METHODS USED FOR SOIL, PLANT, AND WATER ANALYSIS AT THE SOILS LABORATORY OF THE MANITOBA-SASKATCHEWAN REGION

1967 - 1970

by

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INTRODUCTION

At forest research centres in Canada, the analysis of soil, plant, and water samples, through a central laboratory, began only in the last four or five years. Prior to this, each researcher carried out his own analytical work. With the establishment of the central laboratory, most of the analyses are carried out there. However, some analyses which are of interest to only one researcher are seldom carried out in the central laboratory and are done in the individual's laboratory.

If the results obtained in different research laboratories are to be strictly comparable, the techniques must be standardized, as the analytical details vary greatly from one procedure to another for the same determination. There is also a need for standardization of methods of reporting results because certain results may be presented in different forms. Uniformity of terminology is also desirable.

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[1] Head, Soils Laboratory, Northern Forest Research Centre, Canadian Forestry Service, Department of the Environment, Edmonton, Alberta.

This report presents the properties measured and the methods used at the Soils Service Laboratory in the Manitoba-Saskatchewan Region to analyze soil, plant, and water samples submitted by the scientists of the region (Kalra and Ali, 1970). It also contains certain analytical methods which were not used for other researchers.

The procedures have been arranged in the order in which they were generally carried out upon the receipt of samples. All samples were analyzed on the basis of "selective analysis" for specific purposes rather than by "routine analysis".

The selection of the method depended upon the following factors:

1. Purpose of the investigation.
2. Limitations of the method.
3. Availability of equipment.
4. Past experience of the staff with different analytical techniques.
5. Some research scientists in the past had used a particular method or had their samples analyzed from another laboratory where a particular method had been used. In this case the same technique was used on their samples which enabled a valid comparison of results obtained from year to year.

For a certain analysis, when two available methods were similar in most respects, selection of one of the two methods was largely a matter of preference.

Samples came from agricultural areas, shelterbelts, tree nurseries, and forests (forest fertilization projects, forest hydrology, forest stand establishment research, and coniferous and deciduous timber stands). Obviously, for certain soil properties, one method may be best for agronomic soils, but may not be as good for nursery or forest soils. In general, availability-index methods for annual field crops have been used for nursery soils. In most cases, no methods have been developed for the extraction of that fraction of soil nutrient element which is available to trees. However, determination of the total amounts of the element may be carried out on all soils without significant changes irrespective of where the samples were collected.

Methods were selected and in some cases adapted to ensure accuracy and speed. Various techniques were standardized and modified for a variety of analyses. Due to a large number of backlog samples and shortage of staff and space in the laboratory and the fact that the Soils Laboratory was experiencing a large increase in the number of requests for different types of analyses, it was not possible in many cases to evaluate different procedures and select the best method. This report is not intended to show preferred methods.

Blank determinations were made simultaneously with the samples. Calibration curves were prepared under the same conditions prevailing for the samples and the blank determinations.

Trade, company, and model names of the instruments are included only for the readers' benefit and do not in any way reflect their superiority over other instruments available on the market.

Although researchers generally interpreted their own results, certain criteria used to classify grades or groupings for a few analyses have been given in the report for the benefit of individuals not directly involved with soils work.

This report was prepared for the colleagues of the region to provide a ready reference for techniques used in the Soils Service Laboratory. It is hoped that this information will also prove useful to others who are working at other regions. The procedures being used at the Northern Forest Research Centre at Edmonton, formed by the amalgamation of the Manitoba-Saskatchewan and Alberta-Territories Regions, are essentially the same as outlined in this report although some methods have been changed since 1970. More information on the techniques mentioned will be found in comprehensive texts by APHA (1965), Black *et al*.(1965), Boltz (1958), Chapman and Pratt (1961), Jackson (1958), Metson (1956), Piper (1947), Rainwater and Thatcher (1960), and US Salinity Laboratory Staff (1954). Details of the atomic absorption spectrophotometry are available in books by Ramírez-Muñoz (1968) and Slavin (1968).

METHODS FOR SOIL ANALYSIS

S1. Preparation of samples for analyses

Most of the determinations were made on air-dry samples. However, NH_4-N, NO_3-N, and in some cases pH and some other properties, were determined on moist samples immediately after collection. If these analyses could not be done soon after collection, the moist samples were stored in a cold room at ca 2°C.

Large lumps of moist soil were broken and soil spread on a sheet of brown paper to air-dry in a room free from fumes, dust, etc. Soils were air-dried at a temperature of ca 25° to 35°C and relative humidity of ca 20 to 60% (Jackson, 1958). A wooden roller was used to crush large clods. Stones and coarse gravel were removed. After air-drying, the soil was ground to pass through a 2-mm sieve using a modified Rukuhia soil grinder (Day and Dixon, 1965). Remaining gravel and organic residue were removed. These materials were weighed and their percentage in the total sample was determined. A 20-25 g subsample was ground in a Spex mixer/mill[2] and passed through a 100-mesh sieve.

Nearly all the determinations were carried out on the fine earth (< 2 mm) fraction. Organic matter, calcite, dolomite, total nitrogen, etc. were estimated on subsamples pulverized to 100-mesh size.

For Cu, Zn, and other heavy metal determinations, soil was

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[2] Spex Industries, Scotch Plains, N.J.

ground in an agate or porcelain mortar with a pestle. All the soil was passed through a nylon sieve to 2-mm size; the coarse material being returned to the mortar and reground. A portion of 2-mm soil was further ground to pass 100-mesh sieve. Copper and brass utensils were avoided.

The ground samples were stored in moisture-tight cartons. For analysis, the required amounts of soil were taken by the quartering method (Jackson, 1958).

S2. Soil color

The soil samples were matched against standard Munsell Soil Color Charts[3] to obtain hue, value, and chroma combinations (Munsell Color Co., 1950; Shields *et al*., 1968). The color values were obtained for both moist and dry samples.

S3. Moisture content

Air-dry soil samples (> 25 g) were oven-dried overnight at 105°C in a Precision Scientific Thelco, gravity convention oven[4], model 17 or 27. Results were calculated as follows:

$$\text{Moisture factor (M.F.)} = \frac{W_1}{W_2}$$

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[3] Munsell Color Co., Baltimore, Md.

[4] Precision Scientific Co., Chicago, Ill.

$$\text{Hygroscopic moisture (\%)} = \frac{W_1 - W_2}{W_2} \times 100$$

where W_1 = wt. of air-dry soil.

W_2 = wt. of oven-dry soil.

S4. Bulk density

The oven-dry weight of the sample was divided by the volume of the undisturbed sample at field moisture conditions (US Salinity Laboratory Staff, 1954). If the volume was very large, then a subsample was oven-dried and the oven-dried weight of the entire soil calculated.

S5. Soil reaction

The pH was determined on a soil paste or a soil suspension. The soil paste was prepared as given by Doughty (1941) and the US Salinity Laboratory Staff (1954). Soil suspension was prepared using a 1:1 (Peech et al., 1947; Reed and Cummings, 1945) and 1:5 (Piper, 1947) soil-to-water ratio (w/w) and 1 hr of equilibration. Since soils contain varying quantities of salts, pH measurements were also made in the presence of 10^{-2} M $CaCl_2$ with a soil:solution ratio of 1:2 (Schofield and Taylor, 1955) and in a 1:2.5 mixture of soil and 1 N KCl (Puri and Asghar, 1938) to obtain uniformity of results. For organic soils, because of their water retention properties, pH was measured in 1:5 soil-water suspensions or in 1 N KCl with a 1:1 ratio (v/v) of moist peat to solution (Farnham and Finney, 1965). The suspensions were stirred well just before immersing the electrodes (Jackson, 1958).

Soil reaction was measured potentiometrically (Bates, 1964) on a Radiometer pH meter 22 (type PHM 22r)[5]. The electrode combination consisted of a Radiometer glass electrode type G202C and the Radiometer calomel reference electrode type K401. To minimize contamination with KCl, the pH values were measured within 60 sec after immersion of the electrodes in the samples.

The pH determinations were reported as pHsp (saturated paste), pHw (1:1), pHw (1:5), pH-KCl (1:2.5), and pH-$CaCl_2$ (1:2).

The soils were classified on the basis of the following nomenclature and limits, as recommended by the USDA Soil Survey Staff (1951):

Soil reaction class	pH
Extremely acid	< 4.5
Very strongly acid	4.5 to 5.0
Strongly acid	5.1 to 5.5
Medium acid	5.6 to 6.0
Slightly acid	6.1 to 6.5
Neutral	6.6 to 7.3
Mildly alkaline	7.4 to 7.8
Moderately alkaline	7.9 to 8.4
Strongly alkaline	8.5 to 9.0
Very strongly alkaline	> 9.0

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[5] Radiometer, Copenhagen, Denmark.

S6. Salt concentration

Total soluble salts were determined by a conductivity method. For this purpose electrical resistance of the suspension (Piper, 1947), supernatant solution (Greweling and Peach, 1965), or extract (Jackson, 1958; US Salinity Laboratory Staff, 1954) was measured with a conductivity bridge (Model RC-16B2)[6]. The saturation extract and soil suspension were prepared according to the US Salinity Laboratory Staff (1954) and Piper (1947), respectively. The 1:1 soil:water extraction of soluble salts was done according to Jackson (1958). In certain cases, 1:2 soil/water extraction was also done (Merkle and Dunkle, 1944). The results were reported as EC in mmhos/cm at 25°C.

Aqueous extracts of the saturation paste and the soil suspensions were obtained by vacuum filtration. Electrical conductivity of the saturation paste extract was designated as ECspe.

Extracts were analyzed as quickly as possible to prevent microbial activity. If the extracts could not be analyzed at once, toluene or thymol were added to minimize the influence of microorganisms on extract composition for storage for a short time.

A dip-type (immersion-type) conductivity cell was used for soil suspensions and a pipet-type cell for soil extracts. The cell had platinized platinum electrodes.

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[6] Industrial Instruments, Cedar Grove, N.J.

Conductivity and chlorides were determined before carrying out determination for pH, otherwise KCl from the electrode would contaminate the sample and lead to high salt values.

The following salinity grading, as suggested by the USDA Soil Survey Staff (1951) was used:

Class	Salt content (%)	Conductivity of the extract (mmhos/cm)
Nonsaline	0.00 to 0.15	0 to 4
Weakly saline	0.15 to 0.35	4 to 8
Moderately saline	0.35 to 0.65	8 to 15
Strongly saline	> 0.65	> 15

S6.1. Qualitative tests

S6.1.1. Calcium

A few drops of ca 5% ammonium oxalate [$(NH_4)_2C_2O_4 \cdot H_2O$)] solution were added to the extract. The presence of a white precipitate of CaC_2O_4 was noted after warming the mixture for 10 min.

S6.1.2. Magnesium

A few drops of ca 10% sodium ammonium phosphate ($NaNH_4HPO_4 \cdot 4H_2O$) or micro-cosmic salt were added to the extract and made strongly alkaline with NH_4OH. After stirring, the presence of a flocculent precipitate was noted.

S6.1.3. Chloride

The extract was acidified with HNO_3 and a few drops of ca 5% $AgNO_3$ solution added. A white curdy precipitate formed. If presence of carbonate was also suspected, dil. HNO_3 was added to see if it dissolved. Insolubility of the precipitate confirmed precipitate due to chloride. The soils were rated depending upon the visual estimation of turbidity and/or precipitate of AgCl.

S6.1.4. Sulfate

A few drops of ca 10% $BaCl_2$ solution, acidified with HCl, were added to the extract. The presence or absence of sulfate was indicated by the visual estimation of turbidity and/or white precipitate of $BaSO_4$.

S6.2. Quantitative tests

S6.2.1. Calcium and magnesium

They were determined by titration with ethylene diaminetetraacetate and by atomic absorption spectrophotometry as given in Sections S13.2.1, S13.2.2.2, and S13.2.2.3.

S6.2.2. Sodium and potassium

They were estimated by flame photometry and atomic absorption spectrophotometry as given in Section S13.3.

S6.2.3. Chloride

It was determined by argentimetric titration methods. The end point in the titration was detected by either of the following two techniques:

S6.2.3.1. Mohr method

The pH of the extract was adjusted to ca 8 (just acid to phenolphthalein) in a wide-mouthed porcelain crucible or a small porcelain casserole. The solution was then titrated with 0.1 N $AgNO_3$ solution, using a K_2CrO_4 solution (5%) as an indicator to the first permanent reddish-brown color. This would be due to the formation of slightly soluble red Ag_2CrO_4 at the end point (Kolthoff and Sandell, 1952; Reitemeier, 1943).

S6.2.3.2. Potentiometric method

An Ag-AgCl electrode was used (Best, 1950). The equivalence point was indicated when a rapid shift occurred in the potential of the cell. This method could be employed in the presence of soil thus eliminating the need for filtration (Jackson, 1958).

S6.2.4. Sulfate

It was determined by the turbidimetric method using 30- to 60- mesh $BaCl_2$ crystals (Chesnin and Yien, 1951) and preparing a relatively stable colorless suspension. The precipitate was kept in suspension with a gum acacia solution. The absorbance of the $BaSO_4$ suspension was measured, in the period from 5 to 30 min after precipitation had occurred, with a Bausch and Lomb Spectronic

20 colorimeter[7] (cuvettes with 1.3-cm path lengths) using 420 nm wavelength (Rossum and Villarruz, 1961). Since the turbidity of $BaSO_4$ is difficult to reproduce (Willard et al., 1964) the prescribed conditions were carefully observed so that each turbidity was produced under identical conditions.

S6.2.5 Carbonate and bicarbonate

An aliquot of the soil extract was titrated with standard HCl or H_2SO_4, first with phenolphthalein (CO_3^{2-}) and then with methyl orange (HCO_3^-) indicators (Magistad et al., 1945). See Section W6.

S6.3. Estimation of exchangeable-sodium-percentage and exchangeable-potassium-percentage

Sodium-adsorption and potassium-adsorption ratios were calculated as follows (US Salinity Laboratory Staff, 1954):

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

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[7] Bausch & Lomb, Rochester, N.Y.

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

where all concentrations are expressed in meq/l.

These ratios were used to calculate the exchangeable-cation-percentages as follows (US Salinity Laboratory Staff, 1954):

$$\text{Exchangeable-sodium-percentage} = \frac{100\ (-0.0126 + 0.01475\ X)}{1 + (-0.0126 + 0.01475\ X)}$$

$$\text{Exchangeable-potassium-percentage} = \frac{100\ (0.0360 + 0.1051\ X)}{1 + (0.0360 + 0.1051\ X)}$$

where X is equal to the sodium-adsorption-ratio and potassium-adsorption-ratio, respectively.

S7. Particle-size distribution analysis

Particle-size analysis of the fine skeleton of particles under 2 mm was performed by the modified Bouyoucos hydrometer sedimentation technique following H_2O_2 oxidation of organic matter and soluble salt removal (Day, 1956, 1965). If alkaline-earth carbonates were present in soil and if they restricted dispersion, they were removed by sufficient dil. HCl (Piper, 1947). Dispersion was carried out by an electric soil dispersion stirrer. Calgon (sodium hexametaphosphate with sufficient Na_2CO_3 to give a pH of about 8.5 in a 10% solution) was the dispersing agent.

The total sand fraction (soil mineral particles between 50 μ and 2 mm in dia.) was separated from the silt and clay by wet-sieving of dispersed soil suspension through a 300-mesh sieve. For this purpose, the thoroughly dispersed and freshly stirred soil suspension was allowed to stand exactly 40 sec for each 10 cm of its depth and then decanted through the sieve (Jackson, 1956). Finally the sands were swirled in distilled water, poured into one side of the sieve and washed thoroughly (Jackson, 1956).

A total of silt and clay and the content of clay (mineral soil particle with dia. < 2 μ) in the suspension were calculated from the 0 and 2 hr readings of a hydrometer. The silt (soil particles between 2 and 50 μ in dia.) content was determined by the difference. Soil texture classes were obtained from a textural triangle (USDA Soil Survey Staff, 1951). Silty sand class was established within the sandy loam class (Hills, 1957).

Sand fractionation was carried out by dry-sieving on an oscillating American Instrument sieve shaker[8] with several sieves[9], after wet-washing the silt and clay through a 300-mesh sieve, according to following sizes (USDA Soil Survey Staff, 1951):

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[8] American Instrument Co., Silver Springs, Md.

[9] Newark Wire Cloth Co., Newark, N.J.

Sand fraction	Diameter (range) mm	Sieve for obtaining the fraction
Very coarse sand	2.00 to 1.00	1.0-mm round hole
Coarse sand	1.00 to 0.50	0.5-mm round hole
Medium sand	0.50 to 0.25	60-mesh screen
Fine sand	0.25 to 0.10	140-mesh screen
Very fine sand	0.10 to 0.05	300-mesh screen

The soils were classified on the basis of the following nomenclature and limits as recommended by the National Soil Survey Committee of Canada (1965):

Textural grouping	Textures
Coarse textured	sands, loamy sands
Moderately coarse textured	sandy loam, fine sandy loam
Medium textured	very fine sandy loam, loam, silt loam, silt
Moderately fine textured	sandy clay loam, clay loam, silty clay loam
Fine textured	sandy clay, silty clay, clay (40 to 60%)
Very fine textured	> 60% clay

S8. Alkaline-earth carbonates

S8.1. Qualitative

A qualitative estimate of the amount of free lime was obtained by effervescence with ca 10% HCl after saturating the soil with sufficient water. The relative effervescence was described as below (National Soil Survey Committee of Canada, 1968):

Very weakly effervescent - a few bubbles.
Weakly effervescent - bubbles readily observed.
Moderately effervescent - bubbles form a low foam.
Strongly effervescent - bubbles form a thick foam.

S8.2. Quantitative

S8.2.1. Neutralization method

Calcium carbonate equivalence (CCE) of the soil was determined by acid neutralization; digesting with 0.5 N HCl and back titrating with 0.25 N NaOH using phenolphthalein (1% in 60% ethanol) as an indicator (US Salinity Laboratory Staff, 1954).

S8.2.2. Manometric technique for calcite and dolomite

Calcite ($CaCO_3$) and dolomite ($CaCO_3 \cdot MgCO_3$) were determined manometrically using the Burrell "wrist-action" shaker[10]

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[10] Burrell Corp., Pittsburgh, Pa.

and the "differential decomposition rates in acid" technique of Skinner _et al._ (1959). A Lab-Line constant temperature water bath[11] was used. The CO_2 evolved from the reaction was measured at frequent intervals until the reaction was complete. The results were reported as separate percentages of calcite and dolomite. However, in some instances they were reported as $CaCO_3$ equivalent.

Soils having a per cent $CaCO_3$ equivalent of 2 or greater were placed in the calcareous group.

The soils were classified on the basis of the following nomenclature and limits as recommended by the National Soil Survey Committee of Canada (1965):

Calcareous grade	$CaCO_3$ equivalent (%)
Weakly calcareous	2 to 5
Moderately calcareous	6 to 15
Strongly calcareous	16 to 25
Very strongly calcareous	26 to 40
Extremely calcareous	> 40

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[11] Lab-Line Instruments, Melrose Park, Ill.

S9. Loss on ignition

Air-dry or oven-dry soil (100-mesh) was heated slowly in a porcelain crucible in an electric muffle furnace[12] or over a gas burner to about 700°C for 1/2 hr. Loss in weight was expressed as "loss on ignition" (Chapman and Pratt, 1961).

S10. Organic matter

S10.1. "Loss on ignition" method

Approximate organic matter content was calculated from loss on ignition results upon correcting for water lost from clay crystals which is ca 5% of the weight of the clay (Hanna, 1964):

ca o.m.(%) = "loss on ignition" (%) - (0.05 x wt. of clay in the sample)

For organic soils, organic matter was determined by loss on ignition without any correction.

S10.2. Wet oxidation with dichromate

Organic matter was estimated by the Walkley-Black titrimetric wet oxidation method in which the heat of dilution of conc. H_2SO_4 with 1 N $K_2Cr_2O_7$ was the sole source of heat. Initially, barium diphenylamine sulfonate (0.16% aqueous solution) was used as an

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[12] Gallenkamp & Co., London, England.

indicator (Peech et al., 1947). Later, "ferroin" indicator (ortho-phenanthroline ferrous sulfate, 0.025 M solution) was found to be more convenient (Greweling and Peech, 1965). Total organic matter was calculated assuming 77% recovery.

For some investigations, it was more useful to express results as per cent organic carbon.

S11. Nitrogen

S11.1. Total nitrogen

Total nitrogen was determined by the modified macro-Kjeldahl technique as outlined by Jackson (1958). Nitrogen of the sample was converted to ammonia and was present in H_2SO_4 as $(NH_4)_2SO_4$, or more likely as NH_4HSO_4 (Taras, 1958). Kjeldahl digestion flasks of hard well-annealed glass with 800 ml capacity were used. Kelpak #1[13] containing K_2SO_4, HgO and $CuSO_4$[14], was used to raise the temperature of the digestion mixture and as catalysts, respectively (Kirk, 1950). The mercury ammonium complex in the digest was decomposed by sodium

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[13] Matheson Scientific, East Rutherford, N.J.

[14] Each packet of Kelpak #1 contains 9.9 g K_2SO_4, 0.41 g HgO, and 0.08 g $CuSO_4$.

thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$). To minimize pollution, precaution was taken that exposed Hg was not allowed to accumulate.

The source of heat for digestion was able to maintain the digestion mixture at a boiling point of ca 350°C. Ammonia was distilled from an alkaline medium and absorbed in an unstandardized boric acid solution - Winkler modification (Scales and Harrison, 1920) and titrated with standard HCl. Alternatively, ammonia was collected in standard H_2SO_4 and excess acid back titrated with standard NaOH solution (Jackson, 1958). A few Hengar granules[15] were added to prevent bumping.

Known ammonium standard solutions were used for distilling to determine the volume of distillate to be collected for complete recovery.

The Labconco Kjeldahl unit[16] was steamed out before carrying out actual analyses till the distillate from the distilled water was free of ammonia.

If soil nitrates were to be included in the determination, salicylic acid modification was used (Bremner, 1965; Cope, 1916). The resulting nitrosalicylic acid was then reduced with sodium thiosulfate

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[15] Hengar Co., Philadelphia, Pa.

[16] Laboratory Construction Co., Kansas City, Mo.

to form the ammonium compound which was converted to ammonium salt upon digestion (Shuey, 1947).

Carbon-nitrogen ratios were calculated as follows:

$$\frac{C}{N} \text{ ratio} = \frac{\text{Organic C (\%)}}{\text{Total N (\%)}}$$

S11.2. Exchangeable ammonia

The exchangeable NH_4 was determined on moist samples. It was extracted with a 10% NaCl solution (1.7 N), acidified to pH 2.5 with HCl (Peech _et al_., 1947) and determined by one of the following methods:

S11.2.1. Distillation method

It was distilled from a strongly alkalized sample as given in Section S11.1. This method was used when interference was experienced in direct Nesslerization. It was generally preferred to Nessler method for precision and accuracy.

S11.2.2. Nesslerization method

Upon treatment of ammonia with Nessler reagent (alkaline $HgI_2 \cdot 2Kl$ solution), a reddish brown colloidal compound was formed (Nichols and Willits, 1934). The absorbancy of the solution was read[7] after adding the Nessler reagent and standing for at least 10 min. However, if the NH_4-N content was very low, then samples were read 25-30 min after adding Nessler reagent. Since the Nessler-ammonia color system absorbs light over a broad wavelength range (400 to ca 575 nm), optimum wavelength was selected at the point of maximum absorption from the absorption spectrum for the nitrogen range under investigation. Generally, a wavelength of 410 nm was used. See Section W9.1.

S11.3. Nitrate nitrogen

The nitrate nitrogen content was estimated colorimetrically with the phenoldisulfonic acid (PDA) method (Harper, 1924). Nitrate was extracted with 0.02 N $CuSO_4$ solution, 0.007 N with respect to Ag_2SO_4 to prevent chloride interference (Harper, 1924; Prince, 1945). A reciprocating, variable speed (60 to 260 oscillations/min) Utility shaker[17] was used. It was ensured that during sample evaporation a neutral or slightly alkaline medium

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[17] Eberbach Corp., Ann Arbor, Mich.

was present (Taras, 1950). Samples were evaporated on a Lindberg Hevi-duty hot plate[18]. Temperature was controlled such that loss of residue was avoided. The yellow color was developed in the presence of ca 7 N NH_4OH. If NH_4-N was also being determined concurrently, then KOH solution was used in place of NH_4OH to determine NO_3-N. The color intensity measurements were carried out at 415 nm wavelength using a Bausch and Lomb Spectronic 20 colorimeter[7].

S12. Phosphorus

S12.1. Water soluble phosphorus

Water soluble P was extracted according to Bingham (1949) and determined as given in Section S12.2.2.

S12.2. Easily soluble phosphorus

S12.2.1. Extraction

Easily soluble P was extracted by the following two methods:

S12.2.1.1. Easily soluble P in neutral and alkaline soils

Phosphorus was extracted by

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[18] Hevi-duty Heating Equipment Co., Watertown, Wis.

Olsen's method with 0.5 M $NaHCO_3$ solution adjusted to pH 8.5 (Olsen et al., 1954).

S12.2.1.2. Dilute acid-fluoride extraction on acid soils

Adsorbed P was extracted with 0.03 N NH_4F in 0.025 N HCl, Bray-P1 method (Bray and Kurtz, 1945).

S12.2.2. Determination

Phosphate-free detergent was used for cleaning all glassware.

S12.2.2.1. Chlorostannous-reduced molybdophosphoric blue color method in a hydrochloric acid system

The transmittance of the solution after treatment with molybdate in HCl and $SnCl_2$ was determined at 660 nm in a photoelectric colorimeter[7] between 4 and 20 min and the concentration of P determined by reference to a standard curve (Dickman and Bray, 1940; Woods and Mellon, 1941). Phosphorus was determined in the extract after removing organic matter with activated charcoal.

S12.2.2.2. Ascorbic acid method

Phosphorus was estimated colorimetrically as phosphomolybdenum blue with ascorbic acid as reducing agent and Sb added to give a stable Mo-P-Sb compound. After 10 min, color intensity was measured at 882 nm by a Spectronic 20 colorimeter[7] (Murphy and Riley, 1962; Watanabe and Olsen, 1965).

S13. Cation exchange, exchangeable cations, and base saturation

The quantities determined in the usual cation exchange analysis were as follows:

Cation exchange capacity (S13.1)
Exchangeable Ca and Mg (S13.2)
Exchangeable K and Na (S13.3)
Exchangeable H (S13.4)

Total exchangeable bases (S13.5)

Percentage base saturation (S13.6)

S13.1. Cation exchange capacity (CEC)

It was obtained by one or both of the following procedures:

S13.1.1. Saturation with NH_4OAc or $Ba(OAc)_2$ solution

The soil was saturated with 1 N NH_4OAc adjusted to pH 7.0. After leaching excess NH_4OAc from NH_4-saturated soils in a Buchner funnel with 95% ethanol, acidified 10% NaCl solution was used to displace ammonium ions. The amount of exchange ammonium was determined by Kjeldahl distillation (Atkinson _et_ _al_., 1958), as given in Section S11.1.

The NH_4OAc leachate was retained for the determination of exchangeable cations.

Cation exchange capacity of the peat samples was determined by saturation with hydrogen using 0.5 N HCl, equilibrating with neutral 1 N $Ba(OAc)_2$ and then titrating the extract with standardized 0.2 N NaOH to pH 7.0 (MacLean _et_ _al_., 1964).

S13.1.2. Summation method

Exchange capacity was also determined in some cases (distinctly acid soils) to be the sum of the metallic cations (exchangeable bases) and exchangeable hydrogen (exchange acidity). This method was not used for neutral, calcareous, or saline soils (Chapman, 1965).

S13.2. Exchangeable calcium and magnesium

S13.2.1. Compexometric titration method

The NH_4OAc leachate was titrated with 0.01 M disodium versenate (disodium dihydrogen ethylenediamine tetraacetic acid), an organic sequestering agent which forms unionized complexes with Ca and Mg (Tucker and Kurtz, 1961). Ammonium acetate and dispersed organic matter, when present in appreciable quantities, were first removed from the soil extracts by the procedure used by the US Salinity Laboratory Staff (1954). First the total of Ca and Mg was obtained using Eriochrome black T dye (F241) as an indicator (Cheng and Bray, 1951) and a buffer to get a pH of 10.0 (Biedermann and Schwarzenbach, 1948). The NH_4Cl-NH_4OH buffer of pH 10.0 (Cheng and Bray, 1951; Diehl *et al.*, 1950) or odorless 2-amino-ethanol-HCl buffer (Katz and Navone, 1964; Patton and Reeder, 1956) was used. On a separate aliquot, Ca was titrated with EDTA using Cal-Red as an indicator (Patton and Reeder, 1956), after precipitating Mg as $Mg(OH)_2$ by adding NaOH solution (ca 4 N) to increase the pH to 12 (Cheng and Bray, 1951). The titration was performed immediately after alkali addition. Magnetic stirrer and artificial light were used for titrations. In these chelometric titrations, hydroxylamine hydrochloride was used to reduce some of the potential interferences to less objectionable lower oxidation states (Fischer, 1962). Potassium cyanide was used to prevent Fe, Al, Cu, Zn, and Mn interferences by tying up these metals as their cyanide complexes.

Magnesium was calculated from the difference between the above two titrations.

S13.2.2. Atomic absorption spectrophotometry

S13.2.2.1. Instrumentation and related details

Atomic absorption spectrophotometry was used for the determination of Ca, Mg, K, Na, Fe, Mn, Cu, and Zn in soil, plant, and water samples. A double-beam instrument, Perkin-Elmer Model 303 atomic absorption spectrophotometer[19] was used. Intensitron® hollow cathode lamps were employed. An Automatic Null Recorder Readout was also used, especially for low concentrations.

All instrument settings were those recommended in the analytical methods manual (Perkin-Elmer Corp., 1968). However, slight adjustments in the suggested settings were

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[19] Perkin-Elmer Corp. , Norwalk, Conn.

found to give more accurate results for certain analyses. The burner was flushed with water and the "zero absorption" re-established before aspirating each sample. At least 3 standards were prepared to obtain a working curve. Standards were prepared in the same solvent as the samples. Working curve was prepared with every batch of samples.

Solutions were diluted to obtain concentration range as given by Perkin-Elmer Corp. (1968) in their loose-leaf analytical methods manual. To minimize the error due to dilutions, pipets smaller than 2 ml or volumetric flasks smaller than 25 ml were not used (McBride, 1964).

When the concentration of the element was very low, as in the case of Cu in foliage, scale expansion was used to improve readability of small signals and hence improve the detection limit (Perkin-Elmer Corp., 1968). Scale expansion and zero suppression on the Recorder Readout Accessory were also used. The per cent absorption readings were divided by the scale expansion value and converted to absorbance. When absorption readings were less than 10% (using scale expansion) then they were plotted against concentration without prior conversion to optical density.

S13.2.2.2. Calcium

A dual-element hollow cathode lamp containing Ca and Mg was used at 15 ma. Air and acetylene flow rates were set to get reducing (rich, slightly yellow) flame.

Calcium standard stock solution was prepared by dissolving $CaCO_3$ in dil. HCl. A final concentration of 1% La was used to prevent interferences from P and Al in the sample (David, 1960). Lanthanum oxide (La_2O_3) or lanthanum chloride ($LaCl_3 \cdot 6H_2O$ or $LaCl_3 \cdot 7H_2O$) was used. If lanthanum oxide was not available in a sufficiently pure form, it was prepared by heating lanthanum nitrate [$La(NO_3)_3 \cdot 6H_2O$] at 700°C for 2 1/2 hr in a muffle furnace[12] (Perkin-Elmer Corp., 1968).

Wavelength used was 4227 Å. Slit was set to 4 (slit opening = 1 mm, spectral band width = 13 Å). A 10 ppm Ca solution was used to set acetylene flow to obtain maximum absorption.

S13.2.2.3. Magnesium

The Mg-Ca lamp was used. Magnesium standard stock solution was prepared by dissolving its metal in dil. HCl. A 0.5 ppm Mg solution was used to adjust the acetylene flow to obtain maximum absorption (reducing flame). After proper dilution and La addition to remove the potential interference due to Al and P, Mg was determined at 2852 Å line and slit 5 (slit opening = 3 mm, spectral band width = 20 Å).

S13.2.2.4. Calcareous soils

Due to the dissolution of some of the Ca and Mg from $CaCO_3$ (calcite) and $CaCO_3 \cdot MgCO_3$ (dolomite), 1 N NH_4OAc solution could not be used for extracting exchangeable Ca and Mg. Instead a 0.2 N $BaCl_2$-triethanolamine of pH 8.1 was used as extracting solution (Mehlich, 1945; Peech _et_ _al_., 1947). Exchangeable Ca and Mg in calcareous soils were also extracted by 1 N NaOAc, pH 8.2 (Bower, 1955; Bower _et_ _al_., 1952).

S13.2.2.5. Correction for water soluble salts

A correction for water soluble Ca, Mg, Na, Mn, K, Fe, and Zn for an accurate determination of exchangeable quantities of these cations was essential since the forest floor contains a substantial portion of these cations in water soluble form. Exchangeable ions were found by difference between extractable and water soluble ions. However, when analyzing for soil fertility investigations, water soluble ions were not determined separately.

S13.3. Exchangeable potassium and sodium

In nonsaline soils, no correction was needed for the amounts of water-soluble K and Na. For correction in the saline soils, the amount of water-soluble K or Na in a saturation extract (or similar water extract) of the soil was subtracted from the total extracted by 1 N NH_4OAc (Pratt, 1965).

Exchangeable K and Na were determined after extraction with 1 N NH_4OAc, pH 7.0 (Schollenberger and Simon, 1945) by either of the following two methods:

S13.3.1. Flame photometric analysis

Organic matter was destroyed by HNO_3 oxidation. A Beckman model DU flame emission spectrophotometer[20] was used with an oxygen-acetylene flame. Lithium was used as an internal standard (Rich, 1965). Potassium was determined at 7670 Å wavelength and Na at 5885 Å (Dean, 1960).

S13.3.2. Atomic absorption spectrophotometry

S13.3.2.1. Potassium

Standard stock solution was

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[20] Beckman Instruments, Inc., Fullerton, Calif.

prepared by dissolving KCl in water. An oxidizing (lean, blue) flame was used. The final dilution in standards and samples contained 1000 ppm added Na to minimize ionization interference. Potassium was determined at 7665 Å wavelength and slit setting at 4 (slit opening = 1.0 mm, spectral band width = 13 Å). The single element lamp was operated at 25 ma. See also Section S13.2.2.1.

S13.3.2.2. Sodium

Standard stock solution was prepared by dissolving NaCl in water. An oxidizing flame was used. The final dilution in standards and samples contained 1000 ppm added K to substantially overcome ionization interferences. Sodium was determined at 5890 Å wavelength and slit setting of 4 as in the case of K. The single element lamp was operated at 15 ma.

See also Section S13.2.2.1.

S13.4. Exchangeable hydrogen (exchange acidity)

S13.4.1. Barium acetate extraction

Exchangeable H was determined using a 1 N $Ba(OAc)_2$ extracting solution of pH 8.1, adjusted with $Ba(OH)_2$, and back titrating with 0.05 N NaOH solution (Mehlich, 1945; Parker, 1929).

S13.4.2. Ammonium acetate extraction

Exchangeable H was determined by the change in the pH of a 1 N NH_4OAc solution of pH 7.0 (Schollenberger and Simon, 1945).

S13.4.3. Barium chloride - triethanolamine extraction

The soil was leached with a solution consisting of 0.5 N $BaCl_2$ and 0.055 N triethanolamine adjusted with HCl or triethanolamine to pH 8 ± 0.02 (Greweling and Peech, 1965; Peech, 1965). An aliquot of the extract was titrated with 0.1 N HCl using a mixed indicator (bromocresol green-methyl red) to a pink end point (pH 5.1).

S13.5. Total exchangeable bases (TEB)

Total exchangeable bases (the alkali and alkaline earth metals, principally Ca, Mg, Na, and K) were determined by the procedure of Bray and Willhite (1929); appropriate corrections being made for calcium, magnesium, or sodium carbonates and bicarbonates, and nitrates. No correction was needed for chlorides and sulfates.

S13.6. Percentage base saturation (% BS) or exchange status

For certain investigations the results were more useful if expressed as exchange status. Per cent base saturation values were calculated from the sum of exchangeable Ca, Mg, Na, and K and the CEC values as follows:

$$\% \text{ BS} = \frac{\text{TEB (meq \%)}}{\text{CEC (meq \%)}} \times 100$$

$$= \frac{\text{Exch.(Ca+Mg+Na+K)}}{\text{Exch.(Ca+Mg+Na+K+H)}} \times 100$$

S14. Iron

S14.1. Extraction

S14.1.1. Ammonium acetate extraction

Water soluble and exchange Fe in

highly acid or water-logged soils were extracted with 1 N NH_4OAc, pH 7.0 solution.

S14.1.2. Readily soluble iron

Readily-soluble Fe was extracted by the following two methods on 100-mesh soil:

S14.1.2.1. Dithionite - citrate - bicarbonate method for removal of free iron oxides from soil (Mehra and Jackson, 1960)

This method employs sodium dithionite ($Na_2S_2O_4$) for the reduction, $NaHCO_3$ as a buffer, and sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) as a chelating agent for Fe^{2+} and Fe^{3+} (Jackson, 1956).

S14.1.2.2. Acid-ammonium oxalate extraction method of McKeague and Day (1966)

Soils were shaken in darkness with 0.2 M acidified ammonium oxalate $\left[(NH_4)_2C_2O_4 \cdot H_2O\right]$, pH 3.0. After centrifuging the extract was analyzed. An International centrifuge[21], Model MAME, was used.

S14.2. Determination

Aliquots of the extracts from S14.1.2 were digested with HNO_3 and H_2SO_4 to destroy organic matter before Fe determination.

S14.2.1. Colorimetric method

O-phenanthroline ($C_{12}H_8N_2 \cdot H_2O$), also known as 1,10-phenanthroline, was used. Iron was determined colorimetrically as the orthophenanthroline orange-red ferrous complex (Caldwell and Adams, 1946; Fortune and Mellon, 1938). The absorbance was measured[7] in 1.3-cm cells at a wavelength of 508 or 510 nm and varied in the range 480 to 520 nm on the basis of the absorption spectrum (AOAC, 1960; Sandell, 1959).

S14.2.2. Atomic absorption spectrophotometry

Standards were prepared from a stock solution prepared by dissolving

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[21] International Equipment Co., Boston, Mass.

metal in 0.2 N HNO_3. A multi-element hollow cathode lamp containing Fe, Mn, Cu, and Zn was used at a current of 25 ma. Iron was determined in an oxidizing flame at 2483 Å wavelength and slit setting 3 (slit opening = 0.3 mm, spectral band width = 2 Å).

S15. Manganese

S15.1. Extraction

Water-soluble and exchangeable Mn were extracted with 1 N NH_4OAc, pH 7.0 solution.

S15.2. Determination

S15.2.1. Colorimetric permanganate technique

Manganese was determined colorimetrically with periodate as the oxidizing agent, to form permanganate (Cooper, 1953; Kolthoff and Sandell, 1952; Mehlig, 1939). A wavelength of 525 or 545 nm was employed[7], generally 525 nm. A transmittancy curve was prepared to obtain the optimum wavelength. The wavelength giving the least transmittancy and highest absorbance was used (Sandell, 1959). Prior to color development, chloride and other reducing substances such as organic matter were removed by H_2SO_4, HNO_3, and H_3PO_4, as given by APHA (1965). Potassium or Na salt of the periodate employed to develop the permanganate color was potassium meta-periodate (KIO_4) or sodium para-periodate ($Na_3H_2IO_6$), i.e., trisodium periodate [para]. Potassium permanganate ($KMnO_4$) was used to prepare standards.

S15.2.2. Atomic absorption spectroscopic method

A multi-element hollow cathode lamp containing 4 metals (Fe, Mn, Cu, and Zn) was operated at 25 ma. Manganese was determined in oxidizing flame at 2798 Å wavelength and slit setting 4 (slit opening = 1 mm, spectral band width = 7 Å). See also Section S13.2.2.1.

S16. Copper

S16.1. Extraction

Chemical indices of availability of soil Cu were measured by the following methods:

S16.1.1. Versenate and citrate extraction

Extraction with a versenate and citrate mixture containing 20 g ammonium citrate $[(NH_4)_2HC_6H_5O_7]$ and 5 g Na_2EDTA in 100 ml water (Cheng and Bray, 1953).

S16.1.2. Versenate extraction

S16.1.2.1. Versenate, 1% solution

Extraction with 1% solution of Na_2EDTA after shaking for 2 hr (Allan, 1961a).

S16.1.2.2. Versenate, pH 4 solution

Extraction with 1% Na_2EDTA (adjusted to pH 4.0 with HCl) after shaking for 10 min (Cheng and Bray, 1953). This extraction procedure was used for acid soils only.

S16.2. Determination

Copper in the extract was determined by atomic absorption spectrophotometer. A multi-element lamp containing the Cu-Fe-Mn-Zn combination was used. The

Cu resonance line at 3247 Å was employed. Slit setting of 4 (slit opening = 1 mm, spectral band width = 7 Å) was used. The determination was carried out using an oxidizing flame. A standard made by dissolving metal in dil. HNO_3 was used to prepare a calibration curve. See also Section S13.2.2.1.

S17. Zinc

S17.1. Extraction

The following two methods were used for extraction of Zn as an availability index:

S17.1.1. Hydrochloric acid extraction

Zinc was extracted with 0.1 N HCl according to Nelson *et al*. (1959).

S17.1.2. Versenate extraction

A 1% solution of disodium EDTA (ca 0.027M) was also used (Perkin-Elmer Corp., 1968).

S17.2. Determination

The Zn content of the extracts was determined by an atomic absorption spectrophotometer. Standards were prepared from a stock solution prepared by dissolving metal in dil. HCl. Zinc was determined in an oxidizing flame at 2138 Å wavelength and slit setting at 4 (slit opening = 1 mm, spectral band width = 7 Å) using a Fe-Mn-Cu-Zn lamp. See also Section S13.2.2.1.

S18. Total elemental analysis for calcium, magnesium, sodium, potassium, and iron

The total element analysis was carried out on extracts prepared according to Pawluk (1967). The elements were determined as given in previous sections.

S19. Nitric acid extraction of potassium

In some forest soils, index of available potassium was obtained by extraction with boiling N HNO_3 (Leaf, 1958; Rouse and Bertramson, 1950). A 10-g soil sample was boiled for 10 min in 50 ml N HNO_3, cooled, filtered, made up to volume and the K determined as given in Section S13.3.

S20. Extraction and measurement of soil moisture (field capacity and permanent wilting point)

S20.1. Field capacity

S20.1.1. 1/3-atmosphere water tension ($W_{1/3}$)

Laboratory estimate of the amount of water held by the soil at field capacity or 1/3 atm tension was obtained by a 15-bar Ceramic Plate Extractor[22] with 1-bar bubbling pressure plates (Richards, 1949; Richards and Weaver, 1944).

S20.1.2. Soil column wetting procedure

Field capacity was also determined by wetting the soil column until the wetting front reached ca 10 cm from the bottom of the column. The samples were collected 24 hr after wetting.

S20.2. Permanent wilting point (W_{15})

Laboratory estimate of the amount of water held by the soil at the permanent wilting point or 15-atm percentage (FAP) was determined by the 15-bar Ceramic Plate Extractor with 15-bar bubbling pressure plates (Richards, 1947, 1965; Richards and Weaver, 1944).

S20.3. Moisture content after equilibration at other tensions

The 0-1 atm range determinations were carried out with the 1-bar ceramic plate cells and the 1-15 atm range determinations with the 15-bar ceramic plate cells in the 15-bar Ceramic Plate Extractor.

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[22] Soil Moisture Equipment Corp., Santa Barbara, Calif.

S20.4. Oven-drying of equilibrated samples

Moisture contents in samples after equilibration at different tensions were determined gravimetrically after the soil samples were oven-dried[4] overnight at 105°C. The results were expressed as percentage of the oven-dried weight.

S20.5. Available water (W_A)

The available water storage capacity of the soil was obtained by subtracting the moisture held at 15-atm tension from 1/3- atm moisture content. This is assumed to be available water.

S20.6. Calculation of results on volume basis

Moisture weight percentages were converted to a volume basis by multiplication with core bulk density.

S21. Nitrifying capacity

The appraisal of the activity of nitrifying bacteria was done by incubating soil at 28°C for 2 weeks (Wilde and Voigt, 1959) and then determining the NO_3-N content by the PDA colorimetric method as given in Section S11.3. For incubation, water was added to bring the moisture to 0.7 or 0.8 of field-moisture capacity which was kept constant by the twice weekly additions of water and weekly mixing of soil to provide aeration during the incubation period (Jackson, 1958).

S22. Ash content of peat

Oven-dried peat was weighed in a previously ignited dish and kept at 400°C for several hours, cooled, and heated with N HNO_3. After evaporation, the dishes were placed in the muffle furnace[12], cooled in a desiccator and weighed.

S23. Degree of decomposition of peat

The degree of humification in organic soils was determined by estimating the solubility of organic material in sodium pyrophosphate (Farnham and Finney, 1965) as follows:

S23.1. Analysis of moist samples

The pyrophosphate test of Dawson, as described by MacLean *et al*. (1964), was used. The color, developed on treating sample with sodium pyrophosphate solution, on the chromatographic paper was compared with standards of known solubility in pyrophosphate solution. The results were expressed as below (Schnitzer and Desjardins, 1965):

Pyrophosphate solubility (%)	Sample designation
< 0.25	peat
0.25 to 0.75	mucky peat
0.75 to 2.00	peaty muck
> 2.00	muck

In certain cases, colors developed on the paper were compared with Munsell color charts[3].

S23.2. Analysis of air-dry samples

Samples were shaken with a sodium pyrophosphate solution, 0.025 M $Na_4P_2O_7 \cdot 10\ H_2O$, and the absorbance of the filtrate was measured at 550 nm in a spectrophotometer[7] (Kaila, 1956; Schnitzer and Desjardins, 1965). The absorbance readings were multiplied by 100 to give cardinal numbers (Schnitzer and Desjardins, 1965).

S24. Unrubbed fiber content of peat

These determinations were carried out for classification of organic soils. The moist sample was allowed to stand overnight with 1% calgon solution in a sample to solution ratio of 1:20 (w/v) and poured over a 100-mesh screen, then washed once with 2% HCl to dissolve carbonates, if any. The weight of the fiber ($\geq$0.15 mm) was determined after oven-drying[4] at 105°C.

METHODS FOR PLANT ANALYSIS

P1. Determinations on fresh needles or leaves

P1.1. Fresh weight of 100 needles (leaves)

Cold storage at ca 4°C (maximum 2 weeks), if necessary.

P1.2. Oven-dry weight of 100 needles (leaves)

P2. Pretreatment for further analyses

P2.1. Segregation into different parts

Corresponding parts from a few plant samples were composited.

P2.2. Cleaning of samples

Leaves were cleansed with a damp linen rag or gentle brushing with a stiff-bristled brush (Ward and Johnston, 1962). Washing plant tissues with water was avoided, although roots were washed free of soil or sand (Ward and Johnston, 1962).

P2.3. Removing of needles (leaves) from branchlets

Scale-like leaves (e.g., Chamaecyparis and Thuja) were not removed from twigs - the two being analyzed together. Short needles (e.g., *Picea* and *Tsuga*) were analyzed entirely. Long needles (e.g., *Pinus* and some *Abies* spp.) were broken into ca 10 mm lengths prior to subsampling for weighing.

P2.4. Air-drying

Leaves and all other plant material (bark, branches, roots, etc.) were cut into small pieces. Before drying, pine needles and leaves were removed from the twigs; spruce needles were left to dry on the twigs. Contamination by dust was avoided especially when Fe, Mn, Cu, and Zn were to be determined. In some species (e.g., *Pinus sylvestris* L.) the needle base was removed.

P2.5. Oven-drying

The samples were put in an oven[4] and dried overnight at 70°C.

P2.6. Grinding

The samples were ground with an Intermediate Model Wiley Mill[23], with stainless steel contact points, to pass through a 40-mesh sieve. The mill was thoroughly cleansed between grinding individual samples. These samples were used for the determinations of N, P, K, Ca, Mg, Na, etc. For the determination of Fe, Mn, Cu, and Zn the samples

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[23] Arthur H. Thomas Co., Scientific Apparatus, Philadelphia, Pa.

were ground in an agate or porcelain mortar to avoid metallic contamination.

P2.7. Storage

Ground samples were transferred to tightly-capped glass jars, labelled clearly, and stored for further analysis.

P2.8. Subsampling

For anlysis the material was subsampled by quartering (Jackson, 1958).

P3. Root/shoot ratio

For the determination of root/shoot ratio, as in sand culture experiments, the seedlings were washed free of sand, separated into shoots and roots, dried[4] at 70°C, and weighed. For analysis, the roots and shoots were combined if seedling tissue concentration was to be determined; otherwise they were analyzed separately.

P4. Total nitrogen

Total nitrogen was determined using the Kjeldahl digestion method followed by steam distillation (Jackson, 1958). See Section S11.1.

P5. Total ash

Determination of the total ash content was done by ashing at ca 525°C in a muffle furnace[12], as outlined by Jackson (1958).

P6. Preparation of extract for total mineral constituents

A representative sample of the plant material was dry ashed. The samples were ashed in a silica crucible overnight at 450°C in a muffle furnace[12]. Usually, a 1-g subsample was used. For certain analyses such as Cu, a 5 g sample was ashed in a silica dish. Alternately, plant samples were also ashed at 550°C for 2 hr or longer (Chapman and Pratt, 1961) until the tissue was burnt to a greyish-white ash. Ashing for P and S was generally carried out at 450°C. However, when 550°C was used, ashing was carried out in an excess of $Mg(NO_3)_2$ to prevent loss by volatilization (Chapman and Pratt, 1961). In that case, plant sample was charred in a muffle furnace for 2 hr at 300°C. Two milliliters of 50% $Mg(NO_3)_2$ solution were added and the solution evaporated over a steam bath before ashing at 550°C.

Ash was dissolved in 1 N HCl (10 ml 1 N HCl/g sample), warmed, filtered, and the solution diluted to volume (Chapman and Pratt, 1961).

For Cl determination, ashing was done in a basic medium. Piper's method (1947) using CaO was employed. Ash was taken up in dil. HNO_3. In certain cases, samples were ashed at 450°C after wetting with 6% calcium acetate $[Ca(CH_3COO)_2 \cdot H_2O]$ solution and extracted with hot water.

For ashing, the temperature in the muffle furnace was gradually raised to the required temperature.

Certain samples for total P were wet-ashed with HNO_3-H_2SO_4-$HClO_4$(10:1:4) ternary acid mixture according to the procedure outlined by Jackson (1958). The suggested predigestion with HNO_3 was omitted.

P7. Silica

Silica was determined gravimetrically by treating the ash with 1:1 HCl after digesting for ca 30 min on a water bath (Piper, 1947).

P8. Phosphorus

The determination of total P content was made colorimetrically by the vanadomolybdate procedure based on the yellow color of the unreduced vanadomolybdophosphoric heteropoly complex in HNO_3 medium (Barton, 1948: Kitson and Mellon, 1944). The color intensity was determined by the Spectronic 20 colorimeter[7]; generally a light maximum at 470 nm (Jackson, 1958) was employed. All the glassware was washed with phosphate-free detergent.

P9. Potassium and sodium

Total K and Na in the HCl extract were determined flame photometrically and by atomic absorption spectrophotometry as given in Section S13.3.

If only K or Na was to be determined, ashing was not done. Instead, these elements were extracted from the samples with 1 N NH_4OAc, pH 7.0 (Chapman and Pratt, 1961). If they were to be determined by flame photometry, then NH_4OAc solution containing 250 ppm $LiNO_3$ was used and a ratio of 1:500 for sample to solution was employed.

P10. Calcium and magnesium

These cations were determined in the extract by the conventional versenate methods. See Section S13.2.1.

For determination by atomic absorption spectrophotometry, the Ca standards also contained $MgCl_2$. Similarly, Mg standards contained $CaCl_2$ to allow for mutual interference. See Sections S13.2.2.1, S13.2.2.2, and S13.2.2.3.

P11. Iron, manganese, copper, and zinc

Iron, Mn, Cu, and Zn in the filtrate were determined by procedures given in Sections S14.2, S15.2, S16.2, and S17.2, respectively (Buchanan and Muraoka, 1964).

P12. Chloride

Total chloride was determined in the HNO_3 extract of the ash or on a water extract (1:50 sample to water ratio). Determination was done according to the Mohr method by titrating with $AgNO_3$ solution, using K_2CrO_4 indicator, until the first lasting appearance of the colored precipitate. See Section S6.2.3.1.

P13. Total sulfur

Total sulfur was estimated by the $BaSO_4$ turbidimetric method using $BaCl_2$ (Chesnin and Yien, 1951). See Section S6.2.4.

P14. Cation exchange capacity of roots

The root cation exchange capacity was determined by the method reported by Crooke (1964) which employs acid-washing followed by titration of the root-KCl suspension with standard 0.01 N KOH solution to restore the pH to 7.0.

METHODS FOR WATER ANALYSIS

Samples were analyzed as soon after sampling as practicable (1-2 days) because otherwise changes would take place from biological and chemical activity. If analysis was not possible soon after collection, then they were refrigerated. "Plating out" of elements (e.g., Cu) on the surface of the storage container was also prevented by analyzing samples as soon as possible.

For weight-per-weight unit (mg/kg) conversion from weight-per-volume units (mg/l) it was assumed that one liter of water weighs 1 kg and therefore mg/l results are equivalent to ppm. However, if the dissolved solids content is very high, then density correction must be used to compute ppm from mg/l or the results reported in terms of weight of solute per unit volume of solution (Hem, 1959). Concentrations greater than 10,000 ppm were expressed as percentage and concentrations less than 1 ppm as ppb.

W1. Color

"Apparent color", due to substances in solution and due to suspended matter, was determined on samples without filtration or centrifuging.

"True color", due to substances in solution, after removing turbidity, was determined on centrifuged samples[21]. The samples were not filtered because filtration may remove some of the true color. Clear supernatant was obtained by centrifuging for 15-60 min, depending on the nature of turbidity, radius of the centrifuge, and the speed of the motor. If centrifuging was not sufficient to remove all the turbidity, then the method of Lamar (1949) was used.

A 500-unit stock solution (APHA, 1965) was prepared by dissolving platinum (ic) potassium chloride (PtK_2Cl_6) and crystalline cobaltous chloride ($CoCl_2 \cdot 6H_2O$) in HCl and diluting to the required volume. Standards were prepared in 0-70 color unit range. The sample was compared against these standards in Nessler tubes.

Since color value of water is extremely dependent on the acidity of the sample, when reporting color, pH was also reported.

W2. Turbidity

Turbidity was determined on a vigorously shaken sample. A visual comparison was made.

W3. pH

The pH, representing the instantaneous hydrogen ion activity, was determined electrometrically with a glass electode[5]. See Section S5.

W4. Specific conductance

It was determined by the use of a conductivity bridge[6] as given in Section S6. The results were reported as μmhos/cm at 25°C.

W5. Acidity

Acidity, expressing the total reserve or buffering capacity of the sample, was determined by 0.02 N NaOH titration (APHA, 1965; Johnston, 1916). Methyl orange acidity (pH 4.5), phenolphthalein acidity (pH 8.3) and phenolphthalein acidity at the boiling temperature (total acidity) were determined on separate aliquots and expressed as ppm $CaCO_3$. Free available residual chlorine, which would otherwise affect the indicator color response, was removed by adding a drop of 0.1 N sodium thiosulfate solution before titration.

W6. Alkalinity

Alkalinity, expressing the total reserve or the buffering capacity of the sample, was determined by titration of the dissolved carbonate and bicarbonate in water, as given by Dye (1958) and Thomas and Lynch (1960). First $CO_3^=$ was determined by titrating with 0.02 N H_2SO_4 to the bicarbonate equivalence point (pH 8.3) using phenolphthalein indicator (1% in 60% ethanol). Then HCO_3^- (natural and from $CO_3^=$) was titrated to the carbonic acid equivalence point (pH 4.5) using methyl orange (0.1% in water). If hydroxide alkalinity was also present, then it was indicated if $CO_3^=$ titrant volume exceeded the HCO_3^- titrant volume (Rainwater and Thatcher, 1960). The methyl orange titration was continued in the sample titrated using phenolphthalein or on a separate sample.

As in the determination of acidity, free residual chlorine was removed by adding a drop of 0.1 N sodium thiosulfate solution before titration.

Carbonate alkalinity was present when phenolphthalein alkalinity was not zero but was less than total alkalinity. Bicarbonate alkalinity was present when phenolphthalein alkalinity was less than half of total alkalinity.

W7. Hardness

Total hardness was determined by the chelation procedure using the disodium salt of ethylenediaminetetraacetic acid with Eriochrome black T indicator until the first evidence of a blue color (Betz and Noll, 1950; Diehl *et al*., 1950; Schwarzenbach and Flaschka, 1969). See Section S13.2.1. For calculations, it was assumed that all the hardness was due to $CaCO_3$.

"Carbonate" and "noncarbonate" hardness were calculated as follows:

When hardness was greater than the total of CO_3^{2-} and HCO_3^- alkalinities, the amount of hardness in excess of total alkalinity was noncarbonate (permanent) hardness and the remainder was carbonate (temporary) hardness.

W8. Residue (total dissolved solids and loss on ignition)

Resistant-glass bottles or polyethylene bottles were used for storing samples for residue determination.

The procedures given by APHA (1965) were used. For residue determination, the sample was evaporated in a weighed silica or porcelain dish on a steam bath and dried to a constant weight in an oven[4] maintained at 105°C. For the determination of fixed residue, samples from residue determination were then ignited at 500°C in a muffle furnace[12]. For filtrable residue, acid-washed, ashless, hard-finish filter papers were required. For nonfiltrable residue, the filter paper was dried at 105°C before filtering the sample. The drying temperature was also reported with the results of residues.

W8.1. Total residue

A total of filtrable and nonfiltrable residues was obtained by evaporating the sample and drying[4] at 105°C.

W8.2. Filtrable residue

Determination of the dissolved matter or filtrable residue was done by evaporating the filtered sample and drying[4] at 105°C. The approximate amount of total dissolved solids (anhydrous residues of the dissolved substances in water) was also obtained by determining specific conductance as given in Section S6 and calculated, for most waters that could be considered for irrigation, as follows (Rainwater and Thatcher, 1960):

$$\underset{(\text{ppm})}{\text{Dissolved solids}} = \underset{(\mu\text{mhos/cm})}{\text{specific conductance}} \times 0.65 \pm 0.1$$

W8.3. Nonfiltrable residue

For the determination of suspended residue or solids, a known volume of the suspension was filtered, the residue washed thoroughly, dried[4] at 105°C and weighed.

In certain cases, the amount of nonfiltrable residue was obtained by calculation of the difference between the total residue and the filtrable residue.

W8.4. Fixed residue

A measure of organic matter in the water was obtained by evaporating, weighing the residue, igniting, and weighing the ignited residue. Fixed residue was calculated as the difference between the residue on evaporation and the loss on ignition.

For the determination of total, filtrable, and nonfiltrable fixed residues, the residues from W8.1, W8.2, and W8.3, respectively were ignited[12] for 1 hr at 550°C and weighed.

W9. Nitrogen

If analysis of fresh water sample for ammonia, nitrate, and organic nitrogen was not possible then the sample was stored at 4°C after adding 0.8 ml conc. H_2SO_4/1 sample. This acid preservation prevented the changes in the levels of different forms of nitrogen that could have occurred due to biological activity. The sample acidity was neutralized with NaOH solution immediately before carrying out determinations (APHA, 1965).

W9.1. Ammonia

Ammonia nitrogen, that includes nitrogen in the form of NH_3 and NH_4^+, was determined by the color[7] produced by the reaction of ammonium ions with mercuric potassium iodide or Nessler reagent (Kolthoff and Sandell, 1952). The absorption spectrum varied as the intensity of the color varied with a change in the concentration of ammonia. A wavelength range of 400 to 500 nm was used, depending on the concentration of ammonia and the resulting color from the Nessler-ammonia reaction. At low ammonia concentrations, a yellow color was produced and wavelength from the region 400 to 425 nm was selected. At high ammonia levels, a reddish brown color was produced and the wavelength was selected in the 450 to 500 nm range. See Section S11.2.2.

Distillation from a strongly alkalized sample in the Kjeldahl apparatus followed by titration was used for waters containing substances such as Ca, Mg, Fe, and sulfide that interfere with the Nessler reaction (Rainwater and Thatcher, 1960).

W9.2. Nitrate

W9.2.1. Colorimetric method

The PDA colorimetric method (Section S11.3) was used for waters containing less than 30 ppm NO_3 or less than 5000 ppm Cl (Rainwater and Thatcher, 1960). Nitrate was determined colorimetrically[7] with nitrophenolsulfonic acid (Harper, 1924; Taras, 1950) after extracting nitrate from the sample according to Jackson (1958).

W9.2.2. Reduction method

This method was used for waters

containing more than 30 ppm NO_3 or more than 5000 ppm Cl (Rainwater and Thatcher, 1960). Nitrate N was reduced by NH_4-N using Devarda's alloy (Cu 50, Al 45, Zn 5) and a total of this NH_3 and that already in the water was determined by a Kjeldahl procedure.

W9.3. Organic

Organically bound nitrogen, contributed by such biological components as amino acids, polypeptides, and proteins, was determined by the macro-Kjeldahl method (Morgan et al., 1957). See Section S11.1.

The amount of "organic nitrogen" was obtained by subtracting "ammonium-nitrogen" from the "total Kjeldahl nitrogen".

W10. Orthophosphate

Only dissolved phosphates, phosphates in ortho form ($H_2PO_4^-$, $HPO_4^=$, and $PO_4^{\equiv}$), were determined. The "water soluble" and "loosely bound" P in runoff waters was obtained in the clear solution after flocculation of the soil with NaCl solution (Jackson, 1958). Then the P extractable at pH 3 was determined by extracting with 0.002 N H_2SO_4 buffered with $(NH_4)_2SO_4$ (Truog, 1930). The P content was determined by the phosphomolybdate method using $SnCl_2$ as the reducing agent as given in Section S12.2.2.1 (Dickman and Bray, 1940; Woods and Mellon, 1941) or an ascorbic acid reductant as given in Section S12.2.2.2 (Murphy and Riley, 1962; Watanabe and Olsen, 1965). When the P concentration was high, the phosphovanadomolybdate method (Barton, 1948; Jackson, 1958; Kitson and Mellon, 1944), as given in Section P8, was used. The transmittance of the solution after color development was determined in a photoelectric colorimeter[7].

W11. Calcium and magnesium

These cations were determined by Na_2EDTA titration (Katz and Navone, 1964) as given in Section S13.2.1. They were also determined by atomic absorption spectrophotometry (David, 1960; Fishman, 1966) in a solution containing 1% La (w/v) used to inhibit chemical interferences due to phosphate, Al, and Si (Platte and Marcy, 1965). See Sections S13.2.2.1, S13.2.2.2, and S13.2.2.3. Care was taken to redissolve any $CaCO_3$ that may have precipitated on standing during storage (APHA, 1965).

W12. Potassium, sodium, and sodium-adsorption ratio

Samples for K and Na determinations were stored in polyethylene bottles.

Potassium and Na were determined (Fishman, 1965) on filtered samples as given in Section S13.3. Sodium-adsorption ratio, which served as an index of the sodium hazard of irrigation water, was calculated as given in Section S6.3.

W13. Iron, manganese, copper, and zinc

These metals were determined on filtered samples. They were determined by atomic absorption spectroscopy (S14.2.2, S15.2.2, S16.2, and S17.2, respectively) by directly aspirating the aqueous solution into flame. For the determination of Fe and Mn, Si interference was overcome by the addition of Ca to give a final concentration of 50 ppm Ca (Platte and Marcy, 1965). A multi-element hollow cathode lamp containing the Cu-Fe-Mn-Zn combination was set at 15 ma for the analyses.

These metals, when present in low concentrations, were complexed with a chelating agent, the chelate extracted into an organic solvent and the organic phase aspirated into the flame (Perkin-Elmer Corp., 1968). Thus, they were determined by atomic absorption spectrophotometry after extraction with ammonium pyrollidine dithiocarbamate (APDC)-methyl isobutyl ketone (MIBK) (Allan, 1961b; Brooks _et al_., 1967a,b; Malissa and Schöffmann,1955; Mulford, 1966).

W14. Chloride

Chloride was determined by the Mohr method of titrating with standard $AgNO_3$ solution using K_2CrO_4 as an indicator. See Section S6.2.3.1. The samples were titrated in the pH range 7-10 adjusted with H_2SO_4 or NaOH solution (APHA, 1965).

W15. Sulfate

Sulfate was determined by a turbidimetric method by measuring the absorbance of a suspension containing $BaSO_4$ crystals of uniform size; care being taken to form a suspension having a reproducible optical absorbance (Rossum and Villarruz, 1961). See Section S6.2.4.

W16. Saturation and stability with respect to calcium carbonate

W16.1. Langelier's Saturation Index

It was calculated as follows (Langelier, 1936; Larson and Buswell, 1942):

Saturation Index = "pH actual" - "pH saturated"

where "pH actual" is the actual pH of a sample of water and "pH saturated" is the calculated pH the water sample must have, with no change in total alkalinity and Ca content at the same temperature, when just saturated with $CaCO_3$.

W16.2. Ryznar's Stability Index

It was calculated as follows (Ryznar, 1944):

Stability Index = 2 "pH saturated" - "pH actual".

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