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ANIMAL MANURE AS FERTILIZER: CHANGES IN SOIL ATTRIBUTES, PRODUCTIVITY AND FOOD COMPOSITION

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Abstract

Animal manure (AM), such as swine, cattle, sheep, horse, as well as other organic waste materials from recycling agri-food or other processes may be used as nutrient source for horticultural annual and perennial crops, increasing nutrient cycling and reducing costs related to acquisition of industrial fertilizers. Additionally, over the years it is expected to modify chemical, physical, and biological soil attributes such as increasing the nutrient content in the soil, which can affect crop productivity, change the food composition, fruit and vegetable storage aptitudes, and impact on the environment. The present review addresses the effect of AM applications on the soil-plant interface, emphasizing the following aspects: (a) changes in chemical, physical and biological attributes in soils with a history of AM applications, (b) effect of application of AM on annual plant productivity and (c) AM as fertilizer: productivity and food composition of horticultural crops. Successive applications of AM in soils tend to increase the chemical and physical attributes, and, increased production of grain crops. Effect of AM fertilizations on quality and nutritional value of fruits is still uncertain; it depends on several factors, including: 1) characteristics of organic matter, 2) pedoclimatic conditions, 3) time of application and 4) plant species.

Keywords: Pig and Cattle Manure; Soil Organic Carbon; Edaphic Properties; Grain Crops; Quality and Nutritional Value of Agri-Food.

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1. Introduction

The beginning of the 20th century was characterized by the intensive confinement of animals, be they cattle, pigs, birds, among others, aiming to increase productivity in small spaces. In this system, the animals remain at high stocking densities under full confinement until their slaughter (Koneswaran and Nierenberg, 2008; Steier and Patel, 2017). As a consequence of this system, there is a high production of animal waste in the liquid or solid form (Bertora et al., 2008; Koneswaran and Nierenberg, 2008). Among the management practices destined to these wastes, the most accepted and viable, both technical and economical, is the distribution in agricultural soils. However, its use, especially in liquid form, has resulted in environmental liabilities.

The use of organic fertilizers for the man as a source of nutrients for agricultural crops, dates back to the Neolithic period about 12,000 years ago, where the use of plant and animal residues, river humus and human manure was applied to the soil with the aim of nourishing plant crops. From the period 7000 a.c. to the mid-18th century, agriculture depended primarily on organic waste for soil fertilization and maintenance of crop nutrition. In this period, due to the high demand for organic waste, especially animal waste, there was a shortage of the product in certain regions and times of the year (Mazoyer and Roudart, 2010; Singh and Ryan, 2015).

Beginning in the 1950s, the technological advancement of agriculture allowed for increased productivity, crop capacity and storage. This model enabled man to produce large scale animals, especially in a confined and semi-confined form (Naconecy, 2014), resulting in the production of large amounts of animal waste. However, the increased use of industrialized chemical formulas has corroborated the reduction in demand for organic fertilizers, leading to an excess of this type of waste in certain places.

Considering the world production, it is estimated that the United States, Brazil and China own 50% of the production of cut birds, generating around 22 billion tons of litter; and China, the United States, Russia and Brazil hold 70% of pigs production, generating 7.2 billion m³ of liquid slurry. In these countries, due to the agroindustry models, the confinement is carried out in specialized regions, resulting in high animal density in small areas such as watersheds. In the United States, for example, much of the pigs production is located in the West North Central region (USDA, 2012). In Brazil, the Southern region has a prominent role in the production of pigs and birds, where 49% and 62% of the national production is concentrated in small watersheds of this region (Couto et al., 2016, Anualpec, 2017).

In this way, large amounts of animal waste are applied to the soil for long periods, as a source of nutrients to crops and in some situations, due to the lack of adequate facilities, as a form of disposal (Ceretta et al., 2005; Adeli et al., 2008; Broetto et al., 2014). In addition, there is a growing demand for environmentally correct foods, such as agroecological and/or organic foods, which use large amounts of organic waste (Dias et al., 2016).

Successive applications of organic residues, such as in natura or processed animal debris, such as those composted, can cause changes in the chemical, physical and biological characteristics of the soil. For example, in the carbon contents (Hati et al., 2007, 2008; Brunetto et al., 2012, Comin et al., 2013) and nitrogen (Adeli et al., 2003; Bergström and Kirchmann, 2006; Giacomini and Aita, 2008; Giacomini et al., 2013), as well as on soil aggregation (Hati et al., 2006a; Veiga et al., 2009,

Arruda et al., 2010, Comin et al., 2013, Loss et al., 2017) and on biological parameters such as diversity and microbial activity (Marinari et al., 2000, Masto et al., 2006, Liu et al., 2010, González-Mancilla et al., 2013). According to the aforementioned authors, the modifications observed in the soil attributes resulting from the application of animal waste are mainly due to the characteristics of the residue, the soil type, as well as the meteorological characteristics of the site and the cultivated species.

However, there is growing concern about soil health and sustainability in agriculture, and organic fertilizers have gained importance as components of integrated plant nutrient management. As a consequence, the main focus of this management is the management of soil organic matter (SOM) through the integrated use of mineral fertilizers with organic inputs (Bandyopadhyay et al., 2010; Singh and Ryan, 2015). Several types of manure have been applied to soils as a source of nutrients to increase crop yields and improve soil attributes. In addition, increasing fertilizer costs and increasing concerns about soil and environmental quality deterioration have also helped to increase the recycling of organic materials in agricultural areas (Comin et al., 2013, Singh and Ryan, 2015). In this sense, the present review addresses the effect of animal manure applications on the soil-plant interface, emphasizing the following aspects: (a) changes in chemical attributes in soils with a history of animal manure applications, (b) changes in physical and biological parameters in soil areas with a history of animal manure applications, (c) effect of the application of animal manure on annual plant productivity and (d) animal manure as fertilizer: productivity and food composition of horticultural crops.

2. Changes in Attributes in Soils with a History of Animal Manure (Waste) Application

2.1. Changes in Chemical Attributes

Liquid or solid waste from animals such as pigs, cattle, horses and goats can be applied to soils in the most diverse farming systems. The amount of waste to be applied can be established based on the percentage of dry matter, on nutrient concentration, and by the efficiency index, which is related to the total amount of nutrients contained in the waste that can be transformed from organic form to mineral form after its application in the soil (CQFS-RS/SC, 2016).

2.1.1. Total Organic Carbon

The successive applications of waste in soils tend to increase the total organic carbon content (TOC) over the years, especially in degraded soils and, consequently, the soil organic matter. These applications also change the attributes related to soil acidity and increase the nutrient content in the soil, sometimes even above the crop requirements and soil adsorption capacity, especially when the applications are carried out disregarding the established technical criteria (Basso et al., 2005; Ceretta et al., 2010a; Ceretta et al., 2010b; Giroto et al., 2010; Lourenzi et al., 2011; Brunetto et al., 2012; Guardini et al., 2012; Comin et al., 2013; Giroto et al., 2013; Ciancio et al., 2014; Benedet et al., 2016; Couto et al., 2017). In addition, waste applications may increase the content of heavy metals such as copper (Cu) and zinc (Zn) in soils, potentiating plant toxicity, as well as the potential for losses through the solution, especially in soils located in sloping relief, but also by leaching, in sandy soils with low organic matter (Tiecher et al., 2013; Couto et al., 2016).

Animal waste, for example, when used in conservation systems, such as no-till system, perennial pastures and orchards, is applied to crop residues deposited on the soil surface. Thus, a smaller area of contact between the waste and the soil is expected, which may delay the activity of the microbial population, stimulating the accumulation of TOC (Ceretta et al., 2003; Adeli et al., 2008; Lourenzi et al., 2011; Brunetto et al., 2012), especially in the more superficial layers of the soil. However, the increase in TOC content in soils is associated with the composition of the waste, as well as how frequently and how much is applied (Falleiro et al., 2003; Lourenzi et al., 2011; Brunetto et al., 2012). Still, it should be emphasized that part of the nutrients derived from the waste applied to soils can be absorbed by the plants, stimulating the growth of the root system, but also the production of shoot dry matter, for instance, of cover crops species. The deposition of shoot residues or even root senescence may release C to the soil (Comin et al., 2013; Mafra et al., 2015). Lourenzi et al. (2011) observed an increase in TOC up to 60 cm in a soil with sandy texture subjected to 0, 20, 40 and 80 m³ ha⁻¹ of liquid pig slurry over 100 months. This was most likely derived from the wastes, but also from plant residues, such as decomposing roots. On the other hand, Brunetto et al. (2012) reported that applications of liquid pig slurry and deep litter for eight years increased the TOC content up to 30 cm in a soil with sandy texture, with a history of no-till farming.

In general, the application of manure results in an increase in TOC content, both in short (Hati et al., 2006a; Ferreras et al., 2006) and in long term (Pernes-Debuyser and Tessier, 2004; Rauber et al., 2012). The application of manure associated with mineral fertilizers generally increases this effect (Hati et al., 2006b; Zhao et al., 2009), due to the higher crop phytomass production and, consequently, addition of organic carbon to the soil in form of straw and roots. The increase observed, however, is not enough to raise the TOC to the level observed in natural conditions, especially in comparison with native forests (Rauber et al., 2012).

The increase in TOC content is higher in medium textured clay soils than in sandy soils, due to the higher oxidation rate of soil organic matter in the latter (Darwish et al., 1995). For the same reason, the application of manures can minimize the reduction of TOC content in tillage systems that determine high oxidation rate of the soil organic matter, especially those that result in great soil mobilization (Hati et al., 2008). In the literature consulted, the only type of manure that does not necessarily result in an increase in TOC content is the pig slurry (Cenciani et al., 2008; Andrade et al., 2016; Oliveira et al., 2014; Comin et al., 2013), which is associated with the low organic matter content in this type of waste. Thus, a higher increase in TOC is expected when the manure presents high dry matter content and higher C:N ratio, as observed in poultry litter (Ojeniyi, 2008) and cattle manure (Dunjana et al., 2012), as well as in organic compounds (Lynch et al., 2005).

2.1.2. Ph, Al, Ca, Mg, N, P, K and Cation Exchange Capacity (CEC)

The increase in TOC in soils may increase soil cation exchange capacity (CEC), increasing nutrient adsorption (Scherer et al., 2007; Brunetto et al., 2012), which is desirable. Additionally, the increase in TOC in soils may favor the complexation of exchangeable aluminum (Al), especially in the humic and fulvic acid fraction of organic matter (Ceretta et al., 2003), which reduces its toxicity to plants, but also the adsorption of H⁺, which, as a consequence, may be reflected in increased pH values in water (Hue and Licudine, 1999; Lourenzi et al. 2011; Couto et al., 2013). The correction of soil acidity by waste can be further enhanced by the dissociation of CaCO₃

normally found in animal waste (Whalen et al., 2000) and, therefore, an increase in the values of the effective CEC of the soil is expected. Lourenzi et al. (2011) found an increase in pH values in water up to 8 cm with the application of increasing doses of liquid pig slurry (0, 20, 40 and 80 m³ ha⁻¹) for 8 years in a soil with sandy texture under no-till. However, Brunetto et al. (2012) reported that the use of liquid pig slurry for 8 years did not cause acidification or correction of soil acidity, indicating that the effect of this waste on soil acidity attributes were small or null.

Animal waste also has calcium (Ca) and magnesium (Mg) remaining from feed consumed by animals and not absorbed by the digestive tract. Therefore, it is expected that in soils with a history of application of animal waste, such as those of pigs (i.e., liquid pig slurry and deep litter), an increase in the exchangeable contents of Ca and Mg (Ceretta et al., 2003; Assmann et al., 2007; Lourenzi et al., 2011; Brunetto et al., 2012) in the soil profile, which may occur due to the migration of ions, including those bound to water-soluble organic substances, through biopores, such as those derived from root senescence (Kaminski et al., 2005). Thus, it is believed that an increase of the sum of basic cations occurs along the soil profile, which is reflected in increased values of the effective CEC. Consequently, increased values of base saturation and decreased values of saturation by Al is expected and, thus, the chemical environment of the soil will be more favorable to the growth of the root system (Lourenzi et al., 2011; Brunetto et al., 2012; Couto et al., 2013; De Conti et al., 2015). Ceretta et al. (2003) observed an increase in Ca content up to 5 cm and Lourenzi et al. (2011) reported an increase in Ca content up to 16 cm. Both studies were carried out in sandy soils.

Animal waste in soils may increase N, P and K contents. The N present in animal waste (e.g., liquid pig slurry) is typically in the form of N-NH₄⁺, and when applied to the soil it is rapidly transformed into nitrate (N-NO₃⁻) (Aita et al., 2007; Giroto et al., 2013). If it is not rapidly absorbed by the plants, it can be transferred by the solution to the soil surface, but also leached (Basso et al., 2005; Bergström & Kirchmann, 2006; Giroto et al., 2013; Broetto et al., 2014), especially in soils with sandy texture. This is because N-NO₃⁻ forms an outer sphere complex with surface functional groups, which decreases its adsorption energy with organic and inorganic soil particles (Ceretta et al., 2010b; Giroto et al., 2013).

The phosphorus (P) normally contained in animal waste (e.g., liquid pig slurry) is observed in inorganic form (Cassol et al., 2001), which is the preferential fraction of accumulation in soils (Brookes et al., 1997; Chardon et al., 1997; Gatiboni et al., 2008; Ceretta et al., 2010; Guardini et al., 2012; Couto et al., 2017). Phosphorus may be adsorbed at the most avid sites of soil reactive particles, but the remainder may be retained in fractions with lower binding energy (Barrow et al., 1998). As a result, an increase in bioavailable P in soils is expected, part of which is absorbed by the plants, but also part may be lost by surface runoff or even leachate in extremely sandy soils (Ajmone-Marsan et al., 2006; Gatiboni et al., 2007; Couto et al., 2017). The K present in most animal waste is generally found in mineral form, which can readily be available to plants (Kayser and Isselstein, 2005). However, if it is not available, part can be transferred by surface runoff (Ceretta et al., 2010b). Still, since the amounts of K in the waste is lower than those of N and P, coupled with the great absorption and exportation of the nutrient by the crops (Ceretta et al., 2003), it is believed that the quantities transferred by the solution in most soils are small.

2.1.3. Cu and Zn

However, the applications of animal waste in soils can increase the content of other elements, such as Cu and Zn. Cu and Zn, including derivatives of animal waste or other organic waste, are retained by physical-chemical bonds and their lability is dependent on the binder, with emphasis on organic matter and oxides, and on the geochemical condition, especially of the pH values, which define the binding energy (Tiecher et al., 2013; De Conti et al., 2016). Therefore, the two elements are found in different fractions, since they are naturally adsorbed in different degrees of energy. However, increasing Cu and Zn levels in the soil may interfere with its soil distribution fractions. The adsorption of Cu and Zn occurs first at the most avid binding sites, and then the remaining element is redistributed into fractions that are retained with less energy, hence, of greater availability. Thus, frequent applications of waste or organic compost can increase the amount of soluble fractions of these elements, increasing toxicity to plants (Tiecher et al., 2013; Benedett et al., 2016; De Conti et al., 2016). However, the transfer (via sediments to surface and subsurface waters) also potentiates contamination (Adeli et al., 2003; Bergström and Kirchmann, 2006; Gatiboni et al., 2008; Girotto et al., 2010; Couto et al., 2016). Girotto et al. (2010) found that the Cu and Zn content increased in the superficial layers of the soil, in a study of sandy soil subjected to successive applications of liquid pig slurry. These authors observed that 66% of Cu was bound to the organic fraction, 3% to the mineral fraction and only 6% was found in the water-soluble form. On the other hand, 74% of Zn was associated with the mineral fraction, 13% to the organic fraction and less than 1% in the water-soluble form. The results of Cu emphasize the need to maintain the organic matter content to increase Cu complexation, reducing its availability and, consequently, potential toxicity to plants.

2.2. Changes in Physical Attributes

2.2.1. Aggregate Stability

The aggregate stability is one of the properties most affected by the increase in the TOC content, so the effect of the manure application is generally positive on this soil attribute. In general, an increase in the mean diameter of the aggregates (Hati et al., 2006a, Tiarks et al., 1974) and the aggregates stability in water (Hati et al., 2006a, Darwish et al., 1995, Neto et al., 2008, Comin et al., 2013) is observed, even in soils with soluble salts that determine the dispersion of soil particles (Pernes-Debuyser and Tessier, 2004), where incipient aggregation and low stability result in increased susceptibility to degradation. However, these effects seem to be associated with the application of manures at higher doses than those recommended for nutrient supply, since the application of doses for this purpose had no significant effect on the stability of aggregates in a clayey soil (Veiga et al., 2009). The effect on aggregation and aggregate stability is more pronounced with the application of materials with higher C:N ratio, such as the poultry litter (Assis Valadão and Benedet, 2011; Comin et al., 2013), being similar to the cultivation of species with high density of fasciculated roots, such as *Brachiaria brizantha* (Neto et al., 2008). As happened with TOC, the joint application of manure and mineral fertilizers results in increased aggregation and stability (Hati et al., 2008; Hati et al., 2006b).

The reduction in particle dispersion and increase in aggregation occurs in all textural classes, but is more significant in sandy and medium textured soils (Darwish et al., 1995). Soil and climate conditions can be determinant in the results obtained, and there may also have a reduction in the

aggregation and aggregates stability, as observed by (Tejada and Gonzalez, 2008) in a region with precipitation restriction, which may be associated with both the low biological activity in decomposition of this material as with the formation of hydrophobic organic compounds. Reduction of the aggregate stability was also observed in a study with the application of pig slurry (Arruda et al., 2010).

2.2.2. Bulk Density

Bulk density reduces with the application of animal manures, both because the organic matter has a lower particle density than the mineral particles and its increase results in reduction of the soil particulate density as a whole, as because the increase of soil organic matter increases its degree of aggregation, increasing the volume of pores. Tiarks et al. (1974) determined a reduction in particles density from 2.63 to 2.50 g cm⁻³ and in soil density from 1.05 to 0.90 g cm⁻³ with the application of manure, but the effect in depth was dependent on the depth of the tillage. The reduction in bulk density occurs both with the application of manures alone (Celik et al., 2004; Barzegar et al., 2002, Bulluck et al., 2002) and in association with mineral fertilizers (Hati et al., 2006a, Hati et al., 2007; Bandyopadhyay et al., 2010; Hati et al., 2008). However, the application of pig slurry usually does not alter bulk density (Arruda et al., 2010; Oliveira et al., 2014), due to the low percentage of organic matter in the material. The application of poultry litter, bovine slurry and pig slurry at recommended doses to supply nutrients to crops for a period of ten years also did not alter significantly bulk density (Veiga et al., 2007).

2.2.3. Porosity

The results obtained in several studies with application of manure presented divergent results regarding their effects on the total porosity and the classes of pores. When increasing in total porosity was observed, this was due to the increase of pores with larger diameter (macropores), associated with better soil structure (Celik et al., 2004; Rós et al., 2013). Marinari et al. (2000) observed that the increase of macropores in the soil treated with organic fertilizer was mainly due to an increase in the elongated pores, which are considered very important for both soil-water-plant relationships and maintenance of good soil structure. The isolated application of manure is not efficient to physically recover of compacted layers, which is achieved by the association of plants with vigorous root system (Seguel et al., 2013). In a larger number of studies, it was found an increase in the volume of micropores (Hati et al., 2006b; Hati et al., 2007; Hati et al., 2008; Alencar et al., 2015), probably associated with the increase of soil aggregation and, consequently, in intra-aggregate porosity. On the other hand, in some studies there was no significant change in soil porosity (Neto et al., 2008; Veiga et al., 2007), which may be associated with both the applied doses and the soil preparation system used for its incorporation.

2.2.4. Water Infiltration, Retention and Availability

Water infiltration in the soil is another characteristic positively affected by the application of manure in most cases, both when the manure is applied alone (Barzegar et al., 2002; Arriaga and Lowery, 2003; Tiarks et al., 1974; Seguel et al., 2013) and associated with mineral fertilizers (Hati et al., 2006a, Bandyopadhyay et al., 2010), even in soils with salinity problems (Pernes-Debuyser and Tessier, 2004). The application of organic materials increases soil water retention, especially

in the lower tensions (Barzegar et al., 2002; Arriaga and Lowery, 2003; Darwish et al., 1995; Ojeniyi, 2008), which increases the volume of water available to the plants (Hati et al., 2006b; Hati et al., 2007; Hati et al., 2008; Neto et al., 2008; Alencar et al., 2015). According to Hati et al. (2006), the application of 10 Mg of manure increased the efficiency of water use by 103% in relation to the control, increasing the yield of the crops grown in that system. The increase in water retention is dependent on the textural class of the soil, and in fine-textured soils this effect is more pronounced (Darwish et al., 1995).

2.2.5. Physic-Mechanical

The number of studies on the effect of manure application on physic-mechanical properties is less abundant than for other physical attributes. Darwish et al. (1995) determined that the liquid and plastic limits of the three studied soils were higher with the application of manure, however these differences were small in magnitude. On the other hand, the value of the modulus of rupture decreases with the application of manure, which was also observed by Tiarks et al. (1974). Reduction of precompression stress was also observed with the application of poultry litter (Pandolfo et al., 2005), which is associated mainly with the reduction of bulk density (Seguel et al., 2013).

2.3. Changes in Biological Attributes

2.3.1. Diversity

Studies on the effect of manure application on population and biological activity are definitely much scarcer than those conducted to study the effect on soil physical and chemical properties. The microbial population (bacteria, fungi, actinomycetes, ammonifiers and nitrifiers) increases significantly with the application of manure (Ndayegamiye and Cote, 1989), but less or no effect on the edaphic mesofauna was observed (Pandolfo et al., 2005; Oliveira, 2009). This effect seems to be more pronounced on beneficial microorganisms such as *Trichoderma*, including reducing the population of pathogenic microorganisms such as *Phytophthora* and *Pythium* in soils that use the organic production system (Bulluck et al., 2002). González-Mancilla et al. (2013) observed increased density of P-solubilizing bacteria and *Azospirillum*, as well as root colonization by arbuscular and vesicular mycorrhizae.

2.3.2. Activity

The biological activity increases with the application of manure, mainly due to the enrichment in soil organic matter and improvement of soil aeration conditions (Marinari et al., 2000). It was observed a significant increase in microbial biomass (Kanchikerimath and Singh, 2001; Masto et al., 2006), microbial respiration rate (Ferrerias et al., 2006; Masto et al., 2006), quantity of soluble carbohydrates (Tejada et al., 2006) and enzyme activity such as urease, β -glucosidase, phosphatase, arylsulfatase and dehydrogenase (Tejada et al., 2006; Kanchikerimath and Singh, 2001; Hati et al., 2006b; Liu et al., 2010). Mixing straw with low carbon manure may be a suitable strategy to improve their effects on biological activity (Zhao et al., 2009). The increase in biological activity favors the decomposition of the organic material and, consequently, the release of the nutrients contained in it (Kanchikerimath and Singh, 2001; Ndayegamiye and Cote, 1989), accelerating the nutrient cycling.

3. Effect of The Application of Animal Waste on Annual Plant Productivity

Animal waste or other organic waste can be used as a single or complementary organic nutrient source to annual crops (Oliveira et al., 1993; Ciancio et al., 2014). Applications of animal waste tend to increase the availability of nutrients in soils, especially N, P, K, Ca, Mg, which can stimulate plant root growth and, as a consequence, a larger volume of soil may be exploited, which favors the absorption of water and nutrients, reflected in increased production of grain crops, such as maize (*Zea mays* L.), common bean (*Phaseolus vulgaris* L.), and shoot dry matter (DM) of cover crop species such as black oats (*Avena strigosa*) (Ceretta et al., 2005; Chantigny et al., 2008; Ciancio et al., 2014). This may be reflected in a greater accumulation of nutrients in the tissue and even nutrient recovery, which is desirable, since it reduces the potential of nutrient transfer through surface runoff and leaching, potentiating nutrient cycling and nutrient concentration in grains (Doneda et al., 2012), which may be inserted into the animal and human food chain.

According to Giacomini and Aita (2008), animal waste, such as deep litter and liquid pig slurry, applied as a source of N for corn, increased the availability of this nutrient in the soil throughout the crop cycle, compared to the control treatment. However, liquid pig slurry may have a higher rate of mineralization, which may promote increased grain yield. Other studies also report the interference of pig slurry application in crop production (Comin et al., 2007). However, in most studies with animal waste, such as liquid pig slurry, increasing doses were applied and few studies yielded quantities capable of supplying N demand of the crops (Comin et al., 2007; Giacomini and Aita, 2008; Giroto et al., 2010). Therefore, further studies on different types of soil and with different types of organic waste are necessary, establishing doses of animal waste or other organic waste to be applied, such as organic compost derived from the composting of pig slurry, based on the P₂O₅ requirement of the crops. This is because P is one of the determinant nutrients of production, especially in soils of tropical and subtropical regions, and in areas with a history of waste application, where they have been applied in doses to supply the N requirement of the crops. The accumulation of P in the soil has been observed, especially in more labile fractions, which can be absorbed by the plants, but can also potentiate the contamination of waters (Gatiboni et al. 2008; Ceretta et al., 2010; Guardini et al., 2012).

Evaluating the yield of maize grains in the rotation of black oats/maize/wild radish with application of liquid pig slurry, Ceretta et al. (2005) showed that grain yield per m³ of manure was 408, 291 and 188 kg ha⁻¹ in the first year; and 100, 87 and 81 kg ha⁻¹ in the second year, for doses of 20, 40 and 80 m³ ha⁻¹, respectively, evidencing that dose responses may be variable since there is no control over the quality of the waste, as well as the conditions of soil, climate and management can vary influencing the response to the doses of waste.

Evaluated the crop responses to different application rates of animal manure sources, used alone and supplemented with mineral N topdressing, in a no-tillage system, Ciancio et al. (2014) observed that common bean grain yield in the 2005/06 growing season was greater in the soils subjected to the application of 30 m³ ha⁻¹ with pig slurry (PS) + topdressed nitrogen fertilization (TNF) and of 2 t ha⁻¹ with turkey manure (TM) + TNF, with values of 2.31 and 2.08 Mg ha⁻¹, representing increases of 28.1 and 15.1% in relation to the soil without application. To maize grain yields were highest when the plants were grown in soil treated with 30 m³ ha⁻¹ PS + TNF in the 2006/07 growing season, and 20 and 30 m³ ha⁻¹ PS + TNF in the 2007/08 growing season. Grain

yield ranged from 1737 to 4243 kg ha⁻¹ in the 2006/07 growing season, and reached 5102 kg ha⁻¹ in the 2007/08 growing season. The application of 30 m³ ha⁻¹ PS + TNF led to increases in grain yield of 43 and 2441% over the treatment without application, and of 54 and 83 % in relation to the NPK treatment in the 2006/07.

In experiment with fertilization with PS and DL (deep litter) for 10 years in succession black oats/corn in NTS agroecological, Loss et al. (2017) found that, in the average of 10 years, maize grain and black oats dry matter production was 2.9/6.5, 5.0/8.1, 5.5/8.7, 5.6/8.2 and 6.0/8.9 Mg ha⁻¹, respectively, for) treatments Control (no fertilization; PS90 and PS180 (fertilization with PS at rates of 90 and 180 kg N ha⁻¹, respectively); DL90 and DL180 (fertilization with deep litter at rates of 90 and 180 kg N ha⁻¹, respectively).

4. Animal Manure as Fertilizer: Productivity and Food Composition of Horticultural Crops

4.1. Animal Manure Characteristics

The composition of the animal feed and its changes during digestion in the animal gastrointestinal tract are key elements for the knowledge of manure composition and quality causing great variation among different types of manure (Velthof et al., 2000). For example, the concentration of phosphorous (P) in the feces of cow stock is related with the P in diet (Toor et al., 2005).

The characteristics of organic fertilizer can affect soil fertility, fruit production and quality. High quality organic fertilizer presents a complete stability, a carbon:nitrogen (C:N) ratio relatively low (between 10 and 20), low salinity, neutral pH, balanced nutrient composition, and absence of heavy metals, organic pollutants and biological hazards. When one or more of these parameters fall outside the optimal range, then plant production can be impaired and fruit quality negatively affected. Before application, manure should be stabilized since during the stabilization process, the intense redox reactions reduce the availability of oxygen; consequently, if fresh manure is incorporated into the soil, it may induce anoxia at root level. A stabilized manure can be easily recognized by the absence of consumption of oxygen (O₂), the relatively low C:N ratio (< 20), the temperature, that is similar or just a little above room temperature, and the low humidity (30-50%).

4.1.1. C: N Ratio

In general, an improvement of secondary metabolism products such as organic acids and polyphenolic compounds, many of which considered beneficial for human health, occurs in fruits and vegetables because of the application to plants of organic fertilizer (Winter and Davis, 2006), including animal manure. A possible explanation to this response involves the nutritional status of plant and in particular the N availability. The reaction of the plant to soil N deficiency can be explained by the growth: differentiation balance theory (Koricheva et al., 1998). In case of available N, plant moves the metabolic investments toward vegetative growth, increasing N-containing compounds such as aminoacids, terpenes and proteins (Brandt and Molgaard, 2001) reducing the synthesis of carbohydrates, starch, phenylpropanoids, phenolic antioxidants (Mitchell and Chassy, 2004) and C-based secondary compounds. Conversely, a decrease in N availability as well as an increase of CO₂ and photosynthetic active radiation has the opposite effects, with tree

metabolism moving toward a higher synthesis of secondary metabolism compounds such as phenols or terpenoids. As an example, increase of vitamin C with oxidative stress, such as N deficiency, was observed in tomato (Toor et al., 2005). Other authors found an increase of flavonoids, quercetin and kaempferol in tomato fertilized with chicken manure without a decrease of yield, color, soluble solids or other quality characteristics (Mitchell et al., 2004). These authors assessed that flavonoid content in tomatoes is negatively related to available N; as a consequence, plants with limited N, accumulate more flavonoids than those that are well-supplied. However, variety effect is much higher than management system (Woese et al., 1997). The distribution of animal manure often results, depending on the C:N ratio, in a non-prompt availability of N, consequently a switch toward C-based secondary compounds and/or non-N-containing secondary metabolites such as phenolics and terpenoids may happen (Brandt and Molgaard, 2001).

On the other hand, the increase of N availability in soil has a positive effect on β -carotene, vitamin A precursor (Mozafar, 1993), including lycopene (Zhang et al., 2016). β -carotene is located in chloroplast where it acts as an antioxidant, or occurs as colorant, in both situations, its synthesis is depressed by limited N availability (Brandt and Molgaard, 2001).

4.1.2. Biological Hazards

Use of animal manure fertilizer may have microbiological implications, such as fruit and vegetable bacteria contaminations, i.e. the presence of *Salmonella* (Mukherijee et al., 2004) and *Escherichia coli* found in non-certified organic salad and peppers. Ruminants have been identified as the major reservoir of *E. coli* (specifically strain O157:H7), with cattle as the most important source of human infections followed by sheep and goats (Doyle et al, 2006). However, the bacteria was also found in swine, poultry (Heuvelink et al., 1999) and rabbit feces and may contaminate a variety of vegetables such as lettuce, spinach, etc, especially if fresh or not stabilized manure is used. *Campylobacter* has been found more frequently in excrements of organic than conventional cow stock (Winter and Davis, 2006). The best way to reduce the risk of fruit and vegetable biological contamination is the use of composted manure, obtained from a correct stabilization process that employs a temperature of the bulk heap of 65-70°C by regular mixing, a constant oxygenation of the manure and a proper duration (at least 3 months) of the whole process.

4.1.3. Organic Pollutants

Around 90% of antibiotics fed to animals end up in manure (Kumar et al., 2005a; Grote et al., 2007) since they are poorly absorbed by animals' gut, they are excreted in urine and feces. Antibiotics remain stable during manure storage and end up in agricultural fields through manure applications (Migliore et al., 1995). The presence and persistence of antibiotics in manure can lead to environmental problems such as toxicity for soil microflora and fauna; in addition, they can potentially increase the antibiotic resistance in the environment (Smith et al., 2005). Moreover, crops could absorb antibiotics and the consumption of fresh vegetables grown in soil amended with manures could lead to potential risks for human health. The most common antibiotics present in swine, beef and turkey manures are tetracyclines (oxytetracycline and chlortetracycline), tylosin, sulfamethazine, amprolium, monensin, virginiamycin, penicillin, and nicarbazine (De Liguoro et al., 2003; Kumar et al., 2005a) in a concentration that varies from traces to 200 mg L⁻¹ of manure slurry (Kumar et al., 2005a). Greenhouse studies conducted on corn, green onion and

cabbage assessed that plants were able to absorb chlortetracycline but not the large-molecule-size tylosin (Kumar et al., 2005b). In addition, the authors observed a rise of concentration in the plants as the amount of antibiotics present in manure increased (Kumar et al., 2005b). Dolliver et al. (2007) showed a significant difference in sulfamethazine uptaken by lettuce and onions between the control (soil amended with manure with no antibiotics) and the sulfamethazine treatments. Antibiotics were found in roots and leaves of carrots (Boxal et al., 2006; Jones-Lepp et al., 2010), chinese cabbage and turnip (Herklotz et al., 2010), lettuce and spinach (Jones-Lepp et al., 2010) having potential influence on human nutrition. However, field study conducted on 11 vegetable species, showed very low antibiotic concentrations with values lower than $10 \mu\text{g kg}^{-1}$ (Kang et al., 2013), so that, according to the Food and Agriculture Organization (FAO), a person needs to consume 50–75 kg of vegetable to reach a dangerous daily intake (Kang et al., 2013).

4.1.4. Salinity

Animal feed is often enriched with mineral salts, with the results of increasing salinity and ion composition of animal manure (Li-Xian et al., 2007). Once in the soil, ions and salts dissolve in water and increase soil solution salinity. Sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), sulphate (SO_4^{2-}) and chlorine (Cl^-) are the most common ions increased with animal manure, while calcium (Ca^{2+}) was found to decrease after application of chicken and pigeon manure (Li-Xian et al., 2007). Strawberry fertilized with commercial chicken manure-based showed a higher ammonium:nitrate ($\text{NH}_4:\text{NO}_3$) ratio, electrical conductivity and NaCl concentration in the soil solution along with a cation imbalance that were responsible for the decrease of fruit size and the increase of fruit firmness (Pokhrel et al., 2015) compared with the fruits fertilized with the mineral nutrients. On the other hand, these conditions increased fruit dry matter and soluble solid concentrations (Pokhrel et al., 2015). The reason of this response is probably related to the increase of salinity and a consequent decrease in water availability, along with N deficiency, related to the high C:N ratio (Pokhrel et al., 2015).

4.1.5. Heavy Metal

Heavy metal accumulation in soil and eventually in fruits is another major concern related to the use of animal manure fertilizers. Often livestock diet is enriched with heavy metal such as copper (Cu), zinc (Zn), lead (Pb), that may accumulate in soil and contaminate fruits and vegetables (Nawab et al., 2015; Rahman et al., 2014; Singh and Kalamdhad, 2013). However, data from experimental studies showed that the use of manure can decrease the risk of heavy metal contaminations. For instance, application of chicken and cow manure decreased date palm fruit Pb and cadmium (Cd) as well as NO_3^- and nitrite (NO_2^-)-N concentration, compared with mineral N fertilization (Marzouk and Kassem, 2011). This response was related to the lower concentration of Pb and Cd in manure compared to mineral fertilizer where metals are as salt form, more available compared with the organic form (in animal manure). In addition, the carboxyl and phenolic functional groups, proper of organic matter, form stable complexes with metals, therefore the addition of organic material to the soil may lead to a fixation of metals and decrease in their availability for root uptake. Similar results were found in a trial on nectarine tree supplied with cow manure, municipal solid waste compost or mineral fertilizer that showed a decreased of Pb soil accumulation when cow manure was applied and no effect on heavy metal accumulation in fruit (Baldi et al., 2016). It is possible that organic matter promoted the formation of soluble organic form of Pb, that moved to the deeper soil profiles outside the root volume.

4.1.6. Pedoclimatic Conditions

Pedoclimatic conditions affect the rate of animal manure mineralization and consequently, the release of nutrients soil. Soil moisture (Roberts, 2011) and temperature (McCauley et al., 2017) are positively related to mineralization rate, that continues with air temperature near to 0°C (Eusufzai et al., 2013). Clay particles are known to increase the stability of organic substrates and to enhance microbial bio-synthesis (Sørensen, 1981; Wieder et al., 2014). However, there are contrasting evidence regarding the effect of soil structural composition on animal manure turnover. A study on mineralization of different manures (cattle, pig and poultry) conducted in the Netherlands showed a lower mineralization rate in the sandy loam (18% clay) than in sandy (3% clay) soil six months after spring application (Van Faassen and van Dijk, 1987). Moreover, in a different study (Van Veen et al., 1985) organic matter decomposition, mineralization and N immobilization rates were slower in the soil of heavier texture. According to these authors, clay has a greater capacity to preserve or protect soil biomass, provides a closer interaction between micro-organisms and products of their decay and, to a lesser extent, promotes a higher efficiency of utilization of glucose and metabolic products of soil biota. Other authors (Thomsen and Olesen, 2000; Thomsen et al., 1999) did not find a clear relationship between soil clay content (ranging from 11 to 45%) and manure N release. According to Thomsen et al. (1999), manure turnover relies more on water availability than on soil texture. Consequently, the protection effect of clay against decomposition organic matter is probably weaker than the promoting effect related with the increase of soil water-holding capacity (Thomsen and Olesen, 2000).

A rapid mineralization and release of nitrate in soil can severely impairs leafy vegetables quality due to an excessive concentration of nitrate in edible parts (Wang et al., 2008; Bourn and Prescott, 2002). Besides N, manure mineralization also releases P, K and micronutrients useful for plant growth and production; if pedoclimatic condition impairs or stimulate mineralization, the availability of nutrients can diverge from optimal and turn into nutritional disorders. An inverse relationship between concentration of reducing sugar, which are critical precursors for carcinogenic acrylamide and K supply has been observed in potato (Gerendás et al., 2007). In fact tubers grown with high N and low K fertilization showed a higher accumulation of the precursors of acrylamide during frying, than tubers grown with high K availability.

Potassium plays an essential role for wine quality, so that its correct accumulation in berry is important. If K availability is in excess, then a decrease of free organic acids and tartrate: malate ratio, and an increase of pH and tartrate precipitation during wine-making, with a reduction of the overall wine quality is expected (Mpelasoka et al., 2003).

4.2. The Time of Application

The time of application, similarly to pedoclimatic conditions, influences animal manure mineralization and consequently nutrient availability for plants and potential loss from soil. Manure from bedded systems can be correctly applied in autumn since the high lignin content of straw takes long to mineralize; on the other hand, when manure is characterized by high $\text{NH}_4^+\text{-N}$ concentration, such as liquid swine manure, fall applications are not recommended. Manure applied in the spring has less time for nutrient release before crop uptake, consequently this time of application is suitable for manure that contains easily mineralized components so that N and

other nutrients are available for plants at spring vegetative growth. Spring manure application increased soil P and N content if compared to fall manure application; in addition, nutrient runoff losses may be lower during spring and summer compared with fall and winter due to crop nutrient uptake, microbial activity, leaching and evapotranspiration during the growing season (Ahmed et al., 2013). In a two years experiment, organic manure spinach applications were more effective in autumn than in winter (Citak and Sonmez, 2010a). Spring application of poultry manure (15 t ha^{-1}), as well as cow manure (30 t ha^{-1}) supplied adequate N and minerals for the apple trees grown in a sandy soil, since the pattern of release matched the demand of plants in the pedo-climatic condition of the experiment (Amiri and Fallahi, 2009).

It is well known that NO_3^- contents of plants increase with the rate of N application, consequently if manure rapidly mineralize high quantity of NO_3^- are available for plant uptake. The excessive presence of NO_3^- in crops could be dangerous for human health. In detail, NO_3^- convert to NO_2^- in plant tissues, which may cause health problems in infants and form carcinogenic substances. Higher doses of NO_2^- change hemoglobin to methemoglobin and this inhibits the transport of blood oxygen in the human body. Increased rates of N fertilizers also cause the accumulation of oxalic acid in vegetables that causes acute toxicity if taken with Ca since it forms stones in the kidney (Turan and Sevimli, 2005). Total N, NO_3^- and oxalate were higher when cabbage was grown with chemical fertilizers than when farmyard manure was used (Turan and Sevimli, 2005). Furthermore, the NO_3^- concentration of pecan fruit fertilized with mineral fertilizers was lower compared to that obtained with the inorganic fertilizers (Abou, 2004). In addition, on tomato fruit, the NO_3^- concentration increased linearly with mineral N, however, after application of cattle manure the NO_3^- concentration was not influenced by N rates (Ferreira et al., 2006).

4.3. Plant Species

Tomatoes fertilized with chicken manure and grass-clover mulch showed a higher content of total phenolic and ascorbic acid compared to mineral nutrient solution (Toor et al., 2006). Authors explained the response with the slow release of nutrient from chicken manure and grass clover that, also accounted for the relatively slow rate of growth. At the same time, the high light intensity allowed to allocate carbon for C-based secondary compounds like phenols in plants treated with organic fertilizers. Since, in plant there may be a competition between protein and phenolic synthesis, because of the common precursor, L-phenylalanine (Riipi et al., 2002), low N and high light promoted the synthesis of food functional compounds. Other reported that the quality of potted tomato grown with different animal manure (chick, pig, horse and bull) improved when compared with mineral fertilized- and unfertilized-control (Yang and Chu, 2014). In detail, vitamin C and soluble solid content were ordered as: horse manure > bull manure > pig manure > chick manure > chemical fertilizer > control (Yang and Chu, 2014). Sugar: acid ratio was higher in manure than control and mineral even if all manure treatments decreased organic acid content by 22.7–62.1% if compared to chemical or absence of fertilization (Yang and Chu, 2014). Mathur et al. (2010) observed that tomato fruits grown with the high rate ($0.4 \text{ m}^3 \text{ m}^{-2}$) of chicken manure had less vitamin C content than fruits fertilized with the low rate ($0.2 \text{ m}^3 \text{ m}^{-2}$).

The competition between protein and phenolic synthesis was also used to explain the decrease of phenols in juice of passion fruit, as a response of the increase of the rate of poultry manure applied, in the range between 5 and 15 t ha^{-1} (Ani and Baiyeri, 2008). At the same time, the increase of the

rate of poultry manure, with the consequent increase of soil N promoted sugar, vitamin A and vitamin C concentration in juice (Ani and Baiyeri, 2008). Moreover, the concentration of anti-nutrient factors such as tannin, hydrogen cyanide, phytate and calcium oxalate in ripen fruit was negligible and not affected by fertilizers (Ani and Baiyeri, 2008).

In palm dates the application of organic fertilizers (chicken manure and cow dung) alone or in combination with mineral fertilizer increased fruit total soluble solids, palm yield, fruit weight, dry matter, color, and anthocyanin concentration (Marzouk and Kassem, 2011).

Application of cattle, poultry and sheep manures alone or their mixture increased soluble solid, ascorbic acid, total phenol, crude fibers and intensity of red color of bell pepper, compared to mineral (N, P, K) fertilizations. The optimal rate to maximize vitamin C concentration was 5 t ha⁻¹ of poultry manure, with a decline as the manure application rate increased (Ademoyegun et al., 2011). Mineral fertilizer, on the other hand, promoted a higher acidity, water content, fruit size and lycopene concentration (Abu-Zahra, 2011).

A comparison between sheep and cattle manure (both with straw) in sandy soil (Jianming et al., 2008) evidenced that sheep manure compost mineralized a large quantity of organic matter during the early stages, resulting in excessive levels of nutrients becoming available at a time of relatively small plant demand and consequently in a decrease of muskmelon quality. On the other hand, cattle manure released a lower amount of nutrients in the first stages of the vegetative season, but then constantly mineralized all over the season matching the increasing demand of the growing melons (Jianming et al., 2008). In addition, a study conducted on cantaloupe showed that the use of chicken and pigeon manure composts increased fruits vitamin C (Jianming et al. 2008). Probably, the benefit lies in the release of N and P in the soil that was slower in organic amendments if compared to mineral fertilization.

The application of sheep and organic manure reduced the NO₃⁻ concentration in romaine lettuce (Pavlou et al., 2007) and spinach leaves (Ahrens et al., 1983; Citak and Sunmez, 2010b), respectively if compared with mineral fertilization, with an inverse relation between NO₃⁻ level and vitamin C (Citak and Sunmez, 2010b). The application of different manure on cabbage evidenced that the mineral composition of crops was related to the mineral content of the manures (Citak and Sunmez, 2010a); in detail, chicken manure applications caused a high level of P, while farmyard caused a high level of K and N.

Vitamin C content of sweet potatoes peaked when 0.5 t ha⁻¹ of broiler litter was applied and then declined as the rate increased (Gichuhi et al., 2014). For this reason, it is important to define the correct rate of manure application since N rate affects nutraceutical value of crops, i. e. high rates decrease the vitamin C content in fruits and vegetable (Lee and Kader 2000).

Nitrogen soil availability has a great impact also on grape composition and on wine quality (Bell and Henschke, 2005) affecting the fermentation kinetic and the production of aromatic compounds and biogenic amines (Albers et al., 1996). Biogenic amines are organic compounds of low molecular weight, endogenous of plants and with important physiological functions that at certain concentrations can cause headaches, skin irritation, rapid heartbeat, hypertension, hypotension and neurological disorders (Capozzi et al., 2012). According to several authors (Soufleros et al. 2007;

Pérez-Álvarez et al., 2017), an increase of amino acids and biogenic amines concentration in vines is positively correlated to N availability. Moreover, Pérez-Álvarez et al. (2017) showed a positive correlation between N leaf concentration (at bloom and veraison), and total biogenic amines content in wines. Since some amino acids are precursors, through microbial decarboxylation, of the biogenic amines, (Pérez-Álvarez et al., 2017), consequently the excess of N in soil can negatively influence vine quality.

5. Conclusions

The application of animal manure results in an increase in TOC content, both in short and in long term, and associated with mineral fertilizers generally increases this effect, due to the higher crop phytomass production and, consequently, addition of TOC to the soil in form of straw and roots. In the literature consulted, the only type of manure that does not necessarily result in an increase in TOC content is the pig slurry, which is associated with the low organic matter content in this type of waste. Thus, a higher increase in TOC is expected when the manure presents high dry matter content and higher C:N ratio, as observed in poultry litter, deep litter and cattle manure, as well as in organic compounds.

The increase in TOC in soils may increase soil cation exchange capacity, increasing nutrient adsorption, and may favor the complexation of exchangeable aluminum, which, as a consequence, may be reflected in increased pH, and in increased production of grain crops. Aggregate stability is more pronounced with the application of materials with higher C:N ratio. The joint application of manure and mineral fertilizers results in increased aggregation and stability. Bulk density reduces with the application of animal manures, and to total porosity and the classes of pores the results presented are divergent regarding their effects. Water infiltration in the soil is another characteristic positively affected by the application of manure. The microbial population increases significantly with the application of manure, but less or no effect on the edaphic mesofauna was observed. The biological activity increases with the application of manure, mainly due to the enrichment in soil organic matter and improvement of soil aeration conditions.

Although a strength relation between animal manure and fruit and vegetable quality is not established, the most important effects on productivity and food composition of horticultural crops are related to the soil N availability. If animal manure promotes an increase of N, i. e. C:N ratio is relatively low, then an increase of vitamin A and nitrate-N in leaves would be the major effect expected. If C:N ratio is relatively high, then a decrease of N soil availability is promoted and increase of secondary metabolism compounds, such as vitamin C, terpenoids and phenols, is expected. This considering that sub-optimal, optimal and excessive rate of N depends on fruit and vegetable species. To optimize plant growth and crop quality it is important to establish the right animal manure rate and timing of application in relation to soil properties and pedo-climatic condition, so that a synchronization between nutrient release and plant demand is achieved and potential fertilization effect of animal manure is obtained.

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