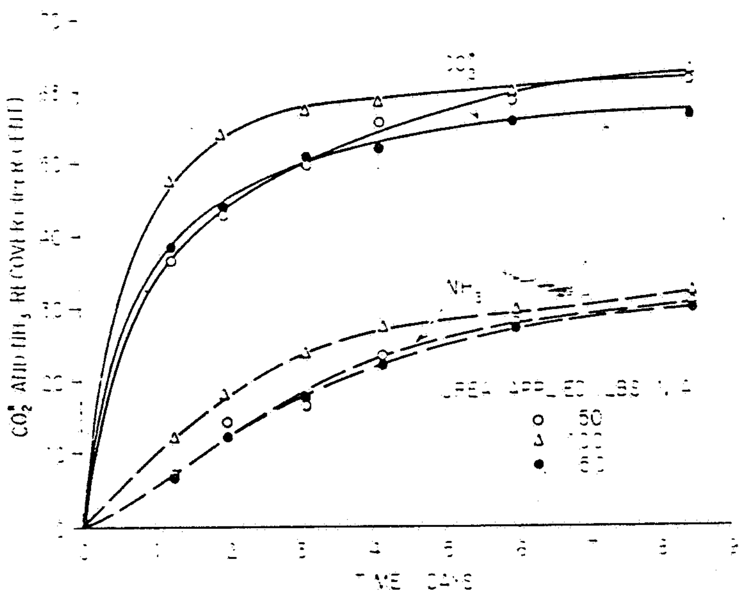

Figure 5–20. The influence of rates of urea applications to a bluegrass sod on the amounts of CO_2 and NH_3 lost to the atmosphere. [Simpson et al., *SSSA Proc.*, **26**:186 (1962).]

TABLE 5–15. The Influence of Nitrogen Source and Sod Treatment on Coastal Bermuda Grass Hay Production in 1958–1960*

Source of Nitrogen (200 lb. A.)	Sod treatment	Relative yield (three-year average)
NH_4NO_3	Burned	100
Urea	Burned	97
Urea	None	86

* Jackson et al., *Agron. J.*, 54:47 (1962).

crease crop yields. Their
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$_2CN_2)_2 - Ca(OH)_2$ (3)

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:ed fertilizers, for it is an

excellent conditioning agent. Its total consumption, however, has steadily declined over the years, for its cost per unit of nitrogen is rather high in relation to the cost of other nitrogen materials.

THE ACIDITY AND BASICITY OF NITROGEN FERTILIZERS

Some fertilizer materials leave an acid residue in the soil, others a basic residue, and still others seemingly have no influence on the soil *p*H. Results of numerous experiments have shown that among the plant nutrients nitrogen, phosphorus, and potassium, the carriers of phosphorus and potassium have little or no influence on soil acidity. The carriers of nitrogen, however, have a considerable effect on both the soil *p*H and the loss of cations by leaching. The development of acidity is illustrated by the nitrification equation given earlier in this chapter (see p. 138).

A method for determining the acidity or basicity of fertilizers was developed by Pierre in 1933. His method is based on the assumption that (1) the sulfur, chlorine, one third of the phosphorous, and half of the contained nitrogen reduce the lime content, hence the *p*H, of the soil and (2) that the calcium, magnesium, potassium, and sodium increase its lime status. He further assumed that half of the nitrogen added to the soil was absorbed by the plant as nitric acid and the other half as a salt, such as calcium nitrate. He accordingly calculated that 1.8 lb. of CP calcium carbonate would be required to neutralize the acidity resulting from the addition of each pound of fertilizer nitrogen. Sources of nitrogen such as sodium nitrate or calcium nitrate would then leave a basic residue because of the nature of the accompanying ion. This method, modified for estimating the equivalent acidity or basicity of complete fertilizers, was adopted by the Association of Official Agricultural Chemists and is recognized presently as the official procedure.

Pierre's method has been criticized by Andrews on the basis that it gives lime equivalent values that are lower than those actually required to neutralize the acid formed by each of the various materials. Andrews maintains that each pound of fertilizer nitrogen as NH_3 will require 3.57 lb. of CP calcium carbonate to neutralize the acidity if converted to the nitrate form. Also every pound of nitrogen leached from the soil as the nitrate (NO_3) takes with it 3.57 lb. of $CaCO_3$ or its equivalent in basic cations. He has accordingly calculated the amounts of limestone he maintains will be required to neutralize the acidity formed by the various sources of nitrogen. These values, along with those determined by the Pierre method, are shown in Table 5-18. The figures currently listed for the acidity or basicity of mixed fertilizers and straight goods are determined by the official A.O.A.C. procedure, which is that of Pierre.

TABLE 5–18. Equivalent Acidity and Basicity of Nitrogenous Fertilizer Materials According to Andrews and Pierre*

Material	Per cent nitrogen	Pure lime necessary to make lime salts†			Pounds of pure lime: official method for neutralizing fertilizers		
		Per lb. of nitrogen	Per 20 lb. of nitrogen	Per 100 lb. of material	Per lb. of nitrogen	Per 20 lb. of nitrogen	Per 100 lb. of material
Inorganic sources of nitrogen							
Sulphate of ammonia	20.5	7.14	143	146	5.35	107	110
Ammo-phos A	11.0	6.77	135	74	5.00	100	55
Anhydrous ammonia	82.2	3.57	72	293	1.80	36	148
Calcium nitrate	15.0	0.42	8	6	1.35B	27B	20B
Calnitro	16.0	0.66	13	11	1.31B	26	21
Calnitro	20.5	1.77	35	36	0	0	0
Crude nitrogen solution	44.4	2.98	60	132	1.20	24	53
Nitrate of soda	16.0	0.00	0	0	1.80B	36B	29B
Potassium nitrate	13.0	0.00	0.00	0.00	2.00B	40B	26B
Manufactured organic nitrogen							
Cyanamid	22.0	1.18B	24B	26B	2.85B	57B	63B
Urea	46.6	3.57	71	166	1.80	36	84
Urea-ammonia liquor	45.5	3.57	71	162	1.80	36	82
Natural organic nitrogen							
Cocoa shell meal	2.7	2.37	47	6	0.60B	12B	2B
Castor pomace	4.8	2.67	53	13	0.90	18	4
Cottonseed meal	6.7	3.17	63	21	1.40	28	9
Dried blood	13.0	3.52	70	46	1.75	35	23
Fish scrap	9.2	2.67	53	25	0.90	18	8
Fish scrap	8.9	1.78	36	16	0.01	2	0
Guano, Peruvian	13.8	2.72	54	38	0.95	19	13
Guano, white	9.7	2.22	44	21	0.45	9	4
Milorganite	7.0	3.47	69	24	1.70	34	12
Tankage, animal	9.1	1.92	38	17	0.15	3	1
Tankage, garbage	2.5	0.93B	19B	2B	2.70B	54B	7B
Tankage, high grade	8.4	2.52	50	21	0.75	15	6
Tankage, low grade	4.3	5.43B	109B	23B	7.20B	144B	31B

Material	Per cent nitrogen	Pe nit
Tankage, packing house	6.0	(
Tankage, process	7.4	3
Tobacco stems	1.4	16
Tobacco stems	2.8	:
Sources of potash		
Manure salts	0	
Muriate of potash	0	
Potassium nitrate	13.0	
Sulfate of potash	0	
Sulfate of potash—magnesia	0	
Sources of phosphorus		
Ammo-phos A	11.0	
Precipitated bone	0	
Superphosphate	0	
Triple superphosphate	0	

* Andrews, *The Response of Cr* 1954 by W. B. Andrews.
† Data to make lime salts from lb. lb. of nitrogen to data for neu
B = lime in excess of that required

In a paper by Raney (1 of percolating or drainage with the amount of base cations in drainage waters the amount of drainage present.

The removal of basic soils become acid. Crop losses of these metallic i clusion that nitrate sourc forming than ammoniacal an acidic anion such as NO_3^- ion, would be mor Experimental evidence h

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y to … er 100 lb. of material	Pounds of pure lime: official method for neutralizing fertilizers: Per lb. of nitrogen	Per 20 lb. of nitrogen	Per 100 lb. of material
146	5.35	107	110
74	5.00	100	55
293	1.80	36	148
6	1.35B	27B	20B
11	1.31B	26	21
36	0	0	0
132	1.20	24	53
0	1.80B	36B	29B
).00	2.00B	40B	26B
26B	2.85B	57B	63B
166	1.80	36	84
162	1.80	36	82
6	0.60B	12B	2B
13	0.90	18	4
21	1.40	28	9
46	1.75	35	23
25	0.90	18	8
16	0.01	2	0
38	0.95	19	13
21	0.45	9	4
24	1.70	34	12
17	0.15	3	1
2B	2.70B	54B	7B
21	0.75	15	6
23B	7.20B	144B	31B

Material	Per cent nitrogen	Pure lime necessary to make lime salts†: Per lb. of nitrogen	Per 20 lb. of nitrogen	Per 100 lb. of material	Pounds of pure lime: official method for neutralizing fertilizers: Per lb. of nitrogen	Per 20 lb. of nitrogen	Per 100 lb. of material
Tankage, packing house	6.0	0.12	2	1	1.65B	33B	10B
Tankage, process	7.4	3.32	66	25	1.55	31	12
Tobacco stems	1.4	16.03B	321B	22B	17.80B	356B	25B
Tobacco stems	2.8	2.53B	51B	7B	4.30B	86B	12B
Sources of potash							
Manure salts	0	0	0	0	0	0	0
Muriate of potash	0	0	0	0.	0	0	0
Potassium nitrate	13.0	0	0	0	2.00B	40B	26B
Sulfate of potash	0	0	0	0	0	0	0
Sulfate of potash —magnesia	0	0	0	0	0	0	0
Sources of phosphorus							
Ammo-phos A	11.0	6.77	135	74	5.00	100	55
Precipitated bone	0	0	0	0	0	0	29B
Superphosphate	0	0	0	0	0	0	0
Triple super-phosphate	0	0	0	0	0	0	0

* Andrews. *The Response of Crops and Soils to Fertilizers and Manures.* 2nd Ed. Copyright 1954 by W. B. Andrews.
† Data to make lime salts from organic sources of nitrogen were obtained by adding 1.77 lb. lb. of nitrogen to data for neutral fertilizers.
B = lime in excess of that required to make neutral salts or neutral fertilizers.

In a paper by Raney (1960) it was pointed out that the nitrate content of percolating or drainage water was the predominant factor associated with the amount of bases in the leachate. The content of these basic cations in drainage waters was only slightly or not at all correlated with the amount of drainage water or the content of sulfates and chlorides present.

The removal of basic cations from soils is, of course, the reason that soils become acid. Crop removal and leaching account for the greatest losses of these metallic ions. *A priori* reasoning would lead to the conclusion that nitrate sources carrying a basic cation should be less acid forming than ammoniacal sources. Further, ammoniacal sources that carry an acidic anion such as SO_4^{2-}, which is not absorbed as rapidly as the NO_3^- ion, would be more acidic than a material such as ammonia or urea. Experimental evidence has shown this to be the case.

Regardless of which method, whether that of Pierre or Andrews, more closely estimates the acidifying effects of the different forms of fertilizer nitrogen, the fact remains that some materials are acid forming and others are not. The importance of this property fades into insignificance in a well-run farming enterprise. In such an operation the maintenance of proper soil *p*H in an adequate liming program is mandatory, and in such an operation the factors determining the choice of fertilizer nitrogen are its applied cost, market availability, and ease of application.

CROP RESPONSES TO VARIOUS SOURCES OF FERTILIZER NITROGEN

Much research has been carried out in the United States to evaluate the effectiveness of various sources of fertilizer nitrogen. By far the greater proportion of these studies has been done on the acid soils of the humid region east of the Mississippi River. It is not the purpose of this book to review individually the results of these various experiments. However, a summary of these findings, as well as of the principles involved in nitrogen fertilization, is given.

1. The continued use of acid-forming fertilizer materials will lead to a decrease in *p*H with an accompanying decrease in crop yields unless lime sufficient to neutralize the acidity formed is applied to the soil.
2. When applied in amounts generally recommended, the use of basic fertilizers may maintain the soil *p*H at its original level, but in general on humid-region soils they will do little to increase the degree of base saturation and, conversely, the soil *p*H. When applied in large quantities over a long period of time, these fertilizers may cause some increase in the soil *p*H.
3. The nitrification pattern of both ammoniacal and natural organic materials provides little justification for the belief that these forms in warm, well-aerated, and moist soils release their nitrogen slowly, thus reducing excessive losses by leaching. In cold, fine-textured soils the water-insoluble forms may be expected to lose less of their nitrogen by leaching than the soluble forms because of reduced mineralization under cold conditions. When early crops are planted on such soils, this difference may be reflected in yields if all the fertilizer nitrogen is applied before planting.
4. The principles of ion exchange generally influence the effectiveness of chemical sources of nitrogen. The ammoniacal form is retained briefly against leaching because of its adsorption by soil colloids. The nitrate form is not so retained. This difference will be greatest in fine-textured and least in coarse-textured soils. The downward

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9. When differences
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Summary

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movement is a factor to consider when top dressing with various sources of solid nitrogen fertilizers on soils of different texture. Differences in the leaching losses of these two forms are reduced when conditions favor rapid nitrification.

5. When conditions favor nitrification, the superiority of one form of nitrogen over the other may be related to the accompanying ion or to some element contained as an impurity. This is illustrated by the use of a material such as ammonium sulfate. If applied on a sulfur-deficient soil, it would give an apparently better response than a nonsulfur-containing nitrogen carrier if sulfur were not included in some other component of the fertilizer. In such cases the way in which the limiting element should be supplied will be dictated by economic considerations.
6. Calcium cyanamide must be applied well before seeding and must be incorporated thoroughly into the soil. The occasional observations of the inferiority of this material can almost always be traced to improper application in the field.
7. Some nitrogen sources such as anhydrous ammonia, nitrogen solutions, urea, and other ammoniacal materials may lose ammonia by volatilization as a result of improper placement, surface application to alkaline soils, or, in the case of urea, surface application to soil or sod. In addition, if placed too close to seed or plants, injury may result from ammonia toxicity. These difficulties can most generally be corrected by proper placement and by adjusting the time of application.
8. Some crops, such as flue-cured tobacco, may be adversely affected by prolonged concentrations of the ammonium ion in the soil which may be caused by the use of soil fumigants that inhibit nitrification. A significant portion of the applied fertilizer nitrogen should be in the nitrate form.
9. When differences in acid-forming properties, secondary or trace element content, and method and time of application and placement are recognized and handled accordingly, one source of fertilizer nitrogen is often as effective as any other in increasing crop yields. The determining factor in the selection of a source of nitrogen is then governed by economic considerations. The material purchased should be that from which maximum return on the fertilizer-nitrogen dollar can be expected.

Summary

1. Atmospheric nitrogen is fixed in soils by various free-living and symbiotic bacteria. The amounts fixed by these organisms are generally

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36

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No claim of confidentiality is made for any information contained in this study on the basis of its falling within the scope of FIFRA Section 10(d)(1)(A),(B), or (C).

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on water and fertilizer.

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B-15

Weights and Common Names
…emical Amendments

…ent …t	Common Name
-	Calcium ion
	Magnesium ion
:	Sodium ion
)	Potassium ion
?	Chloride ion
.	Nitrate ion
3	Ammonium ion
3	Sulfate ion
)	Carbonate ion
2	Bicarbonate ion
)	Calcium chloride
7	Calcium sulfate
9	Gypsum
4	Calcium carbonate
2	Magnesium chloride
9	Magnesium sulfate
5	Magnesium carbonate
5	Sodium chloride
3	Sodium sulfate
0	Sodium carbonate
2	Sodium bicarbonate
6	Potassium chloride
3	Potassium sulfate
0	Potassium carbonate
2	Potassium bicarbonate
3	Sulfur
3	Sulfur dioxide
4	Sulfuric acid
8	Aluminum sulfate
2	Iron sulfate (ferrous)

Table B-16

Average Nutrient Analysis of Some Organic Materials

	N	P_2O_5	K_2O
		(%)	
Fresh manure with normal quantity of bedding or litter			
Duck	1.1	1.45	0.50
Goose	1.1	0.55	0.50
Turkey	1.3	0.70	0.50
Rabbit	2.0	1.33	1.20
Bulky organic materials			
Alfalfa hay	2.5	0.50	2.10
Bean straw	1.2	0.25	1.25
Grain straw	0.6	0.20	1.10
Cotton gin trash	0.7	0.18	1.19
Seaweed (kelp)	0.2	0.10	0.60
Winery pomace (dried)	1.5	1.50	0.75
Organic concentrates			
Dried blood	12.0	1.5	—
Fish meal	10.4	5.9	—
Digested sewage sludge	2.0	3.0	—
Activated sewage sludge	6.5	3.4	0.3
Tankage	7.0	8.6	1.5
Cottonseed meal	6.5	3.0	1.5
Bat guano	13.0	5.0	2.0
Bone meal[1]	<1.0	12–14	—

[1]Bone meal values vary widely because of moisture content and processing. Available P_2O_5, 12%–14%; insoluble P_2O_5, 14%–16%; total P_2O_5, 26%–28%.

Table B-17

The Approximate Amounts of Soil Sulfur (99%) Needed to Increase the Acidity of the Plow-Depth Layer of a Carbonate-Free Soil

Change in pH Desired	Pounds of Sulfur per Acre		
	Sand	Loam	Clay
8.5 to 6.5	2,000	2,500	3,000
8.0 to 6.5	1,200	1,500	2,000
7.5 to 6.5	500	800	1,000
7.0 to 6.5	100	150	300

Table B-18

Tons of Various Amendments Needed to Be Equivalent to 1 Ton of Sulfur

Amendment	Tons Equivalent to 1 Ton of Sulfur
Sulfur	1.00
Lime-sulfur solution, 24% sulfur	3.65
Sulfuric acid (98%)	3.06
Gypsum ($CaSO_4 \cdot 2H_2O$)	5.38
Iron sulfate ($FeSO_4 \cdot 7H_2O$)	8.69
Aluminum sulfate [$Al_2(SO_4)_3 \cdot 18H_2O$]	6.94

Table B-19

Plants Grouped According to Their Tolerance to Acidity

Very Sensitive to Acidity	Will Tolerate Slight Acidity	Will Tolerate Moderate Acidity	Strong Acidity Favorable
Alfalfa	Soybean	Vetch	Blueberry
Sweet clover	Red clover	Oats	Cranberry
Barley	Mammoth clover	Rye	Holly
Sugar beet	Alsike clover	Buckwheat	Rhododendron
Cabbage	White clover	Millet	Azalea
Cauliflower	Timothy	Sudan grass	
Lettuce	Kentucky bluegrass	Redtop	
Onion	Corn	Bentgrass	
Spinach	Wheat	Tobacco	
Asparagus	Pea	Potato	
Beet	Carrot	Field bean	
Parsnip	Cucumber	Parsley	
Celery	Brussels sprouts	Sweet potato	
Muskmelon	Kale	Cotton	
	Kohlrabi	Peanuts	
	Pumpkin		
	Radish		
	Squash		
	Lima, pole and snap beans		
	Sweet corn		
	Tomato		
	Turnip		
	Sorghum		

Amount of Li
the Soil I

Change in pH Desired in Plow-Depth Layer	Sand
4.0 to 6.5	2,600
4.5 to 6.5	2,200
5.0 to 6.5	1,800
5.5 to 6.5	1,200
6.0 to 6.5	600

[a]A dolomitic limestone is preferable wherever

The Neutrali
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Material
Calcium oxide
Calcium hydroxide
Dolomite
Calcium carbonate
Calcium silicate

Use of the neutralizing value ma
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Tons Equivalent to 1 Ton of Sulfur
1.00
3.65
3.06
5.38
8.69
6.94

Tolerance to Acidity

⁄ill Tolerate derate Acidity	Strong Acidity Favorable
⁄etch	Blueberry
Ͻats	Cranberry
⁝ye	Holly
⁝uckwheat	Rhododendron
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Table B-20

Amount of Limestone Needed to Change the Soil Reaction (Approximate)[1]

Change in pH Desired in Plow-Depth Layer	Pounds of Limestone per Acre					
	Sand	Sandy Loam	Loam	Silt Loam	Clay Loam	Muck
4.0 to 6.5	2.600	5.000	7.000	8.400	10.000	19,000
4.5 to 6.5	2.200	4.200	5.800	7.000	8.400	16.200
5.0 to 6.5	1.800	3.400	4.600	5.600	6.600	12,600
5.5 to 6.5	1.200	2.600	3.400	4.000	4.600	8,600
6.0 to 6.5	600	1,400	1.800	2.200	2.400	4,400

[1]A doiomitic limestone is preferable wherever there is a possible lack of magnesium.

Table B-21

The Neutralizing Value of the Pure Forms of Commonly Used Liming Materials

Material	Chemical	Neutralizing Value
		(%)
Calcium oxide	CaO	179
Calcium hydroxide	$Ca(OH)_2$	136
Dolomite	$CaMg(CO_3)_2$	109
Calcium carbonate	$CaCO_3$	100
Calcium silicate	$CaSiO_3$	86

Use of the neutralizing value makes possible the most simple and straightforward comparison of one liming material with another.

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Horst Marschner

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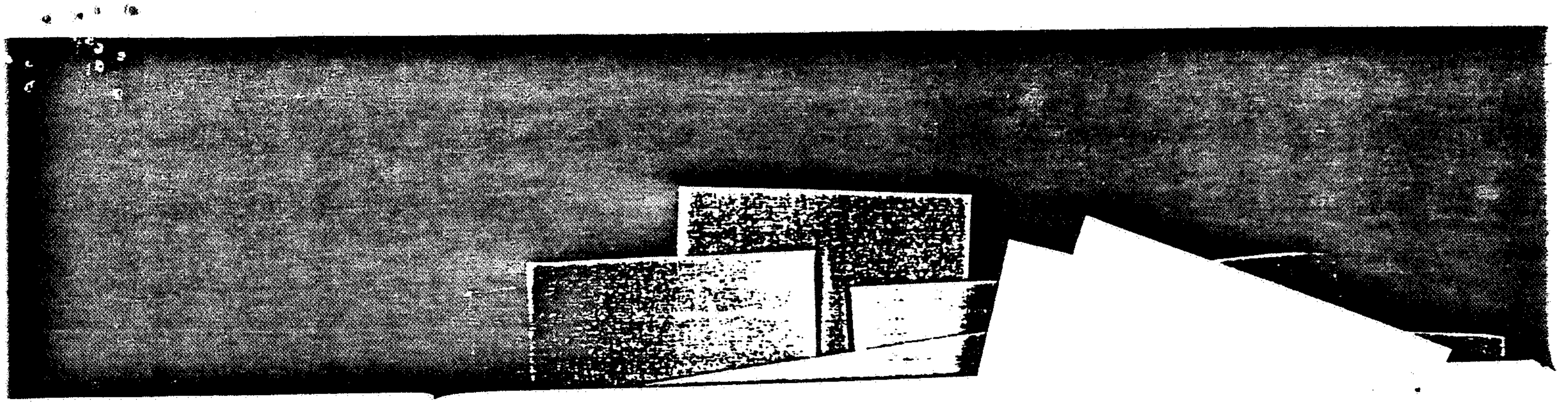

Mineral Nutrition of Higher Plants

Horst Marschner

Institute of Plant Nutrition
University of Hohenheim
Federal Republic of Germany

1986

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Boston Sydney Tokyo Toronto

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1.1

cronutrients for Higher Plants

Discovered by
J. Sachs
J. S. McHague
K. Warington
A. L. Sommer and C. B. Lipman
C. B. Lipman and G. MacKinney
D. I. Arnon and P. R. Stout
T. C. Broyer *et al.*

r mineral nutrient) was proposed by concluded that, for an element to be st be met:

mplete its life cycle in the absence of

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eral elements which compensate for ch simply replace mineral nutrients uch as the maintenance of osmotic described as "beneficial" elements

cussing which mineral elements are icularly obvious when higher and For higher plants the essentiality of lthough the known requirement for number of plant species.

improvements in analytical tech- chemicals, this list might well be hat are essential only in very low micronutrients). This holds true in

Table 1.2
Essentiality of Mineral Elements for Higher and Lower Plants

Classification	Element	Higher plants	Lower plants
Macronutrient	N, P, S, K, Mg, Ca	+	+ (Exception: Ca for fungi)
Micronutrient	Fe, Mn, Zn, Cu, B, Mo, Cl	+	+ (Exception: B for fungi)
Micronutrient and "beneficial" element	Na, Si, Co, I, V	± −	± ±

particular for sodium and silicon, which are abundant in the biosphere. The essentiality of these two mineral elements has been established for some higher plant species (Chapter 10). Most micronutrients are predominantly constituents of enzyme molecules and are thus essential only in small amounts. In contrast, the macronutrients either are constituents of organic compounds, such as proteins and nucleic acids, or act as osmotica. These differences in function are reflected in the average concentrations of mineral nutrients in plant shoots that are sufficient for adequate growth (Table 1.3). The values can vary considerably depending on plant species, plant age, and concentration of other mineral elements. This aspect is discussed in Chapters 8 to 10.

Table 1.3
Average Concentrations of Mineral Nutrients in Plant Shoot Dry Matter that are Sufficient for Adequate Growth[a]

Element	Abbreviation	µmol/g dry wt	mg/kg (ppm)	%	Relative number of atoms
Molybdenum	Mo	0·001	0·1	—	1
Copper	Cu	0·10	6	—	100
Zinc	Zn	0·30	20	—	300
Manganese	Mn	1·0	50	—	1,000
Iron	Fe	2·0	100	—	2,000
Boron	B	2·0	20	—	2,000
Chlorine	Cl	3·0	100	—	3,000
Sulfur	S	30	—	0·1	30,000
Phosphorus	P	60	—	0·2	60,000
Magnesium	Mg	80	—	0·2	80,000
Calcium	Ca	125	—	0·5	125,000
Potassium	K	250	—	1·0	250,000
Nitrogen	N	1,000	—	1·5	1,000,000

[a]From Epstein (1965).