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Review

Organic Fertilizers and Bio-Waste for Sustainable Soil Management to Support Crops and Control Greenhouse Gas Emissions in Mediterranean Agroecosystems: A Review

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Abstract: Agriculture is facing several challenges related to its sustainability. In this regard, the need to reduce its environmental impact related to the use of synthetic inputs and its potential role in mitigating global warming and climate change call for a review of crop management. In this context, and in the framework of achieving sustainable development goals, the use of organic fertilizers and bio-waste represents a valuable contribution to the agricultural transition towards a bioeconomy model by reducing the negative impacts of waste disposal. Farmyard manure, composts, digestate from agrifood processes, and biochar are, among organic fertilizers, commonly used to manage soils and support crop growth. These fertilizers can provide essential nutrients, improve structure, and enhance microbial activity, thus increasing soil fertility and agriculture sustainability. While organic fertilizers offer the benefits of soil fertility and plant nutrition, their impact on greenhouse gas (GHG) emissions is complex and varies depending on factors such as fertilizer type, soil conditions, and management practices. Although organic fertilizers may initially increase GHG emissions, they often lead to carbon sequestration in soils highlighting a negative C balance. Additionally, organic fertilizers promote a reduction in fossil fuel consumption used for synthetic fertilizer production, further contributing to GHG emissions' reduction. Therefore, while organic fertilizers pose challenges in managing GHG emissions, their various benefits warrant careful consideration and strategic implementation in agricultural systems.

Keywords: fertilization; soil fertility; circular economy; carbon dioxide (CO_2) emissions; nitrous oxide (N_2O) emissions; methane (CH_4) emissions

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1. Introduction

Globalization has led to increased industrialization and urbanization, as well as an intensification of agricultural practices, which has contributed to improving food production and the quality of life, but has also led to a considerable increase in natural resources depauperation and waste generation. It is estimated that agriculture produces around 5 billion tonnes of biomass waste globally every year [1]. Waste, often disposed without particular treatment, has a negative impact on the environment [2] and increases the risk of spreading pathogens, heavy metals, and xenobiotics [3]. Moreover, even the treatment of waste through conventional disposal circuits generates residues that are difficult to use and determine environmental impact. For this reason, there is an urgent need to implement strategies that limit the exploitation of environmental resources, reduce the production of waste, and reintroduce it into production systems, transforming it, when possible, into a resource capable of generating income. This vision is fully embraced by the European Union's (EU's) Waste Framework Directive [4] that, from 1 January 2024, obligates all EU nations to separately collect bio-waste with the aim of reaching the target of recycling 65% of waste by 2065. Moreover, this approach plays a fundamental role in aiding the achievement of many of the global Sustainable Development Goals (SDGs) established by the UN 2030 Agenda [5], such as zero hunger, clean water and sanitation, affordable and clean energy, sustainable cities and communities, responsible consumption and production, climate action, and life on land.

Therefore, in this context, agriculture's growth toward a bioeconomy logic, based on the efficient use of renewable biological resources as materials for energy, industrial, and food and feed production, offers an important opportunity to confront environmental challenges.

2. Soil Amendments, Organic Fertilizers, By-Products, and Bio-Waste-Derived Fertilizers

The use of synthetic chemical fertilizers poses a number of critical issues related to their production and their short-, medium-, and long-term negative effects on soil. Indeed, these products can impact the environment during production and/or extraction stages, depending on the cases, or by the unpredictable release of nutrients into agroecosystems in different forms and because of various phenomena (i.e.: leaching and gaseous emissions), with harmful consequences on several environmental components (soil, water, air, and organisms) [6,7]. Secondly, the global fertilizer market has shown considerable instability with prices soaring, linked to the quotations of energetic commodities, putting the economic sustainability of agricultural production in crisis. Based on these considerations, farmers are increasingly paying attention to the possibility of using organic fertilizers, such as soil amendments, by-products, and bio-waste-derived fertilizers. Among this large category, the main products used to manage soil fertility and support crop growth are farmyard manure, composts (from farm waste or from organic fractions of municipal solid waste), agricultural digestate, and biochar.

Farmyard manure is a by-product of livestock farming activity constituted by a decomposed mixture of animal excreta (dung and urine), litter, and residues of forage materials [8]. It can derive from the rearing of different animals (cows, horses, sheep, goats, and swine), be obtained from animals housed on bedding consisting of organic biomasses, typically crop straws (e.g., wheat, barley, and rice straws, and corn stalk), or other organic residues. After collection and mixing, the farmyard manure is left composting in a muckheap for at least six months before being applied to the fields. Farmyard manure represents a good source of nutrients, such as nitrogen (N), phosphorus (P), potassium (K), sulphur (S), magnesium (Mg), and many other microelements. The reported nutrient values are 1–15 g kg^{-1} for N, 1–10 g kg^{-1} for P, 2–20 g kg^{-1} for K [9–11], 1–5 g kg^{-1} for S, and 3–6 g kg^{-1} for Mg, with a total organic carbon (C) content of 40–600 g kg^{-1}, 15–20 dS cm^{-1} of electrical conductivity (EC), and pH above neutrality (7.4–8.6) [11–14]. Farmyard manure has typical average chemical characteristics related to the animal production chain from which it originated, and it is also influenced by several factors depending on animal age, feed composition, the nature of litter used, and manure aging.

Composts are defined as mixtures of wastes stabilized through an aerobic process of decomposition. Raw materials for compost production include kitchen waste, straw and plant residues, manure, and residues from agrifood industries. The composting process typically requires the shredding of raw materials, the addition of water, and the periodic stirring of the mass to ensure good aeration during the process, which is divided into three main stages [15]: the initial mesophilic stage, the intermediate thermophilic stage where the mass temperature reaches temperature above 50 °C (50–70 °C), and the final stage of maturation. As for the farmyard, the chemical composition of these organic fertilizers strongly varies according to the raw materials used, with mean reported values of 9–20 g kg^{-1} for N, 2–10 g kg^{-1} for P, 2–10 g kg^{-1} for K, 10–13 for the C/N ratio, 1–5 dS cm^{-1} for EC, and 6.8–8 for pH [11,16,17]. Among the composts, those derived from the organic fractions of municipal solid wastes (OFMSWs) are gaining popularity due to their low cost, continuous availability, and ecological significance related to the recovery of a material that would otherwise have to be landfilled with a significant environmental impact [17,18].

Digestate represents a by-product of anaerobic digestion, a process where microorganisms degrade mixed organic materials under anaerobic conditions for the biological production of biogas (a gaseous mixture of methane and carbon dioxide), for generating energy and heat [19]. Digestate is ordinarily separated into two fractions according to the dry matter content: a liquid fraction (dry matter of 2–8%) and a solid fraction (dry matter of 22–30%) [20,21]. The liquid fraction has an alkaline pH, total organic C of 0.5–3.2 g L^{-1}, total N of 0.5–3.0 g L^{-1} (18–70% represented by ammonium-N), P of 0.2–2.0 g L^{-1}, and K of 0.5–6.0 g L^{-1} [22–25]. The solid fraction is characterized by an alkaline pH, total organic C concentration of about 400 g kg^{-1}, total N content ranging from 15 to 150 g kg^{-1} mostly represented by the ammonium-N form (up to 67%), P concentration variable of 0.2–70 g kg^{-1}, and a relatively high K content (from 1 to 100 g kg^{-1}) [26–28]. The chemical composition of digestates can vary significantly depending on the characteristics of the raw materials used (industrial, agricultural, and OFMSW digestates). Anaerobic digestate has the potential to be utilized in agriculture either as a replacement for synthetic fertilizers or as a soil conditioner, thanks to its nutrients and partially decomposed organic matter content.

Biochar, according to the International Biochar Initiative (IBI), is defined as a solid material produced from feedstock carbonization [29]. Usually, biochar is obtained from the thermal decomposition of organic materials, like wood, plant leaves, crop residues, and animal manures, under limited oxygenation at temperatures above 250–300 °C [30,31]. Fast pyrolysis, slow pyrolysis, and gasification are the three different techniques applied to produce biochar [32,33]: however, slow pyrolysis, also known as carbonization, is the most used due to its yield. Biochar properties depend on the feedstock characteristics and on the pyrolysis conditions. For example, biochar produced from lignocellulosic biomass, like wood and straw, has fewer nutrients than those obtained from manure biomasses that can provide more N and P [34,35]. Pyrolysis performed at temperatures above 500 °C produces biochar with high hydrophobicity, large surface area, and large micropore volume, while at temperatures below 500 °C, the produced biochar tends to have more oxygenated functional groups and is more suitable for immobilizing inorganic pollutants [36]. Biochar is used for soil amendment, improving fertility and increasing soil anion and cation exchange capacity (CEC), extending the release of fertilizer nutrients over time, increasing the water-holding capacity, decreasing the bulk density, and raising the pH (pH range from 7.5 to 10.3); it also provides N (from 1.4 to 14.1%), P (from 0.05 to 5.9%), K (from 3.9 to 14.7%), and many microelements, such S, Ca, and Mg [35,37,38]. As a result, plant growth and soil microbial activity are enhanced, as shown by different studies [39–41]. Carbon that is present in biochar is characterized by low degradability with a residence time greater than a thousand years, making it a formidable organic fertilizer to sequestrate C in the soil [42].

Considering the bulky nature of the above-mentioned organic fertilizers, their application should be evaluated considering the local production and availability as a determining factor (especially for transport cost) in order to guide actions toward their use in a circular economy implementation context.

3. Effects of Organic Fertilizers on Soil Fertility, Organic Matter, and Nutrient Release for Crops

Organic fertilizer can improve soil fertility by influencing several chemical and biochemical parameters, having positive effects on plant nutrition and on consequential plant growth. Thus, keeping in mind the different organic fertilizers, it is important to highlight their effects on soil properties and the nutrients released.

Farmyard manure is one of the most ancient fertilizers. Scientific evidence trace its use by humans back to approximately 6000 B.C. [43]. Despite technological evolutions, it still represents an important tool for sustaining crops in large cultivated areas worldwide. Indeed, as confirmed by several studies, the majority of N applied to crops worldwide is represented by manure [44–46]. Indeed, manure can provide a large amount of organic N that is susceptible to being transformed into mineral N, available for plants [12,47,48]. Together with the N, farmyard manure provides a high quantity of P (as inorganic orthophosphates), often in higher concentrations than N, causing soil accumulation considering the lower plant uptake values [49,50]. Among other minerals, many micronutrients, like copper (Cu), zinc (Zn), manganese (Mn), and boron (B), are added to soil with manures [51–54], highlighting their higher nutritional value than chemical fertilizers. Considering its pH, farmyard manure can potentially increase soil pH, while the release of soluble minerals may have the effect of raising the EC [55,56]. The release of nutrients from farmyard manure (as from other organic natural fertilizers) depends on its mineralization rate, which is influenced by composition, environmental conditions, and several chemical and biochemical soil properties. Among soil properties, soil CEC increases with the application of manure by promoting the release of nutrients over time [57,58]. Manure has a generally positive effect on soil organic matter determining an increase in the C fraction stored in the soil. However, the persistence of this effect depends on the quality of the manure applied and on the quantitative ratio between compounds and their different degrees of degradability [12,59–61]. Providing C and nutrients, the application of manure promotes soil microbial community, biodiversity, and functionality [62–64]. Usually, according to the chemical characteristics, farmyard manure is applied at variable doses in a range between 15 and 60 Mg fresh weight ha^{-1} without having negative impacts on the soil and the environment.

Composting is a process that stabilizes organic biomasses through the activity of aerobic microorganisms under controlled conditions (humification), consisting of the decomposition of complex organic molecules into a mass constituted of simpler compounds with valuable physical and chemical characteristics [65]. Several benefits are due to its application in soil. Indeed, compost can provide to the crops, according to the raw material used for its production, N, P, K, and micronutrients, while organic matter and the released humic substances can positively affect physical, biological and chemical soil properties [63]. Compost releases between 5 and 60% of N, between 35 and 100% of P, and between 75 and 100% of K applied via mineralization over time within the first year after application. Therefore, it can partially replace mineral fertilizers, according to its maturity and environmental conditions, also influencing soil chemical characteristics, like increasing the pH, EC, and CEC [66–68]. The effects on soil physical properties include the lowering of bulk density, the increase in porosity, the improvement of the structure, and the increase in the water-holding capacity [69,70]. The contribution to increasing sequestered soil C is also significant [68,71,72]. The greater availability of substrates and better soil living conditions lead to the greater size, diversity, and activity of the microbial community in soils amended with compost [73–75]. Generally, C-rich composts (high C/N ratio, e.g., based on cereal straws or wood chips) with lower nutrient concentrations have a greater value as soil conditioners; on the contrary, C-poor composts (low C/N ratio, e.g., those that include poultry manure or kitchen wastes) with higher nutrient concentrations have good fertilizer values [76]. Other benefits related to their use are linked to their natural suppressive capacity against plant diseases (i.e., *Phytium* spp., *Fusarium* spp., *Phytophthora* spp., and *Verticillium* spp.) related to different mechanisms, such as competition among microbial populations, antibiosis, hyperparasitism, systemic acquired resistance, and induced systemic resistance [77,78]. Thanks to these characteristics, numerous studies indicate the use of composts for restoring the fertility of soils degraded and/or contaminated by heavy metals [79,80]. In this regard, composts can remediate soils by affecting the mobility and bioavailability of heavy metals through adsorption, complexation, precipitation, and redox reaction mechanisms [81,82]. However, it is always advisable to assess the intrinsic quality of compost before any application, as poor-quality compost can lead to unexpected EC increases and heavy metal and microplastic contamination [83,84]. The doses used in the literature vary greatly depending on the type of compost applied at a minimum value of 4 to a maximum value of 100 Mg fresh weight ha^{-1} [85–87].

Digestate availability is increasing, and it is related to the spread of using anaerobic digestion plants in the Mediterranean areas, previously only widespread in north-central Europe. Digestates are separated into liquid and solid fractions in order to properly manage their logistics and use. Digestate, as a whole, considering liquid and solid fractions, is characterized by an alkaline pH (7.5–9.0), a total C concentration of about 350–400 g kg^{-1} with small differences among digestates, a total N content ranging from 15 to 150 g kg^{-1} mostly represented by the ammonium-N form (up to 81%), P concentration variable in the range of 0.2–170 g kg^{-1}, and a relatively large K content (from 1 to 400 g kg^{-1}); it also contains many micronutrients [26–28,88]. Considering its properties, solid anaerobic digestate has the potential to be utilized in agriculture as a soil conditioner and as a replacement for synthetic fertilizers, especially to supply N-P-K, owing to its nutrient contents and partially decomposed organic substrates. The relevant organic matter supplied, at different stages of decomposition, increases the soil organic matter concentration [89,90], improves soil structure and promotes aggregate formation [91,92], boosts the soil microbial community, and shapes its structure and functioning [90,93–95]. On the other hand, the liquid fraction, considering its significant concentration of ammonium-N, can serve as a substitute for synthetic chemical N fertilizers. One of the possible risks associated with the use of digestate may be the uncontrolled release of N into agroecosystems through losses by ammonia volatilization (promoted by the alkaline pH of the digestate) and nitrate leaching [27,93,96–98]. Moreover, the high release of soluble minerals can increase the soil EC, threatening plant growth over species' susceptibility limits [99,100]. The application of digestate to the soil is conducted at doses that range between 15 and 60 Mg fresh weight ha^{-1}.

Chars from organic biomasses have become more prominent in the last 15 years due to the benefits that their application can have on soil properties and plant growth. Several studies (i.e., [101–103]) have proven the positive effects of biochar on soil physical, biological and chemical profiles. Indeed, biochar increases the soil water-holding capacity [101], improves porosity, and decreases bulk density [102]. As observed for other natural organic biofertilizers, even biochar increases soil pH [97]. With regards to the nutrient's availability, the release of biochar's own minerals is related to its long and uncertain decomposition dynamics [104]. Its ability to sequestrate nutrients (especially N and P) for a secondary gradual release over time, related to its high CEC, can effectively reduce ammonia loss through volatilization [105] and the mobility of heavy metals or xenobiotics on the soil [106], but in some cases can determine nutrient immobilization [107]. The effect of biochar on soil physical and chemical fertility outcomes enhances soil microbial activity [108–111] and diversity [112]. Its positive role was observed in increasing soil C sequestered into the soil due to the supply of stable/recalcitrant/aromatic C [113–115]. Doses of application vary between 5 and 20 Mg ha^{-1}.

Taking into account their action on soil properties, the use of bio-waste and organic fertilizers can be a useful tool for soil fertility management being able to be integrated into ordinary fertilization plans to support crops as basal or top-dressing fertilizers, according to the matrix nature. In addition, considering the soil degradation of conventionally cultivated cropland in Mediterranean areas, facing a significant loss of nutrients and organic matter, the application of these kinds of fertilizers can represent a recommendable practice to protect soil, restore its functioning and fertility, and increase its productivity in the long term. In particular, considering the cultivation cycle of the main tree and herbaceous crops in Mediterranean areas (citrus, olive, vine, wheat, legumes, vegetables, and hay crops), farmyard manure, composts, and solid agricultural digestate can be used in basal fertilization, applied before spring vegetative growth (early spring) or sowing (fall and early spring), followed by a prompt incorporation by tillage. This last aspect is important in order to control organic fertilizer mineralization in the soil and limit gaseous emissions. Good synchronization between organic fertilizer distribution and the subsequent uptakes of the released minerals by the plant, because of mineralization dynamics, is fundamental in order to optimize the efficiency of nutrient utilization and limit the risks related to its uncontrolled dispersion into the environment. In this regard, higher dosages can be added to soils with a higher CEC and capacity to retain nutrients. Therefore, organic fertilizers can represent the main source of nutrients for crops that can or cannot be coupled with a limited mineral fertilizer top-dressing application. In organic farming systems, which are increasing in Europe and particularly in the Mediterranean region, they can be the exclusive fertilizers.

4. Effects of Organic Fertilizers on Control Soil GHG Emissions

The role of organic fertilizers on GHG emissions has been widely debated by the international scientific community, resulting in conflicting results and opinions. In fact, while some studies have found that the production or use of these matrices can increase emissions of climate-altering gases (i.e., CO_2, N_2O, CH_4, and NH_3), others have shown the opposite results. Other studies claim that, even if they increase GHG emissions, the amount of C stored in the soil is greater than the CO_{2eq} emitted. The discussion on this issue is very important, considering that the application of fertilizers to soils is among the main anthropogenic activities responsible for the emissions of these gases, especially for N_2O, CH_4, and NH_3 [116–118].

The use of natural organic fertilizers, as stated above, can provide soil with both C and N labile molecules that can boost soil microbial community dimension and activity, with effect of differing durations. As a result, CO_2 emissions can increase dramatically with rapid peaks and result in the growth of mean soil fluxes. This result was observed after the application of farmyard manure [119,120], compost [120], and digestate [121,122]. Regarding biochar, Jones et al. [123] highlighted its short-term effect on increasing CO_2 emissions, as observed by Smith et al. [124] and Zimmerman [125], due to its contribution of low-weight molecules to soil.

A further consequence of the sudden release of high amounts of mineral N into the soil is the increase in N_2O emissions related to the denitrification process in soil microsites where there is reduced oxygenation [126]. Moreover, the concomitant increased availability of C, promoting microbial respiration, can cause a decrease in the concentration of oxygen in the soil pores resulting in a higher occurrence of denitrification microsites [127]. This aspect was observed in fields where farmyard manure [128], compost [129], and digestate [93,130,131] were used. By the incorporation of fertilizers, a dilution of N along the soil profile can occur, avoiding the concentration of the N substrate in the superficial soil microsites, which in the condition of reduced aeration can cause denitrification [132]. In the case of digestate, the addition of nitrification inhibitors can significantly reduce N_2O [133,134].

Regarding CH_4 emissions, similar behavior to the other GHGs was observed resulting from manure [135,136], compost [137], and digestate [138,139] amendments.

NH_3 emissions contribute to the formation of fine particulate matter ($PM_{2.5}$) in the atmosphere and leads to N deposition in ecosystems by becoming a secondary source of N_2O emissions. In addition, N loss can be high, decreasing the nutrient efficiency of organic matrices; therefore, the emission of this gas, for which agriculture is one of the main contributors, should also be monitored. From farmyard manure, the emission of NH_3 can be particularly high due to urea and $NH_4{}^+$-N concentrations, and a rapid incorporation into the soil profile is advisable [128]. A significant increase in NH_3 emissions was observed from compost as well [140]. Digestate has a high N concentration, mostly in the form of $NH_4{}^+$-N, susceptible to volatilization in alkaline soils, especially when left on the soil's surface. Therefore, for all organic fertilizers, a prompt injection or incorporation by tillage is required in order to achieve a significant emission reduction of up to more than 90% [141].

As described above, the addition of organic fertilizers to soil can, especially in the short term, increase GHG emissions. However, numerous studies have shown that the C amount emitted is lower than the share of C stored in soil [119], as observed for farmyard manure [12,59,142,143], compost [71,144,145], and digestate [122,130,146]. Regarding biochar, its C-negative impact (low emission/high sequestration) was clearly stated by Glaser et al. [147], while Jones et al. [123] highlighted that only a very small relative amount of biochar C (0.1%) is lost as CO_2 emitted from the soil, promoting C sequestration [148,149]. Thus, this kind of organic fertilizer can play a significant role in climate change mitigation and GHG compensation [150,151]. However, the impact of organic fertilizers on GHG emissions is not uniform, and specific effects depend on factors such as the type of fertilizer, soil conditions, and other management practices [152,153]. Indeed, while organic fertilizers may offer some benefits to reduce GHG emissions, their overall impact is influenced by various variables and requires careful consideration. In other cases, positive synergies can occur between climate-smart cultivation practices, such as reduced tillage and the use of organic fertilizers, with a significant reduction in GHG emissions as observed by Gong et al. [154] and Zhang et al. [155]. Finally, it is important to indicate that organic fertilizers, thanks to their origin (derived from waste products), make it possible to reduce the consumption of fossil and energy raw materials for the production of synthetic fertilizers (and, in many cases, emit fewer GHGs for the same amount of nutrients provided), and they also improve soil fertility, permitting better plant growth and leading to additional CO_2 organication and capture.

5. Conclusions

In the present manuscript, we describe the characteristic properties of four main organic by-product and bio-waste-derived fertilizers, namely farmyard manure, composts, agricultural digestate, and biochar, and their roles in soil fertility management and GHG emissions. As highlighted, these matrices can be usefully applied to soil supplying nutrients for crops and/or improving physical, chemical, biochemical, and microbiological variables. In particular, they can be effectively used to counteract soil fertility loss in Mediterranean soils. However, it is crucial to carefully produce and utilize organic fertilizers to ensure a high-quality and stable product with minimal environmental impacts, during manufacturing, and many beneficial outcomes with minimal negative consequences, during application. Finally, regarding this last aspect, a judicious application of bio-fertilizers must take into account the properties of the soil and the crop that will receive them in order to harmonize their application to each specific agronomical context and achieve the highest efficiency.

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