REVIEW ARTICLE | 1

Influence of Organic and Mineral Fertilization on Soil Greenhouse Gas Emissions. A Review

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Summary

The anthropogenic emission of greenhouse gases including carbon dioxide, methane, and nitrous oxide is bringing about major changes to the global environment. Although most of the anthropogenic emissions originate from industrial processes, agriculture is responsible for a significant portion of the greenhouse gases produced by humans worldwide. The impact of agriculture has become a key issue, considering that the main greenhouse gases are those related to carbon and nitrogen global cycles. This paper presents a review of the scientific literature meant to provide the impact of human management through fertilizers use on CO_2 , CH_4 , and N_2O emissions. The influence of organic and mineral fertilization on greenhouse gas emissions is analyzed, and usage of organic amendments showed a wise potential for protecting the environment and to mitigate greenhouse gas emissions.

Key words

greenhouse gases, emissions, organic fertilization, mineral fertilization, soil properties

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Introduction

Climate change is one of the greatest challenges that the world is facing today (Bilandzija et al., 2014). Changes in the concentration of greenhouse gases (GHG) in the atmosphere such as carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) have been related to the increase in global temperature and are responsible for global warming by increasing the greenhouse effect (IPCC, 2007). By the end of the 21st Century, increases in global temperatures by 1.2°C to 4.8°C are predicted (IPCC, 2013). Although most of the anthropogenic emissions originate from the combustion of fossil fuels and industrial processes, CO2, CH4, and N₂O emissions also come from soils and are related to agricultural activities (IPCC, 2007). This leads to the conclusion that due to its intensity, agricultural production is the cause of climate change (Znaor, 2009). As a part of the biosphere, agricultural soils can play as a sink but also as the source of GHGs which naturally depends on biotic and abiotic factors as well as on anthropogenic impact (agricultural soil management). The primary process that is responsible for emissions releasing from the soil into the atmosphere is diffusion (Buchmann, 2000) that is affected by plant roots (Raich and Tufekgcioglu, 2000), respiration of organisms in the soil, and soil organic matter decomposition (Norman et al., 1992; Xu and Qi, 2001; Epron et al., 2006). Furthermore, studies have shown that factors such as soil temperature, soil moisture, climatic factors, tillage systems, fertilization practices, crop presence and density, presence of organic matter and nutrients influence the GHG production and emission rates from the soil surface (Ludwig et al., 2001; Skiba and Ball, 2002; Lal, 2003; Ball, 2013; Bilandzija et al., 2014).

Moreover, fertilizer induced GHG emissions represent the largest source of total agricultural emissions (Wang et al., 2017). For example, in the UK, 75% of the total emissions from crop production result from the use of organic and inorganic nitrogen fertilizers (Hillier et al., 2009). Therefore, this paper presents the state of agricultural soil and GHG and the influence of human management through fertilizers use on CO2, CH4, and N2O emissions.

Relationship between soil properties and GHG flux

According to Ball et al. (2013), soil properties have a major effect on the emission and exchange of GHGs. The effect of physical-mechanical, chemical or biological properties on soil GHGs is very complex, as it is determined by various factors (Buragienė et al., 2019). These effects came through soil moisture, penetration resistance, soil temperature, structure, porosity, soil organic matter, soil mineralogy, pH and soil nitrogen (Beauchamp, 1997; Evans and Burke, 2013). Soil temperature, soil moisture, mineral N content, soil organic matter content, and pH can directly affect GHGs from the soil surface through microbial activity (Ball, 2013; Bilandzija et al., 2014; Oertel et al., 2016). Increases of soil temperature leads to higher CO₂ emissions (Ludwig et al., 2001; Tang et al., 2003; Galic et al., 2019), N₂O emissions (Liu et al., 2011) and CH₄ emissions (Rosenkranz et al., 2006; Butterbach-Bahl et al., 2013). Soil moisture influences gas diffusion and microbial activity (Lou et al., 2003). In dry soil activity of microorganisms decreases which also affects soil respiration (Galic et al., 2019). According to Brady and Weil (2010), soil organic matter occupies the largest part of carbon

stocks in agroecosystems and plays a very important role in the global balance of carbon and nitrogen cycles where C:N represents an important criterion for evaluating the quality of humus (Kisic et al., 2017), and it also directly affects the GHG emissions from the soil. High soil N concentrations, especially those following fertilization, may induce microbe-mediated N transformation processes leading to high N₂O emissions (Bouwman et al., 2002). The optimal C:N in the soil is 10:1 while in terms of compost, the ideal C:N is 30 and it indicates a sufficient amount of food available to micro-organisms (Kisic et al., 2017). Globally viewed, the soil is the central link in the organic biotransformation chain. As the most important "organ of the agricultural organism" the soil transforms all organic residues through decompositors (Zgorelec et al., 2017). Every transformation of organic matter ends with the emissions into the environment. Several studies reported that N₂O and CO, fluxes increased more after the application of residues with low C:N compared to high C:N (Aulakh et al., 1991; Huang et al., 2004; Jiang et al., 2011). Soil pH is important for mineral decay, the intensity of microbiological processes, OM mineralization, the solubility of substances and other physicochemical processes occurring in soil (Mažvila et al., 1998).

Although the processes of GHG production and emission are considered as mainly biological, soil physical conditions also play a significant role (Gregorich et al., 2006). Thus, soil structure changes can influence its source and sink function (Jungkunst and Fiedler, 2007) while texture and drainage influence emissions indirectly by their influence on the above-mentioned properties (Skiba and Ball, 2002).

Agricultural sector in Europe

Although climate changes and their consequences affect humans, they also affect soil possibility to provide its Ecosystem services in the future (Galic et al., 2019a). Therefore, agriculture represents an important contributor to climate change through emissions of GHGs and air pollutants. Agricultural land accounts for 40 % of total EU land that represents one of the world's leading producers and exporters of agricultural products. Considering that agriculture is also a driver of climate change itself, Europe needs to adapt its agricultural food system and reduce its emissions from agriculture (EEA, 2019). The GHG contribution varies by country (Table 1), but, just less than 44 % of the total agricultural emissions of the 28 EU Member States are released from France, Germany, and the United Kingdom. Between 1990 and 2016, decreases by 20 % in GHG emissions from the agriculture sector are recorded (EEA, 2018).

In the Republic of Croatia, GHG emissions in the Agricultural sector are conditioned by different agricultural activities. As a signatory of the UNFCCC Convention, Croatia has the obligation to write a National Inventory Report (NIR) using the Intergovernmental Panel on Climate Change (IPCC) and Land Use, Land Use Change and Forestry (LULUCF) guidelines. According to the Kyoto Protocol, the EU has taken a leading role in tackling climate change and set the goal of reducing GHG emissions by 80 % by 2050 where the Republic of Croatia shows the possibility to achieve the European goal of reducing GHGs (NIR, 2017). Table 1 presents average greenhouse gas emissions (Kt CO, eq) from the agricultural sector calculated from 1990 -2017 per EU and non-EU countries (FAO, 2019).

Country	Kt CO ₂ eq	
Austria	7392.4	
Bulgaria	5520.6	
Bosnia and Herzegovina	2222.9	
Croatia	2909.6	
France	73735.2	
Germany	62772.9	
Italy	32529.7	
Montenegro	398.3	
Netherlands	18478.9	
Poland	31871.8	
Romania	16439.2	
Serbia	6536.6	
Slovenia	1607.7	

Influence of organic and mineral fertilization on GHG emissions

Despite the influence of physical-mechanical, chemical or biological properties on GHG production, soil management practices affect factors previously described and benefit microbial activity. Among them, the application of mineral or organic fertilizers is of great importance for ${\rm CO_2}$, ${\rm CH_4}$ and ${\rm N_2O}$ emissions which can also be altered by changes in the amount and chemical compositions of manure applied to soils (Rahman et al., 2016).

Soil management systems that add organic wastes and incorporate carbon have been evaluated as important alternatives for increasing the capacity of atmospheric carbon sinks (Tian et al., 2009). The use of organic amendments including manures, composts, crop residues, and biosolids is rapidly increasing, and their share of agricultural land continues to grow (Thangarajan et al., 2013). Organic amendments improve the quality of the soil (Shrestha et al., 2013) through chemical, physical and biological activity (Fereidooni et al., 2013). Organic wastes are usually rich in carbon and nitrogen, and their addition increases the soil content of labile carbon and nitrification and denitrification rates (Jones et al., 2005). However, sustainable application of wastes in agriculture should not only refer to the balanced supply of the necessary nutrients, but also to the minimization of negative environmental impact (Cayuela et al., 2010).

Usage of mineral fertilizers is implemented in order to balance the gap between the nutrients required for optimal crop development and the nutrients supplied by the soil and by available organic sources. On the other hand, the fertilizer industry is a consumer of energy and a GHG emitter. Considering that sustainability of agricultural systems in many parts of the world is threatened by the rapid increase in world population, intensification without suitable management and the use of agrochemicals, including chemical fertilizers has negative

implications for the ecosystem and environment (Abbasi and Khizar, 2012), decreases organic matter (Belay et al., 2002; Nardi et al., 2004; Wu et al., 2004), decreases soil fertility and increases environmental degradation (Tiwari et al., 2008). However, anthropogenic influence on the soil is the factor over which we have the greatest control. By implementing good agricultural practices, which are based on principles of sustainable agriculture, it is possible to reduce GHGs into the atmosphere.

Carbon dioxide emissions (CO₂)

Increased levels of atmospheric $\mathrm{CO_2}$ have prompted research assessing the contributions of industrial, agricultural and environmental practices (Al-Kaisi et al., 2008). Accordingly, $\mathrm{CO_2}$ is recognized as the largest contributor to the greenhouse effect. Since 1750, approximately 35 % of anthropogenic $\mathrm{CO_2}$ emissions have been directly related to changes in land use (Foley et al., 2005). Certain measures, such as the use of different fertilizers can be taken to enhance the capacity of lands to sequester atmospheric C (Janzen et al., 1998; Nadelhoffer et al., 1999; Bowden et al., 2004). Instead of burning crop residues, the applications of inorganic fertilizers and the use of green manures, as well as organic manures can be of great importance in maintaining soil fertility (Ladd et al., 1994). These practices can provide essential nutrients to crops and reductions in the burning of crops can reduce $\mathrm{CO_2}$ emissions into the atmosphere (Edmeades, 2003).

Organic fertilization

Soil CO, emissions are a result of a combination of heterotrophic and autotrophic respiration, and both can be stimulated by the addition of organic compost (Ryals and Silver, 2013). Increases in soil CO, fluxes in agricultural soils after the disposals of organic wastes have been frequently observed by several authors (Scott et al., 2000; Cai et al., 2012; Ryals and Silver, 2013). Accordingly, Cayuela et al. (2010) reported on CO. emissions from six animal-derived wastes (horn and hoof meal, blood meal, hydrolyzed leather, meat bone meal, chicken manure, and a commercial organic mixed fertilizer) and found that soils treated with various animal by-products increased CO₂ emission (the maximum CO₂ fluxes were observed for the organic fertilizer mixture in the sandy soil - 0.031 g CO₂-C kg⁻¹ soil and for chicken manure in the loam soil - 0.189 g CO₂-C kg⁻¹ soil). Heintze et al. (2017) incorporated biogas digestate and cattle slurry to simulate the high-risk situation of enhanced GHG following organic fertilizer application in energy maize cultivation. The application of cattle slurry resulted in significantly higher CO₂ (141.54 mg C m⁻² h⁻¹) compared to the application of biogas digestate (89.95 mg $C m^{-2} h^{-1}$).

Many researchers showed that replacing chemical fertilizer with organic manure significantly decreased the emission of GHGs and pointed out that organic farming can reverse the agriculture ecosystem from a carbon source to a carbon sink (Liu et al., 2014). The substitution of chemical fertilizers with organic fertilizers has become a common practice in agricultural systems. Thus, mitigating GHG emissions through the replacement of chemical fertilizer with organic manure in temperate farmland was investigated by Liu et al. (2014). Results showed that replacing chemical fertilizer with organic manure significantly decreased GHG emissions without crop yield losses which reversed the

agriculture ecosystem from a carbon source (+2.7 t CO₂-eq. hm⁻² y⁻¹) to a carbon sink (-8.8 t CO₂-eq. hm⁻² y⁻¹). Ren et al. (2017) combined data from 379 observations in China and quantified the responses of soil N2O, CO2 and CH4 emissions to manure (Org-M) in comparison to chemical fertilizers (Min-F) or nonfertilizers (Non-F). The results showed that N₂O₂, CO₂, and CH₄ emissions were significantly affected by Org-M compared to Min-F (percentage change: -3, +15 and +60 %) and Non-F (percentage change: +289, +84 and +83 %). Increases in soil CO₂ fluxes in agricultural soils after the organic waste application are also observed by several authors (Scott et al., 2000; Chantigny et al., 2001; Bertora et al., 2008; Johansen et al., 2013; Ryals and Silver, 2013; Galic et al., 2019a).

Mineral fertilization

Using the IPCC methodology, synthetic N fertilizers used in the production of a cereal crop contributed the highest percentage of the carbon footprint, averaging 65 % of the total emissions (IPCC, 2006; Gan et al., 2011). Increases in available N can occur through human-induced N additions or change of land-use and/ or management practices that mineralize soil organic N (IPCC, 2006). The application of N fertilizer and urea has been shown to influence most biological processes in the soil that are important to mineralization, carbon sequestration and nutrient cycling (Bastida et al., 2006; Yan et al., 2007).

Zhang et al. (2014a) identified the characteristics of soil CO, emission and carbon balance in cropland ecosystems after continuous fertilizer applications (no-fertilizer application (SR), nitrogen - phosphorus - potassium chemical fertilizers (NPK), NPK plus pig manure (NPKM) and pig manure alone (M). Authors found that the cumulative CO₂ emission from upland soils in a cropland ecosystem treated with an inorganic fertilizer was higher (8.2 and 11.0 t C ha-1 in 2009, and 7.9 and 11.1 t C ha-1 in 2010) than that emitted from soils without fertilizer (2.5 and 3.4 t C ha⁻¹ in 2009, and 2.1 and 3.7 t C ha⁻¹ in 2010), but lower than that emitted from soils treated with organic fertilizer or with organic and inorganic fertilizers. Furthermore, several authors concluded that increasing the amount of mineral N fertilization such as ammonium nitrate can cause a decrease in soil CO, emissions in agricultural soils (Kowalenko et al., 1978; Wilson and Al-Kaisi, 2008). Mignon et al. (2011) studied the effects of mineral and organic fertilization on CO₂ emission in a potato field including three treatments (control without fertilization, mineral fertilizer (100 kg N of N₁₅P₁₅K₁₅ complex) and organic fertilizer (100 kg N from manure)). Obtained results indicated a higher soil respiration rate in organically fertilized soil (an increase from 153 – 485 %) while in mineral fertilized soil (an increase of 40%) like in control treatments (increase up to 115%) the values of soil respiration were lower. Gregorich and Rochette (1998) studied the effects of three-year application of N fertilizer (200 kg N ha⁻¹) and different manure amendments (stockpiled or rotted manure) on CO, evolution and reported no significant differences between CO, emissions from soil cultivated with maize and mineral fertilized soil compared to unfertilized soil.

Nitrous oxide emissions (N₂O)

Despite the fact that CH₄ and N₂O are present in the atmosphere at much lower concentrations than CO2, these gases potentially cause much more significant greenhouse effects (Forster et al., 2007). According to Desjardins and Riznek (2000), 45% of agricultural $N_{\mbox{\tiny 3}}O$ emission in Canada originates from the collection, storage, and application of animal manure.

To observe the effects of organic manures and crop residues amendments, Baruah and Baruah (2015) used five fertilizer treatments (NPK, cow manure, rice straw, poultry manure, and sugarcane bagasse) and concluded that rice straw, poultry manure, and sugarcane bagasse decreased the cumulative N2O emissions by 14% and 31%, by 1%, and 7%, and 5% and 3%, respectively, in 2012 and 2013 when compared to conventional fertilizer treatment (NPK) in both seasons. Few studies are reporting direct comparison in N₂O emissions between liquid and solid manures. Gregorich et al. (2005) noted that GHG emissions from liquid manure applications differ in emissions from solid manure applications. Solid manure applications resulted in substantially lower N₂O emission (0.99 kg N2O-N ha⁻¹ y⁻¹) than liquid manure (2.83 kg N,O-N ha⁻¹ y⁻¹). However, Mogge et al. (1999) reported higher emissions from the soil with a 30 years' history of repeated application of solid (5.3 kg N₂O-N ha⁻¹ y⁻¹) compared to liquid manure (2.1 kg N₂O-N ha⁻¹ y⁻¹) and concluded that nitrification was the major contributor to N₂O production. Flessa et al. (1995) calculated nitrous oxide emissions of 9.4 kg N₂O-N ha⁻¹ y⁻¹ from soil fertilized with farmyard manure and 50 kg N (calcium ammonium nitrate). Rochette et al. (2008) compared N₂O emissions following the application of liquid and solid dairy cattle manures and found that there was no clear difference in N₂O emissions between liquid and solid manures.

It is generally acknowledged that the nitrogen fertilization leads to an increase in N₂O emissions from agricultural soils through an increase in available N because of nitrification and denitrification enhancement (Hofstra and Bouwman, 2005; IPCC, 2006). Accordingly, Dong et al. (2009) investigated the effect of long-term fertilization (no fertilizer, NK, NP, PK, and NPK) on N₂O fluxes. N₂O flux was significantly higher in treatments with N fertilizer compared to no fertilizer and PK treatments and showed great N fertilization effect on N₂O flux. Changes in N₂O emissions from soil depending on mineral fertilizer quantity and application mode were investigated by Allen et al. (2010). A general trend of increasing N2O emissions with fertilizer N application was observed (maximum in 200 N cane-row - 21.2 mg N₂O m⁻² h⁻¹ while minimum in 0 N between-row positions - 0.01 mg N₂O m⁻² h⁻¹) as well as a cognition that application mode of fertilizer affects N₂O emissions. Zhang et al. (2014) measured N₂O emissions from a maize-wheat field in China investigated for four years. The annual N₂O fluxes ranged for the control treatment (without fertilization) between 1.3 – 2.7 kg N $ha^{-1}y^{-1}$ to 4.0 – 12.5 kg N ha^{-1} y⁻¹ on fertilization plots. The authors showed that the addition of fertilizers increased N2O emissions and proved the relation between emission values and soil precipitation and humidity. Clayton at al. (1997) conducted an experiment on a clay loam including plots fertilized with ammonium sulphate, urea, calcium nitrate, ammonium nitrate, and cattle slurry supplemented with ammonium nitrate. The total emissions from urea were five to six-fold greater (0.8 - 1.4 g N₂O-N ha⁻¹) than from ammonium sulphate, which caused the lowest emissions (0.2 - 0.4 g N₂O-N

Methane emissions (CH₄)

If soil is a net source or sink for methane, it depends on the relative rates of methanogenic and methanotrophic activity (Schimel, 2000; Bodelier and Laanbroek, 2004) where methane-oxidizing microorganisms play an important role in limiting methane emissions from soils (Topp and Patey, 1997). According to Cai et al. (2007), the CH₄ exchange between croplands and the atmosphere is influenced by N fertilizer application, which has varying effects on CH₄ emissions (Sun et al., 2016). In some cases, CH₄ emissions are stimulated (Shang et al., 2011), inhibited (Venterea et al., 2005) or have no significant effects (Mosier et al., 2006). Besides crop growth stimulation, N fertilizers provide more carbon substrates to methanogens for CH₄ production (Inubushi et al., 2003).

Accordingly, a 3-year field experiment was conducted by Zou et al. (2005) to simultaneously measure $\mathrm{CH_4}$ emissions from rice paddies under various agricultural management including water regime, crop residue incorporation and synthetic fertilizer application (urea - 150, 300, 450 kg N / ha x season). Results showed that $\mathrm{CH_4}$ emissions appeared to decrease with increased urea fertilization (150, 300 and 450 kg N ha⁻¹ were 17.3, 7.3 and 4.2 $\mathrm{CH_4}$ -C g m⁻²), which is consistent with the results in some other rice paddies (Krüger and Frenzel, 2003). Lindau et al. (1991), however, found that CH4 emission increased with urea application (maximum $\mathrm{CH_4}$ emissions from the 0, 100, 200 and 300 urea-N treatments were 6.0, 8.9, 9.8 and 11.2 kg $\mathrm{CH_4}$ ha⁻¹ d⁻¹, respectively) while Wang et al. (1993) reported no change in emission with urea application and a decrease in $\mathrm{CH_4}$ production with ammonium nitrate.

The effect of ammonium thiosulphate on the production and emission of ${\rm CH_4}$ from rice soil in India was investigated by Rath et al. (2002). Results suggest the mitigation potential of ammonium thiosulphate on ${\rm CH_4}$ emission from flooded rice paddies without having a significant reduction in yield. In ammonium thiosulphate-applied rice field plots, mean methane efflux decreased by approximately 38 and 60 % at 45.6 and 60 kg N ha⁻¹, respectively, compared to control. Lu et al. (1999) reported a significant reduction of ${\rm CH_4}$ emission from the soil with the application of phosphorus fertilizer where mean emission rates in treatment without P were 19–33 % higher than in those with P fertilization. The use of ammonium sulphate could reduce ${\rm CH_4}$ emission by 10–67 % (Wassmann et al., 2000).

Except for the fact that organic fertilizers application enhances soil nutrient availability, microbial activity and biodiversity (Jannoura et al., 2014), the increased availability of carbon after application of organic fertilizer increases CH₄ emissions (Chen et al., 2014; Pramanik and Kim, 2014; Zhou et al., 2016). In addition, cow manure as a source of organic material is also able to increase the production of methane (Kongchum, 2005). In the research of Nungkat et al. (2015), cow manure did not significantly affect the total methane flux during the first season. Traore et al. (2017) measured the effects of different fertilizers on methane emission including green manure, animal manure, and biogas residue. Methanogenic activities in soils treated with organic manure were higher than those with chemical fertilizers. Among the organic manure fields, the maximum methane emission was from green manure. Conversely, Sampanpanish (2011) studied an effect of organic fertilizers on methane emission in off-season rice farming and reported that the application of 6.25 t ha⁻¹ of manure on rice paddies resulted in lower greenhouse gas emissions than the use of chemical fertilizers.

Conclusion

This paper presents a review of the scientific literature meant to provide information on the influence of human management through fertilizers use on CO_2 , CH_4 , and $\mathrm{N}_2\mathrm{O}$ emissions. Nowadays, the application of fertilizers is inevitable. Considering the global energy demands and increasing cost of inorganic fertilizers, use of organic amendments might be a wise choice for decreasing the intensive use of synthetic fertilizers, protecting environments and to mitigate GHG emissions. Higher soil's organic content will also improve the soil's ability to retain water and nutrients and resist pests and droughts. Intelligent usage of organic manure and inorganic fertilizers is essential to augment productivity, input use efficiency and safeguard soil health.

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