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OPINION

From energy to (soil organic) matter

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Abstract

In this concept paper, we propose a new view on soil organic matter (SOM) formation: microorganisms use most of the organics entering the soil as energy rather than as a source of carbon (C), while SOM accumulates as a residual by-product because the microbial energy investment in its decomposition exceeds the energy gain. During the initial stages of decomposition, the nominal oxidation state of C (NOSC) in remaining litter decreases, and the energy content increases. This reflects the rapid mineralization of available compounds with positive and neutral NOSC (carboxylic acids, sugars, some amino acids). Consequently, the NOSC of the remaining compounds drops to −0.3 units, and the oxidation rate decreases due to the residual relative accumulation of aromatic and aliphatic compounds (which are hydrolized later) and entombment of the necromass. Ultimately, incompletely decomposed plant residues will have 1%–2.5% more energy per C unit than the initial litter. The linear decrease in energy density of a broad range of organic substances by 106 kJ mol^{-1} C per NOSC unit upon oxidation is supported by experimental data on litter decomposition. Preferential recycling of energy-rich reduced (lipids, aromatics, certain amino acids, amino sugars) and the microbial degradation of oxidized compounds (carboxylic acids) also energetically enrich SOM. Despite the high energy content, the availability of energy stored in SOM is lower than in litter. This explains why SOM is not fully mineralized (thermodynamically unfavorable), especially in the absence of plant C to provide new energy (e.g., in bare soil). Energy from litter activates decomposers to mine nutrients stored in SOM (the main ecological function of priming effects) because the nutrient content in SOM is 2–5 times higher than that of litter. This results in only 0.4%–5% $year^{-1}$ of litter-derived C being sequestered in SOM, whereas SOM stores 1%–10% $year^{-1}$ of the total litter-derived energy. Thus, the energy captured by photosynthesis is the main reason why microorganisms utilize organic matter, whereby SOM is merely a residual by-product of nutrient storage and a mediator of energy fluxes.

KEYWORDS
carbon and nutrient cycling, energy and matter fluxes, enzyme activity, microbial turnover, oxidation and reduction processes, priming effect mechanisms, soil organic matter

1 | INTRODUCTION

The transformation of "energy to (soil organic) matter" has long been the focus of scientific attention (Swift et al., 1979), but no definitive conceptual framework exists. Here, we roll the dice again and provide an experiment-based review of the complex processes of microbial conversion of energy and carbon (C) from litter to soil organic matter (SOM).

The classic ecological definition of energy is given by Odum and Odum (Walters, 1977): *Energy is a measure of everything. It measures the amount of stored capability for future processes and the rate at which processes go. The total amount of an accomplished process is measured by the energy used*. This definition is fully applicable to soil processes, given the principles and laws of energy: (i) "the energy entering the system must be accounted as stored or flowing out (law of conservation of energy), (ii) in all processes some of the energy loses its ability to work and is degraded in quality (law of degradation of energy), and (iii) that system survives which gets most energy and uses energy most effectively in competition with other systems (maximum-power principle)" (Walters, 1977).

When applied to soil, the energy transformation associated with the C cycle is evident because organic C is energy stored by plants in the form of chemical bonds of organic compounds, which can then be used by microorganisms and within food webs. Microorganisms regulate the balance of energy and C in the soil through four basic processes: (i) mineralization of root-derived organic matter, easily available SOM compounds and plant residues to CO_2, which involves the loss of both energy and matter; (ii) incorporation of some of the plant-derived C into microbial biomass and accumulation of energy in metabolites and storage compounds (Mason-Jones et al., 2019); (iii) contribution of microbial necromass to soil organic matter (SOM) formation (Kästner et al., 2021; Liang et al., 2017; Zhu et al., 2020) and energy stored in chemical bonds; (iv) decomposition of SOM to obtain nutrients (as its nutrient content is richer than that of plant residues), which again leads to the loss of both energy and matter due to oxidation. Some of the energy is lost during these processes as heat (Herrmann et al., 2014; energy degradation, low quality (see below)), while the matter is lost as CO_2 (H_2O, NH_4^+, etc.), leaving nothing that can be used by microorganisms without new energy input. A small fraction of the residual energy is concentrated in chemical bonds within the SOM (energy conservation, high-quality energy), but the low availability of that energy (see below) limits its full utilization and conversion into heat. Thus, the energy content and fluxes in soil are partially controlled by the same processes as in the case of C, i.e., mineralization and accumulation, but the intensity and energy use efficiency of the energy fluxes that ensure the functioning of the soil system remain unclear.

Although microbial biomass accounts for only 1%–3% of SOM (Joergensen, 1996; Liang et al., 2020), microorganisms drive the cascade of oxidation and reduction processes that alter the C oxidation state in litter and SOM. This is strongly related to the amount of energy stored. Extensive efforts have been made to investigate the transformation of organic C, including its complete oxidation to CO_2 (and reduction to CH_4) and to examine the fluxes to and from the soil (Haddix et al., 2020; Kögel-Knabner, 2002; Lange et al., 2015; Liang et al., 2019; Lutzow et al., 2006; Paul, 2016; Schmidt et al., 2011). However, the simultaneous changes in the C oxidation state and energy content of substances during the formation of SOM from plant residues have never been discussed. The open questions are: (i) How is energy lost during microbial conversion of plant-derived C into SOM? (ii) Can SOM be considered not only as a C sink and nutrient storage, but also an energy sink? (iii) Do microbial residues and SOM have a higher quality and availability of energy than litter, and if so, why? (iv) Can the fate of energy be predicted based on the oxidation state of the substance? and (v) What is the trend of the C oxidation state in litter during SOM formation?

2 | DEFINITIONS

2.1 | Energy quality and availability

Two important terms must be introduced here: *energy quality* and *energy availability*.

The *energy quality* of a substance is a parameter that reflects the maximal portion of the initial chemical energy (which can be understood as the standard molar enthalpy of combustion) that can be stored or transformed into non-thermal energy (heat dissipation) when microorganisms have full access to the substance. This corresponds to the *law of degradation of energy*, which states that in all energy processes, a portion of energy loses its function, i.e., it deteriorates in quality (Walters, 1977). The quality of energy is, therefore, always <1 because according to the law of energy degradation, every energy transformation leads to energy loss.

The e*nergy availability* of a substance or pool of substances is the ratio of the energy obtained and consumed through any activity to the energy that a (micro)organism or community would have to invest to utilize the substance (Equation 1) under real soil conditions. Energy availability ranges from 0 (not available, i.e., the organic compound is not biodegradable and cannot be used by microorganisms at all, e.g., biochar, synthetic rubber, non-decomposable polymers such as Teflon) to more than 1 (more energy is obtained than invested) (Equation 1).

$$E_{\text{availability}} = \frac{E_{\text{obtained}}}{E_{\text{invested}}}. \quad (1)$$

For microorganisms that are limited by nutrients (N, P, K, and S), energy availability can vary between 0 and 1. This is because microorganisms need to invest more energy in mining the nutrients than can be obtained by oxidizing organic matter. Such energy availability is very close to the activation energy (unitless) of a chemical reaction but differs in that the microorganisms must "decide" on their energy investment. Therefore, energy availability should be considered as one of the "decision criteria" for mining energy from organic matter.

Energy availability is reduced by: (i) the irregular and diverse nature of the bonding in polymeric organic compounds, which requires generating a wider range of enzymes than in compounds with regular structures (cellulose, hemicellulose, proteins); (ii) the hydrophobicity of the substance because energy is required to generate (per) oxidases to break down phenolic or heterocyclic ring structures; (iii) binding to clay minerals or Fe (hydr)oxides, which requires energy to reduce iron or to separate organic compounds from clays, e.g., by ligand exchange (Keiluweit et al., 2015); (iv) the distance between

energy-containing organic matter and enzyme-producing microorganisms because both enzymes and hydrolysis products may be lost en route in both directions (Guber et al., 2021); (v) the abundance of microbial cheaters that use hydrolysis products without producing the necessary enzymes (Allison et al., 2011; Kaiser et al., 2015). The first two items relate to the properties of organic substances, while the last three relate to the effects of the microenvironment.

The two energy parameters represent opposite angles of the substrate-microorganism interaction, with *energy quality* representing primarily substance, whereas *energy availability* represents the ability of microorganisms to utilize that substance (or pool of substances) under actual soil conditions.

2.2 | Carbon oxidation state

There are two definitions of oxidation state: one refers to the C atom itself, the other to the nominal oxidation state (NOSC) of all C atoms in a substance. The classical definition of the *oxidation state of a C atom* is: The oxidation state of an atom is the charge of that atom after ionic approximation of its heteronuclear bonds (McNaught & Wilkinson, 1997). The *NOSC value of a substance* is the ratio of the number of electrons transferred in half of the oxidation reaction to the total number of C atoms in the substance (LaRowe & Van Cappellen, 2011):

$$\mathrm{NOSC} = -\left(\frac{-Z+4C+H-3N-2O+5P-2S}{C}\right)+4, \quad (2)$$

where C, H, N, O, P, and S are the stoichiometric numbers of the elements and Z is the net charge of the organic compound. The contents of CNHO can be determined by various methods depending on the nature of the sample (Chadwick et al., 2004; Hockaday et al., 2015; Masiello et al., 2008). Carbon oxidation states vary from −4 (CH_4) to +4 (CO_2), and the NOSC values of organic substances range from −1.7 to +3 (Figure 1). There is a clear linear correlation between NOSC and energy content per C atom (enthalpy of combustion, the total amount of energy stored in a substance), which decreases by 106 kJ mol^{-1} per one NOSC unit (Figure 1).

3 | ENERGY FLUXES, POOLS, AND PROPERTIES

3.1 | Energy fluxes and pools

The fluxes and storage of organic C in soil are not the same as fluxes and storage of energy. SOM stocks depend on (i) annual plant litter input, (ii) its transformation, and (iii) SOM mineralization. The rate of transformation of litter and SOM by microorganisms is influenced by climatic, biotic, and edaphic factors (Paul, 2016), but environmental influences are beyond the scope of this article. Annual plant C inputs can range from 4% to 26% of organic C content in mineral soils (Table S1). Given that the annual energy input from plant litter differs with soil type (Table S1), the energy stocks of SOM are site-specific (Table 1).

The total energy per unit of residual C increases with the decomposition of plant residues (Figure 2a; Cruz & Gabriel, 1974; Kucera et al., 1967; Malone & Swartout, 1969; Rovira et al., 2008). This is because microorganisms preferentially utilize readily available energy sources, i.e., substances that require less energy investment (Equation 1), most of which are hydrophilic (Figure 1; Deng et al., 2021). The paucity of data on energy changes during litter transformation and energy changes in bulk SOM (Barros et al., 2020) prevents a comprehensive assessment of energy accumulation in SOM. Nevertheless, calorimetric measurements of fresh and decomposed litter show that there are two stages of energy conversion. In the first stage, energy is lost (9.6–13.8 kJ g^{-1} for the persisting residues), and in the second stage, energy is accumulated (3.0–3.7 kJ g^{-1} compared to the initial litter). The energy loss in the first stage is associated

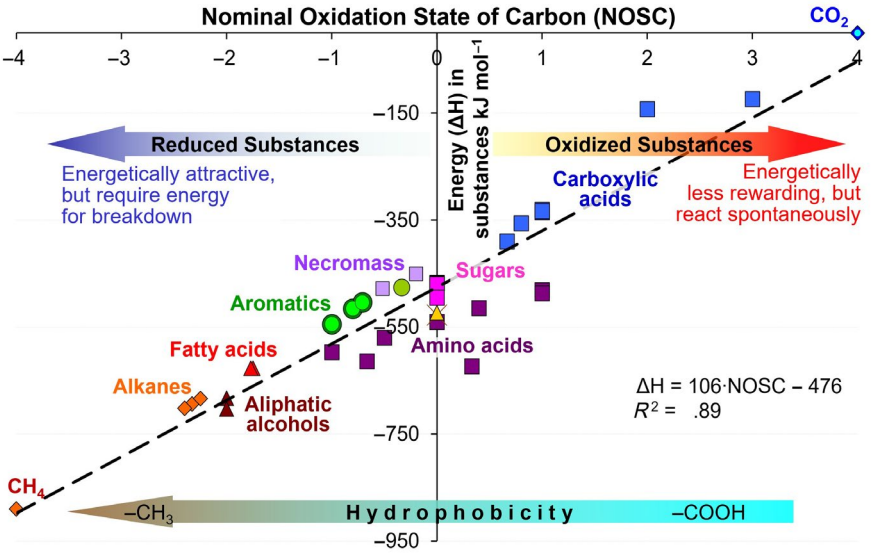

FIGURE 1 Dependence of combustion enthalpy (ΔH) (kJ mol^{-1} C) on NOSC values for the main classes of organic compounds present in soil organic matter. Data for chemical classes are taken from textbooks, and for microbial necromass from Popovic (2019) [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Energy (E) stocks in SOM, the annual loss of energy from SOM mineralization, total input and remaining energy in SOM in selected plant communities for aboveground (litter) and belowground (roots) inputs

Soil/plant community type	E stocks in SOM, GJ ha^{-1}		Loss of E in SOM, GJ ha^{-1} $year^{-1}$	Plant E total input, GJ ha^{-1} $year^{-1}$		Plant E left in the soil, GJ ha^{-1} $year^{-1}$	
	0–20 cm	0–100 cm	0–20 cm	Above	Below	Above	Below
Podzol/Spruce forest	630–910	910–1500	11–16	49 ± 11	18 ± 7.0	3.4 ± 0.8	3.6 ± 1.4
Albeluvisols/ Broadleaf forest	660–1100	910–1700	12–21	76 ± 6.6	28 ± 8.5	6.1 ± 0.5	5.6 ± 1.7
Luvisol/Grassland	690–910	1400–2200	12–16	96 ± 37	260 ± 109	19 ± 7.5	51 ± 22
Chernozem/Grassland	1500–1800	4100–5900	27–33	105 ± 37	240 ± 64	21 ± 7.4	48 ± 13

Note: The energy stocks of SOM are calculated from the mean energy content in SOM (21.2 MJ kg^{-1} SOM; Gorham & Sanger, 1967). The energy loss per year is calculated from the SOM mineralization index = 1.67% $year^{-1}$ (Schmidt et al., 2011). The energy input from plant litter is calculated based on the mean amount (1 t of plant biomass-C contains 1×10^7 kcal of energy (Orlov et al., 1996), 1 kcal = 4184 J). The plant energy remaining in SOM is calculated based on the amount of plant materials remaining in the soil after 1 year (Table S1) while assuming the same energy content as in the initial litter. The data show the ranges of energy stocks and plant energy input (means ± SD).

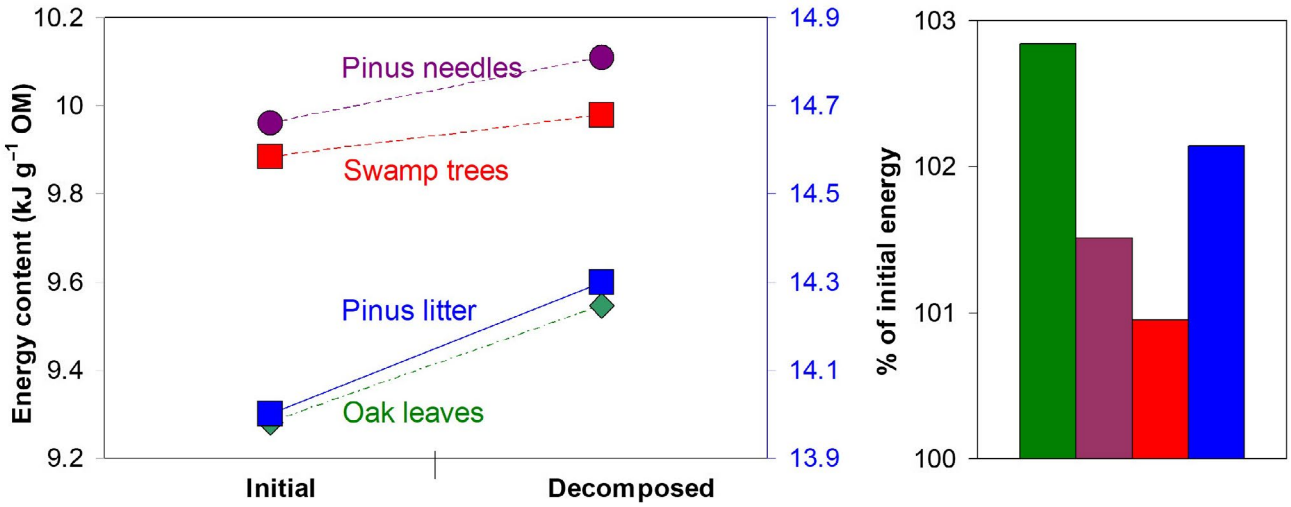

FIGURE 2 Changes in total energy content of plant residues (kJ g^{-1} organic matter) after 1 year of decomposition (left) (right *Y*-axis for *Pinus* litter only), and changes in energy content of decomposed plant residues relative to baseline values (right) (Gorham & Sanger, 1967; Rovira et al., 2008) [Colour figure can be viewed at wileyonlinelibrary.com]

with the mineralization of readily available compounds such as carbohydrates, low molecular weight carboxylic acids, and proteins (all NOSC ≥ 0). Energy accumulation in the second stage is associated with the relative enrichment of litter with poorly degradable hydrophobic compounds such as lignin derivates, lipids, fatty acids, and aromatic compounds (all representing reduced compounds with NOSC < 0): These compounds have a higher energy content (Aliev, 1975) but lower energy availability than the initial plant residues. As a rough estimate, partially decomposed plant residues contain 1%–2.7% more energy than the initial litter (Figure 2b).

Based on the rate of transformation of plant residues (Table S1; Kononova, 1972; i.e., the amount of plant-derived C stabilized or persisting in SOM, including microbial necromass C), the amount of plant-derived energy persisting in soil (after 1 year) ranges from 7% to 20% of total energy input depending on the plant community (Table 1). This represents 0.8%–10% of the energy already stored in SOM, but adds only 0.4%–5% C to the existing SOM pool (Table 2). This calculation was made assuming that the energy content (per unit of OM) in litter during decomposition is constant (implying that NOSC is constant). However, energy can increase up to 300–600 J g^{-1} OM depending on the type of plant residues and edaphic and climatic factors (Figure 2; Gorham & Sanger, 1967; Rovira et al., 2008). Thus, our evaluation of energy accumulation in SOM (Table 2) is conservative, but nonetheless shows that energy accumulation is greater than C accumulation.

3.2 | Properties of energy stored in litter and SOM

The complexity of the problem of determining the quality and availability of energy (see Section 2.1) is explained by (i) the diverse nature of organic substances entering the soil, i.e., carbohydrates, lignin, tannins, lipids, proteins; (ii) the metabolic requirements and constraints of microbes; (iii) the SOM itself, i.e., the existence of

TABLE 2 Contributions of annual energy and plant-derived C inputs to bulk soil pools (0–20 cm), and the energy and SOM balance for selected soils

Soil/plant community type	Total E incorporated/total E storage, % 0–20 cm	Total plant C incorporated/total SOM, % 0–20 cm	E input to SOM—E loss, GJ ha^{-1} $year^{-1}$ 0–20 cm	Plant C input to SOM—loss of SOM, t ha^{-1} $year^{-1}$ 0–20 cm
Podzol/Spruce forest	0.8–1.1	0.4–0.5	−4.0 −9.0	−0.36 −0.60
Albeluvisols/Broadleaf forest	1.1–1.8	0.5–0.8	0 −9.0	−0.28 −0.69
Luvisol/Grassland	7.7–10	3.7–4.8	+58 +54	+1.1 +0.91
Chernozem/Grassland	4–4.6	1.3–1.6	+43 +37	−0.05 −0.34

Note: Data from Table S1 and Table 1 were used in the calculations.

pools with various composition and stability; (iv) edaphic and environmental conditions (Hall et al., 2020). Differential scanning calorimetry combined with thermal gravimetry has shown that the relative amount of labile organic matter does not diminish with litter decomposition and that the energy gain from litter oxidation rises with (i) decreasing polysaccharide content of the decomposing litter and (ii) increasing N content (Rovira et al., 2008). The results demonstrate that microbial necromass accumulates in the decomposing litter because the energy content of necromass is higher than that of plant residues (Malone & Swartout, 1969; Rovira et al., 2008), but the two pools could not be distinguished by the analytical methods described above. The energy quality of soils without organic input or plants (long-term bare fallow) decreases over time due to (1) depletion of C-H-bonds (Barré et al., 2016), (2) decline in SOM aromaticity, (3) increase in the number of -COOH groups (Barré et al., 2016), and (iv) tight binding of persisting SOM to the mineral matrix (Barré et al., 2016; Cotrufo et al., 2013; Lavallee et al., 2020; Plante et al., 2005). As a consequence, the energy/C ratio of SOM in long-term bare fallow is lower than that of litter, which is probably only possible without new C input.

In terms of energy, microorganisms would preferentially use substances or organic pools with an energy availability greater than 1.0 (Figures 3 and 4), i.e., where energy gain is greater than energy investment (Williams & Plante, 2018; Zhang et al., 2021). However, when microbial demand for nutrients (mainly N or P) is greater than the available nutrient pools in the soil, microorganisms may invest more energy to mobilize those limiting nutrients than to obtain the energy per se. In this case, energy availability would be <1.0 because energy investment (e.g., for enzyme production, see below) will be directed to obtaining limiting nutrients, not energy. The main ecological challenge in such a situation would be to reduce the constraints and increase the efficiency of the whole (eco)system (Figure 3). This is the key principle that explains the nutrient mining process in priming effects (Fontaine et al., 2011; Kuzyakov et al., 2000; Meyer et al., 2017; Zhou et al., 2020). Nutrient mining does not necessarily proceed until the full mineralization of organic C as CO_2. Rather, certain components of microbial residues may be reused (Kästner & Miltner, 2018; Kästner et al., 2021). Thus, fatty acids of lipids (Dippold & Kuzyakov, 2016; Kindler et al., 2009; Ruess & Chamberlain, 2010; Ruess et al., 2005), isoprenoid units of cell membranes (Takano et al., 2010), fragments of cell walls (Park & Uehara, 2008) such as amino sugars (Cui et al., 2020; Liang, 2020), and amino acids (Park & Uehara, 2008) may all be taken up directly by cells and used for biopolymer synthesis. This process requires much less ATP than the synthesis of these monomers from precursors, which may explain the preferential accumulation of energy in SOM over the accumulation of C (Table 2).

4 | EXPENSIVE ENERGY INVESTMENT: EXOENZYME PRODUCTION

4.1 | Limitations for microorganisms producing and using exoenzymes in soil

There are two main pathways by which microorganisms obtain energy from organic compounds in litter and SOM: (i) direct substance uptake via mechanosensitive channels that allow the passage of substances smaller than 1000 Da, and ATP (Martinac et al., 2008) or transport systems (Benz, 1994) and (ii) the initial investment of energy (as ATP) and C, N, P, and S to produce extracellular enzymes (exoenzymes) by splitting polymers outside the cells to take up the resulting oligomers or monomers (Schimel et al., 2017). The second pathway is the predominant one in soils, as >95% of organic C in the litter, microbial necromass, organic fertilizers, and SOM are high-molecular compounds. Studies on pure cultures (i.e., *Bacillus licheniformis*) have shown that 1%–5% of assimilated C and N are used for exoenzyme production (Frankena et al., 1988; Schimel & Weintraub, 2003). We, however, hypothesize that the energy investment of soil microorganisms for exoenzyme production is much higher. The energy cost of synthesizing proteins that are excreted extracellularly (7.1 mol ATP per mol of amino acids in the protein, assuming an average molecular weight of amino acids of 138 g mol^{-1}) is 25% higher than the energy cost of synthesizing biomass (5.7 mol ATP per mol biomass, assuming an average molecular weight of microbial biomass of 146 g mol^{-1}; Frankena et al., 1988). This energy was calculated for protein or biomass synthesis from glucose (NOSC = 0), which requires less ATP than, for example, citrate (NOSC = +1.0, oxidized

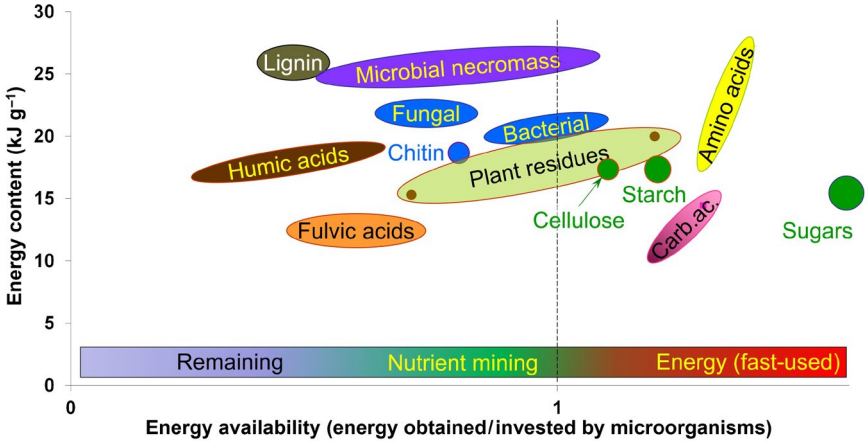

FIGURE 3 Conceptual representation of energy availability (*X*-axis) to microorganisms in monomers and polymers from SOM components versus the energy quantity in various compounds (obtained by differential scanning calorimetry, enthalpy of combustion). In the red zone on the *X*-axis, the energy availability is >1, indicating greater energy gain by microbial decomposition of these substances versus energy investment. The green zone indicates that some energy investment is required for the co-mining of nutrients. The blue zone indicates residual compounds unsuitable for energy mining due to low efficiency that will be partially decomposed by co-metabolism (no energy gain). Note that the placement of substance groups is arbitrary and does not take into account their spatial inaccessibility. Depending on energy availability, the energy contained in the substances can be: (i) used as energy per se (mainly easily decomposable and low molecular weight organic substances) if the energy availability is >1.0; (ii) used for nutrient mining—energy is necessary to invest in exoenzyme production to decompose SOM that is richer in nutrients than plant residues; or (iii) left unspent as residual energy in stable SOM if the energy investment needed to degrade it far exceeds the energy gain [Colour figure can be viewed at wileyonlinelibrary.com]

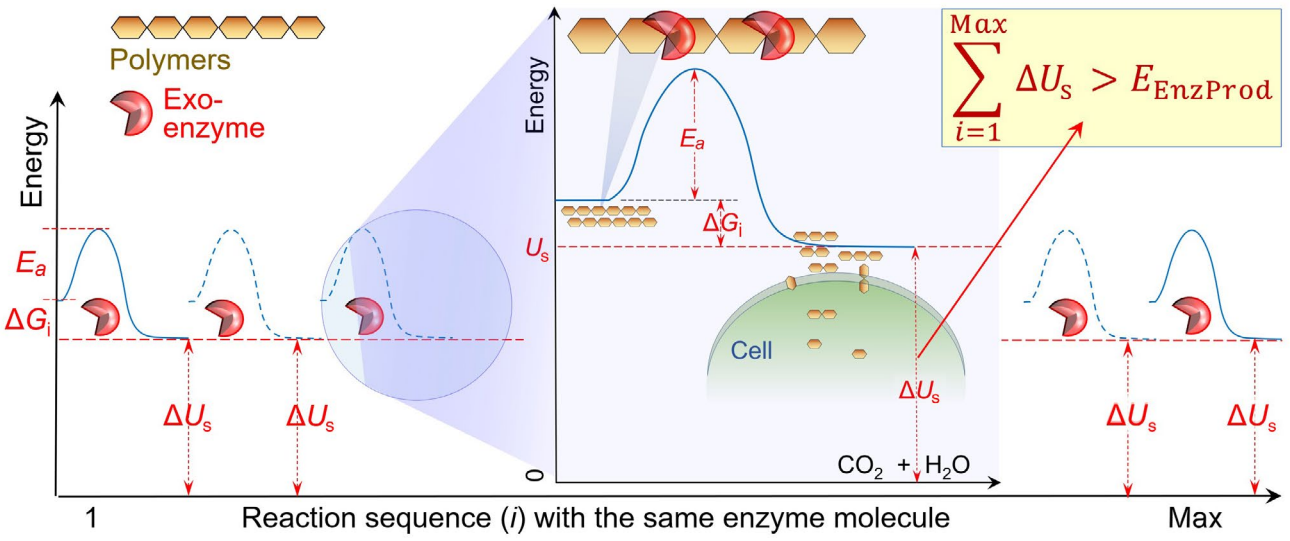

FIGURE 4 The reaction sequence of a single exoenzyme molecule as it breaks down polymers into mono- and oligomers that are further utilized within the microbial cells (Cell). The main energy concept (yellow box) is that the energy used by a microbial cell for exoenzyme production ($E_{EnzProd}$) should be less than the total energy released by utilizing all mono- and oligomers inside the cell (ΔU_s). The activation energy (E_a) that must be overcome to split polymers into mono- and oligomers is important for the efficiency of exoenzymes (reactions outside the cell; V_{max}/K_m), but is not relevant for the amount of energy produced inside the microbial cell. The Gibbs energy (ΔG_i) of individual exoenzymatic reactions (mainly hydrolyses) is much lower than the ATP energy stored and used when mono- and oligomers are utilized inside the cell (ΔU_s). The reaction sequence (*X*-axis) represents the maximal number of exocellular reactions with the same enzyme molecule between its first and last (Max) reaction in the soil before the enzyme is deactivated (e.g., due to sorption, decomposition, or entrapment in micro- and nanopores). The concept that it takes less energy to produce an enzyme than the energy released from monomers may not be valid at the level of the individual microbial cell, but is certainly relevant at the microbial community level [Colour figure can be viewed at wileyonlinelibrary.com]

substance). Despite the same number of C atoms, 56% less glucose (1.6 mol) than citrate (2.5 mol) is required to form and excrete 1 mol of protein (Frankena et al., 1988). This makes the C cost of enzyme production from oxidized compounds high and explains why microorganisms choose to recycle the metabolites of the citric acid cycle (both energy and their own compounds) and invest only a portion of them in enzyme production under C-limited conditions, such as in bare fallow (Nunan et al., 2015).

Not only does enzyme production require considerable energy, but the life cycle, activity, and efficiency of enzymes in soil are constantly hampered by (i) sorption to clay minerals and iron (oxyhydr)oxides, which reduces the activity of enzymes or deactivates them completely; (ii) distribution in micro- and nanopores, which physically separates enzymes from substrates and microorganisms from released products; (iii) uptake of enzyme hydrolysis products by "cheaters" (Allison et al., 2011; Kaiser et al., 2015); (iv) the use of enzymes released from dead cells (Maire et al., 2013) as an N (P and S) source by living microorganisms after hydrolysis by proteases (Burns et al., 2013; Schimel et al., 2017). These processes reduce the number of reaction cycles mediated by exoenzymes (Figure 4) and result in less energy being gained compared to the energy invested by exoenzyme-producing microorganisms.

Despite these deactivation mechanisms, enzyme activity is always present even in bare fallow (Nunan et al., 2015), subsoil (Liang et al., 2019; Thu Hoang et al., 2020), or deep soils (Loeppmann et al., 2016), where enzyme production is energetically and nutritionally particularly expensive. This ubiquitous presence of enzyme activity in the soil can be explained by (1) the slow degradation and deactivation rate of hydrolytic enzymes (measured by inhibiting new enzyme production in sterilized soil): 0.004–0.11 day^{-1} depending on the soil and enzyme type (Schimel et al., 2017); (2) the stabilization of enzymes on mineral or organic matrices without losing their catalytic functions; (3) the rapid recovery of enzyme production when substrates become available again (Guenet et al., 2011). Microorganisms have evolved specific strategies to avoid continuous enzyme production and to increase the likelihood of recovering hydrolyzed products. These include (i) production of inducible enzymes (i.e., enzymes produced only under certain environmental conditions, e.g., certain nutrient constraints); (ii) inhibition of end products (Allison et al., 2011); (iii) very short diffusion range of enzymes from producing cells (Guber et al., 2018), which increases the possibility of recovering hydrolyzed products; (iv) production of enzymes with high catalytic efficiency (low K_m; Razavi et al., 2016); (iv) the formation of microbial colonies in which different microorganisms produce enzymes with specific functions covering the full range of reactions required (Shi et al., 2016).

4.2 | Estimating the energy investment for enzyme production by soil microorganisms

Here, we estimated the energy (ATP content) required to produce β-glucosidase during a 150-day vegetation period (Table 3 gives examples of two other enzymes—acid phosphatase and β-xylosidase—with lower V_{max} but higher k_{cat}). First, we estimated the true enzyme pool (Enz_{total}) to be 2.0 ng of β-glucosidase g^{-1} soil since most studies measure only enzyme activity and not the enzyme pool. Assuming that enzyme activity remains stable over a long period of time (steady-state conditions), the production of β-glucosidase (φ) during one vegetative period was calculated to be between 1.2 and 8.9 ng g^{-1} soil (Table 3). Furthermore, assuming that 7.1 mol ATP is required per mol of amino acids in protein (molecular weight of 138 g mol^{-1}) and that the molecular mass of β-glucosidase is 71 kDa (Table 3), the calculated amount of β-glucosidase requires 0.06–0.46 nmol ATP (during one vegetative period). Since hydrolysis of 1 mol ATP releases 30 kJ mol^{-1} of energy, the ATP energy required for β-glucosidase alone would be 1.9–14 10^{-6} J g^{-1} soil $season^{-1}$ (Table 3).

This is a rough estimate because (i) the k_{cat} value of soil enzymes may differ from the k_{cat} value of purified enzymes (Chen et al., 1992; Eneyskaya et al., 2007; Ullah & Gibson, 1988); (ii) the V_{max} value depends highly on soil properties (Loeppmann et al., 2016; Ndossi et al., 2020); (iii) we do not know the total pool of soil exoenzymes. The estimate has been made for β-glucosidase (see Table 3 for acid phosphatase and β-xylosidase). Given that microorganisms must produce the full range of enzymes to break down the polymeric substances in the litter, microbial necromass, and SOM, the expected energy investment for enzyme synthesis is at least 2 orders of magnitude greater than that estimated here for β-glucosidase. Thus, the energy derived from the intracellular metabolism of oligo- and monomers hydrolyzed extracellularly by exoenzymes should be greater than the energy invested by microorganisms for exoenzyme production (Figure 4).

Assuming that the soil system follows the maximum power principle (see Section 1), the processes that require less energy input by microorganisms to obtain the energy stored in the organic matter should dominate. Accordingly, the 'stability' of the SOM pool can be explained by the disadvantage of enzymatic degradation because the energy input (investment) required for degradation exceeds the energy gain (Figure 4). This inefficiency reflects (i) the irregular structure of SOM compounds (unlike regular polymers in plant residues), which requires a much wider range of enzymes (and thus higher energy and nutrient requirements) to degrade SOM compared to litter and (ii) SOM binding on mineral particles (Williams et al., 2018), which greatly reduces the efficiency of all enzymatic reactions (Mikutta et al., 2019). Therefore, given this new energy perspective, the "inaccessibility concept" used to explain the lack of degradation of SOM should be carefully re-examined (Waring et al., 2020).

5 | NOMINAL OXIDATION STATE OF LITTER, SOM POOLS, AND COMPONENTS

5.1 | Nominal oxidation state of SOM pools

The NOSC value of the organic matter, litter components, and SOM pools increases in the following order: lipids, lignin, amino acids, soluble phenolics (classes include simple phenols,

TABLE 3 Estimated energy requirements of microorganisms for enzyme production (three enzymes were used as examples) during one vegetation period (150 days)

Enzyme	V_{max} (nmol g^{-1} soil h^{-1})*	k_{cat} (s^{-1})	Enz-total$_{to}$, ng g^{-1} soil	k_d (day^{-1})**	φ (ng g^{-1} soil 150 $days^{-1}$)	Enzyme MW (kDa)	ATP energy required (J g^{-1} soil 150 $days^{-1}$)
β-glucosidase[1]	15	144	2.05	0.004–0.029	1.23–8.94	71	$1.9–13.8 \times 10^{-6}$
Acid phosphatase[2]	8	430	0.27	0.002–0.031	0.08–1.27	53	$0.1–2 \times 10^{-6}$
β-xylosidase[3]	0.5	17.5	0.99	0.006–0.062	0.89–9.23	125	$1.4–14.2 \times 10^{-6}$

Note: Enz-total$_{t0}$ (actual enzyme pool) = V_{max}/k_{cat}; φ (enzyme production rate over 150 days) = Enz-total$_{t0}$*k_d*150.

V_{max} is the maximal reaction rate (*data taken from Loeppmann et al., 2016; k_d is the rate of decay of enzyme activity (**data taken from Schimel et al., 2017). Data on k_{cat} (enzyme turnover rate, i.e., how many times each enzyme site converts the substrate to product per unit time) and enzyme MW (Da) are taken from: [1]Chen et al. (1992), β-glucosidase was extracted from *Trichoderma reesei*; [2]Ullah and Gibson (1988), acid phosphatase was extracted from cotyledons of germinating soybeans; [3]Eneyskaya et al. (2007), β-xylosidase was extracted from *Aspergillus awamori* X-100. The k_{cat} of the enzymes was measured with p-nitrophenyl-based substrates.

phenylpropenes, lignans, coumarins, chromones, flavonoids, tannins, quinines, and alkaloids), sugars, and carboxylic acids (Figures 1 and 5a) (LaRowe & Van Cappellen, 2011). NOSC is generally reduced in the early stages of litter transformation because oxidized compounds are preferentially and rapidly degraded (Figure S1; Deng et al., 2021). According to the few NOSC data on bulk SOM (from mineral horizons), the NOSC decreases with the depth from −0.08 (0–2 cm) to −0.225 (5–10 cm; Chadwick et al., 2004) and further varies between −0.24 and −0.5 (upper 20 cm; Clay & Worrall, 2015). These negative NOSC values are only near the soil surface and support the conclusion that many oxidized compounds are hydrophilic (many -COOH and -C=O groups, Figure 1) and, therefore, readily taken up by microorganisms from solutions and lost through mineralization. In contrast, hydrophobic plant and microbial compounds (many -CH_n groups, aliphatics, and aromatics) persist or are only partially degraded, yielding reduced (negative) NOSC values of bulk SOM (Boye et al., 2017).

The successful conversion of certain soil chemical fractions does not support the idea that a decrease in NOSC is due to the residual reducing litter compounds near the soil surface during the initial transformation (Figure 5b; Worrall et al., 2018). For example, the NOSC of NaOH-extractable SOM from automorphic soils (precipitated by HCl from NaOH solution, the equivalent of humic acids) increases from −0.1 (upper 5 cm) to +0.5 at a depth of 30–40 cm (Figure 4b). In this light, the values of both reduced and oxidized NOSC with depth in peat soils have been reported to depend on the site location (Clay & Worrall, 2015; Worrall et al., 2018). The data are also limited on HCl-precipitated and non-HCl-precipitated NaOH-extracted hydromorphic soils extracts (corresponding to humic and fulvic acid-like compounds, respectively; Figure 5c,d; Lodygin et al., 2016). In the first group, there is no detectable oxidation trend with depth, and the NOSC values hover around 0 (Figure 5c). Assuming that humic acid-like compounds do not migrate, we argue that in situ SOM transformation does not have a strong effect on NOSC. In contrast, the NOSC values of fulvic acid-like compounds increased strongly with depth, from +0.4 to +1.7 at 30–40 cm depth (Figure 5d). This reflects the deeper migration of oxidized compounds (here, fulvic acids, DOM) with more polar functional groups (e.g., −COOH, =C=O) and thus higher solubility (Figure 1). Therefore, in most soils, the NOSC of bulk SOM should also increases with depth (i.e., below 20 cm depth) because the ratio of humic-to-fulvic acid-like compounds declines sharply with depth (Figure 5; Guimarães et al., 2013; Orlov et al., 1996, 2005).

The NOSC value of an organic compound not only indicates its susceptibility to microbial decomposition but may also influence energy dissipation and accumulation in soil. The partition of C from LMWOS between microbial biomass (incorporation into polymers, e.g., energy storage) and the mineralization pool (energy loss) depends on the NOSC value of the compound: as the NOSC value of the substance increases, the incorporation into microbial cell compounds and SOM decreases rapidly—these compounds will be utilized and mineralized faster (Gunina et al., 2017). This confirms that microorganisms prefer to incorporate C from reduced rather than from oxidized compounds, even if the uptake rate of the former is slower.

The pattern of metabolic heat release (the sum of complete oxidation of LMWOS to CO_2, incomplete decomposition, and anabolic processes) also depends on the NOSC value of LMWOS (Figure S2, own unpublished data): oxidized substances decompose faster and release less energy than reduced substances. In turn, reduced substances generate more metabolic heat (because they are intensively used to synthesize microbial metabolites) than oxidized substances. Thus, the greater accumulation of energy versus C in SOM (Table 2) reflects the quality of the available C pool and the adaptation of microorganisms to utilize compound specific classes (Nunan et al., 2015).

5.2 | Changes of NOSC and energy content during SOM formation

The principle of decreasing energy with higher (positive) NOSC (Figure 1) applies to the transformations of litter, intermediate states such as live and dead microbial biomass, and SOM. The conversion

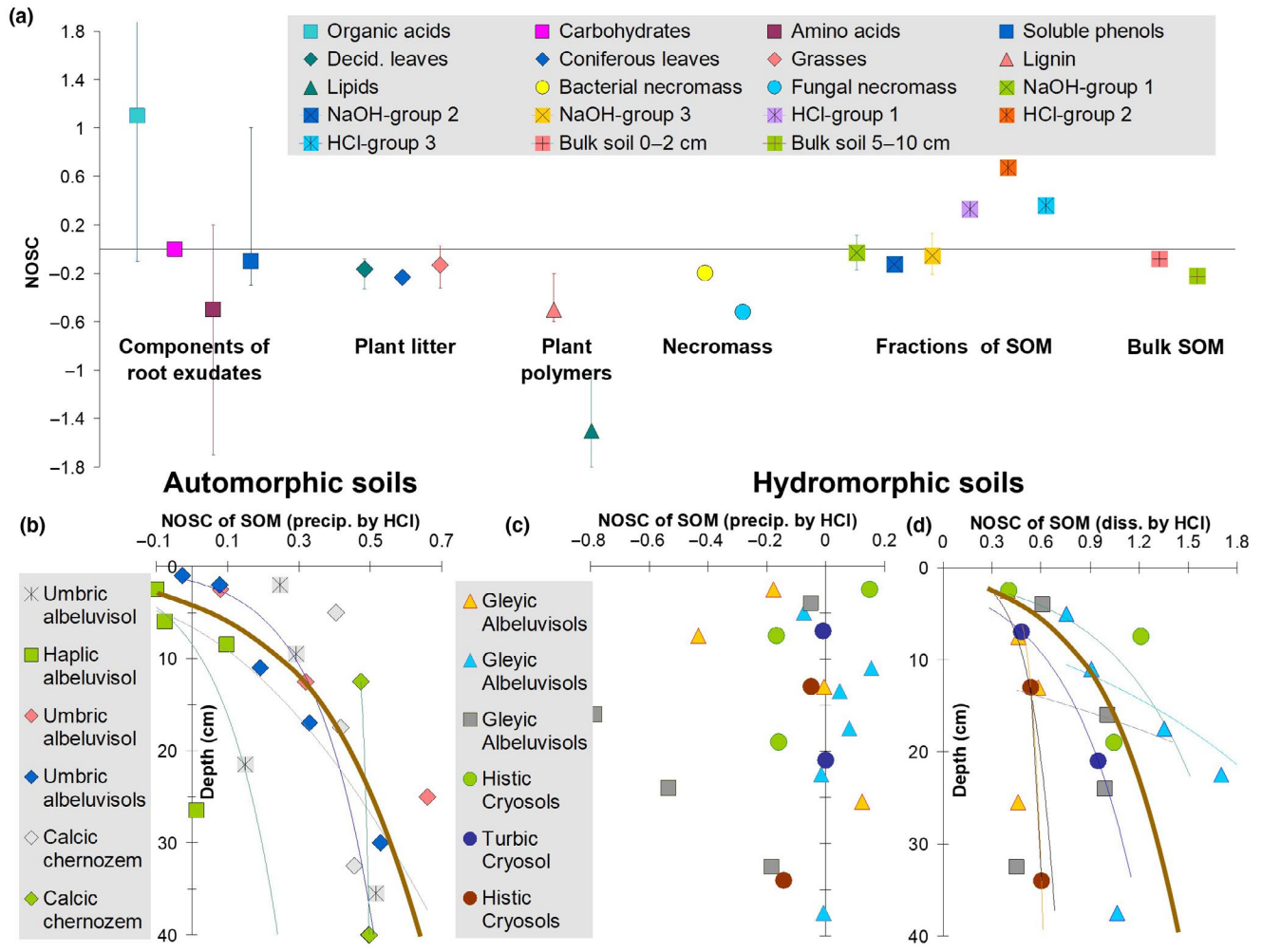

FIGURE 5 Nominal oxidation state of carbon (NOSC) of the main substance classes of root exudates, plant polymers, selected litter types, microbial necromass (pure cultures), SOM fractions (extracted with 1 M NaOH and later precipitated by 6 M HCl (NaOH fractions) or dissolved in HCl (HCl-fractions)), and bulk SOM (0–2 and 5–10 cm). The numbers of NaOH- and HCl-extractable SOM fractions include: group 1 – Podzol, Luvisol, Phaeozem, and Cambisol; group 2 – Histosol and Leptosol; group 3 – Planosols, Chernozem, and Kastanozem (Chadwick et al., 2004; Masiello et al., 2008; Orlov et al., 2005; Popovic, 2019). The NOSC values of pure substances and plant/microbially derived polymers are calculated based on their elemental composition. Error bars: maximum and minimum values. (b) NOSC values of NaOH-extractable SOM (precipitated by HCl from NaOH solution, equivalent to humic acids) from automorphic soils by depth (Bachvalov et al., 2010; Gorbunov & Bezuglova, n.d.; Lodygin et al., 2016). (c) NOSC values of NaOH-extractable SOM (precipitated by HCl from NaOH solution, equivalent to humic acids) from hydromorphic soils by depth (Lodygin et al., 2016). (d) NOSC values of HCl-extractable SOM (NaOH-extractable and HCl-dissolved, equivalent to fulvic acids) from hydromorphic soils by depth (Lodygin et al., 2016). Soil samples are from the following regions: southern taiga (square with a cross inside), middle taiga (square), north taiga (triangles), southern tundra (circles), and temperate forest (rhombus). NOSC values were calculated taking into account the C, H, O, and N molar concentrations of NaOH-extractable and HCl-extractable SOM fractions [Colour figure can be viewed at wileyonlinelibrary.com]

of litter involves a complex of: (i) compositional changes due to the decomposition by micro- and macroorganisms and exoenzymes; (ii) incorporation of some plant-derived C into microbial biomass and subsequently into necromass (Liang et al., 2017; Miltner et al., 2012; Zhu et al., 2020); (iii) mineralization to CO_2. Due to their different degradability and solubility (Figure 1), litter compounds are converted by microorganisms at various rates, shifting the NOSCs of decomposing plant residues (remaining in soil) mainly to reduced states during conversion. For example, the NOSC value of oak roots increased (oxidation) in the initial stages of microbial transformation and decreased in the remaining substances (reduced compounds) during the final stages of SOM formation (Figure S1, left; Hockaday et al., 2015). The NOSC of corn litter declined (was reduced) during the first 300 days of decomposition in forest and agricultural soils and moved in the opposite direction in the intermediate decomposition stages, reaching almost the same NOSC after 600 days (Figure S1, right). Thus, changes in the chemical composition of decomposed plant residues reduce the NOSC value due to remaining persisting compounds and the accumulation of microbial necromass (Figure 5). Accordingly, changes in the NOSC value of the remaining litter cannot be predicted based on the decomposition stage alone (Kuzyakov, 1996, 2002) and depend both on the initial litter composition and

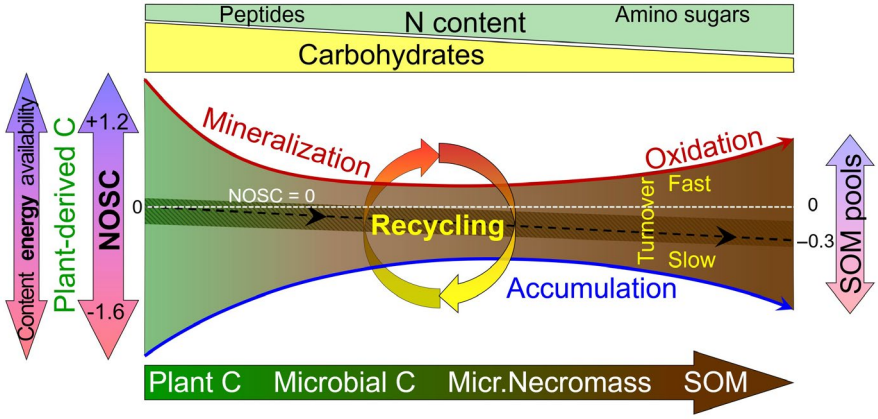

FIGURE 6 Concept showing changes in the nominal oxidation state of C (NOSC) and the energy content of plant residues during decomposition and formation of soil organic matter (SOM). The direction of SOM formation is from left (plant-derived C) to right (microbial-necromass C). Thick arrows: ranges of NOSC of plant residues-derived C and SOM pools. Mineralization, accumulation (red and blue lines, respectively), and recycling processes control both energy and NOSC changes in organic pools. Mineralization processes lead to energy losses and an increase in NOSC, while SOM accumulation increases energy content and decreases NOSC. Recycling can shift both the energy content and NOSC values depending on the environmental conditions of the soil and the quality/quantity of litter input. The SOM (i) has a more diverse composition but a narrower range of NOSC values than plant residues; (ii) consists of microbial necromass and substances recycled by microorganisms; (iii) contains on average substances with a higher energy content than the initial plant residues [Colour figure can be viewed at wileyonlinelibrary.com]

soil properties (e.g. accessibility or thermodynamic constrains under anoxic conditions).

Based on the NOSC and energy content changes of plant residues during microbial transformations—and the ranges of these parameters in SOM (Figures 2 and 5; Figure S1)—we propose the concept that simultaneous changes in energy and NOSC occur when SOM is formed from plant-derived organic matter (Figure 6). Both energy and NOSC changes are driven by shifts in the composition of decomposing litter, which contains substances with a wide range of NOSC and energy content values (Figure 5a) (LaRowe & Van Cappellen, 2011). In early decomposition, readily available soluble compounds are utilized by microorganisms for energy production because of their high energy availability (because of high solubility), even though their energy quality is low. Thus, microorganisms do not need to invest much for substance hydrolysis and solubilization to obtain energy. In the intermediate decomposition stage, the NOSC and energy content of the remaining substrates can shift to (i) a reduced range by the slow decomposition of litter-derived polymers (lignin, waxes) and accumulation of microbial necromass or (ii) an oxidized range because of rapid mineralization of litter and necromass that leads to accumulation/formation of products with high NOSC. Compounds from litter residues or microbial necromass can be recycled by living microorganisms at any time, shifting the NOSC and energy values of the remaining substrates to lower or higher ranges. Finally, SOM contains a wide range of substances (Lehmann et al., 2020) with reduced or oxidized NOSC, but this NOSC range is narrower than that of plant litter due to the predominance of microbial residues (Liang et al., 2020). Thus, the mean NOSC value of SOM is about −0.3 (in the upper horizons) (compared Boye et al., 2017). The average energy content of SOM is expected to be higher than that of litter due to its aliphatic (and partially aromatic) structure and relative enrichment with N-containing compounds in microbial necromass.

6 | CONCLUSIONS

This concept proposes that the formation, stocks, and stability of SOM should be considered in terms of energy and that the SOM pool should be understood not only as a source of C but also as residual energy.

Based on annual sequestration of C from litter into SOM of 0.4%–5% of the total SOM pool, the energy input is equivalent to 1%–10% of the total energy of SOM. Thus, more than 90% of the energy added to the soil by plants is lost during microbial transformation, with SOM representing the residual fraction. This is because microbial energy investment to utilize SOM is inefficient. Therefore, plant litter and rhizodeposition should not be considered as C per se, but rather as energy inputs and stocks that are predominantly used by microorganisms for maintenance, activity (growth and exoenzyme production), and nutrient mining from SOM (the main ecological function of priming effects).

The conversion of plant litter accumulates approximately ~2% of the energy per unit of persisting plant OM. This is the proportion of biochemically stable litter-derived compounds and microbial necromass that become accumulated, while oxidized compounds are completely decomposed or recycled. As a result, SOM has more energy per unit C than plant residues, but the availability of this energy is low. So, it is thermodynamically inefficient for microorganisms to use SOM as a source of C or energy. This is because SOM composition is more diverse with a non-regular structure compared to plant residues and thus requires a wider range of enzymes to break it down.

The microbial transformation of plant residues to SOM is a never-ending continuum governed by processes such as mineralization, recycling, microbial necromass, and residue accumulation, all of which determine the energy content, fluxes, and NOSC values of the residual litter and the resulting SOM. The NOSC and energy content of SOM have a narrower range than litter, with an average NOSC of −0.3 and a higher energy per unit C (Figure 6). At the same time, the NOSC values of available compounds (mainly LMWOS) released from decomposed polymers play a role in the partitioning of C between catabolism and anabolism of microorganisms. These values also affect the energy investment of microorganisms in nutrient mining from SOM.

The conversion of rhizodeposits and plant litter, considered to be the main sources of C in soil, therefore needs to be re-examined from an energy perspective, including energy quality and availability. This would also require assessing energy loss and conservation because almost all microbial processing is directed toward energy acquisition rather than actual C demand. The small amount of plant-derived C and energy that persist in the form of SOM is only an intermediate phase to ensure energy fluxes in the soil system. Thus, the transformation of rhizodeposits and plant litter represents a process of utilizing the energy stored in them, whereby SOM is the residual material that persists because its microbial utilization is energetically inefficient.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

DATA AVAILABILITY STATEMENT

Data openly available in a public repository that issues datasets with DOIs: Gunina (2021), "data_energy_ag", Mendeley Data, V1, https://doi.org/10.17632/fs25cwn9y8.1.

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