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Chapter

Tropical Soil Humus

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Abstract

In strongly weathered tropical soils, humus and humic substances (HSs) appear to play an important role in soil fertility because they represent the dominant reservoir and source of plant nutrients. As the refractory organic carbon form of soil, HSs play a vital role in the atmospheric CO_2 sequestration. Detailed classification of humus forms in tropical ecosystems and the dynamics and function of humus are still poorly understood. Nevertheless, in tropical environment many studies indicated that it is very difficult to differentiate between tropical humus, at least in normally drained soil. Moders, mulls, and Amphimull are the dominant humus forms in the topsoil of tropical environment. Knowing the mechanisms of formation, the dynamics and the methods of characterization of humus in tropical zones are a scientific challenge. This chapter aims to share recent findings from a broad humus in tropical soil and research related to this theme.

Keywords: tropical soil, humus forms, humid substances, fertility, climate

1. Introduction

Soil organic matter (SOM) is a main reservoir and source of plant nutrients, which controls soil's fertility in tropical soil. It also plays a major role in various soil functions in influencing soil chemical and physical properties and carbon storage [1]. Although, in tropical soils, SOM represents only about 1% of the soil mass, the humus is one of the most important fractions of these soils. Approximately 60–70% of organic matter in soil is composed of humic substances (HSs) [2]. As the refractory organic carbon form of soil, HSs play a vital role in the atmospheric CO_2 sequestration [3]. Previous studies summarized the benefits of soil humus and several functions have been assigned to them. These functions include physical, chemical, and biological control, retention of nutriments, metal complexation, and carbon storage [4]. Humus composition in an essential characteristics of HS in SOM [5]. Traditionally, HSs are separated into humic acid (HA), fulvic acid (FA), and humins (HN) based on the solubility characteristics of each fraction, and the humus composition is an essential characteristic of HS in SOM.

Humification is a global process that is implemented in soils [6, 7]. This process of transforming precursors of humification and polymerization of oligomer and monomer molecules into dark-colored, high-molecular-weight macromolecules has been described in terms of organic chemistry [8], environmental dynamics [9, 10], and various zonal soils dynamics., parent rock, vegetation, soil organisms [11, 12]. The

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humus profile comprises different scales, which may be integrated: regional climate. Detailed classification of humus forms has been made for over a century in temperate regions, whereas, in tropical ecosystems, the dynamics and function of humus are still poorly understood.

Although previous works have studied the dynamics and function of humus forms in tropical forest ecosystems, however, these aspects are still poorly understood [5, 13, 14].

The aim of this chapter is to review the current state of knowledge on humic substances in tropical soil, with special emphasis on data concerning humus forms, the factors that control.

2. Humus forms in tropical soil

The humus form reflects the processes of heterotrophic decomposition, nutrient cycling and release [15–17], soil microbial and faunal activity [18, 19], stabilization of soil organic matter, and release of carbon dioxide CO_2 [19, 20]. Humus forms are thus crucial to the functioning of a forest ecosystem, being a key indicator of plant-soil interactions [21]. Under temperate forests, the humus has been studied for over a century, and its three main forms, mull, moder and mor, are well established [22]. In tropical environment, a few investigations have studied the dynamics and function of humus forms [14, 23, 24]). Amphimulls exhibit mixed features of moders and mulls and are widely represented tropical forest ecosystems (**Figure 1**) [14, 25]. Dabin [26] indicated that it is very difficult to differentiate between tropical humus, at least in normally drained soils, on the basis of morphological characters, since we are most often dealing with Mull-type humus with very thin, if not nonexistent, litter, which rests on a mineral horizon where the humus is well decomposed and strongly incorporated. The main criteria are related to the intensity of humic accumulation, which is manifested by the color of the horizon, possibly by its structure, and by the humic penetration in depth [26]. In tropical environments, [14] has evidence that humus forms are more varied and depend on parent rock, litter quality, and millipede activity. For instance, these authors observed two different humus forms in secondary forests in North Grande-Terre (Guadeloupe): a calcareous Amphimull and a Dysmull (**Figure 1**). The first is characterized by a 1.5 cm-thick OH horizon, which has a granular structure and consists of fecal pellets of millipedes. The second has a 7 cm-thick root mat [14]. In tropical humid lowlands, [5] has shown that forest soils generally exhibit the mull humus type and transitions to moder due to the favorable conditions for litter decomposition. According to [27], a great diversity of humus form was found in Atlantic forest (Mesotrophic Tropical Mull, Tropical Ologotrophic mull, Eumoder, Moder-Mull Dysmoder, Mesotrophic Mull), which is a reflection of

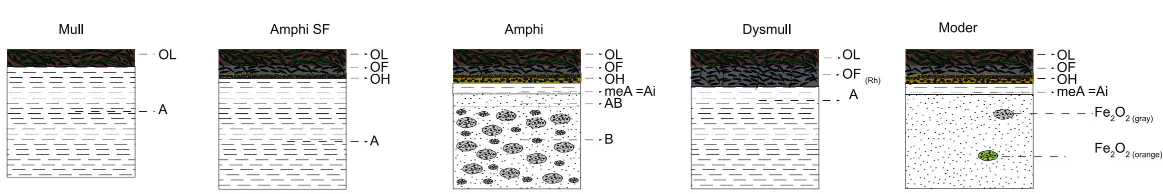

Figure 1.
Representative humus profiles showing Main humus forms identified in tropical soils adapted from [14, 24]. These humus forms reflects the processes of heterotrophic decomposition, nutrient cycling and release, soil microbial and faunal activity, stabilization of soil organic matter, and release of carbon dioxide CO_2.

the complex environmental conditions. In accordance with recent study in tropical environment, the classification of humus forms resulted in the identification of three humus systems: Mull, Moder, and Amphimull [24]. The attribution to an Amphimull system depends on the quality of the A horizon.

3. Humus horizon structure and composition

In tropical soils, humus horizons present some specific characteristics related to decomposition rate and nutrient absorption. For example, [27] found a dark color horizon between organic superficial layers and the first organic-mineral horizon. This horizon, which is of biological origin, was named Ai and had a significant amount of roots [27]. Moder humus forms are characterized by a structured with a juxtaposition of organic and mineral grain, named miA [24]. In opposition, [24] indicated that large organic mineral aggregates are found in Mull humus forms. Amphimull system displayed distinct characteristics similar to that of moder due to the formation of an OH horizon one the one hand and similar to that Mull system due to the presence of organo-mineral part [24]. Others studies indicated that fine roots have been found between horizon OF, which plays a role the development of the humus [14, 23].

4. Factors influencing humus form development in tropical environment

Humification, as well as litter decomposition, is primarily microbially mediated process, mainly controlled by site-specific variables such as temperature, soil water regime, pH, and available nutrients [5]. Biotic and abiotic factors can affect the development of the humus profile by constraining the dynamics of its humus horizons, leading to consequences for the global carbon cycle, climate change mitigation, and forest productivity (**Figure 2**) [28–30]. However, what drives the morphological organization and characteristics of humus horizons in tropical forests is still poorly understood [14, 23, 24].

At the regional scale, due to the effects of temperature and moisture, climate is the best predictor for the decomposition rate and consequently for the formation of humus forms [27]. In tropical environment, the length of the dry season governs the processes of humification [31]. Among these factors, soil moisture is a major factor affecting microbial activity [32]. Previous studies focused on the effects of different soil moisture content on the quantitative and qualitative characteristic of humic fraction, showed that humic fractions decreased with increasing soil moisture [33]. The chemical composition of plant tissues has implications for the recalcitrance of the

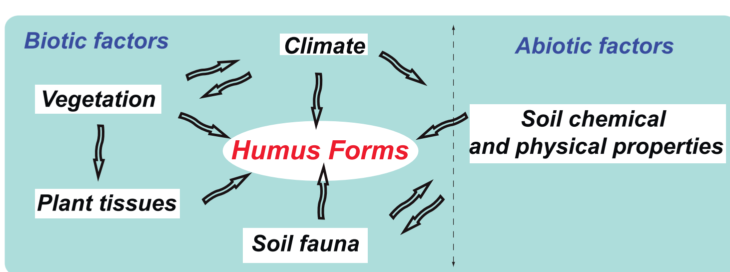

Figure 2.
Factors controlling humus formations in tropical soils.

litter material and thus for humification processes in soils [34–36]. In tropical forests, many authors associated humus forms to litter quality and by the composition of soil macrofauna rather than by edaphic properties [5, 14, 27] has shown that both the litter quality and specific peculiarities are responsible for the humus forms in tropical environment (**Figure 3**). For example, [5] in a study carried out in different land cover in tropical environment showed that there is considerable variability in overall chemical composition of the various plant tissues of tropical forest trees in tropical soil (**Figure 2**).

Besides the litter quality, the soils physical and chemical properties (**Figure 2**) also played an important role in humus forms development [24, 27]. Soil texture is important for humus build-up [24]. These authors showed in recent study that sandy and clayey textures showed pronounced differences in thickness, occurrence, and attributes of humus horizons. In effect, in Amazonian forest, Mull and Amphi represent the dominant humus forms in clayey sites while Amphi forms are found in both sandy and clayey textures, but predominate in clayey ones [24]. This difference could potentially be explained by the activity of earthworms [37] and enchytraeids [38, 39] in clayey and sandy soils, respectively. The presence of fine particles encourages good soil structure resulting in the formation of aggregates, enhancing soil moisture and aeration, and so favors specific faunal development and a consequent Mull humus form [24]. These results confirmed previous data indicating that humus forms are driven by soil texture differentiation [40, 41]. However, without a study including fauna manipulation and an assessment of structure stability, caution must

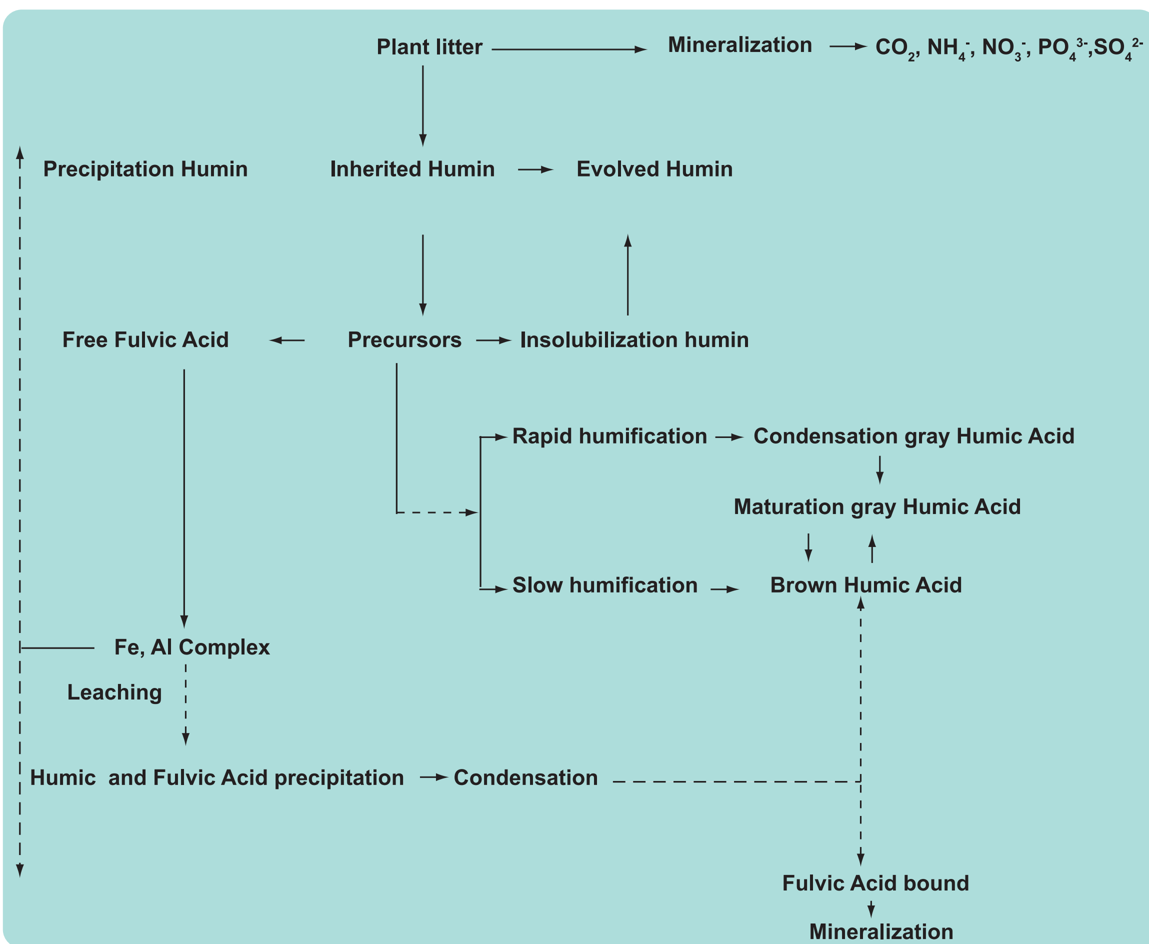

Figure 3.
Formation of tropical humus. These processes are controlled by different factors adapted from [26].

be applied. Because, biological activity could be similar between soil textures but less visible in sandy condition [24]. Regarding vegetation, [14] highlighted an accumulation of organic matter in humus horizons of secondary tropical forests compared with natural forests, which also occurred in forest restoration in bauxite mining areas in the Amazon [42]. For instance, grassland soils are known to possess relatively large amounts of humic acid (~70%) compared with fulvic acid (~30%), whereas forest soils have vice versa [43].

The formation of humic substances (i.e., humification) is primarily a microbially mediated process [5]. In tropical environment, humus forms are determined by the composition of soil macrofauna rather than by edaphic properties [12]. In tropical forest soils, where faunal-mediated mixing between plant/microbial necromass and soil is intense [44]. Animal microbial in the soil fauna are known to influence SOM content in particular in humid climates where HS contributes to the soil moisture and nutrients. Many authors associated microbial and soil animal communities to humus forms [14, 22, 44] showed that mull is associated with high plant, biodiversity, and productivity. Conversely, mor has low productivity and biodiversity and organic layers (OL, OF, and OH) are well identified. Moder, which is an intermediate position, both is characterized by a high level of biological activity [14] showed that tropical semi-evergreen forests, as temperate forests, the activity of endoanecic earthworms gives mull humus profiles, whatever the quality of the litter [5] showed that in biologically active soils with high earthworm population, the mull humus type develops in L-A h horizons only. Many studies have shown that in tropical environments, humus forms contribute to diagnosing both the forest succession and the restoration of degraded areas [14, 24]. For instance, [14] highlighted an accumulation of organic matter in humus horizons of secondary tropical forests compared with natural forests, which also occurred in forest restoration in bauxite mining areas in the Amazon [42]. This accumulation in humus horizons indicates a collapse in the process of organic matter decomposition and incorporation, which results in a decrease in the stabilization of carbon in the soil, as suggested by [42] and [45].

5. Chemical nature of soil humified fractions

The primary contributors to SOM are various plant tissues, which are highly variable among tropical tree species [5]. The chemical composition of the secondary resources (soil fauna and microorganisms) is even more complex, but these sources are quantitatively less important than plants in surface layers of tropical forest soils (**Figure 4**) [46]. So, the structure, nature, chemical composition, and stages humification of the organic material determine molecular size and chemical structure of humic substances [47]. Humic substances in soils consist of heterogeneous insoluble macromolecular compounds, which form complexes with soil mineral surfaces and metal cations [48]. According to their solubility in aqueous solution at different pH values, humic substances can be divided into three main fractions, namely humic acid (HA), fulvic acid (FA), and humin [5].

Stevenson and Olsen [8, 49] studied the humus composition in tropical soils and showed that the bulk of the organic matter in most soils consists of a series of HA, FA, and humin. These authors have found that humified fraction from SOM had high content of insoluble fraction and predominance of fluvic acids. Moreover, the chemical nature of humic and fluvic acids varied with the soil depth. The HA concentration was higher at top soil [49]. The highest biological activity on the surface probably promotes

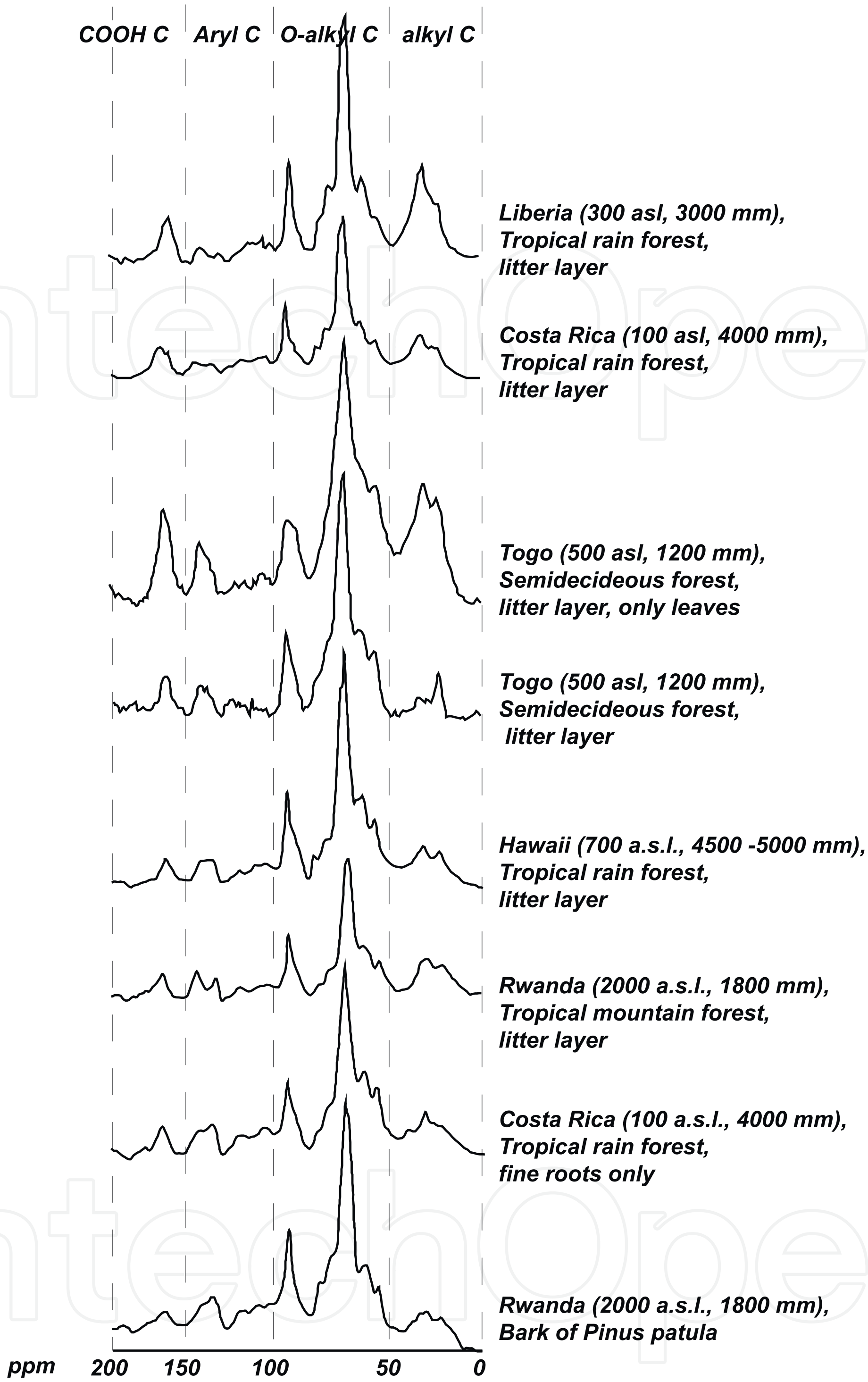

Figure 4.
Carbon distribution of some primary resources of tropical forests according to CPMAS^{13}C NMR spectroscopy adapted from [5].

the formation of condensed alkali-soluble humic substances with greater stability [50]. Studies carried out in Ivory Coast and Senegal showed that fluvic acid content attains and sometimes even exceeds that of humic acids [31]. Using CPMAS ^{13}C NMR analysis, [5] showed the presence of carboxyl fraction groups, aromatic carbon, and O-alkyl carbon in plant tissue of tropical forest. Among them, O-alkyl carbon was shown to be higher (75%) in wood or roots than leaf litter (50%). Moreover, carboxyl and aromatic carbon are low and represent about 5–10% and 10–15%, respectively, of total carbon.

6. Characterization of humic substances: a varied methodological approach

In chemical terms, organic matter consists of three fractions of humic substances (HSs): humin, fulvic acids, and humic acids [51]. The humic substances eventually form between 80 and 90% of all SOM and consist of heterogeneous molecular compounds containing different functional groups [52]. Humic substances (HSs) have received attention from scientists in a wide variety of disciplines [53]. The main precursor of an ecosystem approach for the study of HS in soils has been provided by the work of [48, 54, 55].

Basic information on HS could be accessed through the chemical characterization of SOM. So far, the study of HS composition has been carried out under the action of strong oxidants (alkaline solution) or heat to determine the single structural units. Alkaline extraction remains the most common method for detecting the solubility of HS from soil, according to the International Humic Substances Society (IHSS) [56]. Other extraction procedures using organic solvents are used [57].

Recent methods such as spectroscopic such as infrared, electron spin resonance, and nuclear magnetic resonance (NMR), microscopic, pyrolysis, ionization techniques have also enabled to elucidate various structural characteristics of humic acids, and NMR has recently brought about considerable progress in the study of humic acids [47, 51, 58]. [51] used infrared spectroscopy and nuclear magnetic resonance (NMR) to characterize humic and fluvic acids in aggregates collected from areas under different crop and soil management systems in Brazil. These methods allowed new aspects of research in organic soil chemistry and have been extensively used to quantify the proportions of functional groups as well as the aliphatic and aromatic contents of HS. In an review, [59] stated that the CPMAS technique provides a quantitative measure of aromatic, paraffinic, carboxylic acids, and other groups in fulvic acids (FA) and humic acids (HA). Using solid-state ^{13}C spectroscopy, [5] showed that there is considerable variability in the overall chemical composition of the various plant tissues of tropical forest trees (**Figure 4**). Due to the increasing demands for rapid and quantitative assessments of soil organic matter quality, thermal analysis techniques are a unique means to characterize the complete continuum that comprises soil organic matter. Among the most common thermal techniques, Rock-Eval pyrolysis [60, 61] has been increasingly applied to geologically recent sediment and soils [58, 62–65]. Details of the application of Rock-Eval to soils are provided elsewhere [58, 62, 64, 66, 67]. Rock-Eval provides information on quantity and quality of organic matter without sample preparation. It also gives information on stoichiometric of organic carbon [58, 68]. Disnar et al. [58] provided essential information on the amount and composition of tropical SOM. In addition to information on the abundance of SOM, Rock-Eval provides insight into the composition of SOM and even into its structure [58, 65]. In a recent review on pioneering works on SOM, [53] pointed out the great value of RE pyrolysis for soil scientists.

7. Humics substances and metal micronutrients

Humic substances are able to form stable complexes with metal micronutrients, due to the presence in their structure of oxygen-, nitrogen- and sulfur-containing functional groups [69]. Organic associations of the metals play an important role in storing and stabilizing SOM [e.g. 70, 71]. In the case of Fe, highly stable HS complexes mainly involve O-containing groups (carboxylic and phenolic groups) [72, 73]. More recently, it was shown that carboxylic acids in aliphatic domains are also involved in Fe(III)-HS complexation [74]. Stability and solubility of the complexes are both affected by pH and molar ratio between micronutrients and HS [75, 76]. [77] showed that pH controls Fe-humic substances complexes stability and/or solubility. Therefore, the presence of insoluble complexes may explain plants growth in calcareous soils characterized by limited Fe availability [78]. The stabilization of amorphous Fe oxides HS, which limited Fe availability, has been reported in previous studies [77, 79]. This is the result of co-precipitation of the poorly crystalline Fe phases and its maintenance for a long period in this form [77, 79]. This form would increase Fe reservoir for plant nutrition. [80] reported that the ability of HS to complex Fe can also be important for phosphorous nutrition, since phosphate can be bound to HS by Fe bridges. This process would increase phosphate availability; in fact, complexation of Fe by ligands released by plant roots could promote uptake of both nutrients.

HSs are known to be redox reactive and capable of chemically reducing metals including Fe^{3+} [81, 82]. Very acidic pH values cause the reduction of Fe3+ conversely, this reduction process is limited by formation of Fe3 + -HS complexes. Bioreduction of minerals soils can be accelerate by HS dissolved and solid-phase due to shuttling electrons from bacteria to oxide surfaces [83].

As recently reviewed by [47], the classical view on Al-humus complexes is based on complexation of Al3+ and Fe3+ ions by carboxylic and phenolic groups of humic substances. The degree of "metal–humus" complexation is quantified by ratios of Al, C, and Fe determined in pyrophosphate extracts. Although Al3+ and Fe3+ ions doubtlessly form complexes with carboxylic and phenolic groups [84].

8. Future challenges to humus analysis in tropical soil

Tropical environments share some similarities at the global scale (high productivity, rapid nutrient turnover, highly weathered soil, and low soil pH), but they also exhibit wide variation in soils and associated plant communities. In particular, different tropical regions possess distinct geological histories and plant communities [85]. Variation in climate, geology, and topography can cause diverse patterns and processes of plants, soils, and their interactions [86]. Similarly, the patterns of decomposition process reflected in humus form are highly variable. Most humus studies have been conducted in Amazonian forests [14, 24, 44], few studies have focused on humus in tropical soils in Africa in general and the Congo basin in particular. SOM humification and soil C accumulation are sensitive to climatic and local environmental fluctuations and changes in land use and soil management [87], comparison between tropical regions can provide variation in plant species, soil types, and availability of nutrients with which to investigate roles of soils and functions in tropical environment. Such knowledge is indispensable for the establishment of a sustainable management of the carbon budget maintaining or even improving at the same time major humus functions. In African tropical regions, previous studies focused on classification of humus forms. However, quantitative characteristic of humic substances is poorly studied. These studies can help to assess the role of humic substances in fertility and carbon sequestration in these very sensitive ecosystems.

Complexity of HS and their remarkable properties in agricultural applications has attracted and continues to attain the attention of many investigators, bringing over the years new knowledge on their structure, physicochemical, and biological properties. The effects of HS on plant growth depend on the source, concentration, and molecular weight of humic fractions and mainly on different chemical. Since humus substances might be a source of nutriments for plants, increasing tropical soil OM stocks are also beneficial for soil fertility in these regions known to be poor in nutrients. Many efforts to identify if it is mainly the chemical structure in terms of compounds or the molecular weight of HSs to influence plant growth and development must be carried out. The influence of soil humus in contributing to improve soil quality in its physical stability and capacity to provide nutriments to plants can also be studied.

Regarding tropical soil, humic substances can act as carbon, nitrous oxide, and others greenhouse gases sink playing a role in climate change. This role depends on its quality, quantity, and interaction with soil organo-mineral. Understanding chemical composition structure of humic substances in an ever-evolving environment (changes in land use, agricultural practices, climatic or edaphic conditions, etc.) is essential. To this purpose many research groups are addressing these scientific challenges while striving to overcome scientific knowledge gaps in these mechanisms.

The effect of HS in improving nutrient assimilation and plant metabolism is well recognized. Previous studies indicated that humic fraction increases cell growth, metabolism, and nitrate uptake [88, 89]. [90] has reported that root architecture and nutrients uptake are directed affected by humus, enhancing plant yield. In tropical countries, soils are poor in nutrients leading to the excessive use of fertilizers whose prices are constantly increasing [91]. In order to give the best route for this enormous amount of residues, what are humic substances, new technologies are needed, which in turn could help farmers to cope with the high cost of imported fertilizers.

On the methodological level, analytical techniques such as fluorescence, electron spin resonance, and size exclusion chromatography at high pressure are not yet applied to study humic substances in tropical soil. These techniques can be applied to investigate the molecular changes of humic molecules when in interactions with metals and organic compounds, for example.

9. Conclusions

The dynamics and function of humus forms in tropical forests are still poorly understood. The aims of this chapter were to review new approach tools, methods for qualitative and quantitative evaluation of humus in tropical environment attempting to provide a better understanding of humus forms in tropical. Diverse tools and methods for qualitative and quantitative evaluation of humus coming from diverse sources have been adopted so far to express transformation processes. For the characterization of humus and humic substances, the analytical techniques are applied. Mull, moder, and Amphimull are the dominant humus forms in the topsoil of tropical ecosystems. They differ by the distribution of organic and mineral-organic horizons. The quantity and quality of humic substances formed in soil depend on biotic and abiotic factors. The role and importance of organic matter in soils, and in particular of humus in tropical soils, have been proven. However, few studies have been undertaken in Africa in general and in the forests of the Congo Basin, which is the second largest carbon reservoir in the world. This is why the study of humus in these ecosystems must be carried out.

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Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this chapter.

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