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A PROPOSED CLASSIFICATION OF THE CHEMICAL ELEMENTS WITH RESPECT TO THEIR FUNCTIONS IN PLANT NUTRITION

By the late Professor R. W. THATCHER

MASSACHUSETTS STATE COLLEGE

THE suggestion which is presented in this paper has two purposes in view: First, to systematize and perhaps to simplify the teaching of the subject of the mineral nutrition of plants; and second, to establish a systematic basis for investigations of the specific functions of the different chemical elements in plant nutrition, with special reference to those of the rarer elements discussed in a previous paper.¹

There has been an immense amount of experimental study of the necessity for and specific functions of individual chemical elements in plant nutrition. The general result has been a rough classification of all the elements which have been found in plant tissues into two groups; the so-called "essential" and "non-essential" elements. The segregation of the elements

into these two classes is based upon observed differences in the ability or failure of plants to thrive and reach normal maturity in the presence or absence of each particular element in the nutrient medium and atmospheric environment in which the plants are grown. On this basis, ten elements, namely, carbon, hydrogen, oxygen, nitrogen, sulfur, phosphorus, potassium, calcium, magnesium and iron, are usually listed as "essential," and all others as "non-essential."

As was pointed out in the paper just cited, however, it is now known that other elements are fully as "essential" to plant growth as are these ten; although their physiological function and the actual quantities required for adequate nutrition may be quite different from what is true of those previously included in that class.

Further, so far as the writer is aware, no attempt

¹ R. W. Thatcher, "Some New Aspects of Plant Nutrition," SCIENCE, 76: 1970, 281-285, 1932.

has been made to correlate the known or possible functions of the different elements in plant nutrition with their general chemical properties as functions of their atomic numbers and position in their systematic arrangement in the periodic table. The present proposal constitutes such an attempt.

Any such classification is, of course, subject to criticism as to terms used, assignment of individual border-line cases and validity of the fundamental thesis. Such criticism serves to establish the soundness or unsoundness of the proposal, and its value or futility as a basis for further study. It is to invite such criticism that this particular paper is presented.

Nearly all the chemical elements which are known, or have been suggested, to have any function in plant nutrition are included in the first four orbits of the periodic table. Their places in this table are as follows:

Group	I	II	III	IV	V	VI	VII	VIII
Orbit 1 ...	H	—	—	—	—	—	—	—
2 ...	Li	Be	B	C	N	O	F	—
3 ...	Na	Mg	Al	Si	P	S	Cl	—
4 ...	K (Cu)	Ca Zn	Sc Ga	Ti Ge	V As	Cr Se	Mn Br	Fe Co Ni Cu —

It will be assumed that the reader is familiar with the use of these symbols to represent the names of the corresponding elements and with the general chemical properties of valence, ionic charges, etc., which accompany a particular place in the periodic table.

It is admitted at the outset that the following discussions apply in general only to the green, chlorophyll-containing types of plants and that many exceptions to the statements of fact and of theories here presented are to be found in the nutrition and metabolism of the fungi and other non-chlorophyll containing plant organisms. It is proposed later to make a similar study of the mineral nutrition phenomena of those types of plants whose energy requirements are derived from chemo-synthesis reactions, but for the present the discussion is confined to those plants whose nutrition begins with photo-synthetic reactions.

Also, it is recognized that during the seed-germination and embryo development stage, before chlorophyll production begins, and in the seed-development and maturation stages of the higher plants, many reactions take place in which the functions of the several elements which are under discussion may be quite different from those ascribed to them in this classification. In fact, this is substantially a study of the relation of the chemical elements to the photo-synthetic and accompanying metabolic processes of the higher green plants, which characteristically distinguishes them from all other types of organisms.

Finally, no attempt is made at this time to correlate the observed phenomena with the more recent explanations of atomic structure and chemical reactivity of the elements themselves. On the contrary, in all this discussion, the terms used are always those of the older and more commonly understood properties of valence, acid- or base-forming possibilities, ionic dissociation, etc.

PROPOSED CLASSIFICATION

The proposed classification of the chemical elements with respect to their functions in plant nutrition is based on the general conception that the green plants are the energy-absorbing and energy-storing agents of the cycle of life. Animals use these plants as foods, or as fuels, to supply the energy necessary for their life processes. Of course, green plants respire and otherwise consume energy, but the general result of their growth process, culminating in the production of seeds with their storage reservoirs of energy for the starting of a new generation, is the synthesis of easily oxidizable carbohydrates, fats, proteins, etc., with high energy-producing possibilities. Based on this general conception, the following classification of the elements which are known to, or may possibly, play a definite rôle in the synthetic processes of the higher green plants and hence are required by them as nutrients, is proposed:

- Group I. Hydrogen and oxygen; *energy exchange elements*.
- Group II. Carbon, nitrogen, sulfur and phosphorus; anion (or acid) group formers, with varying valence; *energy storers*.
- Group III. Sodium, potassium, calcium and magnesium; cation (or base) formers, with fixed valence; *translocation regulators*.
- Group IV. Manganese, iron (cobalt and nickel), copper and zinc; cation (or base) formers, with varying valence; *oxidation-reduction regulators*.
- Group V. Boron, aluminium, silicon, arsenic, selenium; ampholytes, with varying valence; *functions unknown*.
- Group VI. Chlorine, fluorine (bromine and iodine); anion (or acid) formers, with fixed valence; *functions unknown*.
- Group VII. Cobalt and nickel; cation (or base) formers, with varying valence; *functions unknown*, but perhaps those of Group IV.
- Group VIII. Germanium, gallium and other rare elements; ampholytes; *functions unknown*.

The following discussions will serve to indicate the general basis for this classification:

GROUP I

Hydrogen and oxygen are universally present in plant tissues. Their separate addition to or removal

from any organic compound results in much greater energy exchange than is true of any other elements. In general, oxidation reactions (addition of oxygen or removal of hydrogen) release energy or are *exothermic*; while the reverse, or reduction, reactions absorb energy or are *endothermic*. The simultaneous addition or removal of two atoms of hydrogen and one atom of oxygen, the so-called "reversible hydrolysis" reactions, do not require energy exchanges of the type here considered and are *isothermic*.

GROUP II

The members of this group, located adjacent to each other in Groups IV to VI of the periodic table, are characteristically anion-formers. They exhibit varying valence and are therefore capable of combination with hydrogen and oxygen in varying proportions, with the consequent possibilities of large energy exchanges in their reactions.

They do not participate in organic reactions as elements, or as elemental ions, but always in groups in which they are linked with oxygen or hydrogen and sometimes other elements to form groups of widely varying complexity, properties and reactivity. In general, they are most easily taken from a nutrient solution by plants when in their most highly oxidized forms. In fact, with the exception of nitrogen, it may be said that they are assimilable by higher plants only when in this form. Further, the first stage in their utilization by such plants is their reduction to a very low, if not the lowest possible, stage of oxidation. (Phosphorus is an exception to this last statement, as will be noted below.) This is a highly endothermic process and is the beginning of photosynthesis, the energy necessary for it being obtained by the absorption of radiant solar energy. In their later oxidation, in both plant and animal tissues, they release their stored energy. Hence, their designation as "energy storers."

Groups I and II might also be called "the protoplasm formers," since they are the essential components of the carbohydrates, fats, proteins and nucleocompounds which constitute the active mass of colloidal matter of cellular tissues. It is for this reason, as well as its place in the periodic table and properties generally similar to those of the other elements of the group, that phosphorus is included in this group, in spite of the fact that it does not, like the others, undergo changes in stage of oxidation during its assimilation and metabolism by plants and consequently probably does not serve as an "energy storer."

GROUP III

The members of this group, while "essential elements" of plant nutrition, are not actual constituents of the principal organic components of protoplasm.

Neither are they involved in the oxidation-reduction reactions which are the basis for energy exchange. This latter fact is probably because of their fixed valence and consequent inability to unite with varying proportions of oxygen and hydrogen.

They are, however, very definitely connected with most of the isothermic transformations of carbohydrates, fats and proteins from simpler (generally more soluble) forms to more complex (generally insoluble) forms and *vice versa*. In fact, they may be considered as serving as catalysts for the reversible hydrolysis of these compounds, whereby they are rendered soluble and capable of translocation from the cells in which they are synthesized to other cells, where they are utilized for energy production or stored in less soluble forms for future use.

Further, these cation-forming electrolytes have very definite effects upon the colloidal properties of cell protoplasm, whereby its permeability, its water imbibition capacity, its power of adsorption and its definite structure-forming capacity are altered so as to influence not only the direction and velocity of the hydrolytic reactions which go on in it, but also the ease or speed of removal from it by osmosis of the various products of such reactions.

In general, therefore, it is apparent that the elements of this group are chiefly concerned with the chemical reactions and colloidal phenomena which are essential to the translocation of compounds through the various tissues of the plant. Magnesium has an additional special and exceptional function in that it enters into the molecular composition of chlorophyll, but its function in this respect is not well understood, since it can be replaced in the chlorophyll molecule by iron, copper or zinc without greatly altering the light-absorbing properties or chemical reactivity of the chlorophyll. Potassium may have highly specific effects other than the general ones attributable to the group as a whole because of its radioactive properties. In fact, it is easily possible to conceive that there are specific functions for each of these elements in addition to those which are described comprehensively under the term "translocation regulators," but the latter seems to express fairly correctly their major function in the energy absorption and storage process.

GROUP IV

The elements assigned to this group, if cobalt and nickel be included in it, constitute the six elements whose atomic numbers (25 to 30) place them adjacent to each other in the periodic table. In other words, their atomic structure differs only by the successive addition of one electron to the proton nucleus. With the exception of zinc (the highest member of the series), they all form both *ous* and *ic* compounds by variations in valence. Manganese and zinc at the two ends of the series both exhibit both acid- and

base-forming properties, but in general these six successive elements in the periodic system exhibit similar chemical properties and undoubtedly perform similar physiological functions in plant nutrition. With respect to cobalt and nickel, these functions have not yet been studied experimentally sufficiently to determine whether they are really important in plant nutrition, and they are therefore tentatively listed both in Group IV and Group VII of this proposed scheme of classification.

With respect to manganese and iron, and copper and zinc, however, I believe that there is sufficient experimental evidence to justify the hypothesis that these are two pairs of mutually coordinating catalysts for oxidation-reduction reactions, the former for biological reactions in which the addition or removal of oxygen is the basis of the energy exchange and the latter for those in which loss or gain of hydrogen is involved. I recognize that the matter has not yet been investigated sufficiently to establish fully the soundness of this hypothesis of the balancing effect of these two pairs of catalysts, but believe that there is adequate proof that their major function is that of catalysts of oxidation-reduction reactions in biological processes. While it is impracticable to cite in detail in this preliminary paper the experimental evidence bearing upon this particular phase of the matter, it may be briefly summarized as follows:

Iron and manganese have been shown to be mutually antagonistic in their production of chloroses of plants due to improper conditions for the production of chlorophyll. This has frequently been explained as a calcium-manganese antagonism, but recent experiments have shown that the true explanation lies in the rendering insoluble and unavailable of iron by excessive proportions of calcium in the nutrient medium or cell protoplasmic contents, thus disturbing the iron-manganese balance, instead of the calcium-manganese balance.

The basis for the belief that copper and zinc are mutually counter-balancing catalysts for hydrogen exchange lies in their recently demonstrated striking and opposite effects upon the reversible oxidation-reduction reactions of both glutathione and ascorbic acid. The theory that these two compounds, which

are now known to be almost, if not quite, universally present together in rapidly metabolizing tissues of both plants and animals, constitute linked factors in the system of oxidation-reductions in protoplasm, has been suggested recently by several different investigators.

In short, it is my hypothesis that the iron-manganese pair constitute the controlling catalytic factors in oxidation-reduction reactions of the oxygen exchange, or chlorophyll and hemoglobin type, and that copper and zinc act similarly in the hydrogen exchange, or glutathione-ascorbic acid type of similar reactions.

In my laboratory, we are now engaged in an experimental study of the soundness of the second phase of this hypothesis, as a part of our study of the general problem of the function of rarer elements in plant nutrition.

GROUPS V-VIII

The functions in plant nutrition of the elements tentatively placed in these groups have not been investigated sufficiently to provide a basis for their grouping according to known uses for this purpose. They are therefore grouped according to their chemical properties as connected with their place in the periodic table, with the thought that this may afford a basis for further study of their possible plant nutrition functions.

It is possible, of course, that further investigational work will show that some of the elements which are found in the higher orbits of the periodic table have definite functions in plant nutrition. In fact, it has been suggested that rubidium, iodine and even lead, for example, may have some such functions; but the observations which lead to such suggestions appear to refer to some abnormal growth or environmental conditions and not to the general normal processes of plant nutrition. The list here presented includes all those elements which have been reported to be frequently found in the ash of plants grown under generally-occurring conditions of soil nutrient supplies the world over, and is therefore believed to include all those elements which need to be considered in a systematic study of this problem.

ENVIRONMENTAL TRANSFORMATION OF BACTERIA¹

By Dr. W. H. MANWARING

PROFESSOR OF BACTERIOLOGY AND EXPERIMENTAL PATHOLOGY, STANFORD UNIVERSITY

RECENT morphological and physiological studies of specific infectious agents have led to tentative conclusions,

¹ Presented as part of the symposium on "Environmental Effects on Plants," Western Society of Naturalists, Asilomar, Calif., December 27, 1933.

which bacteriologists and immunologists are frankly incompetent to harmonize with the currently accepted theories of genetics and organic evolution.

These studies suggest a Lamarckian rather than a