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REVIEW

Enhanced Organic Carbon Triggers Transformations of Macronutrients, Micronutrients, and Secondary Plant Nutrients and Their Dynamics in the Soil under Different Cropping Systems-A Review

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Abstract

Decomposition of soil organic matter (SOM) resulted in the release of mineral nutrients viz. macronutrients (N, P, and K), micronutrients (Zn, Cu, Fe, Mn), and secondary plant nutrients (Ca, Mg, and S) in soils. Loss of SOM can be inherently detrimental to crop productivity due to the adverse impacts on soil's physical, chemical, and biological properties. Therefore, increasing awareness regarding SOM and agricultural sustainability was regained importance in the farming community. The build-up of SOM triggers to chemical transformations of macro, micro, and secondary nutrients in the soil. The SOM is a rich source of secondary nutrients, and its slow release contributes to the dynamics in soil nutrient levels. Integrated use of OM application with mineral fertilizers increased soil organic carbon (SOC) more efficiently and enhanced nutrients in the soil. The present study showed that the build-up of OM affected macro, micro, and secondary nutrients differently. The detailed review of previous research studies concluded that the build-up of OM showed a strong positive correlation with nitrogen, phosphorus, potassium, zinc, manganese, iron, and sulphur availability. However, in some cases, OM build-up demonstrated a negative correlation with copper, calcium, and magnesium availability. Thus, the present review focused on soil's critical role of serving as a complex ecosystem that regulates numerous functions for sustainable agricultural production through nutrient cycling. The review highlighted the importance of OM added to soil in altering soil properties and thus enhanced macro, micro, and secondary plant nutrients transformations.

Keywords Soil organic matter · Macronutrients · Macronutrients · Secondary nutrients · Dynamics · Transformations

1 Introduction

Agricultural intensification remarkably increased food production, but it caused quick depletion of both macro and micronutrients from soils in most progressive agrarian states of India (Dhaliwal et al. 2019a; Zhao et al. 2020b). According to the United Nations report, global human population will be 9.6 billion by 2050 which will demand more agricultural intensification to fulfil dietary needs (Brar et al. 2023). During the Green Revolution, agricultural productivity increased in many regions due to the use of enormous amounts of nitrogenous and phosphatic fertilizers. The increased application of urea and ammonium nitrogen fertilizer on long-term basis cause soil degradation leading to diminished soil organic carbon (SOC) levels, soil acidification, and poor soil physical health (Ali et al. 2009; Walia et

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al. 2024). Additionally, intensive cropping and tillage practices caused a significant reduction in soil organic matter (SOM) levels of many prime agricultural lands throughout the region. This decline in SOM levels negatively impacts soil productivity. In several developing nations, the constant depletion of nutrients by crops without proper replenishment caused soil fertility loss, posing an instant risk to ecological and food security (Voltr et al. 2021). The role of SOM in governing the nutrient fluxes, microbial biomass, and enhancement in soil physical, biological, and chemical properties is already well known Babur et al. (2020). The recycling of plant nutrients is vital in maintaining or increasing SOM content, improving soil physical condition, and environmental sustainability.

The amount and superiority of SOM (and accordingly SOC) determine the amount and activity of soil biota that interacts with plant roots. Hence, SOC influences the soil microbial community structure. The organic matter (OM) application to agricultural soils is a widely used practice. It is an abundant source of essential plant nutrients (Thomas et al. 2019) and a means of improving SOC levels. Bhogal et al. (2018) reported that the use of all organic materials improved the supply of soil nutrients (nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), and magnesium (Mg) within a small timescale (< 3 years), whereas SOC levels were only improved via a long-term basis (9 years or more) with use of bulky organic materials like compost and farmyard manure (FYM). Walia et al. (2024) reviewed various studies and found that in most cases, the short-term use of OM resulted in the enhancement of soil quality (microbial biomass, N, P, and K content).

The advantages of various organic materials used (animal waste such as manure based fertilizers such as composts, biosolids, etc.) for SOC and soil quality enhancement have been well recognized (Bhogal et al. 2018). The organic material's potential as soil conditioners, nutrient source, and source of sequestering carbon to mitigate climate change has also been studied.

The dynamics of micronutrients viz. zinc (Zn), copper (Cu), iron (Fe), manganese (Mn), boron (B), and molybdenum (Mo) in soil are related to the build-up of SOM to a significant extent. Incorporation of organic sources (composts, green manure, livestock manure, crop residues, municipal biosolids) in soil alters the macro and micronutrient content due to additional nutrient supply by organic source, and improve soil structure, water storage, and ion exchange capacity, water drainage, and aeration system (Dhaliwal et al. 2019b). Soil organic matter enhances the microbial biomass carbon, mycorrhizae growth, and other activities of microbes which enhance root development system and promote plant growth (Fig. 1). The application of compost into soils is of significant positive interest for maintaining soil physical properties; however, the possible adverse effect of compost application on cropland is the release of toxic heavy metals into the environment and their transfer from soil to the food chain. Soil organic matter (especially humic and fulvic acids) has a high sorption capacity for soil contaminants, especially heavy metals, resulting in their immobilization and consequently reducing their solubility and/or bioavailability for plants (Malina 2018). Besides, the complexation of metals due tothe addition of organic matterto soil could also decrease the bioavailability of metal species. Zhang and Wang (2007) reported that a high amount of heavy metals in polluted soil could slow down the mineralization rate of SOC and increase hardly biodegradable organic carbon (OC). Diacono and Montemurro (2019) reported that the use of olive pomace compost ensured a similar yield level to the commercial fertilizers.

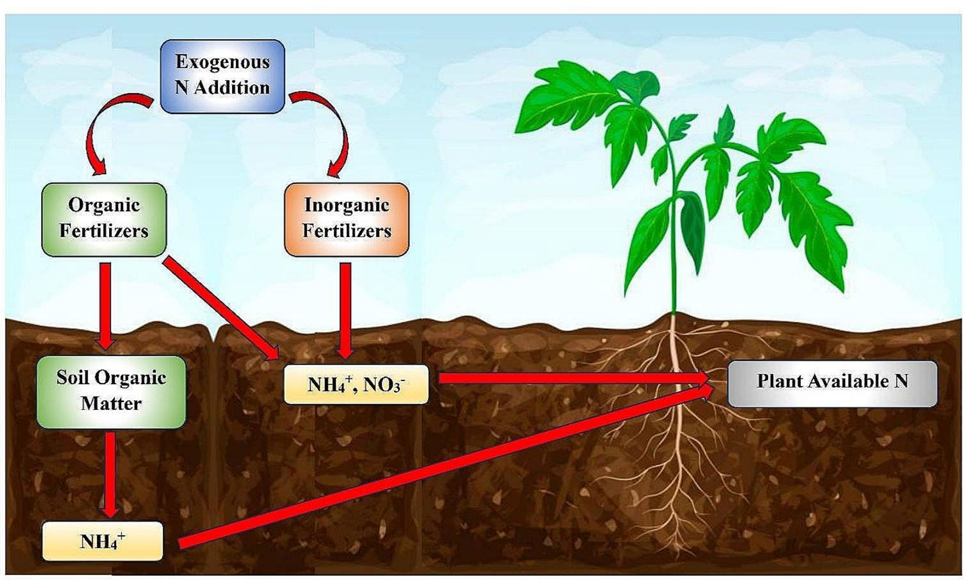

Fig. 1 Impact of soil organic matter (SOM) build-up on exogenous plant-available N forms in soil *Ammonium ions (NH_4^+); Nitrate ions (NO_3^-); Nitrogen (N)

Sustainable soil management deals mainly with SOC management as it plays an essential role in regulating soil processes and properties (Page et al. 2020). The use of OM in cultivated soil becomes more critical for sustainability as cultivation results in higher soil degradation and SOM decomposition (Liang et al. 2012). Substantial improvements in soil's physical, biological, and chemical properties were reported in systems that use OM application (Dhaliwal et al. 2023a). However, not much information is available about the influence of OM on nutrient transformations in the soil. Thus, the present review comprises information regarding dynamics and changes of C, N, P, K, Ca, Mg, and sulphur (S) affected by OM in agricultural soils. Still, significant research and investment efforts are warranted to increase the in-depth knowledge regarding agro-ecological complexities associated with the sustainable use of SOM and, thus, harness the full benefits of macro and secondary plant nutrients to crops.

2 Impact of SOM Build-Up on SOC Level in the Soil

The incorporation of OM is a well-known and effective way of increasing SOC levels and improving soil quality. Hou et al. (2020) showed that sustainable management of soil was mainly about managing SOC. The addition of compost has been widely practiced organic amendment as an alternative nutrient source in crop cultivation. Green manure, particularly legumes, is also a widely used soil management practice to minimize the application of N fertilizer applied in/or N-fixing plants. Soil amendment using peat lowers SOM decomposition by microorganisms by enhancing its resistance to degradation. Studies regarding the use of numerous organic amendments comprising crop residues, municipal solid wastes, peat, composted farmyard manure (FYM), and green manure (GM) to enhance different crop yields and soil quality have been reported earlier (Gomez-Sagasti et al. 2018). Organic matter must be applied to cultivated soil because the soil degradation and decomposition of SOM increase with the cultivation. Brar et al. 2023; described that organic manure application along with chemical fertilizer in subsequent ratoon crops of sugarcane increased the SOC. On the other hand, it has been stated that the integrated use of N, P, and K fertilizers and livestock manure increased the mint and mustard yield along with N, P, and K contents in soil. Walia et al. (2024) studied the effect of applying chemical fertilizer alone and in combination with organic manure in farmland rotating sorghum and wheat on various nutrients and found that fertilizer application in combination with organic manure increased the concentrations of organic C, N, P, and K in the soil. Murmu et al. (2013) carried out a study on tomatoes and corn in acidic soil and revealed that soil health, crop productivity, and nitrogen utilization efficiency were increased with organic manure application compared to chemical fertilizer. It was reported that the content of N, P, K, and main cations in the soil increased by using organic manure containing 30% OM content (Han et al. 2016).

The OM present in manure allows plants to use the nutrients over a long time because of the slow decomposition of OM and limits the loss of nutrients that the plants cannot utilize. Dhaliwal et al. (2023b) found that SOC content was higher under manure application than inorganic fertilizer on sandy loam soils. Liang et al. (2012) revealed that the use of FYM for 15 years increased SOC compared to control (no application) on silty loam soil under winter wheat-summer maize crop rotation.

The addition of FYM, green manure, and wheat-cut straw with *Dhaincha* green manure (*Sesbania aculeate* L.) slightly increased the SOC over the chemical fertilizer application (Walia et al. 2010). Kumar and Prasad (2008) reported a significant build-up of SOC using green gram residue and GM in the rice-wheat system. Singh et al. (2012) studied the impact of organic and integrated modes of cultivation on soil fertility and observed that the organic cultivation method was superior in improving the SOC followed by integrated nutrient management. It was observed that an increase in SOM occurred over the control with the use of pig manure and incorporation of straw into the field (Li et al. 2009). Application of compost alone or with chemical fertilizer is reported to enhance SOC levels (Sarwar et al. 2008). The use of organic fertilizers along with chemical N fertilizers is an extensively used practice in agricultural production reported by Wei et al. (2006) who described that manure and N fertilizer on a long-term basis led to an escalation in SOC content in maize-wheat cropping sequence. Ali et al. (2009) reported a positive impact of organic manure or crop residue incorporation in the integrated management of nutrients on SOC status. The manures like FYM, poultry manure, and sugarcane filter cake, when applied either alone or with chemical fertilizers for seven years under pearl millet–wheat cropping sequence, showed significant enhancement in SOC status. Ozlu and Kumar (2018) studied SOC concentrations under different manure and inorganic fertilizer applications and reported that these treatments significantly impacted SOC for all the soil depths.

The results from previous studies provide strong evidence of the beneficial effects on soil quality through recycling organic materials to agricultural land. However, the extent of impact relies significantly on the quantity (carbon content) and quality (decomposition ability) of the applied organic source. Thus, organic materials may prove

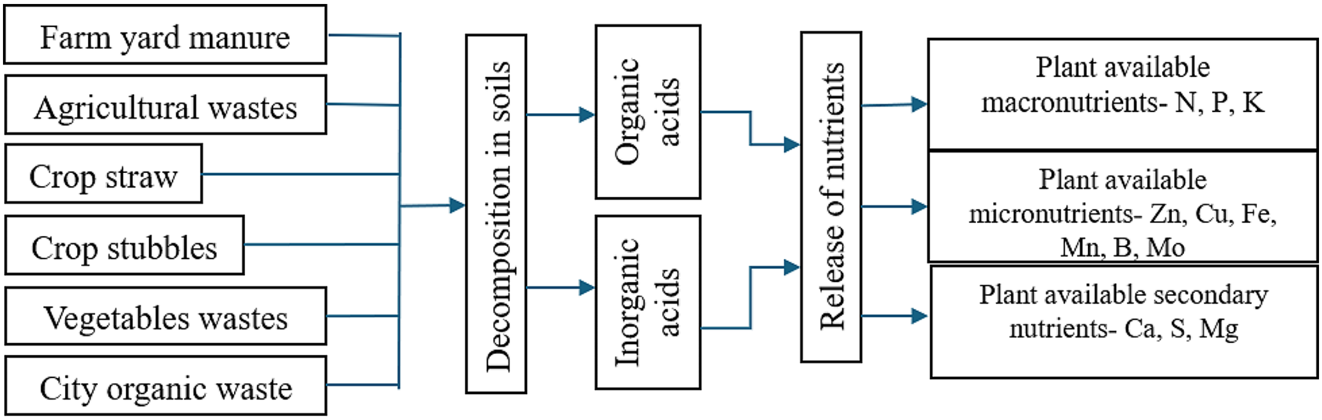

Fig. 2 Build-up soil organic matter (SOM) triggers the release of plant available nutrition in the soil
*N-Nitrogen; P-Phosphorus; K-Potassium; Zn-Zinc; Cu-Copper, Fe-Iron, Mn-Manganese, B-Boron, Mo-Molybdenum; Ca-Calcium; S-Sulphur; Mg-Magnesium

Table 1 Impact of soil organic matter (SOM) build-up on plant-available nitrogen

Source of nutrients	Impact on plant-available *N*	Reference
Organic manures (FYM* and vermicompost) + Inorganic fertilizers	Increased N level	Dhaliwal et al., 20023b
FYM, wheat cut straw and GM with *Sesbania aculeata*	Increased level	Walia et al. 2010
Mixture of wheat straw and grass	Reduced N losses	Shi and Schulin 2018
80% Urea and 20% pig manure /compost	Increased N along with SOC	Liu et al. 2020
Organic manure	Reduced N losses	Mensik et al., 2018

*Farmyard manure (FYM); Green manure (GM); Soil organic carbon (SOC); Nitrogen (N)

advantageous for declined use of synthetic fertilizers as they serve as a valuable source of plant nutrients.

3 Impact of SOM Build-Up on Plant Available Macro Nutrients (N, P, and K) in Soils

3.1 Impact on Plant Available Nitrogen (N)

Nitrogen (N) is one of the significant elements essential for plant life, stimulates above-ground growth, and produces a rich green colour. About 78% of the atmosphere is covered by molecular nitrogen (N_2) unavailable to plants. This molecular nitrogen combines with oxygen or hydrogen to produce ammonia or nitrate or some other organic form of nitrogen. Soil nitrogen is nearly present in OM and is mainly utilized in the NO_3^- form in arable soils (Ladha et al. 2000). Soil microorganisms convert organic forms of N to mineral forms upon decomposition of OM and fresh plant residues (Fig. 2). Plants require more N than any other nutrient, but only a small portion of N in soil is available to plants, and 98% of the N in soil is in organic forms. Significant quantities of N are annually applied globally, directly to soils as fertilizer (Dhaliwal et al. 2024a). Therefore, considering the effects of such N addition on the SOC and N cycles are important. The effect of the addition of N in the soil through different sources has been proposed in Fig. 1. The long-term use of inorganic fertilizers along with organic manures was found to be more beneficial. Zhang et al. (2019) reported that N and P application management is crucial for improving grain yield, maintaining soil C and N levels, and meeting plant needs. A substantial rise in available N was perceived when organic manures were used in combination with N or N and P fertilizers compared to the application of N and P fertilizers alone. Several studies have shown that SOM levels increased prominently in areas receiving FYM and constant use of inorganic fertilizers containing N, P, and K on a long-term basis (Sharma and Subehia 2014). Narwal and Antil (2005) reported that escalation in plant-available N level with the application of organic manures might be related to the breakdown of organic matter, leading to N's release. Walia et al. (2010) reported that the use of manures and fertilizers resulted in a significant enhancement in available N content build-up on subsurface soil (Table 1).

Soil OC and N build-up are estimated by the quantity and quality of the organic residue inputs and their decomposition rate (Dhaliwal et al. 2023d). Soil OC and N showed a similar trend attributable to the high correlation (Shi and Schulin 2018). The N losses due to the addition of OM were comparatively much less than the only fertilizers treated plots on a long-term basis (Eleftheriadis et al., 2018). The SOC to N ratio suggested that the level of humification and degree of OM decomposition in forests generally possess higher values than the agricultural sites (Solomon et al. 2000). Dhaliwal et al. (2012) studied the positive impact of different organic manures on the N status of the soil. Application of N through 80% urea and 20% pig manure/compost resulted in a simultaneous increase in SOC and total N content, which might be due to the high content of biodegradable organic compounds compared with inorganic fertilizer. Another possible reason for increased SOC content might be the improved crop growth, which enhanced the SOC in the soil via crops (Liu et al. 2020). The comparative efficiency of organic and inorganic fertilizers to alter soil properties has also been studied. Inorganic NPK fertilizers without organic input boosted humus mineralization and soil degradation and lowered nutrient availability, nitrogen leaching, energy for micro-organisms activity, etc., by lowering soil pH. On the contrary, organic inputs help to maintain optimal soil properties (Mensik et al., 2018). While another study reported that the application of inorganic fertilizer, either balanced or unbalanced, was not related to any significant effects on SOC or its fractions (Walia et al. 2024).

3.2 Impact on Plant Available Phosphorus (P)

Phosphorus (P) is the critical nutrient after N, which significantly impacts plant growth and metabolism processes, i.e., enzyme regulation, respiration, energy storage and transfer. Phosphorus is also a structural component of deoxyribonucleic acid (DNA), ribonucleic acid (RNA), and cell membranes (Guo et al. 2000). This nutrient is widely distributed in nature as it occurs in living organisms, soil, minerals, and water but is not found in elemental form. Soil P is of two types: organic and inorganic phosphorus (Fig. 2). Both forms of P have low solubility in soils. However, P from inorganic fertilizers is pretty soluble and accessible to plants, but various reactions in the soil reduce its solubility and accessibility (Vu et al. 2008).

Types of soil parent material, degree of weathering, and climatic characteristics greatly influence soil P concentration (Fuentes et al. 2008). Though the total P levels in the soil are high (2–3 g P kg^{-1} of soil), the available P levels in the soil solution are significantly less, representing a small portion of total P (Dhaliwal et al. 2024b). The release of orthophosphate anions from organic and inorganic P is influenced by sorption-desorption, dissolution-precipitation, mineralization-immobilization, and soil pH (Mkhabela and Warman 2005). The effect of organic fertilizers on plant-available P content in soil under SOM build-up has been well documented by the researchers (Fig. 3). Generally, 70–90% of added P through fertilization or mineralization in the soil is fixed depending on soil characteristics, resulting in reduced plant-available P, causing an increase in P fertilizers application rates in agricultural fields (Fink et al. 2016). The chief stable organic P compounds are inositol phosphates, phospholipids, nucleic acids, orthophosphate diesters, monoesters, and organic polyphosphates (Jones and Oburger 2011). Mineralization of soil organic P to plant-available P is carried out in the presence of phosphatase enzyme secreted by soil microorganisms and plant

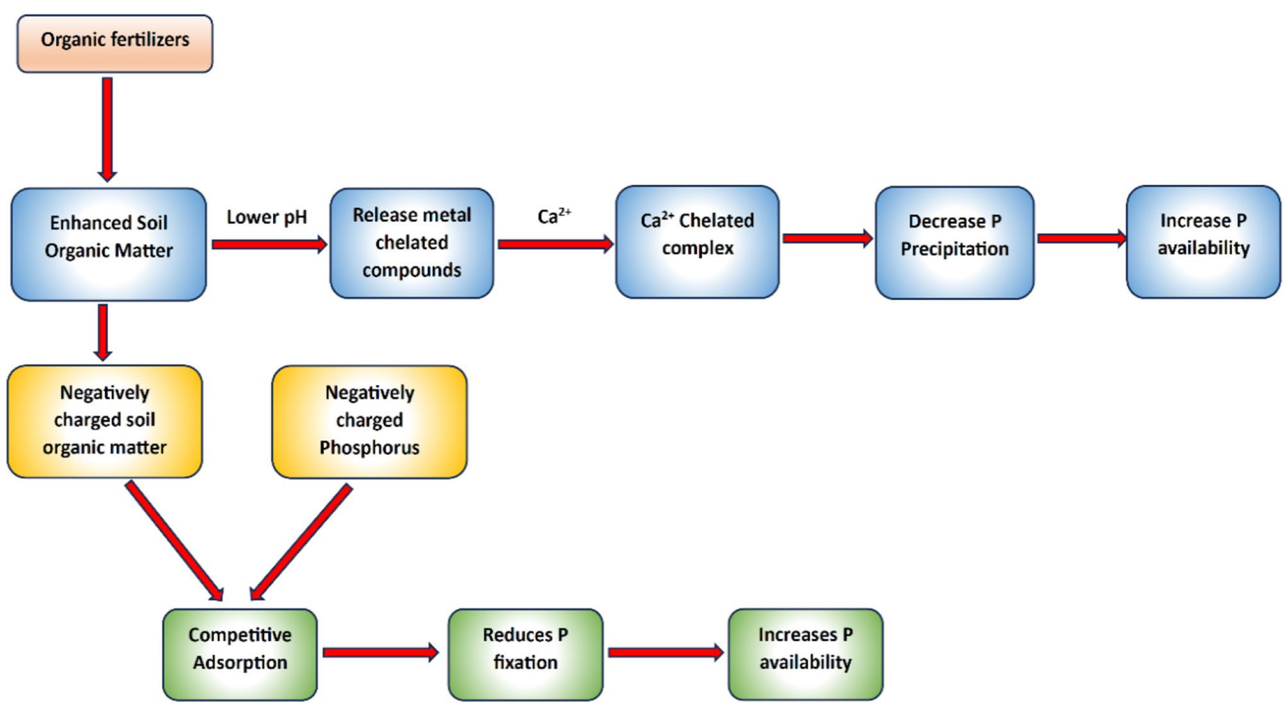

Fig. 3 Impact of SOM build-up to plant-available P forms in soil

roots. The enzymatic reaction is influenced by environmental conditions such as soil pH, temperature, moisture, and surface area of soil particles. Several potential direct and indirect mechanisms affect P and SOM on soil surfaces. Added SOM decomposes, and its products can adsorb to the mineral surface's binding sites, resulting in reduced P sorption and increased P concentration in soil solution and available P for plant uptake (De Bolle 2013).

Phosphate sorption in the soil relies on various factors and soil conditions viz. soil texture, pH, clay mineralogy, and sorption capacity determined by oxide or hydroxide of Al and Fe, and SOM (Yan et al. 2013). The P's chief adsorbents for P in sandy soils are Fe and Al (hydroxides) (Fink et al. 2016). The addition of organic matter to the soil may alter the P sorption depending on the type of SOM, inert P concentration, and the quantity of P added via fertilization (Dhaliwal et al. 2023c). The SOM can hinder P sorption since SOM and phosphate anions are both negatively charged and they bind on the same binding sites in the soil sorption complex (Yan et al. 2013). On the other hand, Dhaliwal et al. (2024b) reported that lower molecular weight organic acids produced from the decomposition of poultry manure in the presence of microbes increased available P content in the soil. The results were due to the competition between anionic forms of organic acids and P for the adsorption sites on soil particles which lower the P adsorption and thus increased the levels of soil available P. Similar results were found by Adler and Sikora (2003) that the application of organic fertilizer produces organic and humic acids, which increased the soil available P content.

Plant remains, manures, and by-products of grazing animals added phosphorus to both the organic and inorganic phosphorus pools. Around 70% of the P present in residues is in soluble form and released when the leftovers are included in the soil (Habashy et al. 2008). The decomposition of organic residues is slow; therefore, P's release occurs relative to the rate of decomposition. Thus, the C: P ratio of organic matter was used to determine whether P will be released or immobilized during organic matter decomposition. Net immobilization of inorganic P is more likely if residues added to soil have a ratio of more than 300. As the ratio drops, P is more than microbial needs, causing a net release of the plant-available form of P. Microbial decay of crop residues with a P content of more than 0.24% leads to increased P mineralization. In contrast, crop residues with P content lesser than 0.07% lead to P immobilization (Iqbal 2009).

At the present rate of rock phosphate consumption, a non-renewable and limited resource, reserves will be exhausted in the next 50–100 years (Steen 1998). However, some of the plant P needs can be supplemented by the addition of organic sources. Organic P sources like manure, compost and plant residues are becoming popular due to the cost and environmental risk linked with inorganic fertilizers. Soil amendment with materials like manure, compost, and plant residue can improve soil P availability directly as a source of P and indirectly via the production of organic acids due to the microbial decomposition of organic material that results in the blocking of P fixing sites, which increases mobilization and decreases P fixation. Composts can affect soil P availability when applied to the soil (Bortoluzziet al. 2015). However, its decomposition rate depends upon quality, soil properties, and weather conditions (Fink et al. 2016).

The maximum bioavailability of P in soil is at soil pH 6.5 (Barrow 2017). Higher soil pH favours P fixation on metals (Al^{+3} and Fe^{3+}) in acidic soils and accelerates the P precipitation with Ca^{2+} in calcareous soils. The slow decrease in available P content with organic P supply and aging time may be related to the lower precipitation rate of less soluble Ca-phosphate complex (Delgado et al. 2000). The application of organic matter such as compost or manure showed a significant impact on decreasing soil pH due to OM hydrolysis and this process lead to the production of anions (citrate or oxalate) that undergo complexion with Ca^{2+} ions, thus elevating P availability in soil solution by lowering precipitation reaction. Ahmad et al. (2018) observed that Ca^{2+}actsas a major hindrance in P availability to plants in calcareous soils as it tends to fix applied P because of the higher soil pH. Several studies reported the synergistic effect of manure and P fertilizer application to improve soil P levels (Garg and Bahl 2008). The presence of humic acid and fulvic acids in organic amendments facilitated the increased recovery of applied P using bicarbonate (Olsen-P), resulting from a decrease in the precipitation rate of poorly soluble calcium phosphate by organic amendments (Delgado et al. 2000). Various studies reported the synergistic effect of manure use alongside P fertilizer on increased soil P concentration (Garg and Bahl 2008). The organic nutrition sources helped to improve mineralizable N, labile C, microbial biomass, dehydrogenase, and phosphatase activity (Dhull et al. 2004).

Dhaliwal et al. (2023a) showed that the application of animal manures increased the concentration of soil-dissolved OC and resulted in increased bioavailability of soil P. Also it was observed that incorporation of organic manures with inorganic fertilizers enhanced the overall plant growth, yield, and soil P availability than the solitary application of either of these nutrients. Use of organic manures alone or in integrated nutrient management increased N, P, and K content of the soil compared to recommended fertilizer-treated plots. Further studies reported that the soil P status improved considerably with FYM substituted for 25 and 50% N and build-up P status to a very high level, ranging from 30.46 to 46.54 kg ha^{-1} (Dhaliwal et al. 2012). On the other hand, Singh et al. (2013) also reported the positive impact of integrated use of fertilizers and manures on OC and available P in the soil compared to bare mineral fertilization. Wei et al. (2006) reported that after 18 years of cropping and fertilization, soil pH and calcium carbonate ($CaCO_3$) levels were lower in the cropped and fertilized treatments than fallow treatment. Continuous twelve-year addition of lantana (*Lantana acamara*) biomass addition in rice-wheat cropping system increased the available P by about 23–71% over no lantana addition (Manikandan and Subramanian 2010). Application of FYM as N source evidenced the maximum improvement in post-experiment soil fertility due to elevated SOC and NPK content. The apparent P and K balance was positive for organic farming treatments. Manna et al. (2006) reported that available P content increased with the integrated use of manures and fertilizers than FYM equivalent to N and the use of inorganic fertilizers, respectively (Chandrakala 2008). Whereas, Kumar (2003) revealed that integrated manurial treatment recorded significantly higher N, P, and K contents. Also it was suggested that the use of composted manure and cattle manure, based on the N needs of corn, could ultimately result in soil accumulation of P, because the N to P ratio of manure or compost is usually smaller than the N to P uptake ratio of corn. The application of dairy manure improved the available plant P over the inorganic fertilizers and without fertilizer treatment in podzol soil (Ali et al. 2019).

The impact of SOM content on P sorption in sandy soil has shown dependence on certain soil properties along with initial P content as P sorption was higher in top soils than in deeper soil horizons. The P saturation and P sorption affected P sorption to a greater extent along with SOM content due to the presence of low-energy sorption sites, which were occupied in the later stages of the P sorption process. The decrease in SOM from top soil lowered the sorptive capacity in most examined samples (Debicka et al. 2016). The amount of humic acid present in SOM has been identified as a primary factor that affects P adsorption and thus alters the amount of plant-available P. In this context, exogenous addition of humic acid was done to modify the SOM content and adsorption-desorption of P was monitored in the black soil of Northeast China. The study concluded that enhanced SOM content released a higher amount of adsorbed P under the typical amount of P fertilizer application. In contrary, the application of an excess amount of P fertilizer along with higher SOM content increased P fixing capacity (Table 2). Thus, to improve plant-available P content in the soil, SOM content must be present in excess with sufficient P fertilizer for a long period (Yang et al. 2019).

3.3 Impact on Plant Available Potassium (K)

Potassium (K) is one of the three essential nutrients that influence plant growth. The quantity of K required for plant growth is almost similar to N but higher than P. Potassium is the seventh most abundant element that constitutes about 2.1–2.3% of the earth's crust (Ali et al. 2019). It has a vital role in various physiological processes is well recognized, such as opening and closing of stomata, uptake and transport of nutrients, and biotic and abiotic stress resistance (Fig. 2). Thus, it plays an integral part in agricultural product quality and plant growth (Dhaliwal et al. 2024a). The soil is the most direct and essential K source for crops (Wang et al. 2010). However, despite the higher contents of K in soils, large agricultural areas of the world are found to be deficient in available K, including about 75% of the paddy soils of China and 66.67% of the wheat belt of Southern Australia (Walia et al. 2024). In recent years, with the expansion in the number of high-yield crop varieties, development of more intensive agricultural practices, and an increase in multiple cropping indices, K uptake by crops from the soil also increased, resulting in an escalation of K deficient soils.

Table 2 Impact of soil organic matter (SOM) build-up on plant-available phosphorus

Source of nutrients	Impact on plant-available *P*	Reference
Poultry manure, FYM, GM and maize residue	Increased P levels	Garg and Bahl 2008
FYM + Vermicompost + NPK	Increased P levels	Dhaliwal et al. 2023d
FYM + Inorganic fertilizers	Increased P levels	Dhaliwal et al. 2012
Poultry manure + Inorganic fertilizers	Increased P levels	Singh et al. 2013
Dairy manure	Increased P levels	Ali et al. 2019
Humic acid (Higher SOM content) + controlled amount of P fertilizer	Increased P levels due to increased desorption	Yang et al. 2019
Humic acid (Higher SOM content) + excess amount of P fertilizer	Increased P fixation and thus decreased plant-available P	
Humic acid (Excess SOM content) + enough P fertilizer	Maintain P supply to crops	

*Farmyard manure (FYM); Green manure (GM); Nitrogen, phosphorus and potassium fertilizers (NPK); Soil organic matter (SOM); Phosphorus (P)

Thus, soil K depletion is gradually becoming a more serious concern.

To sustain agricultural crop production, soil K fertility must be considered, and the application rate of K fertilizer should be based on soil K content, crop requirements, and potential crop yields (Niu et al. 2013). Studies have found that the addition of biotite to K-deficient soils may enhance soil available K contents, in contrast to other macronutrient fertilizers. Nevertheless, another study suggested that the addition of rock K materials may improve soil's long-term fertility by increasing K deposit (Basak and Biswas 2009). The use of non-exchangeable K sources is an essential factor that affects the K uptake efficiency of crops and various plant species have been reported to possess the variable capability to use this resource efficiently (Wang et al., 2011). The low status of available K may be attributed to higher yield targets and more removal from soil. The analogous trends of variation to soil properties under the rice-wheat system were also reported in other studies (Ladha et al. 2000). On the other hand, Sood et al. (2008) reported that fertilizers and organic amendments' continuous implication enhanced all the K fractions in soil over control.

4 Transformations of Macro Plant Nutrients (N, P and K) with Soil OM Build-Up

4.1 Impact on Nitrogen (N) Transformations

Nitrogen is a dynamic nutrient, and it is being continuously rotated between the atmosphere, soil, and living organisms. Within the soil, N can exist either as unreactive gases N_2, N_2O, ions NH_4^+(ammonium), NO_3^-(nitrate) or organic forms like amino acids, lignin, and several other compounds in living organisms, residues, and SOM. There are several N pools in soils (Dhaliwal et al. 2023b). Other transformations of N are mineralization of N, i.e., conversion of organic N to inorganic forms; N immobilization, defined as the uptake or assimilation of inorganic forms of N by microbes and other soil heterotrophs; nitrification, i.e. conversion of ammonium ion (NH_4^+) to nitrite (NO_2^-) and then nitrate (NO_3), and denitrification, which is the conversion of nitrate to nitrous oxide (N_2O) and further dinitrogen gas (N_2). The fact of N_2 fixation, biological and industrial, now far-out spaces historical rates of denitrification is the principal reason nitrogen becomes a major pollutant (Galloway et al. 2013). No other vital element exists in as many forms in the soil as N, and microbes mostly intervene in transformations amongst these forms. The productive capacity of the ecosystem can be measured by the rates at which N transforms to plant-usable forms by soil microbes. Nitrogen undertakes several transformations in the soil while it is used, recycled, and made accessible by soil microbes.

In a study, Robertson and Vitousek (2009) reported that major environmental challenges observed like creating managed ecosystems for N conservation and removing N from wastewater streams, such as urban and industrial effluents, require necessary information about N transformations by soil microbes. Recognizing the fact that plants can take up simple, soluble organic forms of nutrients forced us to widen our description of mineralized products to include all the simple, soluble N forms that can be taken up by plants (Masunga et al. 2016). There are a number of methods for the measurement of mineralization and immobilization (Lin et al. 2016). Nitrogenous compounds contain roughly 20–35% of the SOC. Amino sugars are essential component of SOM that contains C and N.

Earlier humic-formation theory suggested that amino acids interact with sugars and phenol through the Maillard and condensation reactions, respectively (Horwath 2015). But later, SOM stabilization theories propose direct adsorption of amino acids to clays. It is a general belief that most soil N is composed of protein derivatives and cell wall constituents (Nannipieri and Paul 2009). Prominent concentrations of cyclic N monomers in soil were observed in pyrolysis analysis. The probability that these compounds were formed in the duration of analysis was also considered, but now it is thought that significant amounts of these non-plant N compounds do exist in soil (Gillespie et al. 2014). Amino sugars derivatization permits separating and measuring the compounds and associated. Manure constitutes many nutrients required for crop production, out of which N is the most essential and widely added nutrients to the soil for high yields.

4.2 Impact on Phosphorus (P) Transformations

Phosphorus is one of the essential nutrients and it was estimated that about 40% of total P exists in the form of organic compounds in the SOM; however, this percentage may vary from 25 to 80% (Dodd and Sharpley 2015). Plant roots absorb P from the soil solution primarily in the form of orthophosphate anions. All P compounds undergo mineralization either from the mineral phase or from the SOM to convert to orthophosphates in the presence of the enzymatic action of extracellular phosphatases (Lemanowicz et al. 2016). The chemical environment of the rhizosphere is different due to the existence of various enzymes, variable pH, partial pressure of CO_2, and ions activities, which affects the available form of P. Soil OM could also affect the amount of P that is fixed by oxides of Al, Fe, and Ca as the OM prevent the occurrence of this process. The properties of organic compounds possess a significant effect on the quantity of

P fixed. Dhaliwal et al. (2023d) stated that the relation of SOM to P is not as straightforward as it is for N. Although elevated SOM levels are expected to be beneficial for stored P supply but also offer carbohydrates for microbial populations that could upsurge access to P sources. As for N, an identical type of mineralization and immobilization process which transports P amongst the soluble and organic pools exists for P. However, there exists a crystallization/fixation process as an alternative to the denitrification process that converts the soluble P to the insoluble mineral pool of the soil to cause P fixation (Chatterjee et al. 2014). The P held in the SOM or humus, organic residues, and microbial biomass does not exist in plant-available form and thus, the OM undergoes mineralization to convert into plant-available P forms. The movement of P into a fixed P pool varies with soil characteristics. Soils with high Fe and Al sesquioxide have shown the greatest capacity to fix P. Finer root systems and the range of mycorrhizae hyphae could upsurge the access of plants to P sources (Pauwels et al. 2020).

Phosphorus is one of the important nutrient elements for life, and its transformation during the development of the ecosystem employs a decisive influence on soil fertility and environmental properties (Chen et al. 2015). The decrease in inorganic P amounts and availability during the constant development of soil increases C: P and N: P ratio and causes the accelerated limitation of P in terrestrial ecosystems (Mishra et al. 2017). Thus, at a more advanced stage of weathering, soil cycling of organic P becomes necessary for regulating P bioavailability and rates of C and N changes. Although the significance of organic P as an essential nutrient source for soil ecosystem and its key role in ecosystem functioning is well documented, yet there is a lack of in-depth knowledge regarding chemical properties and the transformation reactions as compared to inorganic P. As stated, previous P transformation models during natural pedogenesis suggested that the extracted organic P serves as a sole functional pool with limited plant availability (Huang et al. 2017). In direct contrast to the simple explanation of this operationally defined term, soil organic P contains several compounds that differ prominently in their bioavailability and behavior in the natural environment (Dhaliwal et al. 2023c). The limited understanding of the sources and types of organic P and its transformations in soils not only constrain the implementation of sustainable management strategies, but also restrict the prediction of ecosystem functioning responses towards the variation in nutrient stoichiometry (e.g. C: N: P). Organic P is defined as the P present as a constituent of organic compounds having C-H bonds and results primarily from biological activities involving the assimilation of orthophosphate and subsequent release as plant and animal residue. Based on P bonds, soil organic P has been categorized into three groups i.e. phosphate esters, phosphonates, and phosphoric acid anhydrides (Tian et al. 2021). Many methods have been reported to determine soil organic P, including the measurement of total organic P by ignition/alkaline extraction, estimation of specific organic P compound after extraction using a particular reagent, and the identification of different organic P forms by sequential fractionation or ^{31}P NMR spectroscopy (Alam et al. 2021).

The estimation of total soil organic P mineralization rates reduces due to the rapid sorption of released phosphate (Bunemann 2015). The study used the isotopic dilution approach to measure gross and net organic P mineralization rates under steady-state conditions for estimating P transformation rates. Isotopic dilution studies showed that isotopically exchangeable P, in the period of incubation, could partially or even largely (20–90%) result from biochemical and biological processes rather than physicochemical ones. With the increase in time, the relative importance of mineralization of soil organic P increases, whereas the estimation of extracellular hydrolysis remains unclear. Thus, apart from enzyme activity assays, other approaches are required to evaluate phosphomonoesterase activity in soil that interferes with organic P mineralization rates.

4.3 Impact on Potassium (K) Transformations

Potassium (K) is an essential macronutrient for plant growth and strongly influences the quality attributes. The K ions are involved in many processes and often provide positive contributions (Bell et al. 2021). Potassium is essential for the improvement of soil fertility; however, the organic amendment may differ from mineral K fertilization with respect to modifying the soil. Soil K generally occurs in four pools viz. soil solution K, exchangeable K, interlayer K, and mineral K. The readily available K forms for plant uptake are exchangeable K (1–2%) and solution K (0.1–0.2%)], which represents only a very small fraction of the total soil K. To improve the utilization efficiency of K fertilizers, the investigation studies not only the amounts of different K fractions that other fertilizers had on the K balance in soils but also the movement and transformation of K in soils were required. Most researchers focused on leaching and transporting K in field experiments. However, there is little research available on the diffusion and transformation of K in fertilizer microsites. Potassium in plant material is not bonded to carbon materials and does not undergo microbial mineralization or immobilization processes. As well, because K is readily soluble, it is not subject to significant precipitation reactions.

In an investigation, Bhattacharyya et al. (2006) reported the effect of 30 years of continuous cropping, fertilization and manuring on the K balances, the soil K pools, and the non-exchangeable K release in a *Typic Haplaquept* soil under a rainfed soybean–wheat cropping system. The results showed a net depletion of exchangeable K (80 kg K ha^{-1}) in soil depth (0–45 cm) under the NPK-treated plots and observed a substantial decrease in non-exchangeable K content in 0–45 cm soil layer after 30 years of cropping in the NPK + FYM and NPK treatments. Thus, long-term application of non-revised recommended fertilizer rates may threaten the sustainability of the continuous rainfed soybean–wheat system. In North China Plains, the non-significant alteration in soil K pools and soil K-bearing minerals with K fertilizer application for 25 years has been reported. Thus, fertilization and tillage management practices posed a negligible impact on soil total K and mineral K contents due to excess concentration of feldspar and hydromica contents in soil. The weathering of K-bearing minerals and fertilization significantly altered slowly available K and readily available K contents in soil (Li et al. 2017).

5 Effect of Cropping Systems and Fertilizers on Micronutrients (Zn, Cu, Fe, and Mn) Distribution in Soil

5.1 Effect on Available and Total Zn, Cu, Fe, and Mn in Surface Soils

Compared to a conventional rice-wheat system (Sc1), different scenarios showed significant variations in available zinc (Zn) and iron (Fe) concentrations in the soil. In a CA-based maize-wheat-mungbean system (Sc4), available Zn content was 51% higher. Similarly, in a conventional rice-wheat system (Sc2) and CA-based rice-wheat-mungbean system (Sc3), the available Zn content was 57 and 93% higher, respectively, than in Sc1. However, the available copper (Cu) concentration remained consistent across all scenarios and soil depths. Regarding available Fe, Sc2 exhibited 10% increase compared to Sc3, 13% increase compared to Sc1, and a significant 69% increase compared to Sc4. On the other hand, the manganese (Mn) concentration was 13% higher in Sc3 compared to Sc4, 21% higher compared to Sc1, and 32% higher compared to Sc2 (Jat et al. 2018). The rise in Zn concentration within the CA-based scenarios (Sc2, Sc3, and Sc4) may be attributed to elevated Zn incorporation facilitated by crop residues, leading to subsequent accumulation in the surface soil as reported by Dhaliwal et al. (2019b). The soil micronutrient status of rice crop in Alfisol was significantly improved by the combined application of rice straw (2.5 t ha^{-1}) and leaf residue (2.5 t ha^{-1}), together with 100% NPK (Palkar et al. 2022).

In a 40-year-long study conducted on Alfisols, Prashanth et al. (2019) reported that the combination of FYM (10 t ha^{-1}) in addition to RDF (100%), along with maize residue (5 t ha^{-1}), led to a significant enhancement in the availability of DTPA-Mn and Zn in the soil when compared to the application of only RDF (100%) and the control (Kumari et al.,. 2017). Application of crop residues and fertilizers considerably increased the amount of DTPA-Fe in soil compared to control and its original status. Dhaliwal et al. (2024b) also reported the combined effect of crop residue and fertilizers on Cu availability that significantly increased because of increased microbial activity in soil, which led to the production of complex organic compounds that might have stopped precipitation, fixation, oxidation, and leaching of micronutrients (Fig. 2). The Zn content of the soil was significantly increased after crop residues were continuously incorporated for 18 years at a rate of 100% straw as reported by Kumari et al. (2018). The increase in Zn availability resulting from the incorporation of crop residues occurs due to the addition of Zn from the residues themselves and the release of native Zn through chelation facilitated by the decomposition products of the crop residues. Sharma and Dhaliwal (2020) observed an enhancement in DTPA-extractable Zn, Fe, and Cu in the soil with the application of N (120 kg ha^{-1}) and incorporation of rice straw (7.5 t ha^{-1}), as compared to not incorporating any crop residue except Mn, at 0–15 cm depth. The study suggested that this increase could be attributed to the limited depth of rice straw incorporation, mainly confined to the top 10–15 cm of soil layer, leading to the buildup and distribution of carbon from straw within the upper layers of the soil. Singh et al. (2014) observed that the root biomass density of both rice and wheat was notably greater in the upper 0–15 cm layer of soil in comparison to the deeper soil layers. The micronutrients absorbed by wheat and rice crops can be recycled by crop residue to some extent (between 50 and 80%). A significant increase in DTPA-extractable micronutrients was also found in the topsoil layer when rice residue was used as surface mulch in a zero-tillage wheat system as opposed to conventional or zero-tillage systems without rice residue. Furthermore, this increase in micronutrient availability was particularly pronounced for Fe and Cu, which showed an improvement of 12–14%, while Zn and Mn demonstrated relatively lower increase of 3–6% (Kharia et al. 2017). Residue retention led to 11% increase in DTPA-extractable Zn as compared to residue removal, after a six-year period (Nandan et al. 2019). Retention and incorporating of rice residue resulted in a significant increase in DTPA-extractable Zn, Mn, and Cu content at 0–15 cm soil depth was juxtaposed to burning or removing of rice straw. Furthermore, it was found that DTPA-extractable Fe was found significantly higher when rice residue was retained on the surface as compared to other residue management techniques (Zahid et al. 2020). When conventional tillage is compared with reduced tillage, in reduced tillage DTPA-extractable Zn (0.59 to 0.67 mg kg^{-1}), Fe (8.25 to 11.16 mg kg^{-1}), Mn (15.65 to 17.73 mg

kg^{-1}) and Cu (1.54 to 1.80 mg kg^{-1}) was found higher as compared to conventional tillage 0.57 to 0.62 mg kg^{-1}, 7.56 to 9.58 mg kg^{-1}, 15.04 to 15.91 mg kg^{-1} and 1.37 to 1.80 mg kg^{-1}, respectively, at 0–15 cm depth (Fig. 3). It is because in reduced tillage, crop residue was recycled which favored the micronutrient availability at the surface soil layer (Jayaraman et al., 2021).

Zinc and Fe availability in the surface soil tended to rise as the biochar treatment dose was increased while with increasing doses of biochar, the availability of Mn and Cu in the soil tended to decline. Furthermore, the amount of total Fe and Mn in the surface soil was decreased (17.1–19.3 g kg^{-1} and 336.8-424.9 mg kg^{-1}) due to the application of biochar to the surface soil,. On the other hand, total Fe and Mn in surface soil were lower as compared to deeper layer, respectively, this decrease occurred due to different doses of biochar application on surface soil (Xu et al. 2022). It is possible that the release of Fe and Mn led to the administration of a sizable amount of biochar at high doses and a potential chemical reduction of Fe and Mn oxides, which was made possible by phenolic hydroxyl groups, and the interaction of functional groups with the dissolved organic C from biochar may have helped to create soluble metal-organic complexes (Murtaza et al. 2022). Although there was no discernible effect from the application of biochar in either soil type, soil total Zn and Cu levels tended to be higher in the topsoil in comparison to the subsoil, with increasing biochar doses. The topsoil's total Zn concentration first increased, but thereafter decreased, this might be explained by the fact that Zn frequently forms complexes with different chemical ligands, has less reducibility, and has a tendency to precipitate, whereas the total Zn content in the surface soil increased as a result of the application of an intermediate (6 t ha^{-1} yr^{-1}) dose of biochar (Xu et al. 2022). In the other hand, Dhaliwal et al. (2024a) observed that the addition of rice hull biochar to a mining soil led to increased concentrations of dissolved Fe, Mn, Cu, and Zn. Similarly, Ippolito et al. (2014) demonstrated that the application of hardwood-derived biochar enhanced the availability of Fe and Mn in the soil but did not affect the availability of Cu and Zn. These findings suggest that the dosage of biochar plays a crucial role in influencing soil micronutrients. The highest levels of micronutrients (Zn, Fe, Mn, Cu, B and Mo), along with sulfur (S), were observed when sunflower straw was added at a rate of 4 t ha^{-1} in combination with recommended doses of fertilizers (125% N+100% P) during the cultivation of green gram, as reported by Raut et al. (2010).

5.2 Effect on Available and Total Zn, Cu, Fe, and Mn in Sub-Surface Soils

Available Fe was found highest under Sc2 treatment (38%, 50% and 55%) as compared to other treatments Sc1, Sc3, and Sc4, respectively, while available Zn and Mn were found to be consistent across all four scenarios at sub-surface depth. Furthermore, regardless of the scenarios, there was a noticeable reduction in the content of all the micronutrients with increasing soil depth (Jat et al. 2018). On the other hand, Sharma and Dhaliwal (2020) investigated the impact of residue incorporation with Napplication on DTPA-extractable Mn levels in the subsurface layer. In a research experiment, Dhaliwal and Singh (2013) revealed that the rice-wheat cropping system led to higher Mn concentrations in the subsurface layer, primarily because of leaching, wherein a significant portion of Mn content moved down to the deeper layer due to its increased solubility under rice crop due to submerged conditions. This phenomenon was observed to cause severe deficiencies in the succeeding wheat crop. Jayaraman **e**t al. (2021) observed that the concentrations of available Zn, Fe, Mn, and Cu decreased with increasing depths in both conventional tillage and reduced tillage systems, however, there was no statistically significant difference between the two tillage systems or the various cropping systems in the concentrations of readily available Fe, Mn, Zn, and Cu at depths of 5–15 cm, 15–30 cm, and 30–45 cm, while in the reduced tillage system, the cropping combination of soybean + pigeon pea (2:1) exhibited higher available Fe concentration across all depths compared to other. Xu et al. (2022) conducted an experiment on different doses of biochar on soil and found that available Zn and Fe content was significantly lower while available Mn was higher in sub-surface soil by the application of biochar, whereas biochar application doesn't affect the total Fe and Mn in sub-surface soil. Total Fe and Mn were found higher in sub-surface soil as compared to surface soil, respectively, furthermore, when a high dose of biochar was used, soil total Fe and Mn were higher in the sub-surface soil (19.3–19.8 g kg^{-1} and 491.6-603.3 mg kg^{-1}) as compared to surface soil, respectively, while total amounts of Zn and Cu in the subsurface soil were unaffected by biochar. Brar et al. (2023), the findings demonstrated a clear trend in the vertical distribution of DTPA-Zn content, showing a decrease with increasing soil depth. Notably, the rice-lentil cropping system exhibited a distinct ability to impede the downward migration of DTPA-Zn and organic carbon within the soil profile when compared to the rice-wheat and rice-maize systems.

The relationship between DTPA-Zn and organic carbon content was observed to be positively correlated, suggesting that the adoption of CA practices, which involve retaining crop residues and minimizing surface soil disturbance, led to increased organic matter content. This increase in organic matter content facilitated the presence of chelating agents that contributed to the complexation of native Zn. To summarize, the implementation of practices such as zero tillage and permanent bed cultivation had a notable impact on constraining the movement of both DTPA-Zn and organic carbon to lower soil depths as compared to conventional tillage methods. Similarly, Ansari et al. (2022) observed that the available concentration of micronutrients in the surface soil was notably higher compared to the subsoil layers, this concentration exhibited a linear decline with increasing soil depth. Moreover, retaining crop residues showed a significant increase in micronutrient content (including available Zn, Fe, Mn, and Cu) in comparison to removing the residues. The micronutrient levels in the retained residue scenario were lower by 10.9, 6.4, 9.5, and 5.1%, respectively, compared to the levels found in the surface soils.

5.3 Effect on Transformations of Zn, Cu, Fe, and Mn in Soil

Majority of the total Zn content was found in the residual form, with only a small portion present in easily available forms (WS + EX form). The incorporation of crop residues in the soil led to a remarkable increase in various Zn fractions, but the effect was minimum on the amorphous fraction. The majority of the Zn recycled through crop residue, whether alone or with additional Zn, ended up accumulating in the residual form, followed by the crystalline fraction. Approximately 81% of the total native Zn was present in the residual fraction. The ranking of Zn fractions, irrespective of the treatments, was as follows: Res-Zn > AFeOX-Zn > OM-Zn > MnOx-Zn > SpAd-Zn > WS + EX Zn as reported by Kumari et al. (2018) who reported thata major portion of Zn, whether naturally occurring or added externally, existed in a residual state, while smaller fractions are found in easily soluble forms such as exchangeable, water-soluble, and organic complexes, Additionally, the incorporation of crop residue or the application of residual Zn led to a significant increase in different Zn pools. Karimi et al. (2019) observed the effect of different biochar applications on Zn fraction in soil and found that biochar generated at 200 °C resulted in higher Zn levels in organic, exchangeable, and Fe-MnOx Zn fractions compared to the control, which could prove beneficial for Zn-deficient calcareous soils. Conversely, biochar produced at 350 and 500 °C led to an increased organic and carbonate Zn fractions while reducing exchangeable Zn fraction in the soil. Furthermore, about 64% of the soil's total zinc was found in the residual fraction, while about 22.5% was present in the Fe-Mn and Ox-Zn fraction. Sharma and Dhaliwal (2020) revealed that the incorporation of rice straw in wheat had a significant impact on the availability of micronutrients compared to the removal or rice straw.

Among the various Zn fractions, the crystalline Zn fraction (CRYOX) exhibited the highest level, followed by the OM-bound fraction, and amorphous (AMOX) fraction, and the lowest were the water-soluble and exchangeable Zn fractions. This impact primarily stemmed from the process of native soil insoluble Fe solubilization, accompanied by enhanced diffusion and mass flow in the immediate vicinity of plants, as highlighted in the study by Dhaliwal et al. (2012). As for the Fe fractions, the AMOX fraction was slightly higher than the CRYOX and OM-bound fractions, which were higher than the water-soluble and exchangeable (WSEX) as well as the specifically adsorbed (SPAD) fractions. Notably, when different treatments were considered, the application of N (120 kg ha^{-1}) and rice straw (7.5 t ha^{-1}) resulted in significantly higher levels of all Zn and Fe fractions compared to unfertilized or removal of straw treatment. The incorporation of rice residue led to an increase in Mn fractions. The highest increase in CRYOX and MnOX was observed under rice straw (10 t ha^{-1}), with levels 2.6 and 22.3% higher than straw removal, respectively. The CRYOX and OM-bound fractions of Mn were significantly higher under N (120 and 150 kg ha^{-1}) compared to unfertilized plot. Additionally, among the Cu fractions, the CRYOX fraction showed maximum increase under N (120 kg ha^{-1}) and rice straw (10 t ha^{-1}) compared to unfertilized or straw removal treatment. Addition of crop residues led to an increase in SOM content, resulting in the formation of strong complexes between Fe and SOM. As a consequence, reduced amount of oxides was available for Zn adsorption. Walia et al. (2024) reported a decrease in the binding of Zn to both crystalline and amorphous Fe oxides was evident. The presence of agricultural crop residues exerted a significant influence on augmenting the solubility and accessibility of Fe in the soil. Furthermore, the increase in the organic fraction observed in plots where residues were retained can be attributed to the development of organic complexes involving Mn and organic acids generated during the decomposition of organic matter.

The incorporation of crop residues affects the reduction of soil pH, leading to increased solubility of Cu compounds (Dhaliwal et al. 2017). Additionally, it enhances the organic matter content of the soil and promotes the formation of complexes, resulting in higher availability of Cu and Mn. The elevated content of WSEX-Cu and SPAD-Cu fractions in residue-retained plots compared to other treatments can be attributed to the increased organic carbon content and cation exchange capacity (CEC) of the soil. These factors are known to rise with the application of organic manures. Similarly, Sharma and Dhaliwal (2019) conducted an experiment to understand the impact of sewage sludge and rice straw compost on soil micronutrients fractions. Among Fe fractions, OM-bound fraction showed edge over the crystalline Zn fraction (CRYOX), amorphous Fe Oxide (AMOX), and Mn-oxide (MnOX) and was higher as compared to water soluble and exchangeable (WESX) and specifically adsorbed (SPAD) fractions. Among different Zn fractions, CRYOX showed higher range followed by AMOX, OM-bound, SPAD, MnOX and minimum in WESX Zn fraction are 21.2–31.2 mg kg^{-1}, 4.93–9.33 mg kg^{-1}, 4.53–7.07 mg kg^{-1}, 1.69–3.65 mg kg^{-1}, 1.40–2.03 mg kg^{-1} and 1.27–1.87 mg kg^{-1}, respectively. Among various treatment options, the application of sewage sludge and rice straw compost resulted in significantly higher levels of all Zn, Fe, Mn, and Cu fractions compared to the recommended use of fertilizers. However, among organic treatments, those with 50% N substitution through sewage sludge (10 t ha^{-1}) exhibited greater micronutrient transformations compared to treatments using rice straw compost. For Mn fractions, higher Mn fraction was recorded in CRYOX followed by as compared to other fractions, while AMOX fraction shows highest increase in Cu fractions. The concentrations of organic-bounded micronutrient fractions were found to be higher compared to the other fractions, particularly in treatments where organics (sewage sludge and rice straw compost) were incorporated along with inorganic fertilizers. Dhaliwal et al. (2019b) revealed that the prevalence of alternative oxidized and reduced conditions in the rice-wheat system led to a decline in the content of CFeOX forms of Mn, while the easily reducible AFeOX forms of these micronutrients increased thereby enhancing their availability. Moreover, the long-term application of farmyard manure in the soil also increases organic matter content, subsequently enhancing the availability of Zn and Fe (Dhaliwal et al. 2023a).

6 Impact of SOM Build-Up on Secondary Plant Nutrients (Ca, Mg, and S) in Soils

6.1 Impact on Available Calcium (Ca)

Calcium (Ca) is an essential plant nutrient required for root health, the growth of new roots and root hairs, and leaf development. Calcium is required in large amounts by all plants to form cell walls and cell membranes, In addition to its role in plant nutrition, Ca also plays an important role in maintaining soil physical properties and reclaiming sodic soils (Liu et al. 2000). The five available form of Ca in the soil can vanish when it dissolved and removed in drainage water, taken by plants, absorbed by soil organisms, leached in rainwater and absorbed by clay particles. A significant quantity of Ca-compounds is necessary to establish the carbonate equilibrium in soil water and create a proper buffering system of the soil water (Medhe et al. 2012). Rainfalls and the respective elution leads to a continuous repetition of these processes. The process of Ca-compound ingestion to create CaCO3 equilibrium is controlled wholly by the amount of mineralizing OM liability, however, the role of soil properties is only minimal. Better the reserve of oxidizable OM in soil and lower the stability of OM, higher is the consumption of Ca-compounds to establish equilibrium between CO_2 and HCO_3^- and higher production of water-soluble $CaHCO_3$(increase in the available form of Ca). However, soils quality and potential fertility decreases due to the loss of labile OM (Oldham 2017).

Organic matter use integrated with mineral fertilizers provides the potential for increasing soil fertility and eventually crop yields (Vanlauwe et al. 2002). The nutrients' release and their availability to the plants can be changed by adjusting the quality and quantity of OM. The role of Ca in microbe-mineral-organic matter interactions and related transformations is still unnoticed and needs to be explored (Shabtai et al. 2023). Shabtai et al. (2023) reports a positive correlation between Ca and SOC stocks in mildly acidic to alkaline soils. This is because of Ca moderate various physiochemical associations such as co-precipitation, occlusion within soil aggregates, sorption, and complexation between soil minerals and organic compounds. These associations decreased SOC availability and enhanced soil SOC stocks. Organic matter enriched with $CaCO_3$ and calcium oxide (CaO) helped crops via acidity correction of soil, though the intensity of acidity correction depends on the initial pH of the soil and the amount of OM added to the soil (Dhaliwal et al. 2024b). The short-term organic liming effect, caused by N, is strongly dependent on OM decomposition, which is further mediated biologically. The decomposition of organic molecules consisting of Ca had affected pH similarly as effected by lime (Larney and Angers 2012).

The compost and vermicompost addition to slightly acidic soil significantly improved the soil available Ca content due to high Ca content in organic amendments (Angelova et al. 2013). The trend for increased Ca content was vermicompost > compost > control and showed significant correlation with TOC ($r=0.59$) and soil pH ($r=0.90$). The enhancement in available Ca content might be due to the favourable formation of DOC-cation complexes in high pH soil due to vermicompost addition, thus enhancing macronutrient mobility. The addition of organic amendment through Corresal Plus to calcareous saline-sodic soil resulted in non-significant enhancement in exchangeable Ca^{2+}, whereas the addition of bio-stimulant slightly decreased the exchangeable Ca^{2+} (Table 3). The results of SOM addition showed a reverse trend to that of exchangeable Ca^{2+} (Karapouloutidou

Table 3 Impact of soil organic matter (SOM) build-up on plant-available calcium

Source of nutrients	Impact on plant-available Ca	Reference
Vermicompost, Compost	Increased significantly	Angelova et al. 2013
Corresal plus	non-significant increase	Karapouloutidou and Gasparatos 2019
Biostimulant (Actiwave)	Non-significant decrease	
Sewage sludge, Poultry litter, and Swine	Increased significantly	Dhaliwal et al. 2017
Organic fertilizer	Significant increase	Zhang et al. 2020

Table 4 Impact of soil organic matter (SOM) build-up on plant-available magnesium

Source of nutrients	Impact on plant-available Mg	Reference
Animal manure	Significant increase	Ano and Agwu 2005
Vermicompost, Compost	Significant increase	Angelova et al. 2013
Corresal plus	Non-significant increase	Karapouloutidou and Gasparatos 2019
Bio-stimulant (Activate)	Non-significant increase	
*Lime, CMP, OF, OFC	Significant increase	Zhang et al. 2020

*Calcium magnesium phosphate fertilizer (CMP), Organic fertilizer (OF); Organic fertilizer combined with calcium magnesium phosphate fertilizer (OFC)

and Gasparatos 2019). The incorporation of organic matter into the municipality soil through sewage sludge, poultry litter, and swine manure raised available Ca content in the soil by 44%, 38%, and 36%, respectively. Thus, poultry litter may prove as a potential source to improve the nutrient content of soil (Faria et al., 2019). The bare organic and in combination with inorganic amendments of *Udic Ferralsol* was done through different sources to monitor the variation in soil properties. The soil amendments, irrespective of the source used, improved the soil exchangeable Ca concentration (691–3876 mg kg^{-1}) over the control (208–497 mg kg^{-1}). Non-significant variation among soil amendments was observed except for treatment which possessed significantly lower Ca content than in the lime (Zhang et al. 2020).

6.2 Impact on Available Magnesium (Mg)

Magnesium (Mg) is the second dominant ion on the exchange complex of the mineral soils. Various factors that affect the concentration of plant-available Mg include distribution and chemical properties of the parent rock material, its grade of weathering, anthropogenic factors, and site-specific climatic conditions, agronomic practices such as cropping intensity, cultivated crop species and crop rotation, and fertilizer management practices through organic or inorganic sources (Chaudhary et al., 2021). Available Mg is the primary source of Mg for plants. Except in some acidic sandy soils, Mg is rarely a limiting nutrient as far as its availability is concerned. Organic matter accounted for about 10.6% of the total variability on available Mg content in soil and a single unit increase of OM decreases the available Mg by 13.39 units (Khadka 2016).

The organic matter (compost and vermicompost) treatments significantly raised available Mg content in soil. Vermicompost is enriched with most nutrients in plant-available forms such as phosphates, exchangeable Ca, Mg, and soluble K (Orozco et al. 1996). However, there has been variable correlation reported earlier between OM and available Mg contents (Table 4). The negative but non-significant correlation was obtained by Medhe et al. (2012). An increase in available Mg accompanied an increase in soil pH. Similarly, animal manure showed significant improvement in soil pH, which increased with an increase in levels of Mg (Ano and Agwu 2005). The organic amendments to slightly acidic soils through compost and vermicompost treatments significantly increased the soil available Mg content due to exogenous addition through organic matter, which contained significant amount of Mg. The increment was highest in vermicompost treatment followed by compost and control treatments, and the trend showed a significant correlation with TOC and soil pH. The amendment of *Udic Ferralsol* through lime, calcium magnesium phosphate fertilizer (CMP), organic fertilizer (OF), and organic fertilizer combined with calcium magnesium phosphate fertilizer (OFC) treatments was done to monitor the variation in soil properties. In general, soil exchangeable Mg concentrations followed the trend CMP (58.2–1159 mg kg^{-1}) > OFC (41.4–945 mg kg^{-1}) > OF (24.4–398 mg kg^{-1}) > lime (17.3–59.8 mg kg-1) > control (11.8–49.1 mg kg^{-1}) at all sampling times and both soil depths (Zhang et al. 2020).

6.3 Impact on Available Sulphur (S)

Sulfur (S) is the 4th major nutrient in crop production after N, P, and K. In recent years, S has become more important as a limiting nutrient in crop production (Lipiński et al. 2003). Plants can absorb S only through their root systems in the sulphate (SO_4^{2-}) form. Soil OM contains S in an organic form, which releases its S for plants' use on decomposition. The SOM decomposition releases non-anionic S

(SO_4^{2-}forms). Most of the agricultural land soils (70%), showed S fraction content in the range 5.0–20.0 mg kg^{-1}in the soil sampled from the crop rotation enriched with SOM. Organic matter application (FYM), when applied for many successive years, increased sulphatesin soil and the highest content was observed when OM was used at a rate of 60 t ha^{-1}. Farmyard manure contains S in the range of 0.9 to 1.2 kg ha^{-1}. On average, 20% of total S exists in the form of plant-available sulphate form, 40% accounts for the organic bonds, and another 40% in organic-inorganic sulphates (Kaczor and Zuzańska 2009).

About 90 to 95% of the S is in the SOM. An inverse relationship has been observed between SOM and available S (Khadka 2016). Organic matter describes around 3.6% of the total variability in available S form. Similarly, by increase in OM content, available S decreases gradually and vice-versa. Furthermore, increasing organic matter by one unit reduces the available S by 0.37 units and vice-versa. Soil microorganisms are responsible for the movement of the nutrients between the SOM pool and the soil solution in plant-available form. Thus, high populations of microorganisms (*Thiobacillus* sp.) mineralizing S on the low OM site might result in high S availability. On the other hand, a significant but positive correlation was obtained by Habtamu et al. (2014). On the other hand, a negative but non-significant correlation was obtained by Patel et al. (2014). Enzyme response towards alteration in soil management may be more rapid than other soil variables and thus might be used as early indicators of changes in soil biology (Gianfreda and Ruggiero 2006). Arylsulphatase catalyses the hydrolysis of O-S bond and releases plant-available inorganic S as SO_4^{2-}. Arylsulphatase activity, similar to other hydrolases, alters due to crop rotation and organic matter addition. The enzymatic activity of sulphohydrolases strongly influences the balance between microbial synthesis and degradation of ester sulphates, and thus the ester sulphate pool in soils.

Incorporating organic fertilizers to *Alfisol* for long term (37 years) resulted in significant enhancement in total S content of the topsoil layer compared to lower layers (Gao et al. 2017). Moreover, higher levels of fertilizers showed prominent results compared to lower levels followed by no fertilizer treatment. Integrated application of organic fertilizers with NPK fertilizers showed superior results for improving the total S content of soil. Addition of organic amendments to the two S deficient soils belonging to the series reported that S significantly increased plant available S content due to the development of SO_4^{2-} sorption sites in the soil. The chief components of organic amendments were TOC, LOC, total S, and extractable S, which affected S availability in soil. The trend for available sulphate was in the sequence sugarcane filter cake > poultry litter > FYM (Malik et al. 2020). In another study, combined application of S and organic matter were reported to enhance the content of plant-available S (12.87 to 16.66 mg kg^{-1}) in soil despite a non-significant variation in total S (Table 5). Oxidizable OC decreased (1.31 to 1.27 g 100 g^{-1}) significantly with the incubation period due to mineralization of OC and carbon losses in the form of CO_2. Also, negative correlation between oxidizable OC and non-sulphate S was observed (Saren et al. 2016). In acidic soil (pH = 5.5), rice cultivation led to the depletion in plant-available S content in the absence of fertilization. Integrated application of organic and chemical fertilizers showed superior results as compared to the application of chemical fertilizers alone. Among organic sources, FYM and GM were found to be more potent sources to improve the available plant S in soil (Sharma et al., 2020). Application of FYM to *Haplic Luvisols* recorded an increased activity of arylsulphatase and high content of plant available S content over the untreated soil along with an increase in organic matter content.

7 Soil OM Build-Up Influencing Transformations of Secondary Plant Nutrients (Ca, Mg, and S) in Soil

7.1 Impact on Calcium (Ca) Transformations

Organic matter contains black humicacids, which exhibit a strong chemical affinity to Ca; hence where Ca is present in solution, humic acid may react with Ca and form an insoluble Ca-humic acid complex (Zhao et al. 2020a). The Ca ion combination with humic acid formed in hydration causes difficulty for Ca crystallization, which is accountable for the increase of cement soil strength to take place. Organic matter also contains fulvic acid that combines with mineral particles containing Al, Ca, and induces layered crystal lattice decomposition.

Table 5 Impact of soil organic matter (SOM) build-up on plant-available sulphur

Source of nutrients	Impact on plant-available S	Reference
Organic fertilizer + NPK	Significant increase	Gao et al. 2017
Sugarcane filter cake, FYM	Significant increase	Malik et al. 2020
Organic fertilizer + Inorganic S	Significant increase	Saren et al. 2016
FYM/GM + Inorganic fertilizer	Significant increase	Sharma et al., 2014
FYM	Significant increase	Siwik-Ziomek et al. 2016

*Farmyard manure (FYM); Green manure (GM); Sulphur (S); Nitrogen, phosphorus and potassium fertilizers (NPK);

7.2 Impact on Magnesium (Mg) Transformations

Application of OM (compost and vermicompost) significantly enhanced soil available Mg content. The maximum improvement was observed after the addition of vermicompost. Vermicompost is enriched with most nutrients in plant-available forms such as phosphates, exchangeable Mg, Ca, and soluble K (Ramnarain et al. 2019). Increasing the compost and vermicompost application rate increased DTPA-extractable Mg. Organic matter application has also been reported to change the pH of the soil. A high positive coefficient of correlation between exchangeable Mg and soil pH has been observed as an increase in soil pH resulted into an increase in Mg (Orozco et al. 1996). The addition of animal manure has also shown significant improvement in soil pH with increased values for exchangeable Mg. Sorption of dissolved organic carbon (DOC) and formation of DOC cation complexes may be pH-dependent (Steinberg et al., 2018). As soil pH increases above neutrality, DOC sorption to soil becomes weaker, and the potential for the formation of DOC-cation complexes increases. At higher soil pH, vermicompost addition likely promoted the formation of DOC cation complexes, subsequently increasing macronutrient mobility (Romkens et al., 1996). To date, scanty information is available on the contribution of SOM to the soil Mg levels, plant minerals, and nutrition. In terms of plant Mg nutrition, SOM has been widely known to increase soil cation exchange capacity by providing variable charges to soils. However, in some specific soils, the organically bound Mg can act as an important source of Mg. Nevertheless, the lack of knowledge on the contribution of Mg mineralization to Mg nutrition of crops again points to the importance of future research efforts to be put on this topic.

7.3 Impact on Sulphur (S) Transformations

In fertile agricultural soils, S mainly exists in organic form in roots, humified OM, and undecomposed litter. In SOM and plant litter, S is mainly present in sulphydryl form in proteins, sulpholipids and nucleic acids and bonded directly to C (Samanta et al. 2020). Mineralization and subsequent oxidation of S in SOM proceed via the generation of protons. As soil bacteria and fungi grow on plant litter and SOM rich in C and poor in S, soil solution SO_4^{2-} may be immobilized. In an intervallic anaerobic environment that arises, succeeding aerobic production of SO_4^{2-}, O_2 concentration might be depleted by quickly growing bacteria. Some bacteria could use $SO_4^{2-}$for fermentation as a terminal electron acceptor. The process leads to the consumption of H^+ for reduction of $SO_4^{2-}$to H_2S along with the generation of intermediate compounds. The produced H_2S is well known to precipitate metal ions to metal sulphides (Dhaliwal et al. 2024a). As this is a reversible reaction, thus the produced metal sulphides are reoxidized to generate H^+, resulting in soil acidification. These reactions are prevalent for lowland rice cultivated soils and result in a phytophillic neutral pH when waterlogged, but can create low phytotoxic pH when the soil is in the aerobic state (Li et al. 2001). In agricultural systems, where S inputs from fertilizer and atmospheric deposition are low, the release of S from organic forms is important for the constant supply of S to plants.

8 Conclusions

Application of organic matter resulted in significant soil health improvement in terms of soil organic matter and available nutrient status. However, excessive application of fertilizers not only adversely influenced soil biological communities but might also elevate the residual inorganic N level, which enhance SOC mineralization and thus result in the loss of SOC. As there is huge spatial and temporal variability in soil nutrient supply, thus crop response to fertilization also varies. Organic matter addition, either alone or in combination with inorganic fertilizers, significantly increased different fractions of P and K in soil. Organic matter application was reported to affect nutrients, including macronutrients (N, P, K), micronutrients (Zn, Cu, Fe, Mn, Mo, B) and secondary nutrients (Ca, Mg, S) in the soil. Various forms of organic amendments were used to increase the nutrient availability to plants. For secondary nutrients, mixed results were reported in the literature in case of the effect of organic matter, Ca, and Mg. It could be established that the impact of organic matter on secondary nutrients depends on the area, type of soil, and soil properties. Thus, the direct positive or negative correlation between organic matter and secondary nutrients could not be concluded. Overall, the review illustrated that the addition of organic matter to soil alters its physical, chemical, and biological properties, which strongly affected the nutrient dynamics and transformations to plant-available forms.

9 Future Perspectives

- Different methods for incorporation of agricultural waste and residue in soil are being followed throughout the production of crops.
- With increase of organic matter strongly influenced the transformations of macronutrients in soil under different cropping systems.

- Enhanced organic carbon lowers the pH of soil which directly affected the micronutrients and secondary plant nutrients under different cropping systems.
- Organic carbon alters nutrients transformations their dynamics in the soil under different cropping systems.
- It is difficult to maintain the organic carbon status of soil via efficient management of crop residues properly and return them to the soil in some way to avoid various environmental problems.
- Soil microorganisms capable of breaking down lignocellulose contribute significantly to the decomposition of organic matter within soil or during composting.
- With increase in soil organic carbon, nutrients transformation and their dynamics varied in the surface soil as compared to sub-surface soil.
- Overall, it is crucial to manage crop residues properly and return them to the soil in some way to avoid various environmental problems caused by their improper management as well as to make agriculture sustainable.

Abbreviations

FYM Farmyard manure
GM Green manure
SOC Soil organic carbon
SOM Soil organic matter

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Declarations

Conflict of Interest The authors declare that they have no conflict of interest.

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