



Review

The Central Role of Soil Organic Matter in Soil Fertility and Carbon Storage

Jörg Gerke

Ausbau 5, 18258 Rukieten, Germany; gerke.rukieten@t-online.de

Abstract: The aim of the paper is to give an overview on the chemistry of soil organic carbon (SOC) affecting nutrient availability, the emission of greenhouse gases and detoxifying harmful substances in soil. Humic substances represent the stable part of SOC, accounting for between 50 and more than 80% of organically bound carbon in soil. Humic substances strongly affect the soil solution concentration of several plant nutrients and may increase P-, Fe-, and Cu- solubility, thereby increasing their plant availability. Soil organic carbon, mainly humic substances, can detoxify monomeric Al in acid soils, can strongly bind toxic heavy metals, making them unavailable to the plant roots, and may strongly bind a vast variety of harmful organic pollutants. Increasing SOC is an important goal in agriculture. The inclusion of mixtures of semi-perennial plant species and cultivars may strongly increase SOC and humic substance content in soils. To increase SOC, farmyard manure and its rotted or composted forms are superior compared to the separate application of straw and slurry to soil. The storage of carbon, mainly in organic form, in soils is very important in the context of the emission of greenhouse gases. Worldwide, soils release about 10 times more greenhouse gases compared to fossil fuel combustion. Small increments in SOC worldwide will strongly affect the concentration of atmospheric CO₂. The public discussion on soil fertility and greenhouse gas emissions has been politically controlled in a way that leaves the important and positive contribution of soil organic carbon and mainly humic substances partly misinterpreted and partly underestimated.

Keywords: humic substances; nutrient availability; soil solution nutrient species; carbon storage; greenhouse gas emission; four per thousand goal



Citation: Gerke, J. The Central Role of Soil Organic Matter in Soil Fertility and Carbon Storage. *Soil Syst.* **2022**, *6*, 33. <https://doi.org/10.3390/soilsystems6020033>

Academic Editor: Yam Kanta Gaihre

Received: 21 January 2022

Accepted: 28 March 2022

Published: 31 March 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The production of human food is principally based on cultivation on arable soils and grassland. Additionally, the future of food production for human civilization also will be based on productive and sustainable cultivation on agricultural soils.

These basic statements are in strong contrast to several kinds of science fiction that tells us that soil-based food production may be overcome by new and more “modern” forms of food production, e.g., by using artificial substrates, by cultivation in nutrient solutions or by “vertical farming”.

A simple calculation may support the first statement that most of these science fiction scenarios are unrealistic if they are considered to contribute to human food production in a quantitative way.

A recent investigation of the phosphorus (P) status of German arable soils found reserves of on average 8 tons of P per hectare within 1 meter depth [1]. Considering the annual inorganic P fertilization of about 8 kg P/ha in Germany, this annual P input accounts for about onethousandth of the P reserves in soil. Soil P reserves are the dominant P source for plants. In countries with less P fertilization, the role of soil P reserves in actual plant P nutrition may be even more important. The availability of soil P to plants is often limited due to the strong fixation of P species such as orthophosphate and inositol phosphate species in the soil solid phase [2]. Phosphorus is an essential plant macronutrient, the

reserves of which are strongly limited [3–5]. Cordell and White [4] estimated the maximum production of phosphate fertilizers—P peak—for the year 2037.

In the case of P, it is evident that the soil P reserves are by far greater than the reserves for the production of P fertilizers. The production of artificial plant substrates will fail, partly due to the lack of sufficient P reserves worldwide. Moreover, these reserves are concentrated in a few countries, mainly Morocco, with 85% of soil P reserves [5]. The existing agricultural soils are the principal sites where most of the P reserves and food production are concentrated. Further, the supply of food for a growing human population strongly depends on the agricultural soils, today and in the future.

For the macronutrients N, S, K, Ca and Mg, the reserves worldwide are less limited. However, these reserves are unequally distributed over the world, which may lead to high fertilizer transport costs in the case of K, S, Ca and Mg. In the case of nitrogen (N), N₂-fixation by legumes accounts for an important part of the N supply available to cultivated plants. In ecological agriculture, N nutrition with mineral N fertilizers based on the Haber–Bosch synthesis is forbidden, which makes N₂fixation the main source by which N is introduced into agronomic rotations in ecological agriculture.

From the viewpoints of soil science and plant nutrition, two important aspects may be considered: the supply and cycling of plant nutrients at a high level, which is strongly affected by soil organic matter, and the management of soil organic matter for high soil fertility and high carbon storage in soils, which may compensate for increasing CO₂-concentrations in the atmosphere.

2. Organic Matter and the Cycling of Mineral Plant Nutrients

Soil organic matter, its stable components (humic substances) and its transient components can strongly improve nutrient availability and acquisition by higher plants. Soil organic matter also strongly affects nutrient storage and its availability in soils. For nitrogen (N) and sulfur (S), and in many soils for P, soil organic matter is the main pool of nutrient storage. In the case of micronutrients, especially iron (Fe) and copper (Cu), and to some extent zinc (Zn), soil organic matter determines the availability of these micronutrients to plants.

High yields in agriculture require adequate to high supplies of plant mineral nutrients—both macronutrients and micronutrients.

The role of soil availability and of plant acquisition in the uptake of both macro- and micronutrients by the roots of higher plants has been extensively investigated and described by several scientific groups, mainly those of S.A. Barber, USA [6], the group of P.H. Nye from England [7] and the group of A. Jungk from Germany [8].

The transport of the nutrients in soil takes place via mass flow and diffusion in the soil solution. Plant roots cannot absorb all species of a nutrient present in the soil solution. The uptake is restricted to only a few species. In the case of P, the two orthophosphate anion species, H₂PO₄[−] and HPO₄^{2−}, but probably not organic P species, are absorbed by the roots.

Therefore, the concentration of nutrients in the soil solution and the chemical species of the different nutrients in solution are of central importance for nutrient uptake by the roots. Mathematical nutrient uptake models using mechanistic models (see [6–8] and references therein) show the great sensitivity of nutrient soil solution concentrations for the calculated uptake by roots.

Additionally, the fraction of soil nutrients in the soil solid phase that is in equilibrium, either thermodynamically or kinetically controlled, with the soil solution is important since together with the nutrients in solution, it forms the quantity of plant-available nutrients.

Table 1 summarizes the most important chemical species of selected plant macro- and micronutrients in the soil solution and the mechanisms for their transfer from the soil solid phase to the soil solution.

Table 1. Selected chemical macronutrient and micronutrient species in the soil solution and the mechanisms of transfer into the soil solution.

Nutrient	Soil Solution Species	Transfer Mechanism
Nitrogen (N)	NO_3^- ; NH_4^+ Organic N	mineralization, nitrification desorption
Phosphorus/ Phosphate (P)	H_2PO_4^- ; HPO_4^{2-} ; organic P, humic-metal- P complexes	desorption; mineralization dissolution of humic-metal- P complexes
Potassium (K)	K^+ ; humic-K species?	desorption
Sulfur (S)	SO_4^{2-} ; organic S heterocyclic S?	mineralization; desorption dissolution of humic-S
Iron (Fe)	Fe(III), Fe(II) species humic-Fe complexes other organic Fe complexes	mineral dissolution, reduction dissolution of humic-Fe complexes desorption
Copper (Cu)	Cu(II), humic-Cu complexes other organic Cu- complexes	dissolution of humic-Cu complexes desorption, mineralization
Manganese (Mn)	Mn (II), Mn (III), Mn (IV) organic (humic)-Mn species?	reduction, desorption, dissolution

The central importance of soil organic carbon (SOC) and especially of humic substances for the soil solution concentrations of most of the mineral plant nutrients that are considered here is remarkable. Only in the case of K and Mn is the contribution of humic association to the solubility of the nutrients probably of minor importance.

For Fe and Cu, organic complexation is essential to increase Fe and Cu soil solution concentrations to meet plant requirements. In the case of Fe (III), soil solution concentrations in equilibrium with Fe-oxide such as goethite or ferrihydrite at $\text{pH} > 6.0$ are between 10^{-9} and 10^{-13} mol Fe/L, whereas Fe soil solution concentrations required to satisfy the needs of plant roots are 10^{-6} mol Fe/L or higher [9–11]. At soil pH values above 6, most of the Fe (III) in solution is organically complexed Fe (III). Among the organic complexants, humic-Fe complexes play a dominant role [12]. Even small additions of humic substances to calcareous soils may strongly improve Fe uptake by the plant roots by increasing the solubility of Fe (III) through the formation of humic-Fe (III) complexes. For a detailed discussion on the effect of humic substances on Fe acquisition by higher plants, see Zanin et al. [13].

Ecological farming systems are based on the cycling of organic N built up in the years when legumes and their mixtures, e.g., alfalfa/clover/grass mixtures, are cultivated within an agronomic rotation. In the subsequent years, organic N, e.g., that recovered in farmyard manure or directly accumulated in soil by semi-permanent legumes, may be mineralized to provide the non-legume crops with N. Such rotations may deliver a high level of nitrogen during the agronomic cycle without any application of mineral-N fertilizer. For N availability, the contribution of labile soil organic matter is evident. As a consequence, the organic to conventional yield gap may be small or even disappear [14,15].

In the case of P availability and P acquisition by higher plants, a strategy has been described that includes the formation of ternary humic-Fe (Al) P complexes in soil [16,17] and the excretion of di- or tricarboxylic acids by P-starving higher plants such as white lupin, yellow lupin, alfalfa, or red clover [18]. Humic-Fe(Al)-P complexes can account for more than 50% of soil P [19] and may be especially important in Podzols and Andosols [16]. Humic-P complexes may be split by carboxylates, releasing the orthophosphate anion into the soil solution [2]. Further, the reduction of Fe (III) to Fe (II) may release Fe from the humic complexes and simultaneously release adherent P ions. In P fixing soils, the increase in SOC as humic-C and the cultivation of carboxylate-excreting crops may be a promising way to improve P and Fe uptake by the plants. Both P and Fe are poorly soluble nutrients. Low Fe and P solubility, and not low absolute concentrations of both elements in soils, are the factors limiting their availability to plants.

Soil organic carbon plays, therefore, a central role in nutrient soil availability, strongly affecting N and probably S delivery to the plant roots and strongly affecting P, Fe and Cu availability. Increasing SOC and humic substance content in soils is considered to be a main factor to increase plant yields without or with less negative side effects [20].

3. Ecological Effects of Soil Organic Carbon

Soil organic carbon not only improves soil nutrient bioavailability but also affects soil fertility by various other mechanisms and is of central importance for the global C-cycle, which may strongly affect atmospheric CO₂-concentrations. Therefore, (a) soil organic matter management will be considered, and (b) its effect on soil fertility and (c) soil organic matter effects on greenhouse gas emissions will be discussed.

3.1. Soil Organic Matter Management

The content of soil organic matter and humic substances (HS) in agricultural soils strongly depends on the way these soils are cultivated. The aim is to maintain a high SOC level, from which organically bound nutrients such as N or S can be delivered to the plant roots at adequate and even high rates, through which the availability of plant nutrients may satisfy the demand of the plants. Thus, both high SOC levels and high rates of nutrient delivery from decomposing organic matter should be achieved.

Two agronomic instruments are especially important to achieve and maintain high SOC levels in soils. Soil fertilization with organic fertilizers containing stable organic carbon helps to increase SOC. Among these fertilizers, rotted farmyard manure, its composts, or composts from other sources may be very efficient [21,22]. The application of rotted farmyard manure and its composts is much more efficient for increasing SOC levels than the separate application of cattle, poultry or pig slurry separate from the application of straw [21]. Schrama et al. [15] showed, in a field trial with conventional versus ecological rotations, that organic matter content in the upper 20 cm was higher in the ecological than in the conventional treatment (5.5 vs. 4.4% *w/w*), probably due to the application of stable composts in the ecological treatment and to the very high quantities of compost that were applied. A key reason for the stability of organic carbon in rotted or composted farmyard manure is the formation of stable humic substances during the transformation process [23,24]. There is a close positive correlation between compost ripening and the humification/formation of humic substances [24–30].

Humification is initiated by radical formation by phenolic substances in soil and polymerization [31]. The aromatic oligomers or polymers can further react to incorporate labile organic molecules such as carbohydrates [32], amino acids, peptides and proteins [33,34]. Often, aromaticity of the HS is increased during composting [24–27,29], and the content of polycyclic aromatic carbon (PAC) may also be increased during compost ripening [26,35]. Ikeya et al. [36,37] suggested that PAC in HS may be responsible for the persistence of these organic molecules. The group of P. Hatcher has recently shown in several papers that PAC units of HS are formed from lignin [38–40]. Thus, the assumption that PAC in soils is indicative of pyrogenous carbon is wrong, as shown by Chang et al. [41]. This is further considered in Sections 3.3.2 and 3.3.3.

Because of the central role of HS for high SOC stocks in soils, there are efforts to add HS to soils. One way is to recover and add oxidized coals, which represent rather stable humic substances—Leonardite—to soils. Additionally, humification products from plant residues [42] or especially from lignin [43] are suggested. The question with respect to SOC is the effect of such additions, i.e., what quantities of humic amendments remain stable in soil and to what extent can the added humic molecules bind and stabilize additional organic carbon in soil. This question will be considered again in II.c.

Crop rotations are also of central importance in maintaining increasing soil organic carbon content. If semi-perennial cultivars such as alfalfa, clover and grass species as well as their mixtures are integrated into the agronomic rotations, then a combination of zero or reduced tillage, high production of organic residues, e.g., dead roots, litter and leaves,

and root-released organic carbon and photosynthetic activity during the whole vegetative period may strongly increase SOC content in arable soils. Further, if mixtures of deep rooting cultivars (alfalfa) together with grasses that show high rooting density in the upper layers of soil are cultivated, the additive effect on soil organic carbon from these mixtures may be even higher. These factors make years of alfalfa/clover/grass mixtures within a rotation highly valuable to maintaining and increasing soil fertility. Könnecke (p. 22, [44]) summarized root masses of different crops and mixtures and showed that alfalfa released high quantities of root residues that are partly located in the subsoil below 1 m. Red clover showed a similar but less-pronounced rooting pattern. There are a variety of perennial or semi-perennial legume species that may be cultivated for this purpose in temperate soils, among them alfalfa, red clover, white clover, Swedish clover, and in special situations, medic clover species.

Gattinger et al. [45] compared carbon stocks in ecologically and conventionally managed soils and found higher SOC stocks and higher SOC accumulation rates in the ecologically managed soils. They attributed the differences to the incorporation of alfalfa/clover/grass mixtures within the rotation, since in ecological farming, no mineral fertilizers from the Haber–Bosch production are allowed. The N input into soil principally requires N₂-fixation by legumes such as alfalfa and clover species, among them red clover, white clover, Swedish clover or medic clover. The results that Gattinger et al. [45] observed were based on a meta-analysis of existing data.

Forstreuter [46] proved that plants such as alfalfa integrated within an agronomic rotation can increase SOC stocks. In most of the field trials comparing ecological and conventional agriculture, the mechanisms by which carbon accumulation in soil may occur were not resolved. Ecological agriculture differs from conventional agriculture by three main characteristics: no mineral N fertilizer, no organic pesticides, and legumes in the rotation to satisfy crop demand for N. In a field trial at the Georg-August-University of Göttingen from 1982 to 1998, the parameters of N-fertilization, pesticide application and with or without alfalfa in the rotation were treated as independent factors. After 2.5 rotations, the SOC concentrations within the upper 20 cm of the soils were about 10 t SOC/ha higher in the treatment with alfalfa in the rotation [46]. This difference on this high-yielding fertile soil may be even higher considering not only the upper 20 cm of soil but the whole rooting zone.

Ghabbour et al. [47] compared results for soil organic matter (SOM) and humic substance concentrations in organically and conventionally managed soils in the USA. They included 659 and 728 samples, respectively, of organically and conventionally managed soils represented in a large database. The average concentration of SOM was (*w/w*) 7.37 for the conventional and 8.33 for the organic soils. The humification rate (%) was also higher in the organic soils compared to the conventional soils, at 57.3 vs. 45.6. They explained their results in terms of intensive, conventional agriculture as a “known source of greenhouse gas emissions, . . . decline in SOM” and characterized organic farming as including “many of the practices which are known to maintain or to increase SOM are central to organic agriculture” [47]. This statement regarding intensive conventional agriculture may be indeed justified. It should, however, be mentioned that recent developments in organic agriculture seek to copy some of the developments of conventional agriculture, including the separation of cattle production and crop production together with inputs of organic fertilizer nitrogen from conventional farms, which make it easier to abandon alfalfa/clover/grass mixtures in the rotation and instead focus on the cultivation of cash crops.

For loess soils in a semiarid environment (annual precipitation of about 380 mm), Song et al. [48] found that after 17 years of differential cultivation, the soil sown with alfalfa contained about 10 t more SOC/ha compared to fallow soil. However, in the experiment described by Song et al. [48], alfalfa was not harvested or grazed. Even under these conditions, alfalfa dominated the vegetation [49]. Another deep-rooting legume, medic clover, showed similar but less-pronounced effects compared to alfalfa, probably due to smaller soil cover of the species in the experiment [49]. These results underline the potential

of deep-rooting, perennial plants to increase SOC stocks in soils. Humification processes may be central for this process, since stable organic molecules may be formed that may additionally bind and stabilize labile carbon molecules in soil [34,50,51].

3.2. Soil Organic Matter and Soil Fertility

Besides the prominent role of SOC, and especially of humic substances on soil nutrient availability, as evident for N, S, P, Fe and Cu, there are additionally important chemical features by which SOC and mainly humic substances may improve soil fertility.

Soil humic substances affect several biochemical pathways in plants. They act like plant hormones [11,20,52,53]. Humic substances increase root growth, the formation of root hairs and lateral roots, and the release of organics by the roots [20]. Humic acids sometimes act similarly to auxins, which induce mitotic sites in the roots and induce root proliferation [54–56]. One central plant physiological process that is affected by HS is the increase in the activity of the plasma membrane H⁺-ATPase [57], which in turn induces acidification of the rhizosphere, promotes root growth, and activates nutrient transporters in the roots and the release of organic acids [58].

Strong interactions between soils and roots exist and are called soil/root crosstalk mediated by soil HS [52,53,59]. Root exudates such as organic acids affect humic substances by dissolving them and by exposing plant hormone-active sites that in turn affect, among other factors, the release of organic acid anions from the roots. The extent of this process depends on the physiology of the plants and on the chemical characteristics of the HS.

Humic substances can bind inorganic and organic xenobiotics. For example, heavy metals may be bound to HS due to their high content of acidic groups (2–12 meq/g) and to the fact that heavy metals such as Pb, Cd, Zn or Hg may be specifically bound to HS. By this detoxification, soils may become more fertile. Spark et al. [60] investigated the interaction of humic acids with Cu (II), Zn (II), Cd (II) and Co (II) in the pH range 3–8.5. They showed the dominant effect of humic acids on the solubility of the four metals in the considered pH range. At low pH, around 3, the metal solubility was high. By increasing the pH, first the sorption of the metals to the precipitated humic surface decreased metal solubility. At higher pH, often above 7.0, metal solubility was increased due to the dissolution of the humic–metal complexes [60].

Soil humic substances can alleviate Al toxicity, which is relevant in acid soils with pH values below 5.0, where monomeric Al species are present in the soil solution. Humic substances in the soil solid phase can bind monomeric Al. Humic fractions in the soil solution may complex and detoxify monomeric Al (Haynes and Mokolobate [61]). Suthipradit et al. [62] investigated the root growth-inhibiting effect of monomeric Al in the range of 0–50 µmol/L. Without organic ligands in the soil solution, roots reacted to higher Al concentrations with a strong reduction in root length. Oxalate and malate in concentrations from 0–50 µmol/L had a small curative effect; however, fulvic acid (65 mg C/L) fully eliminated Al-induced root growth limitations. The chosen fulvate concentration is often found in the soil solution of soils relatively rich in HS. If the chosen concentration is calculated in carboxylate equivalents, it may account for about 200 µeq–COOH/L, assuming 3 eq–COOH/g humic matter, which may help to understand the strong positive effect of fulvate in alleviating Al toxicity. The humic fraction of fulvic acids often represents by far the most dominant source of carboxylic groups in the soil solution.

Organic soil contamination by pesticides, surfactants or other xenobiotics may be reduced by sorption to and incorporation into the humic molecules, thereby inactivating the xenobiotics. However, the development of “bound residues” may also accelerate the accumulation of xenobiotics in soils. For deeper insight, the reader is referred to a recent review by Chianese et al. [63].

3.3. Soil Organic Matter and Greenhouse Gas Emissions

The discussion on greenhouse gas emissions and their consequences is not simply a dispute between scientists alone, but is strongly politically affected and controlled,

which means that correct and important scientific arguments sometimes considered of less relevance if they are in contrast to dominant political interests.

I will consider three aspects that may underline the above statement and will present arguments for a more scientifically based discussion concerning soil organic carbon and greenhouse gas emissions.

3.3.1. First: Carbon Dioxide Emission Sources!

In many western countries including the USA and Germany, the political focus towards greenhouse gas emissions is on the CO₂-released by fossil energy combustion. For the reduction of CO₂-emissions from this source, strongly restrictive policies have been formulated and partly already applied. However, soil organic matter represents the greatest carbon pool, which is reported to be between 2 and more than 3 [kg C * 10¹⁵], [64,65]. Soils contain more carbon than the atmosphere and vegetation combined [66]. Because soil carbon is by far the greatest C pool, consequently changes in soil organic carbon will strongly affect CO₂- concentrations in the atmosphere.

From this point of view, what Hayes and Clapp [67] stated already about 20 years ago is realistic, namely, that worldwide the net release of CO₂ from soils is higher by a factor of 10 than CO₂ evolution from fossil fuel combustion.

In a more recent review on greenhouse gas emissions, Oertel et al. [68] calculated that worldwide, annual CO₂ net emissions from soils are 350 [kg CO₂ equivalents * 10¹²] compared to the CO₂ released by fossil fuel combustion of 33.4 [kg CO₂ * 10¹²]. Worldwide, today greenhouse gas emissions from soils are, by a factor of more than 10, higher than those from fossil fuel combustion. In the future, fuel combustion will be restricted by political decisions, whereas efforts to reduce net CO₂ (and N₂O and CH₄) released from soils will, despite its quantitative importance, be a matter of scientific discussion and political statements but not actions.

At present, changing routines in agriculture, horticulture and cultivation of forest soils to reduce emissions is a neglected option within the political discussion today. Industrialized agriculture, increasing mineral N application, soil compaction by heavy machines in agriculture and forestry, separation of plant production and domestic cattle production, the increasing irrelevance of farmyard production and composting within the frame of industrialized agriculture, and cultivation without years of alfalfa/clover/grass in the rotations will further increase greenhouse gas emissions from soils. However, industrializing agriculture is a core political goal of many governments worldwide. This conflict probably led to a political declaration.

3.3.2. Second: The 4 per 1000 Initiative of the Paris Agreement!

During the discussion of the Paris Agreement in 2015, a 4 per 1000 target was announced, aiming for the storage of more carbon in soils worldwide. Accordingly, it was recommended to increase the organic carbon stocks in agricultural soils yearly by about 0.4% of their already existing organic carbon stocks. This target may have been formulated by scientists with participation by soil scientists.

In 2017, soil scientists from different regions of the world published a paper in which regional case studies from all over the world presented the status quo on SOC and estimated the potential of increasing carbon stocks in the respective regions [69]. In their introduction, they mentioned reduced tillage in combination with legume cover crops as a principal instrument to increase soil organic carbon [69]. They did not mention compost, rotted farmyard manure or alfalfa/clover/grass mixtures in temperate soils as instruments for sustainable, organic carbon-increasing agriculture. Under “legumes”, such plant species were summarized as those with high and deep rooting intensity (e.g., alfalfa, *Medicago sativa*) or extremely low rooting intensity (e.g., pea, *Pisum sativum*). Thus to call “legume” cultivation an instrument to increase soil organic carbon is at least misleading.

Rumpel et al. [70], in discussing “Paris climate pledges”, also mentioned the cultivation of “nitrogen-fixing plants” and included in this group oilseed rape! Lack of agronomic

knowledge was also evident in another paper related to the 4 per 1000 goal, the paper of Wiesemeier et al. [71]. They discussed the feasibility of the 4 per 1000 initiative in Bavaria, Germany. They mentioned the instruments agroforestry and cover crops as the most effective management options, but did not consider years of alfalfa/clover/grass within a rotation or farmyard manure or compost instead of separate slurry and straw applications to soil.

Ernst Klapp, one of the most influential German agronomists of the 20th Century, wrote in the 6th edition of his “Lehrbuch des Acker- und Pflanzenbaus” (scientific textbook on agronomy and crop production) about the effects of farmyard manure on humus/SOC content. Yearly applications of 8–12t farmyard manure increased the humus content by about 0.022% each year (on a weight basis related to the whole soil (Klapp, p. 184, [72]). He further noted that the organic matter content of arable soils is often between 2 and 5%, but can be increased in soils with rotations including clover/grass to about 7–8% (Klapp, p. 179, [72]). In permanent grassland, the organic matter content can be higher than 10% (Klapp, p. 179, [72]). Considering these well-known results, it is astonishing that present-day soil scientists talking and writing about the 4 per 1000 initiative did not discuss the potential of farmyard manure and years of semi-permanent alfalfa/clover/grass in crop rotations. These results are well-known. One additional aspect of alfalfa, or medic clover and to some extent, red clover, is their ability of deep rooting, which may induce stable organic C in soil depths below 1m, as evident from the results reported by Könnecke (p. 22, [44]). Könnecke also reported root masses for different crops. Under alfalfa or clover/grass mixtures, 40–80 dt root dry matter per hectare were found, which is between 250 and 333% of the root matter found under cereals (Könnecke, p. 23, [44]). Additionally, different cover crops strongly vary in their ability to produce root matter, increasing from stubble cover crops over winter cover crops to undersown cover crops that have root masses similar to cereals grown as cash crops (Könnecke, p. 22, [44]). The conclusion is that cover crops represent a wide variety of crops and cultivation methods with different abilities to produce root mass, which should be treated differently with respect to their rooting patterns and effects on soil organic carbon content.

Baveye and White [73], among others, recently criticized the 4 per 1000 initiative. Their main argument is that the goal is unrealistically high and may lead to inactivity, e.g., toward reducing fossil fuel consumption. In my opinion, the basic knowledge on SOC accumulation in soils has been buried or lost in the past, which make the discussion on the 4 per 1000 goal somewhat arbitrary. Another, even more important aspect has not been considered. The accumulation of SOC under the 4 per 1000 initiative is a goal that aims for higher SOC stocks in soils. However, plant nutrients, i.e., N, S, and P, are stored in the organic matter. High SOC levels and high transformation rates of SOC should be balanced. This is the real task of the discussion on SOC stocks in soils.

A corollary statement on the 4 per 1000 initiative is that the desired increase in SOC is related to actual SOC stocks in soils, which leads to the next point.

3.3.3. Third: According to the 4 per 1000 Goal, the Increase in SOC Should Be Higher in Soils Where the SOC Is High Compared to Other Soils!

Evidence for such an assumption requires a concept where additional SOC binding in soils depends on the level of organic matter in the soils. The 4 per 1000 initiative implicitly refers to the concept of humic substances as a major component of stable organic carbon in soils. According to Piccolo [74] or Ghabbour et al. [75], humic substances make up between 50 and more than 80% of SOC. Humification is, after photosynthesis, the second largest process in the carbon cycle [76].

One key feature of HS that may give sense to the 4 per 1000 initiative is the ability of soil humic substances to bind, to incorporate and to stabilize additional organic molecules even if they are labile [32–34]. The underlying mechanisms and the quantitative effects have been described by Martin and Haider [34], Swift [50], Piccolo et al. [51] and Gerke [31] (Figure 2). For example, decomposition of the free amino acids glycine and lysine was

reduced from 85 to 22% and 78 to 17%, respectively, if the amino acids were linked to humic acid polymers (34).

Considering HS in soils, there are attempts to use their potential to increase SOC. The group of the Italian soil chemist Alessandro Piccolo developed a model of humic substances where supramolecular associations of relatively small humic units are stabilized by weak chemical forces [74,77]. The induction of polymerization of the humic associates leads to true humic polymers [78–80]. This process of humic polymerization may increase the SOC content by 2.24–3.90 t SOC/year, since the humic polymers are much more resistant against degradation than supramolecular associates stabilized by weak chemical forces [81]. The induction of polymerization reactions described by Piccolo and coworkers may not be restricted to supramolecular associates, since polymerization of humic matter may be limited either by lack of substrate or of catalyst required for the polymerization reactions. For example, Fuentes et al. [24] stated that humic macromolecules and humic supramolecular structures may both be present in soils. The initiation of polymerization of humic units as an instrument to stabilize humic matter and, consequently, to increase SOC in soils has been well-known for a long time. However, it plays no role in the discussion of how to increase SOC in agricultural soils.

The frequently recommended zero tillage, minimum tillage or reduced tillage practices as instruments to increase SOC should be discussed more carefully. In a detailed overview, Ogle et al. [82] evaluated where and under what conditions no-till management may increase SOC content. They compared no-till and full-till management in 0–80 cm soil depths for various soils and climatic conditions. Soil organic carbon stocks were higher for no-till in the 0–20 cm depth, whereas below 20 cm, in many cases the SOC stocks were higher in the full-till treatment. Higher SOC stocks in the upper horizons for the no-till treatment may be compensated by higher SOC stocks below 20 cm for the full-till treatment [82]. Tillage effects on SOC are rather complex and not as simple as assumed by Rumpel et al. [70] and Wiesemeier et al. [71].

Some key question sare to what extent soil organic carbon will accumulate in soil and to what extent soil organic carbon will be mineralized and contribute to the delivery of mineral plant nutrients. This question needs to be resolved within a scientific discussion on the 4 per 1000 initiative, aside from the question of whether the 4 per 1000 goal is realistic.

Another mechanism of SOC accumulation is related to recent humic substances. The application of oxidized brown coals such as leonardite introduces very stable humic substances into soil. Erro et al. [83] suggested a chemical structure for leonardite. Such substances may act as soil amelioration for increasesin SOC. Leonardite molecules may also act as binding agents for labile organic molecules. Moreover, leonardite molecules with their aromatic sites may act as nuclei for further humification reactions in soil, which in turn may strongly increase SOC content. The initial step for the polymerization of soil humic substances is the formation of phenolic radicals (Ziechmann, p. 142, [84]; Gerke [31], Figure 1). Adding highly oxidized and polymerized humic substances such as leonardite introduces specific redox systems into soil. Humic substances are reported to have standard reduction potentials (E°) between 0.15 and 0.80 V (Ziechmann, pp. 50–52, [84]). The E° of the reaction hydroquinone—quinone is about 0.703 V (Ziechmann, (p. 53, [84]). Humic substances must, however, act as oxidizing agents for phenols, which is not very probable considering the reported E° values. Additionally, Visser [85] found that with increasing humification, E° is lowered. However, natural humic substances also act as complexing agents for Fe (III) and probably Mn (IV) or (III). Leonardite may bind phenolic compounds, and Fe (III) complexed by leonardite may induce radical formation of phenolic compounds as a first step to humic polymerization. Leonardite may act as catalyst mediated by metals at the humic surface, as shown by Trommler [86] for the (catalytic?) oxidation of polycyclic aromatic hydrocarbon species by coal humic acid and by synthetic humic acids from hydroquinone. Leonardite as a catalyst for the formation of humic substances in soils? This may be a relevant hypothesis that should be tested!

Under the assumption, and only under the assumption, that a great portion of SOC is made up by humic substances, the goal of increasing carbon binding in soil by increasing SOC content as an included condition of the 4 per 1000 initiative may be justified. The problem, however, is that despite their relevance in soil science, and especially in organic soil chemistry, humic substances are mainly ignored within political discussions.

A prime example: One year after the Paris agreement, in 2017, the FAO published a paper: Soil organic carbon, the hidden potential (FAO [87]). In this paper, the authors define a specific carbon saturation of soils (FAO, p. 7, [87]), but soil humic substances are not even mentioned. In the FAO paper, the positive role of biochar, i.e., manufactured black/pyrogenic carbon is mentioned. It is evident that the FAO paper was formulated by ignoring the research and results of the great group of soil scientists working on humic substances. Two of the most experienced organic soil chemists, M.H.B. Hayes and R.S. Swift, recently gave an extended overview on humic substances in the environment and proved that these chemical molecules are not to be ignored in the description of chemical, biochemical and biological processes in soil (Hayes and Swift [88]).

As for the FAO report, the recommendations to apply biochar to introduce stable organic carbon into soils, which also are assumed to increase soil fertility, are based on publications that linked high soil content of black carbon to the fertility of these soils, among them Amazonian dark earths (Glaser et al. [89]), European chernozems (Schmidt et al. [90,91]) and soils in the USA (Skjemstad et al. [92]). However, the methods by which BC contents in soils were measured overestimated BC by a factor of 10 or more (Chang et al. [41]; Gerke [93]). Moreover, the effect of biochar on soil fertility was recently evaluated by Jeffrey et al. [94], who showed that the positive biochar effect on yield is restricted to tropical soils and is exclusively a nutrient and pH effect even at high application rates. In cases where biochar was positive for plant yield, the organic matter may be better used for composting in order to produce stable humic substances.

4. Conclusions

At present, it seems that changing the management of agricultural and forest soils to support sustainable methods to improve soil fertility and reduce greenhouse gas emissions is deliberately only a scientific and political goal and nothing more. Industrialized agriculture is highly energy- and resource-consuming and may reduce soil fertility and increase greenhouse gas emissions. Sustainable methods of agriculture should be adopted in the future. Managing soil organic matter and increasing the content of humic substances in soils the right way will be of central importance for sustainable agriculture.

Funding: This research has received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The author declares conflict of interests.

References

1. Gocke, M.I.; Don, A.; Heidkamp, A.; Schneider, F.; Amelung, W. The phosphorus status of German cropland—An inventory of top- and subsoils. *J. Plant Nutr. Soil Sci.* **2021**, *184*, 51–64. [[CrossRef](#)]
2. Gerke, J. The acquisition of phosphate by higher plants: Effect of carboxylate release by the roots. A critical review. *J. Plant Nutr. Soil Sci.* **2015**, *178*, 351–364. [[CrossRef](#)]
3. Römer, W. Ansätze für eine effiziente Nutzung des Phosphors auf der Basis experimenteller Befunde. *Ber. Landw.* **2009**, *87*, 5–30.
4. Cordell, D.; White, S. Peak phosphorus. Clarifying the key issues of a rigorous debate about long-term security. *Sustainability* **2011**, *3*, 2027–2049. [[CrossRef](#)]
5. Cordell, D.; White, S. Life's bottleneck: Sustaining the world's phosphorus for a food secure future. *Environ. Res.* **2014**, *39*, 161–168.
6. Barber, S.A. *Soil Nutrient Bioavailability*; John Wiley: New York, NY, USA, 1995.
7. Tinker, P.B.; Nye, P.H. *Solute Movement in the Rhizosphere*; Oxford University Press: Oxford, UK, 2000.

8. Jungk, A. Dynamics of Nutrient Movement at the Soil-Root Interface. In *Plant Roots, the Hidden Half*; Waisel, Y., Eshel, A., Kafkafi, U., Eds.; Dekker: New York, NY, USA, 2002; pp. 587–616.
9. Schwertmann, U. Solubility and dissolution of iron oxides. *Plant Soil* **1991**, *130*, 1–25. [[CrossRef](#)]
10. Gerke, J. Mathematical modeling of iron uptake by graminaceous species as affected by iron forms in soil and phytosiderophore efflux. *J. Plant Nutr.* **2000**, *23*, 1579–1587. [[CrossRef](#)]
11. Gerke, J. The effect of humic substances on phosphate and iron acquisition by higher plants: Qualitative and quantitative aspects. *J. Plant Nutr. Soil Sci.* **2021**, *184*, 329–338. [[CrossRef](#)]
12. Gerke, J. Aluminum and iron (III) species in the soil solution including organic complexes with citrate and humic substances. *J. Plant Nutr. Soil Sci.* **1997**, *160*, 427–432. [[CrossRef](#)]
13. Zanin, L.; Tomasi, N.; Cesco, S.; Varanini, Z.; Pinton, R. Humic substances contribute to plant iron nutrition acting as chelators and biostimulants. *Front. Plant Sci.* **2019**, *10*, 675. [[CrossRef](#)] [[PubMed](#)]
14. Ponisio, L.C.; M'Gonigle, L.K.; Mace, K.C.; Palomino, J.; deValpine, P.; Kremen, L. Diversification practices reduce organic to conventional yield gap. *Proc. R. Soc. B* **2014**, *282*, 1396–1403. [[CrossRef](#)] [[PubMed](#)]
15. Schrama, M.; De Haan, J.J.; Kroonen, M.; Verstegen, H.; Van der Putten, W.H. Crop yield gap and stability in organic and conventional farming systems. *Agric. Ecosyst. Environ.* **2018**, *256*, 123–130. [[CrossRef](#)]
16. Gerke, J. Humic (organic matter)-Al(Fe)-phosphate complexes: An underestimated phosphate form in soils and source of plant available phosphate. *Soil Sci.* **2010**, *175*, 417–425. [[CrossRef](#)]
17. Urrutia, O.; Erro, J.; Guardado, L.; San Francisco, S.; Mandado, M.; Baigorri, R.; Claude Yvin, J.; Garcia-Mina, J. Physico-chemical characterization of humic-metal-phosphate complexes and their potential application to the manufacture of new types of phosphate-based fertilizers. *J. Plant Nutr. Soil Sci.* **2014**, *177*, 128–136. [[CrossRef](#)]
18. Gerke, J. *Chemische Prozesse der Nährstoffmobilisierung in der Rhizosphäre und ihre Bedeutung für den Übergang vom Boden in die Pflanze*; Cuivillier-Verlag: Göttingen, Germany, 1995.
19. Gerke, J.; Jungk, A. Separation of phosphorus bound to organic matrices from inorganic phosphorus in alkaline soil extracts by ultrafiltration. *Commun. Soil Sci. Plant Anal.* **1991**, *22*, 1621–1630. [[CrossRef](#)]
20. Canellas, L.P.; Olivares, F.L. Physiological responses to humic substances as plant growth promoter. *Chem. Biol. Technol.* **2014**, *1*, 1–11. [[CrossRef](#)]
21. Körschens, M.; Albert, E.; Baumecker, M.; Ellmer, F.; Grunert, M.; Hoffmann, S.; Kismanyoky, T.; Kubat, J.; Kunzova, E.; Marx, M.; et al. Humus und Klimaveränderung—Ergebnisse aus 15 langjährigen Dauerfeldversuchen. *Arch. Agron. Soil Sci.* **2014**, *60*, 1485–1517. [[CrossRef](#)]
22. Gerke, J. Carbon accumulation in arable soils: Mechanisms and the effect of cultivation practices and organic fertilizers. *Agronomy* **2021**, *11*, 1079. [[CrossRef](#)]
23. Inbar, Y.; Chen, Y.; Hadar, Y. Humic substances formed during composting of organic matter. *Soil Sci. Soc. Am. J.* **1990**, *54*, 1316–1323. [[CrossRef](#)]
24. Fuentes, M.; Baigorri, R.; Garcia-Mina, J. Maturation in composting process, an incipient humification-like step as multivariate statistical analysis of spectroscopic data shows. *Environ. Res.* **2020**, *189*, 109981. [[CrossRef](#)]
25. Chen, Y.; Inbar, Y. Chemical and spectroscopic analyses of organic matter transformation during composting in relation to compost maturity. In *Science and Engineering of Composting: Design, Environmental, Microbial and Utilization Aspects*; Hoitink, H.A.J., Keener, H.M., Eds.; Ohio State University: Wooster, OH, USA, 1993; pp. 551–600.
26. Baddi, G.A.; Hafidi, M.; Gilard, V.; Revel, J.C. Characterization of humic acids produced during composting olive mill wastes: Elemental and spectroscopic analyses (FTIR and ¹³C NMR). *Agronomie* **2003**, *23*, 661–666. [[CrossRef](#)]
27. Huang, G.F.; Wu, Q.T.; Wang, J.W.C.; Naggar, B.B. Transformation of organic matter during co-composting pig manure with saw dust. *Biores. Technol.* **2006**, *97*, 1834–1842. [[CrossRef](#)]
28. Adani, F.; Genevini, P.L.; Tambone, F.; Montoneri, E. Compost effect on soil humic acid. A NMR study. *Chemosphere* **2006**, *65*, 1414–1418. [[CrossRef](#)] [[PubMed](#)]
29. Adani, F.; Spagnol, M. Humic acid formation in artificial soils amended with compost at different stages of organic matter evolution. *J. Environ. Qual.* **2008**, *37*, 1608–1616. [[CrossRef](#)] [[PubMed](#)]
30. Smidt, E.; Meissl, K.; Schmutzer, M.; Hinterstoisser, B. Co-Composting of lignin to build up humic substances—strategies in waste management to improve compost quality. *Industr. Crop Product.* **2008**, *27*, 196–201. [[CrossRef](#)]
31. Gerke, J. Concepts and misconceptions of humic substances as a stable part of soil organic matter: A review. *Agronomy* **2018**, *8*, 76. [[CrossRef](#)]
32. Piccolo, A.; Spaccini, R.; Nieder, R.; Richter, J. Sequestration of biologically labile organic carbon in soils by humified organic matter. *Clim. Change* **2004**, *67*, 329–343. [[CrossRef](#)]
33. Verma, L.; Martin, J.P.; Haider, K. Decomposition of ¹⁴C-labelled proteins, peptides and amino acids: Free and complexed with humic polymers. *Proc. Soil Sci. Soc. Am.* **1975**, *39*, 279–284. [[CrossRef](#)]
34. Martin, J.P.; Haider, K. Influence of Mineral Colloids on Turnover Rates of Soil Organic Carbon. In *Interactions of Soil Minerals with Natural Organics and Microbes*; Huang, P.M., Schnitzer, M., Eds.; Soil Science Society America: Madison, WI, USA, 1986; pp. 283–304.

35. Chen, Y.; Chefetz, B.; Hadar, Y. Formation and properties of humic substances originating from composts. In *The Science of Composting*; De Bertoldi, M., Sequi, P., Leumes, B., Papi, T., Eds.; Springer: Dordrecht, NL, USA, 1996; pp. 382–393.
36. Ikeya, K.; Sleighter, R.L.; Hatcher, P.G.; Watanabe, A. Characterization of the chemical composition of soil humic acids using Fourier transform ion cyclotron resonance spectroscopy. *Geochim. Cosmochim. Acta* **2015**, *153*, 169–182. [[CrossRef](#)]
37. Ikeya, K.; Maie, N.; Han, X.; Wang, G.; Watanabe, A. Comparison of skeletal structures in black humic acids from different soil origins. *Soil Sci. Plant Nutr.* **2019**, *65*, 109–113. [[CrossRef](#)]
38. Waggoner, D.C.; Chen, H.; Willoughby, A.S.; Hatcher, P.G. Formation of black carbon-like and alicyclic aliphatic compounds by hydroxyl radical initiated degradation of lignin. *Org. Geochem.* **2015**, *82*, 69–76. [[CrossRef](#)]
39. Di Donato, N.; Chen, H.; Waggoner, D.; Hatcher, P. Potential origin and formation for molecule components of humic acids in soils. *Geochim. Cosmochim. Acta* **2016**, *178*, 201–222.
40. Waggoner, D.C.; Hatcher, P.G. Hydroxyl radical alteration of HPLC fractionated lignin: Formation of new compounds from terrestrial organic matter. *Org. Geochem.* **2017**, *113*, 315–325. [[CrossRef](#)]
41. Chang, Z.; Tian, L.; Li, F.; Zhou, Y.; Wu, N.; Steinberg, C.; Dong, X.; Pan, B.; Xing, B. Benzene carboxylic acid—A useful marker for condensed organic matter but not only for pyrogenic black carbon. *Sci. Tot. Environ.* **2018**, *626*, 660–667. [[CrossRef](#)]
42. Yang, F.; Tang, C.; Antonietti, M. Natural and artificial humic substances to manage mineral ions, water, and soil microorganisms. *Chem. Soc. Rev.* **2021**, *50*, 6221–6239. [[CrossRef](#)] [[PubMed](#)]
43. Lee, J.G.; Yoon, H.Y.; Chu, J.-Y.; Kim, W.-Y.; Kim, P.J.; Jeon, J.-R. Artificial humification of lignin architecture: Top-down and bottom-up approaches. *Biotechnol. Adv.* **2019**, *37*, 107416. [[CrossRef](#)]
44. Könnecke, G. *Fruchtfolgen*; DeutscherLandwirtschaftsverlag: Ostberlin, Germany, 1967.
45. Gattinger, A.; Müller, A.; Haeni, M.; Skinner, C.; Fließbach, A.; Buchmann, N. Enhanced topsoil carbon stocks under organic farming. *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 18226–18231. [[CrossRef](#)]
46. Forstreuter, T. Bodenfruchtbarkeitskennwerte und Kulturpflanzenenertrag in zwei Bodennutzungssystemen. Ph.D. Thesis, Georg-August-Universität, Göttingen, Germany, 1999.
47. Ghabbour, E.A.; Davies, G.; Misiewicz, T.; Alami, R.A.; Askounis, E.M.; Cuzzo, N.P.; Filice, A.J.; Haskell, J.M.; Moy, A.K.; Roach, A.C.; et al. National comparison of the total and sequestered organic matter contents of conventional and organic farm soils. *Adv. Agron.* **2017**, *146*, 1–35.
48. Song, X.; Fang, C.; Yuan, Z.-Q.; Li, F.-M. Long-term growth of alfalfa increased soil organic matter accumulation and nutrient mineralization in a semi-arid environment. *Front. Environ. Sci.* **2021**, *9*, 649346. [[CrossRef](#)]
49. Yuan, Z.-Q.; Yu, K.-L.; Epstein, H.; Fang, C.; Li, J.-T.; Lui, Q.-Q.; Lin, X.-W.; Guo, W.-J.; Li, F.-M. Effects of legume species introduction on vegetation and soil nutrient development on abandoned croplands in a semi-arid environment on the loess plateau, China. *Sci. Tot. Environ.* **2016**, *541*, 692–700. [[CrossRef](#)]
50. Swift, R.S. Sequestration of carbon by soils. *Soil Sci.* **2001**, *166*, 858–871. [[CrossRef](#)]
51. Piccolo, A.; Spaccini, R.; Drosos, M.; Vinci, M.; Cozzolino, V. The molecular composition of humus carbon: Recalcitrance and reactivity in soils. In *The Future of Soil Carbon*; Garcia, C., Nannipieri, P., Hernandez, T., Eds.; Academic Press: London, UK, 2018; pp. 87–124.
52. Nardi, S.; Ertani, A.; Francisco, O. Soil-root crosstalk: The role of humic substances. *J. Plant Nutr. Soil Sci.* **2017**, *180*, 5–13. [[CrossRef](#)]
53. Urrutia, O.; Erro, J.; Fuentes, M.; Olaetxea, M.; Garnica, M.; Baigorri, R.; Zamarreno, A.M.; Movila, M.; De Hita, D.; Garcia-Mina, J. The effect of soil organic matter on plant mineral nutrition. In *Achieving Sustainable Crop Nutrition*; Rengel, Z., Ed.; Burleigh Dodds: Cambridge, UK, 2020; pp. 1–11.
54. Zandonadi, D.B.; Canellas, L.P.; Facanha, A.R. Indole-acetic acid and humic acids induce lateral root development through a concerted plasmalemma and tonoplast H⁺ pump activation. *Planta* **2007**, *225*, 1583–1595. [[CrossRef](#)]
55. Zandonadi, D.B.; Santos, M.P.; Dobbss, L.B.; Olivares, F.L.; Canellas, L.P.; Binzel, M.L.; Okorokova-Façanha, A.L.; Façanha, A.R. Nitric oxide mediates humic acid induced root development and plasma membrane H⁺-ATPase activation. *Planta* **2010**, *231*, 1025–1036. [[CrossRef](#)] [[PubMed](#)]
56. Trevisan, S.; Pizzeghello, D.; Ruperti, B.; Francioso, O.; Sassi, A.; Palme, K.; Quaggiotti, S.; Nardi, S. Humic substances induce lateral root formation and expression of the early auxin-responsive IAA 19 gene and DR 5 synthetic element in Arabidopsis. *Plant Biol.* **2010**, *12*, 604–614.
57. Pinton, R.; Cesco, S.; Iacoletti, G.; Astolfi, S.; Varanini, Z. Modulation of NO₃-uptake by water-extractable humic substances: Involvement of root plasma membrane H⁺-ATPase. *Plant Soil* **1999**, *215*, 155–161. [[CrossRef](#)]
58. Canellas, L.P.; Olivares, F.L.; Aguiar, N.O.; Jones, D.L.; Nebioso, A.; Massei, P.; Piccolo, A. Humic and fulvic acids as biostimulants in horticulture. *Sci. Hortic.* **2015**, *30*, 15–27. [[CrossRef](#)]
59. Canellas, L.P.; Teixeira Junior, L.R.L.; Dobbs, L.B.; Silva, C.A.; Medici, L.O.; Zandonadi, D.B.; Facanha, A.R. Humic acids crossinteractions with root and organic acids. *Ann. Appl. Biol.* **2008**, *153*, 157–166. [[CrossRef](#)]
60. Spark, K.M.; Wells, J.D.; Johnson, B.B. The interaction of humic acid with heavy metals. *Aust. J. Soil Res.* **1997**, *35*, 89–101. [[CrossRef](#)]
61. Haynes, R.J.; Mokolobate, M.S. Amelioration of Al toxicity and P deficiency in acid soils by addition of organic residues: A critical review on the phenomena and the mechanisms involved. *Nutr. Cycl. Agroecosyst.* **2004**, *59*, 47–63. [[CrossRef](#)]

62. Suthipradit, S.; Edwards, D.G.; Asher, C.J. Effects of aluminum on tap-root elongation of soybean (*Glycine max*), cowpea (*Vigna unguiculata*) and green gram (*Vigna radiata*) grown in the presence of organic acids. *Plant Soil* **1990**, *124*, 233–237. [[CrossRef](#)]
63. Chianese, S.; Fenti, A.; Iovino, P.; Musmarra, D.; Salvestrini, S. Sorption of organic pollutants by humic acids: A review. *Molecules* **2020**, *25*, 918. [[CrossRef](#)] [[PubMed](#)]
64. Stevenson, F.J. *Humus Chemistry: Genesis, Composition, Reactions*; John Wiley: New York, NY, USA, 1994.
65. Batjes, N.H. Harmonized soil property values for broad-scale modeling with estimates of global carbon stocks. *Geoderma* **2016**, *269*, 61–68. [[CrossRef](#)]
66. Weber, J.; Chen, Y.; Janroz, E.; Miano, T. Preface: Humic substances in the environment. *J. Soils Sediments* **2018**, *18*, 2665–2667. [[CrossRef](#)]
67. Hayes, M.H.B.; Clapp, C.E. Humic substances: Considerations of composition, aspects of structure and environmental influences. *Soil Sci.* **2001**, *166*, 723–737. [[CrossRef](#)]
68. Oertel, G.; Matschullat, J.; Zimmermann, F.; Erasmi, S. Greenhouse gas emissions from soils—A review. *Geochemistry* **2016**, *76*, 327–352. [[CrossRef](#)]
69. Minasny, B.; Malone, B.P.; McBratney, A.B.; Angers, D.A.; Arrouays, D.; Chambers, A.; Chaplot, V.; Chen, Z.-S.; Cheng, K.; Das, B.S.; et al. Soil Carbon 4 per mille. *Geoderma* **2017**, *292*, 59–86. [[CrossRef](#)]
70. Rumpel, C.; Asmirasami, F.; Koutika, L.-S.; Smith, R.; Whitehead, D.; Wollenberg, E. Put more carbon in soils to meet Paris climate pledges. *Nature* **2018**, *564*, 32–34. [[CrossRef](#)]
71. Wiesemeier, M.; Mayer, S.; Burmeister, J.; Hübner, K.; Kögl-Knabner, I. Feasibility of the 4 per 1000 initiative in Bavaria: A reality check of agricultural soil management and carbon sequestration scenarios. *Geoderma* **2020**, *369*, 11433. [[CrossRef](#)]
72. Klapp, E. *Lehrbuch des Acker- und Pflanzenbaus*; Paul Parey: Berlin/Hamburg, Germany, 1967.
73. Baveye, P.C.; White, R.E. The “4p1000” initiative: A new name should be adopted. *Ambio* **2019**, *49*, 1–2. [[CrossRef](#)] [[PubMed](#)]
74. Piccolo, A. The supramolecular structure of humic substances: A novel understanding of humus chemistry and implications in soil science. *Adv. Agron.* **2002**, *75*, 57–134.
75. Ghabbour, E.A.; Davis, G.; Daggett, J.L., Jr.; Worgul, C.A.; Wyant, G.A.; Sayedbagheri, M.-M. Measuring the humic acid content of commercial lignites and agricultural top soils in the international soil project. *Ann. Environ. Sci.* **2012**, *6*, 1–12.
76. Hedges, J.I.; Oades, J.M. Comparative organic geochemistry of soils and marine sediments. *Org. Geochem.* **1997**, *27*, 319–361. [[CrossRef](#)]
77. Piccolo, A.; Conte, P. Molecular size of humic substances. Supramolecular associations versus macromolecular polymers. *Adv. Environ. Res.* **2000**, *3*, 508–521.
78. Piccolo, A.; Cozzolino, A.; Conte, P.; Spaccini, R. Polymerization of humic substances by an enzyme catalyzed oxidative coupling. *Naturwissenschaften* **2000**, *87*, 391–394. [[CrossRef](#)]
79. Cozzolino, A.; Piccolo, A. Polymerization of dissolved humic substances catalyzed by peroxidase. Effects of pH and humic composition. *Org. Geochem.* **2002**, *33*, 281–294. [[CrossRef](#)]
80. Nuzzo, A.; Piccolo, A. Oxidative and photo-oxidative polymerization of humic superstructures by heterogeneous biomimetic catalysis. *Biomacromolecules* **2013**, *14*, 1645–1652. [[CrossRef](#)]
81. Piccolo, A.; Spaccini, R.; Cozzolino, V.; Nuzzo, A.; Drosos, M.; Zavattaro, L.; Grignani, C.; Puglisi, E.; Trevisan, M. Effective carbon sequestration in Italian agricultural soils by in situ polymerization of soil organic matter under biomimetic photocatalysis. *Land Degrad. Dev.* **2018**, *29*, 485–494. [[CrossRef](#)]
82. Ogle, S.M.; Alsaker, C.; Baldock, J.; Bernoux, M.; Breidt, F.J.; McConkey, B.; Regina, K.; Vazquez-Amabile, G.G. Climate and soil characteristics determine where no-till management can store carbon in soils and mitigate greenhouse gas emissions. *Sci. Rep.* **2019**, *9*, 11665. [[CrossRef](#)] [[PubMed](#)]
83. Erro, J.; Urrutia, O.; Baigorri, R.; Fuentes, M.; Zamerreno, G.; Garcia-Mina, J. Incorporation of humic-derived active molecules into compound NPK granulated fertilizers. *Chem. Biol. Technol. Agric.* **2016**, *3*, 18–33. [[CrossRef](#)]
84. Ziechmann, W. *Huminstoffe*; Verlag Chemie: Weinheim, Germany, 1980.
85. Vissser, S.A. Oxidation-reduction potentials and capillary activity of humic acids. *Nature* **1964**, *204*, 7–11. [[CrossRef](#)]
86. Trommler, U. Einfluss von Huminstoffen auf Chemische Reaktionen bei der Reinigung von Kontaminierten Wässern. Ph.D. Thesis, Universität Leipzig, Leipzig, Germany, 2007.
87. FAO. *Soil Organic Carbon, the Hidden Potential*; FAO: Rome, Italy, 2017.
88. Hayes, M.H.B.; Swift, R.S. Vindication of humic substances as a key component of organic matter in soil and water. *Adv. Agron.* **2020**, *163*, 1–37.
89. Glaser, B.; Haumeier, G.; Guggenberger, G.; Zech, W. The terra pretaphenomen: A model for sustainable agriculture in the humid tropics. *Naturwissenschaften* **2001**, *88*, 37–41. [[CrossRef](#)] [[PubMed](#)]
90. Schmidt, M.W.I.; Skjemstad, J.O.; Gehrt, E.; Kögl-Knabner, I. Charred organic carbon in German chernozemic soils. *Eur. J. Soil Sci.* **1999**, *50*, 351–356. [[CrossRef](#)]
91. Schmidt, M.W.I.; Skjemstad, J.O.; Jäger, C. Carbon isotope geochemistry and nano morphology of soil black carbon: Black chernozemic soils in central Europe originate from ancient biomass burning. *Glob. Biogeochem. Cycles* **2002**, *16*, 1123–1131. [[CrossRef](#)]
92. Skjemstad, J.O.; Reikovsky, D.C.; Wilts, A.R.; McGowan, J.A. Charcoal carbon in US agricultural soils. *Soil Sci. Soc. Am. J.* **2002**, *66*, 1249–1255. [[CrossRef](#)]

-
93. Gerke, J. Black (pyrogenic) carbon in soils and waters: A fragile data basis extensively interpreted. *Chem. Biol. Technol. Agric.* **2019**, *6*, 13. [[CrossRef](#)]
 94. Jeffery, S.; Abalos, D.; Prodana, M.; Bastos, A.C.; Van Groenigen, J.W.; Hungate, B.A.; Verheijen, F. Biochar boosts tropical but not temperate crop yield. *Environ. Res. Lett.* **2017**, *12*, 053001. [[CrossRef](#)]