

HUMUS CHEMISTRY

GENESIS · COMPOSITION · REACTIONS

F. J. STEVENSON

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PREFACE

Whereas interest in the chemistry and reactions of organic substances in soils, sediments, and natural waters is of long-standing, significant advances of the past two decades, partly caused by the application of new and powerful analytical techniques, has served to rekindle interest in the subject. A considerable body of information has now accumulated and the time has arrived to prepare an account of this work for classroom use. To the author's knowledge there is no comprehensive textbook on humus chemistry that is suitable for students or new researchers. Although specific reviews and monographs are available, most of them are addressed to the senior investigator or specialist.

Essentially, the book is designed as a reference text for graduate students and advanced undergraduates taking a one-semester course in soil organic matter chemistry and soil biochemistry and is based upon the experience of the author in teaching a course at the University of Illinois. It is assumed that the student has had prior training in organic and analytical chemistry. Since emphasis is given to the basic organic chemistry and reactions of naturally occurring organic substances in the environment, the book will be of considerable value to investigators in several scientific disciplines, including all aspects of soil science, geochemistry, sanitary engineering, environmental science, and others. It is also hoped that the book will be of value to advanced researchers, though they may detect omissions and deficiencies arising in part from an attempt to present as broad a coverage of the subject as possible in a single volume. That much remains to be done will be evident to all readers of the volume.

The subject matter is conveniently arranged into four sections. The first part (Chapters 1 and 2) covers organic matter transformations (emphasis on carbon-14 studies) and methods of extraction and fractionation. The second part (Chapters 3 through 7) deals primarily with the chemistry and distribution of known classes of organic compounds in soil such as saccharides, lipids, and constituents containing nitrogen, phosphorus, and sulfur. Chapter 4 of this section is devoted to the dynamics of soil nitrogen transformations as revealed by nitrogen-15 studies. The basic organic chemistry of the so-called humic substances (humic acids, fulvic acids, etc.) is presented in Chapters 8 through 13 of part three. Portions of this section may be too

advanced for the average student. A particularly important section of the book (part four: Chapters 14 through 18) deals with organic matter associations and interactions, such as combinations with polyvalent cations, clay minerals, and pesticides.

As with most advanced texts, the book contains somewhat more material than can be covered in any one course on soil organic matter or soil biochemistry. Arrangement of the subject matter is such that certain sections or chapters can be omitted in formal study. Inclusion of the added material increases the usefulness of the book to researchers and the serious student. The book may prove valuable as a reference text for related courses in soil chemistry, soil microbiology, geochemistry, sanitary engineering, and environmental science.

One of the functions of this book has been to present a critical account of our knowledge of each topic, and, for this reason, rather extensive use has been made of references within the text. Because of space limitations, complete documentation was not feasible and selection of references was rather arbitrary; in some cases a full search of the literature for establishing priorities was not possible. The author apologizes for any omission of important work.

In an undertaking of this nature errors will undoubtedly creep in and the author may have inadvertently misrepresented some of the research discussed. Corrections and suggestions for improvement will be welcomed.

Appreciation is expressed to graduate students and staff members at the University of Illinois for encouragement and assistance in preparation of the text. Special thanks go to Kathryn Biondic for preparing many of the illustrations.

F. J. STEVENSON

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ORGANIC MATTER TRANSFORMATIONS, DISTRIBUTION, AND FUNCTION IN SOIL

The decomposition of plant and animal remains in soil constitutes a basic biological process in that carbon (C) is recirculated to the atmosphere as carbon dioxide (CO_2), nitrogen (N) is made available as ammonium (NH_4^+) and nitrate (NO_3^-), and other associated elements (phosphorus, sulfur, and various micronutrients) appear in forms required by higher plants. In the process some of the C is assimilated into microbial tissue (the soil biomass) and part is converted into stable humus. Some of the native humus is mineralized concurrently; consequently, total organic matter content is maintained at some steady-state level characteristic of the soil and management system.

This introductory chapter places into proper perspective those aspects of organic matter transformations that relate to humus synthesis and composition. Emphasis is given to modern studies using ^{14}C -labeled substrates. Other topics include factors affecting the organic matter content of the soil, the overall decay process, and the function of humus in soil. For background reading, the reviews of Campbell,¹ Jenkinson,² Paul and Veen,³ and Stevenson,⁴ and Wagner⁵ are recommended.

THE ORGANIC MATTER CONTENT OF THE SOIL

Soils vary greatly in organic matter content. A typical prairie grassland soil (e.g., Mollisol) may contain 5 to 6% organic matter in the top 15 cm; a sandy soil less than 1%. Poorly drained soils (Aquepts) often have organic matter contents approaching 10%. Tropical soils (Oxisols) are known for their low content of organic matter.^{4,6}

For all practical purposes the organic matter content of the soil parallels the N content. The C/N ratio of organic matter generally falls in the range of 10 to 12 although higher values are not unusual. Because of the ease with

which a Kjeldahl determination can be made, N is often used as an index of organic matter content.

The quantities of C in various reservoirs at the earth's surface and to a depth of 16 km are recorded in Table 1.1. It can be seen that the mass of soil C exceeds the amount found in all other *surface* reservoirs combined. However, the reservoir of soil C (30 to 50×10^{14} kg) is small when compared to the total amount contained in sediments ($200,000 \times 10^{14}$ kg).

For supplementary information regarding global aspects of the C cycle, the works of Bolin⁷ and Garrels et al.⁸ are recommended.

Natural processes leading to the development of soils having variable organic matter contents are related to the so-called factors of soil formation.

$$\text{O.M.} = f(\text{time, climate, vegetation, parent material, topography, . . .})$$

where the letter *f* stands for "depends" or "function of" and the dots indicate that other factors may be involved.

In the classical studies of Jenny⁹⁻¹² each soil forming factor was treated as an independent variable.

$$\text{O.M.} = f(\text{climate})_{\text{time, vegetation, parent material, topography, . . .}}$$

Evaluation of any given factor requires that all other factors remain constant, which seldom if ever occurs under natural conditions. Despite this shortcoming, studies of the type initiated by Jenny⁹⁻¹² have contributed substantially to our understanding of the factors influencing the organic matter content of soils. According to Jenny⁹ the order of importance of the soil-forming factors in determining the organic matter and N contents of

Table 1.1
Amount of C in Various Reservoirs^a

Reservoir	Amount of C, 10^{14} kg
At Earth's surface	
Atmospheric CO ₂	7
Biomass	4.8
Fresh water	2.5
Marine, above thermocline	5-8
Soil organic matter	30-50
At depths to 16 km	
Marine organic detritus	30
Coal and petroleum	100
Deep sea solute carbon	345
Sediments	200,000

^a From Bolin.⁷

loamy soils within the United States was: climate > vegetation > topography = parent material > age.

The Time Factor

Organic matter does not accumulate indefinitely in well-drained soils and, with time, an equilibrium level is attained that is governed by the soil-forming factors of climate, topography, vegetation, and parent material. The numerous combinations under which the various factors operate account for the great variability in the organic matter content of soils, even in a localized area.

Information on the rate of organic matter accumulation in soil has come from studies of time sequences, or chronosequences, on mud flows, spoil banks, sand dunes, road cuts, and the moraines of receding glaciers. This work, reviewed by Stevenson,⁴ shows that the rate of organic matter accumulation is rapid during the first few years, diminishes slowly, and reaches equilibrium in periods of time which vary from as little as 110 years for fine-textured parent material to as much as 1500 years for sandy areas.

Although several reasons have been given for the establishment of equilibrium levels of organic matter in soil, none has proven entirely satisfactory. Included with the explanations are: (1) organic colloids (e.g., humic acids) are produced which resist attack by microorganisms, (2) humus is protected from decay through its interaction with mineral matter (e.g., polyvalent cations and clay), and (3) a limitation of one or more essential nutrients (N, P, S) places a ceiling on the quantity of stable humus that can be synthesized.⁴

Influence of Climate

Climate is the most important single factor which determines the array of plant species at any given location, the quantity of plant material produced, and the intensity of microbial activity in the soil; consequently, this factor plays a prominent role in determining organic matter levels. Considering climate in its entirety, a humid climate leads to forest associations and the development of Spodosols (Podzol) and Alfisols (Gray-Brown Podzolic and Red-Yellow Podzolic); a semi-arid climate leads to grassland associations and the development of Mollisols (Brunizem, Chernozem, and Chestnut). Grassland soils exceed all other well-aerated soils in humus content; desert, semi-desert, and certain tropical soils have the lowest.

Soils formed under restricted drainage (Histosols and Inceptisols) do not follow a climatic pattern. In these soils O₂ deficiency prevents complete destruction of organic residues by microorganisms over a wide temperature range.

Extensive studies were made by Jenny and his co-workers^{9,10} on the effect of climate on organic matter and N levels in soil. For soils along a

north to south transect of the semi-humid region of the Central United States, the N content of the soil decreased 2 to 3 times for each rise of 10°C in mean annual temperature. Whereas this relationship cannot be extrapolated directly to other areas,¹³ it is widely known that soils of the warmer climatic zones generally have low organic matter contents.

Several explanations have been given for the decrease in soil organic matter content with an increase in mean annual temperature. Jenny^{9,10} attempted to relate organic matter levels to the effect of temperature on microbial activity, but this approach can be criticized on the grounds that consideration is not given to temperature effects on photosynthesis (production of raw material for humus synthesis). Senstius¹⁴ attributed the low levels of organic matter in tropical soils to the high activities of microorganisms at the warmer temperatures.

Enders¹⁵ presented a unique concept concerning the synthesis of genuine stable humus. He concluded that the best soil conditions for the synthesis and preservation of humic substances having high N contents were frequent and abrupt changes in the environment (e.g., humidity and temperature); consequently, soils formed in harsh continental climates should have high organic matter and N contents. Harmsen¹⁶ used this same theory to explain the greater synthesis of humic substances in grassland soils, as compared to arable land, claiming that in the former the combination of organic substrates in the surface soils and frequent and sharp fluctuations in temperature, moisture, and irradiation leads to greater synthesis of humic substances.

The effect of increasing rainfall (moisture component of climate) on soil organic matter content is to promote greater plant growth, and, consequently, the production of larger quantities of raw material for humus synthesis. The quantity of vegetable material produced, and subsequently returned to the soil, can vary from a trace in arid and arctic regions to several tons per hectare in warm climates where plant growth occurs throughout the year. Both roots and tops serve as energy sources for humus synthesis.

For grassland soils along a west to east transect of the central United States, a definite correlation exists between the depth of the root system and the thickness of the grass cover with depth of penetration of organic matter.⁴

Vegetation

It is widely known that, other factors being constant, the organic matter content of grassland soils (e.g., Mollisols) is substantially higher than for forest soils (e.g., Alfisols). Reasons given for this include: (1) larger quantities of raw material for humus synthesis are produced under grass, (2) nitrification is inhibited in grassland soils, thereby leading to the preservation of nitrogen and carbon, (3) humus synthesis occurs in the rhizosphere, which is more extensive under grass than under forest vegetation, (4) restricted

aeration occurs under grass, thereby contributing to organic matter preservation, and (5) the high base status of grassland soils promotes the fixation of NH_3 by lignin.⁴ A combination of several factors is probably involved, with item (3) being of major importance.

In the case of forest soils, differences in the profile distribution of organic matter occur by virtue of the manner in which the leaf litter becomes mixed with mineral matter. In soils formed under deciduous forests on sites that are well-drained and well-supplied with calcium (Alfisols), the litter becomes thoroughly mixed with the mineral layer through the activities of earthworms and faunal organisms. In this case mineral particles in the top 10 to 15 cm of soil become coated with humus. On the other hand, on sites low in available calcium (Spodosols), the leaf litter does not become mixed with the mineral layer, but forms a mat on the soil surface. An organic-rich layer of acid (mor) humus accumulates at the soil surface and only the topmost portion of the mineral layer becomes stained with humus.

Parent Material

Parent material is effective mainly through its influence on texture. It is a well-known fact that, for any given climate zone, and provided vegetation and topography are constant, organic matter content depends upon textural properties. The fixation of humic substances in the form of organo-mineral complexes serves to preserve organic matter. Thus heavy-textured soils have higher organic matter contents than loamy soils, which in turn have higher organic matter contents than sandy soils.

Organic matter has several characteristics, such as resistance to attack by microorganisms and to removal by chemical extractants, which suggests that it occurs in intimate association with mineral matter. Retention may also be affected by the type of clay mineral present. Montmorillonitic clays, which have high adsorption capacities for organic molecules, are particularly effective in protecting nitrogenous constituents against attack by microorganisms.

Topography

Topography, or relief, affects soil organic matter content through its influence on climate, runoff, evaporation, and transpiration. Local variations in topography, such as knolls, slopes, and depressions, modify the plant microclimate, defined by Aandahl¹⁷ as the climate in the immediate vicinity of the soil profile. Soils occurring in depressions, where the climate is "locally humid," have higher organic matter contents than those occurring on the knolls, where the climate is "locally arid."

Naturally moist and poorly drained soils are usually high in organic matter, because the anaerobic conditions which prevail during wet periods of the year prevent destruction of organic matter.

Effect of Cropping

Marked changes are brought about in the organic matter content of the soil through the activities of people. Usually, but not always, organic matter levels decline when soils are first placed under cultivation.^{1,4}

Early findings, such as those of Salter and Green,¹⁸ showed that loss of N (and organic matter) was the least with rotations containing a legume and greatest under continuous row cropping. An item of some significance was that losses were more or less linear with time. Therefore, unless a change occurred, organic matter content would ultimately reach an absolute minimum, e.g., approach zero. The following equation was derived by Salter and Green to describe N loss

$$N = N_0 K^t, \quad \text{or} \quad \frac{dN}{dt} = -rN$$

where N_0 is the initial N content, K is the fraction of the N remaining after a single year's cropping, and r is the annual rate of N loss.

Jenny's¹⁹ results for losses of soil N under average farming conditions in the cornbelt section of the United States are in general agreement with the findings of Salter and Green¹⁸ and others in that cropping caused a decline in organic matter levels. On the other hand his finding suggested that destruction of organic matter is far from complete and that new *equilibrium levels* are ultimately attained. For the cornbelt soils, Jenny found that about 25% of the N was lost the first 20 years, 10% the second 20 years, and 7% during the third 20 years. Jenny¹⁹ modified Salter and Green's¹⁸ equation by including a factor for the annual return of nitrogen to the soil.

$$\frac{dN}{dt} = -rN + A$$

where A is the annual rate of addition.

This equation can be written in the form

$$N = \frac{A}{r} - \left(\frac{A}{r} - N_0 \right) e^{-rt}$$

A plot of N vs e^{-rt} should, therefore, yield a straight line in which the "y" intercept (A/r) would describe the expected equilibrium value and the term $(N_0 - A/r)e^{-rt}$ the change process. The change in the magnitude of the latter with time provides a measure of the rate of establishment of equilibrium.

Graphical methods were used by Bartholomew and Kirkman²⁰ to obtain the constants A and r for the experimental plots of several long-time rotation experiments. In brief their findings were in agreement with Jenny's obser-

vation that equilibrium levels can be expected to be attained within a 50- to 100-year period of cultivation.

The decline in the N (and organic matter) content of the soil when land is cultivated cannot be attributed entirely to a reduction in the quantity of plant residues available for humus synthesis. Improved aeration, resulting from cultivation, may lead to increased microbial activity and loss of organic matter. A temporary increase in respiration rate occurs each time an air-dried soil is wetted, and since considerable amounts of fresh soil are subjected to repeated wetting and drying through cultivation, losses of organic matter by this process could be appreciable. A major effect of cultivation in stimulating microbial activity may be the exposure of organic matter previously not accessible to microbial attack.

Results of numerous studies have shown that, for most agricultural soils, organic matter can only be maintained at high levels by inclusion of a sod crop in the cropping sequence, or by frequent addition of large quantities of organic residues (e.g., animal manure).¹⁴

Whereas numerous investigations have shown losses of soil organic matter through cropping, few have shown increases.^{1,4} When increases have occurred, they have been attributed to additions of plant and animal residues, or to the introduction of leguminous crops on soil initially low in organic matter.

Jenkinson²¹ demonstrated a continuous increase in soil N content through long-time applications of manure to soil under permanent barley at the Rothamsted Experiment Station in England. The plots were established in 1852 and equilibrium levels had still not been attained by the time they were terminated 94 years later (in 1946).

THE OVERALL DECAY PROCESS

Several stages can be delineated in the decay of organic remains in soil. Earthworms and other soil animals play an important role in reducing the size of fresh plant material; further transformations are carried out by enzymes produced by microorganisms. The initial phase of microbial attack is characterized by rapid loss of readily decomposable organic substances. Depending on the nature of the soil microflora and quantity of synthesized microbial cells, the amount of substrate C used for cell synthesis will vary from 10 to 70%. Molds and spore-forming bacteria are especially active in consuming proteins, starches, and cellulose. By-products include NH_3 , H_2S , CO_2 , organic acids, and other incompletely oxidized substances. In subsequent phases organic intermediates and newly formed biomass tissues are attacked by a wide variety of microorganisms, with production of new biomass and further C loss as CO_2 .²² The final stage of decomposition is characterized by gradual decomposition of the more resistant plant parts, such as lignin, for which the actinomycetes and fungi play a major role.