Commercial Humates for Agriculture and the Fertilizer Industry

EVERETTE M. BURDICK[1]

The humate content of soils must be maintained for optimum productivity. Skilled agriculturists are aware of this and accomplish it by indirect and costly methods. The same can be achieved through the use of humate concentrates, which are salts of the humic acids obtainable from natural sources, that can be added directly to soils along with regular commercial fertilizers.

Introduction

The humates are so important in garden and crop production that practically all modern soil management practices are designed to increase their content. The necessity of maintaining an adequate concentration of humate material in productive soils has been recognized by agriculturists for many years. As far back as 1786, Achard (1) conducted and published research on humus. Sprengel (50) showed it could be extracted from soil in 1826, but little or nothing of significance along this line was added during the next 100 years.

The fertilizer industry has long emphasized the importance of maintaining the humic content of soils to ensure good productivity (40). Extension and research agronomists have engaged in the study of these humic substances for many years, and many scientific data regarding them are common knowledge to most agricultural workers. *Humus* is the Latin word for soil. Humus and its related chemical derivatives are mainly responsible for the brown or black color of fertile soils. Humic materials are the partly decayed and otherwise transformed organic matter built up or accumulated in soils through natural biochemical processes over the ages, and which convert mineral dusts into soils. Humic matter is continuously being formed in soils, and at the same time, it is continuously being destroyed (33). Modern cultivation practices greatly accelerate the rate of destruction of humic material, which must be replaced in some manner if the productivity of the soil is to be maintained.

Crop rotation, adequate fertilization, planting legumes, plowing under of green manures, application of animal manures, inoculation with microorganisms, and the use of expensive organic fertilizers are some of the more acceptable ways of maintaining adequate amounts of humic materials in soils. These practices are quite effective, but they are indirect, time consuming, wasteful, and costly. Simple analysis of this situation suggests that the humates be added directly to the soil exactly as is done with fertilizers. The obvious difficulty with this suggestion lies in the fact that adequate supplies of highly concentrated and purified humates are relatively unavailable commercially. Humates have been produced commercially in Austria and Japan for some time, and in the United States for use in oil well drilling muds for several years (6, 11, 12), but only recently have suitable ones become available for the agricultural industry. Production is somewhat limited at present, although it is expected to increase rapidly, since various salts of the humic acids, such as the ammonium humates and the potassium humates, can be added to standard commercial fertilizer formulas to make them more complete. Recent developments along these lines in this country should soon make the humates available in large volume and at costs low enough to permit their direct application to farmlands (5).

[1] Consulting Chemist, 4821 Ronda Street, Coral Gables, Florida.

Received for publication June 5, 1964.

Unique Properties of the Humates

Humus is the organic matter of soils that has decayed sufficiently to have lost its identity with regards to its origin. The most important and biochemically active group of the many degradation products of soil organic materials is the alkali-soluble fraction commonly called the humic acids. The salts of these humic acids are known as the humates. Humates supply growing plants with food, but they serve in much more important ways to make soils more productive and farming more profitable. They increase the water holding capacity of soils (40, 61), and thus soils containing relatively large amounts of humate material resist droughts more effectively and produce better yields where rainfall or irrigation may be insufficient. They improve the tilth or workability of the soil (52, 19), and thus heavy clay soils can be worked into satisfactory seed beds and marginal soils into profitable ones. Soils are more friable and suitably sized particles are formed in the aggregate (52). They reduce soil erosion. They retain water soluble inorganic fertilizers (32, 42) and release them to the growing plants as needed. For these reasons alone, it is easy to understand why the humic acids have been so extensively studied by soil scientists and the technical literature is replete with references to the unique properties of these materials so widespread in nature.

The chemical structure of the humic acids is not definitely known, in spite of the great amount of research and study on them and their biochemical effects. It is extremely interesting that so little is really known about the chemical structure of these very important natural chemicals, which are as fundamental and necessary to man's existence as the chlorophylls. In 1938, Waksman thoroughly reviewed the literature in his book on the origin, chemical composition and importance of these materials (61), but only minor reviews have appeared since (7, 13).

In general, the humic acids have been shown to possess fairly high molecular weights, and to be polymeric polyhydroxy acids derived from celluloses, lignins, and proteins (30, 31, 61). They form water-soluble or dispersible colloids with ammonium, sodium, and potassium hydroxides, but calcium, aluminum, and iron salts are quite insoluble. Various humic fractions are often classified according to their carbon to nitrogen ratios (61). These ratios indicate somewhat the degree of humification and are influenced by the particular biochemical processes involved in their formation; for example, the ratio averages about 10 to 1 in the more humid regions of the world, and considerably higher in the semi-arid regions, but rarely exceeds 14 to 1 (54,61). Fractionation of the humic acids can be effected by the use of various solvents (44), distribution between immiscible solvents (26), chromatographic techniques (14, 17, 41), fractional precipitation techniques (2,3), and electrophoresis (8). Spectrographic (15) and electron paramagnetic resonance studies (57) have yielded considerable information regarding chemical structure.

Viscosity and specific gravity changes can be effected in soils through the addition of small amounts of the humates (12, 19, 23, 52). This is especially true of clayey soils. Colloidal properties and surface tension effects are readily observed in dilute solutions, which practically defy filtration, and in more concentrated ones which form thixotropic gels. The ability of the humates to poise or regulate the water-holding capacity or content is probably their most significant property so far as agriculture is concerned (24), since from a quantitative point water is the most important plant material derived from the soil. In conjunction with this water regulating effect, the humates possess extremely high ion-exchange capacities (21, 27, 29, 32, 42, 45), and it is this property that makes possible better retention and utilization of fertilizers by preventing excessive leaching away from the root zones and ultimately releasing them to the growing plants as needed. The humates reduce soil erosion by increasing the cohesive forces of the very fine soil particles (61). The desirable friable character of fertile soils is maintained through the formation of colloidal mineral complexes, which assist in aeration and the prevention of large clods and stratification.

Very low concentrations of purified humates have been shown to stimulate seed germination and viability (16, 60), root respiration and formation (16), root growth, especially lengthwise (4, 16, 37, 38, 47, 48).

Significant increased yields have been reported for many crops, such as cotton, potatoes, wheat, tomatoes, mustard, and nursery stock (23, 24, 25, 34, 35, 39, 49, 51, 55, 56). They have also been shown to stimulate growth and proliferation of desirable soil microorganisms (20, 59) as well as algae and yeasts (9, 22, 28). A number of workers have reported that the humic acids can solubilize and make available to plants certain materials that are otherwise unavailable, such as the rock phosphates (21, 29, 58). The humates seem to play an important role in plant utilization and metabolism of the phosphates (25, 27, 53). The humic acids apparently can liberate carbon dioxide from soil calcium carbonates and thus make it available to the plant through the roots for photosynthesis. The humates are known to stimulate plant enzymes (25).

The preceding list is impressive, but by no means complete. It does make it easy to understand why soil scientists, chemists, and others have tried in vain to produce materials possessing similar properties. As a result, several "synthetics" have been produced, marketed and used with some success. Some of these materials have been produced by drastic degradation of natural carbohydrates and proteins, but most have been polymers of such things as vinyl acetate and maleic acid, polylvinyl alcohol, hydrolyzed polyacrylonitrile, carboxymethylcellulose, polyacrylates, isopropyl acrylamide plus acrylic or maleic acid, and poly-quaternary ammonium compounds (10, 18, 36, 43, 46). Some of these synthetics have proven to be quite effective under certain conditions, but their high cost and other limitations, such as loss of effectiveness upon drying, ageing, exposure to the elements, and often stabilize the soil too much (36). The humates, on the other hand, are nature's soil conditioners "par excellence."

Commercial Humates

Why haven't the agricultural and fertilizer industries developed the humates commercially? This question is not easily answered, especially, in view of the apparently recognized importance of the humates to both, and more so, since the market potential is so great. More baffling is the fact that high purity humic acids and humate concentrates have remained as laboratory curiosities for so long. The successful production and marketing of any chemical depends upon an economical and practical manufacturing process. A number of suitable methods for recovering the humic acids have been available for some time, so this has presented no serious problem. However, suitable raw materials such as the peats, peat mosses, mucks, forest soils, brown coals, and certain lignites generally do not contain high enough concentrations of the humates to make them attractive for commercial production, but suitable sources in the United States are now known to have commercial possibilities. These include certain deposits in Arkansas, Arizona, Florida, Louisiana, New York, North Dakota, Michigan, Minnesota, Texas, and Wyoming. Rich deposits exist also in Mexico. The organic-mineral soil called *"aguja"* found in the Big Bend area of Texas appears to be most promising, and although these extensive deposits have been surveyed and studied by competent geologists, they have not been classified and named scientifically. In many areas these deposits contain over 50% organic matter, two-thirds or more of which is readily recoverable humic acid. Similar deposits surely exist in other arid and semi-arid parts of the world and only await discovery.

Literature Cited

1. Achard, F. K. 1786. Chemische Untersuchung des Torfs. Crell's Chem. Ann. **2:** 391–403.
2. Beckley, V. A. 1921. The preparation and fractionation of humic acid.. J. Agr. Sci. **11:** 66–8.
3. Berthelot, M. and G. Andre. 1892. Recherches sur les substances humiques. Ann. Chim. Phys. **25** (6):354-403.
4. Bottomley, W. B. 1913. Ammonium humate as a source of nitrogen for plants. J. Soc. Chem. Ind. **32:** 920–4.
5. Burdick, E. M. 1961. Process for treating humus materials. U. S. Pat. 2,992,093.
6. Caraway, W. H. 1953. Domestic substitutes for quebracho in oil-well drilling fluids. Petroleum Engr. **25** (12) B:81–92.
7. Carls, H. 1953. Present state of humic acid research. Pharm. **8:** 161–3.
8. Duchaufour, P., and F. Jacquin. 1963. The extraction and fractionation of humic compounds controlled by electrophoresis. Ann. Agr. **14** (6):885–918.

9. Dzierzbicki, A. 1910. Influence of humus substances on the development of yeast and ethyl alcohol fermentation. Biochem. Centr. 9: 704–10.
10. Erickson, J. G. 1957. Polyquaternary ammonium compounds as soil conditioners. U. S. Pat. 2,807,910.
11. Fischer, P. W. 1955. Electrically conductive drilling fluids. U. S. Pat. 2,721,841.
12. Fisher, H. B. 1950. Drilling mud clay. U. S. Pat. 2,515,207.
13. Flaig, W. 1960. Chemistry of humus materials. Suomen. Kemistilehti **33A**: 229–51.
14. Forsyth, W. G. C. 1947. Studies on the more soluble complexes of soil organic matter. I. A method of fractionation. Biochem. J. **41**: 176–81.
15. Fujii, Shuya. 1959. Infrared absorption of humic acid and alkali treated humic acid. Nenryo Kyokaishi **38**: 267–73.
16. Guminski, S. 1960. Influence of humin materials on the respiration of roots. Acta Agrobotan. **9**: 123–7.
17. Hock, A. 1937. Chromatographic separation of brown and grey humic acids. Bodenk. Pfl. Ernahr. **5**: 1–8.
18. Huge, P. 1960. Production of humic acids under controlled conditions. Bull. Inst. Agron. Sta. Rech. Gembloux **28**: 177–9.
19. Inukai, Toyoharu, and Yutaka Shibuya. 1959. Industrialization of the manufacture of humic .acids and their salts. Nenryo Kyokaishi **38**: 296-300.
20. Iswaran, V. 1960. Effect of humified organic matter on nitrogen fixation by Azotobacter. J. Indian Soc. Soil Sci. **8**: 107–13.
21. Kaindl, K., and H. H. Mayr. 1958. Inhibiting effect of humus on the fixation of phosphates in soil. Atom praxis **4**: 407–11.
22. King, C. J., and H. F. Loomis. 1929. Cotton root-rot investigations in Arizona. Jour. Agr. Res. **39**: 199–221.
23. Kononova, M. M., and K. V. D'yakonova. 1958. Effect of humus fertilizer on plant growth. Intern. Soc. Soil Sci., Trans. II and IV Comm. Hamburg, **2**: 56–9.
24. Kortleven, J. 1961. Organic matter in humus. Landbouwvoorlichting **18**: 130–5.
25. Kristeva, L. A., et al. 1954. The reciprocal relation between mineral and organic nutrition of higher plants and the utilization of humic acids as fertilizers. Pochvovedenie (12): 1–10.
26. Kosaka, Jiro, et al. 1961. Fractionation of humic acids by organic solvents. Nippon Dojo-Hiryogaku Zasshi **32**: 333–7.
27. Kotlyuba, V. G., and V. A. Reutov. 1963. Effect of humic acid on assimilation of phosphorus by plants as a function of the surrounding temperature. Zh. Biol. Abstr. No. 14 G 24.
28. Linford, M. B., et al. 1938. Reduction of soil populations of the root-knot nematode during decomposition of organic matter. Soil Sci. **45**: 127–41.
29. Mack, K. 1922. The influence of humic acid upon the assimilation of phosphorus. Chem. Ztg. **46**: 73–5.
30. Marcinek, J. 1962. Chemical composition of the organic matter of peat soils. Zeszyty Probl. Postepow Nauk Rolniczych No. 34: 127–38.
31. Marcusson, J. 1922. The structure and formation of humic acids and coals. Z. angew. Chem. **35**: 165–6.
32. Misterski, W., and W. Loginow. 1959. Physiochemical properties of humic acids. Sbornik Ceskoslow. akad. zemedel, ved, Rostlinna vyroba **5**: 457–78.
33. Monnier, G., et al. 1959. Dynamic approach to the organic materials of the soil. Compt. rendu. **248**: 138–41.
34. Mukanova, V. L. 1961. The effect of humate fertilizers prepared from lignite on growth, development and yield of cotton. Akad. Nauk. Uz.SSR, Inst. Khim. 142–60.
35. Mukhersee, P. N., et al. 1961. Fertilizers from coal. I. Production. II. Field trials. Proc. Natl. Acad. Sci., India Sect. **A 31**: 124–6.
36. Okuda, Azuma, and Katsuihiko Tokubo. 1957. Seepage-preventing effect of synthetic soil conditioners in paddy fields. Soil and Plant Food **2**: 215–19.
37. Pivovarov, L. R. 1962. The nature of the physiological activity of humic acids in relation to their structure. Primeneniya (Kiev: Gas. Izd. Sel'skokhoz. Lit. Ukr. SSR). pt. 2, 101–21.
38. Rerabek, Jiri. 1960. Humic acid interactions in the growth process. Biol. Plant. Acad. Sci. Bohemoslov. **2**: 88–97.
39. Ronsal, G. A. 1963. Biological activity of soluble humates obtained from humus. Produktivnosti Roslin Sb. 68–70.
40. Sauchelli, V. 1944. Humus: the working partner of chemical plant food. Amer. Fertilizer **101** (8):11–12, 26–28.
41. Scharpenseel, H. W. 1960. Paper chromatography of humus substances and of humic acid products and model substances. Z. Pflanzenernahr. Dung. Bodenk. **88**: 97–115.
42. Scheffer, F., et al. 1957. Determining the complexing and chelating capacity of or-

ganic materials in soils. Z. Pflanzenernahr. Dung. Bodenk. **78:** 168–77.
43. Scheffer, F., et al. 1958. Synthetic humic acids from polyoxybenzenes. Z. Pflanzenernahr. Dung. Bodenk **82:** 193–205.
44. Scheffer, F., et al. 1960. Extraction of humus fraction by mild organic solvents. Z. Pflanzenernahr. Dung. Bodenk. **90:** 58–69.
45. Seitz, D. S., et al. 1960. Ion exchange resins from lignite coal. Ind. Eng. Chem. **52:** 313–4.
46. Shearer, N. H. 1957. Soil conditioner. U. S. Pat. 2,816,083.
47. Smidova, M. 1960. The influence of humic acid on respiration of plant roots. Biol. Plant Acad. Sci. Bohemoslov. **2:** 152–64.
48. Smidova, M. 1960. Influence of humates on wheat respiration. Acta Agrobotan. (Warsaw) **9:** 129–43.
49. Smidova, M. 1962. Effect of sodium humate on swelling and germination of winter wheat. Biol. Plant., Acad. Sci. Bohemoslov. **4:** 112-18.
50. Sprengel, C. 1826. Extraction of humus from soil. Kastner Arch. ges. Naturlehre (Nurnburg) **8:** 145.
51. Strmecki, E. L., and P. C. De Kock. 1954. Factors contributing to the growth-promoting properties of Velenje lignite. Zemljiste i Biljka **3:** 1–20.
52. Swíetochwski, B. 1960. Significance of humus for the fertility increase of light soils. Acta Agrobotan (Warsaw) **9** (1): 159–170.
53. Szymanski, S. 1961. Phosphate-humate compounds and phosphoric acid nutrition of plants. Prague, Brno, Studies About Humus, Symp. Humus Plant, 289-90.
54. Takijima, Yasuo, and Kiichi Konno. 1959. Soils of peaty paddy fields. VII. Properties of soil humus. Nippon Dojo Hiryogaku Zasshi **29:** 541–4.
55. Tello, F. Dueso. 1953. Increment of gluten in wheat due to the influence of activated lignite. Anales bromatol (Madrid) **5:** 203–26.
56. Tichy, V. 1960. Influence of some humus fractions on the growth and sugar metabolism of plants. Acta Agrobotan. (Warsaw) **9:** 145–58.
57. Tollin, G., et al. 1963. Structure of humic acid. IV. Electron paramagnetic resonance studies. Biochim. Biophys. Acta **66:** 444–7.
58. Torok, L. 1961. Dissolution of phosphates in humate solutions. Agroke. Talajtan **10:** 465–78.
59. Voicu, J. 1923. Effect of humus in weak and strong doses upon the fixation of nitrogen by Azotobacter chrooccum. Compt. rendu. **176:** 1421–3.
60. Volna, M., and V. Dlouhy. 1956. Humus extract improves the quality and increases the yield of nursery stock. Lesnicka prace **35:** 205–10.
61. Waksman, S. A. 1938. Humus, origin, chemical composition, and importance in nature. 2nd Ed. Williams and Wilkins, Baltimore.