AVAILABLE SULFUR IN SOME MANITOBA SOILS AS ESTIMATED BY PLANT GROWTH AND CHEMICAL ANALYSES

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ABSTRACT

Measurement of the water soluble sulfate content of several Manitoba soils indicated that most of the soils contained adequate amounts of sulfur. The lowest water soluble sulfate contents encountered were in the soils of the Stockton association. A more detailed study involving 9 sampling sites within the Stockton association showed that these soils are generally much lower in water soluble sulfate and soil sulfur content than other Manitoba soils.

In a greenhouse experiment the yield of rape was significantly increased by sulfur fertilization on 7 of 11 surface soils involved. All those soils that yielded significant responses to sulfur fertilizer contained less than 2.0 p.p.m. water soluble sulfate. Sulfur uptake by rape was significantly correlated with the amount of water soluble sulfate, heat soluble sulfate and sulfate present after mineralization. The soil sulfur, HCl soluble sulfur, and organic matter contents of the soils were not correlated with sulfur uptake.

A second greenhouse experiment determined the critical level of sulfur in rape as .10% total sulfur, and 200 p.p.m. water soluble sulfate sulfur.

Studies of the sulfate adsorption characteristics of Manitoba soils indicated that adsorbed sulfate is not an important sulfur fraction in these soils. Water soluble sulfate should be a good measure of the sulfate that is available to plants.

In a field experiment, consistent but not statistically significant increases in yield of rape seed were obtained by broadcasting 20 to 40 pounds of sulfur fertilizer on a Stockton soil. This soil contained 252 pounds of water soluble sulfate in the upper 48 inches. Most of the

Stockton soils studied contain less than that amount of water soluble sulfate.

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I INTRODUCTION

Sulfur is an essential plant nutrient. In plants sulfur is an essential component of proteins, and is thought to be associated with the production of chlorophyll, the development of the root system, and nodulation in legumes (20). The occurrence of sulfur deficient soils in several areas of the world has resulted in an increased interest in the soil chemistry of sulfur. Detailed investigations into methods of analysis for plant available sulfur, the nature of the various sulfur fractions, and the adsorption chemistry of the sulfate ion, have been reported in the last two decades.

In North America soil sulfur deficiencies may be encountered on strongly leached, acid soils such as the Podzols of Eastern United States, or the Grey Wooded soils of Alberta. Sulfur deficiencies are not restricted to degraded soils. Some well drained Chernozemic soils in Washington and Oregon have been shown to contain insufficient amounts of sulfur (23). Little is known of the sulfur fraction of Manitoba soils. This study is an attempt at assessing the sulfur status of these soils, determining the nature of this sulfur, and devising a means of estimating the plant available fraction.

Soils that contain large amounts of water soluble sulfate were considered to be sulfur sufficient, and few investigations were made on these soils. Since preliminary analyses indicated that the coarse textured, well drained Chernozemic soils of the Stockton association contained small amounts of water soluble sulfate, a more detailed study was made of these soils. In devising a chemical soil test for plant available sulfate, several different methods were investigated. The sulfur measured by each method was correlated with uptake of sulfur by rape plants grown on these soils in the greenhouse. A second greenhouse experiment involved the determination of the critical level of total sulfur, and water extractable sulfate sulfur in rape plants. Studies were also conducted on the adsorption of sulfate ions by several representative Manitoba soils. A field experiment measured the effect of sulfur fertilizers on rape grown on a Stockton soil.

II REVIEW OF LITERATURE

Early workers in Soil Science, although recognizing sulfur as an essential plant nutrient, made few studies of sulfur in soils. There were several reasons for this apparent dearth of research on sulfur. Some of these reasons are: early methods of plant analysis underestimated the sulfur content of plants, thereby underestimating plant requirements of sulfur; sulfur was added incidentally to many soils as impurities in lime and phosphorus fertilizers; and, sulfur deficiencies are not general and widespread, as are nitrogen deficiencies, but more localized and specific to certain areas and soils. However, responses to sulfur fertilizer in many areas of the world, new methods of plant analysis and the removal of sulfur impurities from phosphorus fertilizers, has shown workers that supplies of soil sulfur are not always adequate for maximum plant growth. Consequently an increased interest in the soil chemistry of sulfur has developed within the past two decades.

A. NATURE OF SULFUR IN SOIL

The total sulfur fraction in soils comprises both organic and inorganic forms. Organic sulfur, generally estimated as the difference between total sulfur and inorganic sulfate, accounts for nearly all the sulfur present in the surface horizons of most soils (18). Several workers have estimated amounts of organic sulfur in soils, and related the amount of organic sulfur to amounts of other soil constituents. Evans and Rost (15) working with Chernozemic soils in Minnesota, report organic sulfur contents ranging from 216 to 428 p.p.m. Nelson (32) reports that most of the sulfur of the surface horizons of soils is in the organic form. He measured the sulfur content of some surface soils of Mississippi, which varied in texture from sandy loam to clay, and in pH from 5.2 to 7.4. These soils contained 127 to 564 p.p.m. total sulfur, of which 64 to 353 p.p.m. was present in the organic form. The soils had an average C:N:S ratio of 126:10:1, and amounts of organic carbon, total nitrogen and total sulfur were positively correlated. Work by Harward et al. (22) shows that the bulk of the sulfur of surface soils is in the organic fraction. The organic sulfur levels ranged from 77 to 765 p.p.m. The amounts of organic carbon and organic S were positively correlated. The average C:N:S ratio was 145:10:1. Lowe (29), working with soils of Quebec reports that 53 to 90 per cent of the sulfur is organic. His more recent work on soils of Alberta reports a mean value of 435 p.p.m. total sulfur in the Ah, and 273 p.p.m. in the Bm of Chernozemic soils. The mineral horizons of the Grey Wooded soils contained much less total sulfur than did equivalent horizons in the Chernozemic soils (28).

Little is known about the compounds of the organic sulfur fraction. The sulfur compounds of plants, such as proteins, polypeptides and amino acids are assumed to be present, but it is not known how long they persist. Lowe and Delong (30) and others (16,40) suggest that a considerable amount of the soil sulfur is covalently bound to the polysaccharides, or sulfate esters of phenol. Small amounts of amino acids methionine and cysteine have been detected in hydrolyzates of soil (18).

Most soils contain significant amounts of inorganic sulfur. In the lower horizons, especially where soils are imperfectly drained, calcareous or gypsiferous, inorganic sulfates constitute nearly all the total sulfur. The sulfate may be present in the soil solution as sulfate ions, or occur as relatively soluble salts such as gypsum or

$MgSO_4$ (18). This sulfur fraction is readily available to plants, and consequently on many soils, chemical soil tests which employ water or dilute electrolytes as extractants are suitable for measuring plant available sulfur. In other soils, especially those which are strongly acid and contain appreciable amounts of clay and sesquioxides significant amounts of sulfate may be retained by processes of adsorption (14,21,26). A third form of inorganic sulfate is that sulfate which is coprecipitated with $CaCO_3$. Williams and Steinbergs (40) have shown that in calcareous soils of Australia this fraction comprises an important portion of the total sulfur. This soil sulfur fraction, generally extracted with N HCl is thought to be relatively unavailable to plants. Sulfur may also be present as very insoluble forms such as $BaSO_4$ or pyrite, FeS_2 (18,7).

B. MINERALIZATION OF SULFUR

Soil microorganisms convert the organic sulfur of soil to inorganic sulfate by a process similar to the mineralization of organic nitrogen to nitrate. Although one would expect the release of nitrate and sulfate to be in a ratio of their content in the soil organic matter, several studies have shown that this often does not occur. Barrow (3,4) found that some sulfur deficient soils did not release sulfate although nitrate was mineralized. Nelson (32) reports that mineralization of nitrogen and sulfur are related, but that release of sulfate lags behind release of nitrate. The addition of materials of high organic carbon: organic sulfur ratio may result in fixation of sulfate (32). Incubation studies have estimated the amount of sulfate mineralized as 1.2 pounds per acre per month (32), 9.8 pounds in a 4 week period (22), and 24 pounds in a 100 day period (4). These findings indicate the variable nature of sulfur mineralization. It is difficult to apply results from studies with various soils under laboratory and greenhouse conditions to particular soils under field conditions.

C. SULFUR BALANCE IN SOILS

The amount of plant available sulfate in soils depends upon the relative rates of addition and loss of sulfate. Where losses of sulfate exceed the amounts released or supplied, sulfur deficiencies result.

On imperfectly drained soils, especially under conditions of low rainfall, soluble sulfate, salts of calcium, magnesium and sodium contribute to the supply of sulfate (18). The mineralization of the sulfur of the organic fraction is an important source of sulfate in many soils. Significant amounts of sulfate are added in rainwater. Workers in the southern United States estimate yearly additions of an average of 12.7 pounds sulfur per acre near industrial areas, and 5.4 pounds sulfur per acre in rural areas (24). Yearly additions of a mean of 27 pounds sulfur per acre per year are reported for Indiana (6). In western Australia about 1 pound per acre per year is added in rainwater (18). It has been shown that plants can adsorb SO_2 from the atmosphere (24). Very little of a crop's requirement is realized from this source. Small amounts of sulfate are added in insecticides and as impurities in some fertilizers. The most common sulfur fertilizers are gypsum and ammonium sulfate.

Removal of sulfate from the soil is principally by two processes; crop removal and leaching. Removal by crops has been estimated at forty pounds per acre per year for members of the Brassica family, twenty pounds per acre per year for legumes, and ten pounds per acre per year for cereals and grasses (6). Loss of sulfate by leaching may be extensive. Studies with lysimeters have shown that as much as 55 pounds per acre per year may be leached from sandy soils (23). Since sulfate adsorption is negligible at pH greater than 6.0 (26,14), sulfate is easily leached from most neutral or alkaline coarse textured soils.

D. SULFATE ADSORPTION

Many soils have the ability to retain sulfate ions by processes of adsorption. Kamprath et al.(26)found that soils have the capacity to adsorb significant amounts of sulfate ions. Greater amounts of sulfate are adsorbed by soils that are strongly acid than are adsorbed by soils that are less acid or neutral. Clay minerals, sesquioxides and organic matter appear to be the soil constituents responsible for the sulfate adsorption phenomena. The species of clay mineral is important. Aluminium saturated kaolinitic clays with a 1:1 type lattice are able to adsorb a great deal more sulfate than 2:1 lattice type clay minerals such as montmorillonite. The amount of adsorbed sulfate increases with increasing concentration of sulfate ions in the soil solution. Phosphate ions can replace adsorbed sulfate, and phosphate is adsorbed preferentially to sulfate.

Work by Chao et al.(8,9) at Oregon indicates that a kinetic equilibrium exists between sulfate retained by soil, and the sulfate in solution. These adsorption phenomena can be described by the Freundlich adsorption equation which considers the relationship between the concentration of an adsorbate, and the amount of its adsorption by an adsorbent. The good fit of adsorption of sulfates by soils suggest that there are no adsorption maxima, and therefore no definite anion exchange capacity.

This discounts the role of anion exchange in sulfate adsorption. Sulfate is easily desorbed; as much as 45 per cent of the sulfate adsorbed by soils from soil-sulfate solution suspensions can be removed by one extraction treatment with water. The exchange reactions are rapid; from 87 to 93 per cent of the exchange has taken place after one minute.

Harvard _et al._ (21) used soil column chromatographic techniques to demonstrate sulfate retention by soils. They report that S^{35} tagged sulfate ions were much less mobile, and hence adsorbed to a greater degree in those soils of low reaction, especially where aluminum saturated clays were present. The destruction of organic matter in these soils resulted in the sulfate adsorption capacity being reduced by one-third to one-half. The removal of iron and aluminum oxides also reduced the amount of sulfate adsorbed. They postulate that the mechanisms of sulfate adsorption are:

1. Anion exchange involving hydrous oxides of iron and aluminum, and the crystal edges of clay as positively charged sites capable of attracting sulfate ions.
2. Retention of sulfate ions by coördination with hydroxy-aluminum complexes.
3. Salt or molecular adsorption, resulting from attraction between the soil colloids and salts of sulfate.
4. Retention by amphoteric organic compounds. That is, at acid pH, positively charged sites are available on organic matter components for the adsorption of sulfate ions.

E. CHEMICAL SOIL TESTS FOR SULFUR

The development of a chemical soil test to measure supplies of plant available sulfur has been investigated in several areas in