Smart fertilizers as a strategy for sustainable agriculture

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Abstract

In the coming decades there will be increasing pressure on global food systems, and agriculture will have the challenge to provide food security for a growing world population without impacting environmental security. Accordingly, it will be necessary to use modern technologies in agroecosystems in order to supply sufficient food and decrease the negative impacts on the environment induced by chemical fertilization and by inadequate disposal or reuse of agricultural wastes. A combination of biotechnology and nanotechnology has the potential to revolutionize agricultural systems and provide solutions for current and future problems. These include the development and use of smart fertilizers with controlled nutrient release, together with bio-formulations based on bacteria or enzymes. This study was designed to provide a critical review of information related to current food security issues and the role of smart fertilizer development in future food production. We concentrate on advances in the development of controlled release biofertilizers and the use of harvesting residues as coating and carrier materials.

Keywords: biofertilizer; bio-formulations; carrier materials; harvesting residues; food security; nanofertilizers; slow/controlled release; wheat straw.

Contents

1. Introduction

Agricultural land systems (cropland, managed grassland, permanent crops including agro-forestry and bio-energy crops) cover about 40–50% of the Earth’s land surface (Smith et al. 2007), on which humanity needs to secure food production. The global population is expected to increase from 7.2 billion to 9.6 billion by 2050 (UN, 2013), which will increase food demand and fodder requirements for feedstock. In 2015, the UN adopted 17 sustainable development goals, aiming to eradicate hunger and extreme poverty by 2030, while at the same time preserving the environment and global climate. This implies sustainable intensification on existing agricultural land through innovation and collaboration between multiple sectors (Chabbi et al., 2017). One option to achieve greater crop production could be the improvement of plant fertilization strategies.

Nitrogen (N) and phosphorus (P) are essential nutrients for plant growth and consequently the application of these nutrients as chemical fertilizers has been growing since the green revolution in the 1960s and determines crop productivity (Haygarth et al. 2013; Mora et al., 2007; Stewart et al., 2005). Continued fertilizer inputs are essential to sustain and increase food production. However, there are problems associated with mineral fertilizer use because of relatively low nutrient uptake by crops in productive systems (Trenkel, 1997). High fertilization rates lead to N and P losses with negative impacts on atmospheric greenhouse gas (GHG) concentrations and water quality (Haygarth et al. 2013). There is an urgent need to improve nutrient use efficiency in agricultural systems, and to manage biogeochemical cycles in a sustainable way (Rumpel et al., 2015a). This includes the development and application of modern biotechnological tools, such as plant growth promoting rhizobacteria (PGPR) and diazotrophic N_2-fixing bacteria as alternatives to conventional fertilization.

Many different agricultural commodities are produced worldwide and will be needed to assure a diverse, healthy nutritious diet. However, global food security will continue to depend most heavily on stable foods, which are the three cereal crops rice (*Oryza spp*), wheat (*Triticum spp*) and maize (*Zea mays spp*). Global cereal production has to increase with the objective to satisfy the growing global demand (He et al., 2014). Higher production will in turn increase the amounts of harvesting residues (e.g. straw, stubble) that can be used as biomass feedstock or for animal feeding (Jiang et al., 2012; Habets et al., 2013). Unfortunately, one of the most important practices globally is the removal of these residues by *in-situ* burning with significant environmental, economic and human health impacts (Gupta et al., 2016; Singh et al., 2010). Harvesting residues should be considered as a resource that can be utilized as organic raw material, which could be used to improve soil quality and productivity. One way to take advantage of these residues is their use as composting agents (Medina et al., 2017; Roca-Pérez et al., 2009). Pyrolysis of harvesting residues to produce biochar has also been suggested as a win-win practice leading not only to energy generation but also to a soil conditioner with the potential to increase plant growth and soil carbon (C) sequestration (Abiven et al., 2014). Another strategy may be the transformation of harvesting residues into raw materials for fertilizer production.

The aim of this review is to present innovations related to smart fertilizer technology as a response to food security scenarios under growing global population and the environmental impacts of current agricultural systems. Smart fertilizers may be a solution to enhance food production and environmental quality. In the sense of a circular economy, we suggest that these smart fertilizers may be based on the innovative use of harvesting residues.

2. Food security: Agricultural management and its environmental footprints

2.1 World food demand associated with a growing global population

Three cereals (rice, wheat and maize) account for 58% of the annual crop area and provide about 50% of food calories (Fischer et al., 2009). Rice and wheat are essential suppliers of energy for the population of developing countries, and maize makes up over 60% of commercial animal feeds (Fischer et al., 2009). Based on projected global population growth, an annual increase of the world cereal production of 0.9% reaching 3,009 billion tones (3,009,000 Tg) will be required to meet the demand (He et al., 2014). Average global cereal yields will need to increase from 3.32 t/ha to 4.30 t/ha, with wheat yields rising from 2.8 t/ha to 3.8 t/ha (He et al., 2014). Agricultural land needs either to be expanded or used more efficiently in order to increase the global food production by 60-110% to meet the rising demand of the global population in 2050 (Ray et al., 2013). Expansion of agricultural land may not be a good option, as non-agricultural land area is needed for other purposes, for example to provide habitat for endangered species (Balmford et al., 2005). Thus sustainable intensification leading to production increase on existing land area seems to be the best option (Godfray et al., 2010).

Cereal yields were increased during the green revolution due to genetic improvement and intensive utilization of mineral fertilizers (Pingali, 2012). However, yields have not increased further since the 1990s (Brisson et al., 2010; Grassini et al., 2013; Ray et al., 2012). Amongst the factors responsible for yield stagnation is climate change, principally increases of temperature and prolongation of summer droughts. Depletion of soil reserves due to soil organic matter (OM) losses and the prolonged and intensive use of agrochemicals may also have contributed (Baishya, 2015; Lal, 2004; Lipper et al., 2014).

It is therefore highly uncertain if current crop improvement and management practices will be able to achieve food security in the future. Moreover, the future demand for agricultural products will be further affected by other factors such as the decline in rural workforce and the requirements of the biofuel market and climate change, which could have a huge impact on food productivity (FAO, 2009). Moreover, the negative environmental impacts of the green revolution due to massive fertilizer use call for the adaptation of more sustainable technologies (Pingali, 2012).

2.2 Availability of chemical fertilizer to support food production

The food production is strongly dependent on N and P, which are essential and irreplaceable nutrients for plant growth and to maintain life in the world. For example, long term data obtained between 1960-2010 estimated that around 48% of crop N was contributed by inorganic fertilizers, considering maize, rice, and wheat production systems (Ladha et al., 2016). Nevertheless, N and P present a significant difference in terms of their availability. In this sense, the supply of N is currently unlimited due to the production of urea by the Haber Bosch process, (Dawson and Hilton, 2011), which industrially produces around 100 TgNyr^{-1} (Ladha et al., 2016). On the other hand, phosphate rock reserves are finite and there is a critical concern about the availability and cost of phosphate rock in the future (Cordell et al., 2009; Dawson and Hilton, 2011; IFDC, 2010; USGS, 2016). In this sense, Elser and Bennett (2011) stated: “More important than the amount of P in the ground is how much it will cost to get it out”. Figure 1 shows the principal reserves of rock phosphate, most of which are located in Morocco.

Despite the fact that P is a finite resource, continuous inputs are needed to maintain the productivity of agroecosystems under current scenarios (Ostertag et al., 2016; Valkama et al., 2016). A recent meta- analysis carried out by Valkama et al. (2016) showed that yield response to P fertilization varied considerably in grassland systems and initial soil tests for P do not always predict this behavior. They described that the major sources of variation in yield responses to annually applied P were soil type specific. Under this context, only about 40% of the variation in yield could be attributed to fertilizer P applications (Valkama et al., 2016). In many situations P-fertilizer inputs, especially in tropical areas are rapidly fixed by the soil matrix and not available for plant uptake. Therefore, the emerging global challenge of the issues associated with P supply is to improve the overall P-use efficiency of plants (Cordell and White, 2011).

2.3 Conventional fertilization practices: their environmental consequences

The type of soils and its management has a strong influence on the conventional fertilizer use efficiency. For example, it has been reported that Cambisols, which are one of the major soil types under agricultural use with an estimated surface of about 1.5 billion ha under cropland (FAO, 2001), are deficient in nutrients such as P (Dabin, 1980).

Moreover, in some Cambisols from central Africa, the continuous application of N and P fertilizers in addition with the unbalanced and suboptimal fertilization (e.g., by the exclusive application of N and P containing fertilizers such as urea and di-amonium phosphate) for long periods of time, has led to soil nutrient depletion, especially when the entire crop biomass is removed from land (Tesfay and Gebresamuel, 2016). Moreover, nowadays, often fertile soils are lost for agricultural production through urbanization.

Agriculture, as a result, is conferred to marginal land with low OM and nutrient content (Ngo et al., 2014). On such soils, the application of mineral fertilizers can cause accelerated acidification and further nutrient and OM losses (Lal, 2006; Marschner et al., 2002). Other soil types such as Andisols, which represent 0.84% (around 110 to 124 million ha) of global soil area (FAO, 2001), are characterized by high OM content (1–25% w/w) and high capacity to immobilize P. In this sense, their clay fraction makes up 35–60% of the soil, and is dominated by allophane (Besoain and Sepúlveda, 1985; Escudey et al., 2001). Agricultural management to obtain productive systems and the allophanic nature of these soils leads to acidification as a result of the use of urea and other ammonia (NH_3) fertilizers (Mora et al., 2007, 2005). For example, about 50% of the Chilean Andisols are acidic with pH values between 4.5 and 5.5 (Jorquera et al., 2014; Mora et al., 2006, 2002, 1999). Soil acidity is one soil property contributing to P-fixation (Mora et al., 2004), decreasing its availability for plant nutrition. More than 50% of P incorporated in these soils is fixed as organic P (Borie and Rubio, 2003) and may contribute to the residual fraction (Velásquez et al., 2016). Thus, huge amounts of conventional P-fertilizer need to be applied annually to maintain available P levels in soil-plant systems.

N- and P-fertilizer application at levels exceeding plant requirements due to low acquisition efficiency leads to significant environmental consequences in many parts of the world due to N losses, such as: nitrate (NO_3^-) and phosphate (PO_3-) leaching, NH_3 volatilization, and nitrous oxide (N_2O) emission (Muñoz et al., 2010; Núñez et al., 2010; Saggar et al., 2013; Vistoso et al., 2012). Transport of P and N from agricultural soils to surface waters has been linked to eutrophication of freshwater and estuaries (Entry and Sojka, 2007; Liu et al., 2013; Riley et al., 2001; Smith and Schindler, 2009). These negative environmental consequences associated with fertilizer inputs further emphasize the need of technological approaches to improve nutrient management in modern agriculture. In addition, current agricultural activities contribute up to 20% to the annual atmospheric emissions of GHG, such as methane (CH_4) and carbon dioxide (CO_2) (Lemke et al., 2007). Even higher contribution was noted for N_2O (about 60%) (Smith et al., 2007), which is a potent GHG and catalyst for stratospheric ozone depletion (Yang et al., 2014), with more than 300 times the global warming potential than CO_2 (Crutzen, 1981; Kennedy et al., 2004). Its emission is closely related to mineral fertilizer input. In some countries, GHG emissions from conventional agriculture have increased by 33% between 1984 and 2003 (González et al., 2009).

One way to mitigate these GHG emissions could be the sequestration of C and N in soils in form of OM (Lal, 2003). Soils contain about three times more C than the above-ground vegetation, and approximately 75% of the terrestrial C pool and play a key role in the global C cycle (Calabi-Floody et al., 2015, 2011; Paustian et al., 2016; Le Quéré et al., 2015; Rumpel et al., 2015b; Schlesinger, 1986). The importance of the sink function of agricultural soils for GHG depends on the biophysical processes, incorporation/decomposition of organic residues, fertilizer application and environmental factors (Muñoz et al., 2010). In this sense, if mismanaged with intensive tillage and fertilization soil may lose OM and become a source of CO_2. Agricultural wastes such as dairy slurry or manure (Muñoz et al., 2010; Rochette et al., 2008; Saggar et al., 2009), and biomass after harvesting (Garay et al., 2009; Taladriz and Schwember, 2012) may also be a source of GHG emissions. Improvement of organic residue recycling in agriculture may be a solution in view of sustainable intensification of agricultural practices and could contribute to increase soil C storage, thereby improving soil quality and to some extent mitigating atmospheric GHG concentrations (Chabbi et al., 2017).

2.4 Management of crop waste after harvesting

Worldwide, the annual production of agricultural residues amounts to 3.7 Pg dry matter (Bentsen et al., 2014). Straw, roots, shaft and other tissues of corn, wheat and rice as the main crop residues account for about 40.6%, 24.2% and 15.7% respectively (Medina et al., 2015). Burning of large amounts of crop residues produced worldwide in open fields leads to soil fertilization in form of ash input. Residue burning accounts for 27 % (1900 Tg dry matter) of global biomass burned annually (Crutzen et al., 2016). It is a source of atmospheric pollution with significant impacts on atmospheric chemistry, global climate and with great threat to human health (Brühl et al., 2015; Pongpiachan et al., 2015; Udeigwe et al., 2015). For example, burning wheat residues generates huge amounts of particulate material less than < 2.5 µm ($PM_{2.5}$), GHG (i.e., CH_4, N_2O, CO_2), volatile organic carbon (VOC), NH_3, sulfur dioxide (SO_2) and other pollutants (Crutzen et al., 2016; Sun et al., 2016; Zhang et al., 2015, Koppmann et al., 2005, Li et al., 2008).

China is one of the main crop residues producers with around 18% of the total global production (He et al., 2014; Kung et al., 2015; Zhang et al., 2016, 2015). Studies conducted by Sun et al. (2016) investigated CO_2 emissions in China from 1996 to 2013, including the contribution from combustion of maize, wheat and rice residues. They calculated that these sources accounted for 22.5% of total emissions. In the USA, over 1.2 million ha of cropland is burnt annually. This has been estimated to produce 6.1 Tg of CO_2, 8.9 Gg of CH_4, 232.4 Gg of CO, 10.6 Gg of NO_2, 4.4 Gg of SO_2, as well as 28.5 Gg of particulate matter of less than 10 µm in diameter (PM_{10}), and 20.9 Gg of $PM_{2.5}$ (Udeigwe et al., 2015). Although open straw burning occurs primarily in rural areas, it also has a serious impact on urban air quality under the effect of air circulation (Chen et al., 2015).

Taladriz and Schwember (2012) reported that in Chile stubble burning is the most common management practice with 80 to 90% of wheat stubble being burned. It has been estimated that straw burning generates nutrient losses by volatilization of 98-100% for N, 20-40% for P and potassium, and 70-90% for sulfur (Heard et al., 2006), affecting their potential incorporation into the soil. The associated cost is US$125 per ha, and considering post-burn runoff the cost is US$225 per ha.

While the main effect of straw burning is on the atmospheric chemistry and air quality, this practice has additionally negative consequences on soils affecting the soil OM quantity and quality, the activity and colonization of topsoil by microorganisms, biological diversity and nutrient dynamics among other negative environmental implications (Borie et al., 2006, 2010).

2.5 Potential economic benefits to reusing harvesting residues

Cereal straw, one of the most important harvesting residue globally, is biodegradable and a natural source of cellulose, hemicellulose and lignin, which in turn may be used for paper, biofuel and biogas production (Bhatnagar and Sillanpää, 2010; Hansen et al., 2014; Huang et al., 2007; Liu et al., 2013; Ma et al., 2011; Risberg et al., 2013; Talebnia et al., 2010; Xie et al., 2011), livestock bedding, animal feed (Dunford and Edwards, 2010) and for direct incorporation into the soil for nutrient recycling (Aulakh and Rennie, 1987; Garay et al., 2009; Li et al., 2011; Misselbrook et al., 2012; Taladriz and Schwember, 2012; Tan et al., 2007). The straw incorporated into the soil is an important energy and C source, which can positively influence the biological, chemical and physical properties, improving soil quality and productivity (Mulumba and Lal, 2008; Wei et al., 2015). The incorporation of crop straw residues may increase N mineralization and available N, as well as organic C and total N stocks in soil (Cassman et al., 1996; Wei et al., 2015; Zhang et al., 2015). Moreover, increased availability of some nutrients such as P and K has been also reported for soils in semiarid areas (Wei et al., 2015). Nevertheless, it has been demonstrated that the excessive incorporation of fresh residues into soils may have adverse effects on the soil environment and crop yields (Jiang et al., 2012), because many soil functions require a mature and stable OM (Medina et al., 2015; Plaza and Senesi, 2009). Some adverse effects of straw incorporation include (i) an increase of the mineralization rate of native soil organic C, (ii) the induction of anaerobic conditions by mineralization of large amounts of non-stabilized organic C, (iii) the associated extended O_2-consumption, (iv) the alteration of soil pH (Senesi and Plaza, 2007), (v) the stimulation of NH_3 and GHG emissions and (vi) the biotic and abiotic immobilization of N (Luo et al., 1999; Said-Pullicino et al. 2014; Yan et al., 2005; Zhang et al. 2015). In this sense, considering its high polymerization degree due to cellulose and lignin content and high C/N ratio, low decomposition may occur when wheat straw is incorporated into soil (Li et al., 2011; Taladriz and Schwember, 2012) and lead to N deficiency due to high microbial demand (i.e. immobilization). Therefore, pretreatment through aerobic or anaerobic degradation is necessary to initiate wheat straw decomposition, improving its physiological, biochemical and morphological characteristics, increasing its nutrient content and reducing its C/N ratio (Pan and Sen, 2013).

Wheat straw is one of the best-known fibers and despite its low reutilization, its industrial potential is increasing. Recent studies suggested that structural modification of wheat straw by grinding can influence its degradation, porosity and surface area (Silva et al., 2012; Wang et al., 2016). Moreover, different chemical and biological treatments have been investigated to modify some properties of these materials for smart fertilizer design

(Panthapulakkal and Sain, 2015). Therefore, wheat straw is potentially valuable after a series of chemical modifications, such as esterification, etherification and copolymerization, and shows a broad potential for applications in superabsorbent material production (Liu et al., 2013; Ma et al., 2011; Xie et al., 2012). In recent years, researchers have focused on superabsorbent and slow-release fertilizers, as summarized below.

3. New technologies to ensure food security and environmental health for the expanding world population

In order to enhance nutrient use efficiency, new types of smart fertilizers with controlled nutrient release are needed. The development of such fertilizers could be based on the use of microorganisms (biofertilizers) and/or nanomaterials (nanofertilizers).

In this context, nanotechnology is a promising, rapidly evolving field of interdisciplinary research that has potential to revolutionize food systems (Sastry et al., 2011). Nanotechnology involves the design, synthesis and use of materials at nanoscale level, ranging from 1 to 100 nm (EPA, 2007). At this scale, the physical, chemical and biological properties of materials differ fundamentally from the properties of individual atoms, molecules or bulk matter (Cao, 2004; Mansoori, 2005). The ability to manipulate matter at the nanoscale can lead to improved understanding of biological, physical and chemical processes and to the creation of improved materials, structures, devices and systems that can be used in agroecosystems (Sastry et al., 2011; Qian and Hinostroza, 2004).

The application of nanotechnology to agriculture and food industries is growing rapidly as shown by increasing numbers of publications and patents (Fig. 2).

Nanotechnology has a number of potential benefits ranging from improved food quality and safety to reduced agricultural inputs and improved processing and nutrition (Veronica et al., 2015). The development of smart fertilizers based on nanotechnology is a recent phenomenon (Manjunatha et al., 2016), with an emphasis on controlled release and/or carrier/delivery systems to synchronize nutrient availability with the plant demands, thus reducing losses to the environment (Fig. 3) (Bley et al., 2017; Chinnamuthu and Boopathi, 2009; DeRosa et al., 2010).

3.1 Slow / controlled-release fertilizers

According to Trenkel (1997) slow or controlled-release fertilizers are those containing a plant nutrient in a form, which either a) delays its availability for plant uptake and use after application, or b) is available to the plant significantly longer than a reference ‘rapidly available nutrient fertilizer’ such as ammonium NO_3^- or urea, ammonium phosphate or potassium chloride (AAPFCO, 1995). There is no official differentiation between slow-release and controlled-release fertilizers. However, the microbially-decomposed N products, such as urea-formaldehydes, are commonly referred to as slow-release fertilizers, and coated or encapsulated products as controlled-release fertilizers (Trenkel, 1997). Delayed availability of nutrients or consistent supply for extended time periods can be achieved through a number of mechanisms. These include semi-permeable coatings for controlled solubility of the fertilizer in water, protein materials, occlusion, chemicals, slow hydrolysis of water soluble compounds of lower molecular weights and some other unknown means (Naz and Sulaiman, 2016). Other options include utilization of semi-permeable materials and sensors of chemical or biological origin within the fertilizer (Fig. 4a). These are advanced materials, whose physical or chemical properties can change in response to an external stimulus such as temperature, pH, and electric or magnetic fields (Foster, 2013; Mastronardi et al., 2015; Roy and Gupta, 2003).

Many coating materials can be used to slow nutrient release, including natural materials such as clays and nanoclays (e.g., allophane), non-degradable (polysulfone) and biodegradable polymers (e.g., alginate beads) (Table 1). Several studies have shown that urea based coatings can have variable efficiencies depending on the material used (Du et el., 2006; Naz and Sulaiman, 2016; Shaviv, 2005). In addition, they can be highly expensive in some cases, pollutants, or toxic (i.e., polymer coated urea) and mostly difficult to degrade with potential environmental impacts (accumulation) as the major concern. As a consequence, formulation with environmentally safe and biodegradable coating materials seems to be necessary (Ni et al., 2009). In this sense, natural polymeric carbohydrates appear as an alternative to non-biodegradable materials acting as permeable or impermeable membranes with tiny pores in slow release fertilizers (e.g., urea) (Butzen, 2013). These highly degradable materials have also received attention because of their low cost and low environmental damage due to biodegradability and low accumulation in the environment (Naz and Sulaiman, 2016). However, these polymers may need some modifications to be included into the coating design because of their hydrophilic properties and their weak coating barrier, for example in the case of starch.

3.2 Bioformulation fertilizer: plant growth promoting and nutrient use efficiency

One group of microorganisms beneficial for plant growth are PGPR, a heterogeneous group of bacteria that can be found in the rhizosphere, at root surfaces and in association with roots (Ahmad et al., 2008). These bacteria have several functions, including production and regulation of phytohormones, release of nutrients to plants (e.g., P-, N-fixation, siderophores, among others), and control of phytopathogens (production of antibiotics and siderophores) (Egamberdieva and Adesemoye, 2016; Martínez-Viveros et al., 2010; Zahid et al., 2015).

Phosphobacteria, phytate-mineralizing bacteria, and phosphate-solubilizing bacteria have been commonly isolated from soil and proposed as inoculants for agricultural improvement (Jorquera et al., 2008). For example, a large diversity of microbes in Andisoils under pastures and cereal crops are capable of mineralizing phytate (Jorquera et al., 2008; Martínez-Viveros et al., 2010; Menezes-Blackburn et al., 2014). They may be used to develop bacterial or enzyme systems as biofertilizers to overcome the limitations of conventional fertilizers in acidic soils, as well as for developing added value products from agricultural wastes. To this end, Calabi-Floody et al. (2012) studied the effect of enzyme-nanoclay complexes on P availability of composted cattle dung and showed that it increased the inorganic P content. Moreover, Menezes-Blackburn et al. (2014) suggest that inoculation of cattle manure with enzyme-nanoclay complexes enhances the organic P cycling and P nutrition of plants grown in P deficient soils.

Low N acquisition by plants is a limiting factor in agricultural ecosystems and there is interest in using N_2-fixing bacteria as an alternative to conventional fertilization. Diazotrophic bacteria are capable of converting atmospheric dinitrogen (N_2) into NH_3, which can be used by plants (Ilsam et al., 2009). Among them, a number of free-living soil bacteria are considered to be PGPR, because of their competitive advantage in C-rich and N-poor environments (Kennedy et al., 2004). Free-living N_2-fixing bacteria have been considered as an alternative to conventional N-fertilizer for promoting plant growth, and several research studies reported significant increases in grain and shoot biomass yield from plants inoculated with free-living diazotrophic bacteria (Andrade et al., 2013; Barua et al., 2012; Kennedy et al., 2004; Park et al., 2005). Moreover, Vadakattu and Paterson (2006) reported that under intensive wheat rotation at Avon, South Australia, free-living N_2-fixing bacteria contributed 20 kg N per ha per year, which represented 30–50% of total crop requirements. This response was attributed to a combination of factors including enhancement of root development, production of growth regulators, and N fixation (Naiman et al., 2009). However, it is well known that bacteria directly inoculated in the soil system could be adversely affected by competition with native microorganisms, unfavorable physicochemical conditions and fluctuating pH and temperature (Bréant et al., 2002).

Encapsulating microorganisms in carrier materials (bioformulation) is designed to protect them during storage and from adverse environmental condition (pH, temperature, etc) (Fig. 4b), thus ensuring a gradual and prolonged release (Bashan, 1986; Kim et al., 2012). A wide range of microorganisms have been investigated and a framework for selecting suitable organisms for specific purposes has been developed (Table 2).

Materials suitable for immobilization and preservation of bacteria include alginate gels, synthetic gels (Sol-Gel), polyacrylamide, agar and agarose, polyurethane, vermiculite and polysaccharides (Bashan, 1998; Liu et al., 2008). In addition, composite materials based on biodegradable polymer-clay or nanoclays are being studied, including nanocomposites (Calabi-Floody et al., 2009). For example, encapsulation of free-living diazotrophic bacteria has been considered as one of the possible alternatives for inorganic N-fertilizer for promoting plant growth and crop yield (Ivanova et al., 2005).

4. Smart fertilizer formulations

4.1 Nanofertilizers

Nanofertilizers, as smart fertilizers are designed to increase nutrient use efficiency and consequently reduce adverse effects on the environment compared to application of conventional mineral fertilizers (Manjunatha et al., 2016; Sharpley et al., 1992; Wurth, 2007). According to Mastronardi et al. (2015) there are three main types of nanofertilizers: nanoscale fertilizer (synthesized nanoparticles), nanoscale additives (bulk products with nanoscale additives), and nanoscale coating or host materials (product coated with nanopolymer or loaded with nanoparticles) (Table 3).

Slow-release nanofertilizers and nanocomposites are suitable alternatives to soluble fertilizers. Nutrients are released at a slower rate during crop growth, thereby reducing loss. Slow release of nutrients in the environments could be achieved by using zeolites (natural clays), which acts as a reservoir for nutrients that are released slowly (Manjunatha et al., 2016). The mineral nutrients required for plant nutrition can be encapsulated inside nanomaterials such as nanotubes or nanoporous materials, coated with a thin protective polymer film, or nanoscale particles (DeRosa et al., 2010; Manjunatha et al., 2016).

Depending on the application, it is possible to use synthetic or natural nanoparticles obtained from various sources, including plants, soils and microorganisms (Table 3) (Calabi-Floody et al., 2011, 2009; Panpatte et al., 2016; Tarafdar et al., 2012). Nanoclays, which naturally occur in soils, have been considered important tools in modern agriculture due to their physicochemical properties (Sekhon, 2014). Nanoclays can be used to stabilize enzymes and thereby increase their catalytic activity for different biotechnological purposes (Calabi-Floody et al., 2009; Kim et al., 2006; Moelans et al., 2005; Wang, 2006). For example, Menezes-Blackburn et al. (2011) studied the effect of synthetic allophane, synthetic iron-coated allophanes and natural montmorillonite as solid supports of phytases and observed that immobilization patterns at different pH values were strongly dependent on both enzyme and support characteristics. In addition, they concluded that montmorillonite appeared as a good immobilizing support only for the *Escherichia coli* phytase, while it was an inhibitor for *Aspergillus niger* phytase activity. Calabi-Floody et al. (2012) evaluated and implemented the use of natural clays and nanoclays (from montmorillonite and allophanic clays) as support materials for acid phosphatase (AP) in nanoclay-cattle dung-AP complexes. They found a clear stabilization of AP by these materials through encapsulation. The authors reported an increase of both specific activity (up to ~ 48%) and V_{max} (up to 38%) of the enzyme. They also observed that AP immobilized on allophanic nanoclays enhanced the release of inorganic P from cattle dung compared with free AP. Positive growth responses were found for P nanoparticles applied to basil (*Ocimun basilicum*) under salt stress (Alipour, 2016) and for synthetic apatite nanoparticles (solid P nanofertilizer) applied to soybean (*Glycine max*) (Liu and Lal, 2014).

Nanocomposites are hybrid materials consisting of a continuous (polymer) phase or matrix and a dispersed (nanofiller) phase. The dispersion of a small amount (< 10%) of nanomaterial in the polymer matrix can lead to marked improvement in physical and mechanical properties (strengths, pH tolerance, storage stability, heat distortion, break elongation) compared with a single polymer matrix (Calabi-Floody et al., 2009). Currently research is focused to develop nanocomposites to supply essential nutrients through smart delivery system (Manjunatha et al., 2016), synchronizing the release of them with the crop uptake, so preventing undesirable nutrient losses to soil (e.g., leaching and volatilization) (Bley et al., 2017; DeRosa et al., 2010). Coating and cementing of nano and subnanocomposites can also be used to regulate the release of nutrients from the fertilizer capsule (Liu et al., 2006). Therefore, the future development should focus on materials allowing for nutrient release from nanofertilizers triggered by an environmental condition or simply at specific time (Gruère, 2012). In this context, nanodevices or additives (e.g., nanotubes, aptamers, double hydroxide-nanocomposites, urease enzymes, nanosize titanium dioxide, nanosilica particles) can be associated to nanofertilizers to synchronize the fertilizer release with plant demand (DeRosa et al., 2010; Foster, 2013).

4.2 Other smart fertilizers formulations

4.2.1 Polymers: Polymers are widely used in agriculture especially for fertilizer development. Smart polymeric materials have been applied to smart delivery systems of a wide variety of agrochemicals (Puoci et al., 2008). A broad range of synthetic materials, such as petroleum based polymers have been used to encapsulate water-soluble fertilizers. Polysulfone, polyacrylonitrile, polyvinyl chloride, polyurethane and polystyrene are the main materials currently used for coating (Ibrahim and Jibril, 2005; Lü et al., 2016; Tao et al., 2011). Jarosiewicz and Tomaszewska (2003) compared the use of the synthetic polymers polysulfone and polyacrylonitrile and the biodegradable cellulose acetate for the development of slow release fertilizers. They observed that physical properties of the coatings can influence the release rate of macronutrients (N, P, and K), which are present in the core of the coated fertilizers. They found that synthetic non degradable materials had a slower release rate than cellulose acetate based ones. Tao et al. (2011) studied the use of a triple polymer fertilizer to encapsulate and enhance the mechanical properties of urea. They suggested that polyethylene in a first layer, poly (acrylic acid-co-acrylamide) as superabsorbent in a second layer, and poly (butyl methacrylate) in the third layer improve the controlled release of urea. They also observed that the incorporation of this triple polymer fertilizer into soil improved its water holding capacity, which in turn enhanced nutrient uptake and crop yield. Liu et al. (2008) replaced sulfur with dicyclopentadiene to improve coating properties, moisture resistance, abrasion resistance and mechanical strength of slow release fertilizers. They found that the mechanical strength of the coating was directly related to the dicyclopentadiene content, which ameliorated nutrient release efficiency.

4.2.2 Biodegradable polymers: These materials have increasingly been used as substitutes of others polymers in agriculture. Devassine et al. (2002) divided them in two main groups according to their water vapor permeability, namely degradable synthetic polymers with a small permeability coefficient (K<3000 cm^{2} s^{-1} Pa^{-1}) (biopols, polylactic acids and polycaprolactone), and modified polysaccharides with a higher permeability coefficient (K>4000 cm^{2} s^{-1} Pa^{-1}) (alginates, starchs, agar). Several studies have reported on the utilization of these degradable polymers for a wide range of nutrients. For example, Perez and Francois (2016) prepared macrospheres with chitosan and chitosan-starch blends using sodium tripolyphosphate aqueous solution as the crosslinking agent. They observed that these materials could be used as slow release N and K fertilizers. Zhang et al. (2016) have reported the development of polymer-coated N-fertilizer using bio-based polyurethane derived from liquefied locust sawdust as coating material. They found that this fertilizer was more efficient at supplying N to maize than conventional urea.

Biodegradable polymers have also been used in bioformulations, acting as microbial carriers. These carriers protect microbial inoculants from various stresses and prolong shelf life (Ardakani et al., 2010; Egamberdieva and Adesemoye, 2016; Kumar et al., 2007). For example, calcium alginate gel may protect microbial cells with a concomitant increase in shelf life (Wu et al., 2011). Sodium alginates are widely used for bioformulations (i.e., bacterial fertilizers) and with pesticides (Liang et al., 2007; Liu et al., 2008; Singh et al., 2009). Despite the low cost and the environmental friendly properties of biodegradable polymers, in many cases the properties of these materials need to be blended with synthetic materials to improve their performance (Puoci et al., 2008)

4.3 Use of harvesting residues for smart fertilizer formulations

4.3.1 Lignocellulosic straw as carrier and coating material: Low-cost materials such as wheat straw are abundantly available resources in current agricultural systems (Jiang et al., 2012). These harvesting residues contain lignin, hemicelluloses, and cellulose (Hubbe et al., 2010). Cellulose fibrils and lignin impart mechanical strength properties (Panthapulakkal and Sain, 2015). Wheat straw contains surface carboxyl, hydroxyl, ether, amino and phosphate, which enhance its reactivity and physicochemical properties, useful in the preparation of adsorbent materials for the treatment of wastewater (Wang et al., 2016) and slow release fertilizers (Liu et al., 2013; Xie et al., 2011). Moreover, some researchers have found that wheat straw can be used as reinforcements and/or fillers for nonstructural and structural composites, (Panthapulakkal and Sain, 2015).

Xie et al. (2011) noticed the potential use of wheat straw for the development of slow release N and boron fertilizers with water-retention properties. The authors prepared and used the straw as skeletal material in copolymerization with other monomers to form a superabsorbent material. They introduced inorganic fertilizers (urea and borax) in order to develop an organo-mineral fertilizer within a core/shell structure. They found that the final product contained 23.3% N and 0.65% boron with potential slow release characteristics. Wang et al. (2016) designed a multifunctional strategy for the development of a slow release compound fertilizer, which was prepared by recovery of NH_4^+ and $P_2O_4^-$ from aqueous solutions onto an amphoteric straw cellulose adsorbent. The maximum NH_4^+ adsorption capacity of the material was 68.4 mg g^{-1}, whereas the adsorption capacity for $P_2O_4^-$ was 38.6 mg g^{-1} at pH 7 and 5, respectively.

On the other hand, cellulose obtained from agricultural residues has been also used in bioformulations as carrier for bacterial inoculants with broad-spectrum antifungal activity and suppression of fungal pathogens (Egamberdieva and Adesemoye, 2016; Negi et al., 2005). Albareda et al. (2008) studied the survival of different PGPR strains on various carrier and liquid formulations and found that compost and perlite were very effective. However, lignocellulose and compost are subject to rapid decomposition once incorporated into soil. In order to further improve their properties as slow release fertilizers, they could be combined with clay minerals or biochar to reduce their decomposition (Barthod et al., 2016; Ngo et al., 2016).

4.3.2 Biochar as carrier and coating material: Harvesting residues, such as straw may also be used as feedstock for energy producing pyrolysis systems with biochar generation. Considering its physicochemical properties, carbonaceous materials like pyrogenic carbon (biochar) have been widely used as soil ameliorant with several applications in both laboratory and field studies (Glaser, 2015; Wiedner et al., 2015). Biochar is obtained through pyrolysis of agricultural or other lignocellulosic biomass at temperatures ranging from 350 – 700°C (Glaser et al., 2002; Lee et al., 2013; Lehmann and Joseph, 2009). Biochar was found to increase the C sequestration potential of soil through its high stability and the reduction of native soil OM mineralization (Naisse et al., 2015; Ventura et al., 2015) and to be an excellent microbial habitat (Lehmann et al., 2011). González et al. (2015) studied the influence of different polymers and biochar produced from oat hull as support material on the release and leaching of N from urea under greenhouse conditions. They found that urea formulated together with biochar slowed down the release of this fertilizer. Nevertheless, biochar did not act as a nutrient release retarder agent and may need other polymeric materials as encapsulating agent to control N leaching from controlled release fertilizers. Cai et al. (2016) found that biochar produced from corncob, banana stalk and pomelo peel displayed an excellent retention ability in holding NH_4^+ associated to the presence of carboxyl and keto groups when the material was prepared at 200 °C, suggesting that this material could be used as a slow release carrier for N. Zhao et al. (2016) observed that the combination of P fertilizers (triple superphosphate and bone meal) pre-mixed with sawdust and switch grass biomass prior to biochar production was a good strategy for the production of an effective slow release P fertilizer.

Recent studies have also investigated the use of biochar and charcoals as carriers in combined formulations with beneficial microorganisms. Biochar was a useful carrier for the bacterial population of *Enterobacter cloacae (*Hale et al., 2015) and *Azospirillum lipoferum* (AZ 204) (Saranya et al., 2011).

The use of biochar as carrier for smart fertilizers could be highly beneficial, as it combines nutritional benefits for plants with improvement of many other soil functions due to the addition of biochar itself. In particular, biochar addition to soils has positive effects on water holding capacity as well as C sequestration. However, biochar properties vary widely depending on feedstock and production conditions (Wiedner et al., 2013). Thus, the use of these kinds of formulations presents new challenges related to the optimal combination of carrier materials and inoculants. Considering the varying properties of carrier materials here reviewed and the variety of potential utilization for smart fertilizers designs, more research is needed for their development.

5. Conclusions and future directions

In order to meet sustainable development goals, agricultural production needs to be increased and the pollution and GHG emissions related to farming activity need to be decreased. We suggest that advances in the application of biotechnology and nanotechnology have the potential to facilitate improved nutrient management and use efficiency in agroecosystems. Smart fertilizers based on slow/controlled release and/or carrier delivery systems have been shown to improve crop yields, soil productivity and lower nutrient loss compared with conventional fertilizers. Several materials such as clays, nanoclays, non-degradable and degradable polymers, and agricultural wastes are suitable for the development of smart fertilizers by acting as carrier matrices for nutrients and bacterial inoculants. Future research should continue to explore and evaluate the composition, manufacture, and agronomic and environmental performance of various smart fertilizers, especially those that utilise organic waste materials. We suggest that lignocellulosic organic waste, such as straw after chemical, physical or thermal transformations may be an excellent carrier or coating material for fertilizer formulations. Such organic wastes occurring as harvesting residues in agricultural systems should be used in the sense of a circular economy to create innovative fertilizers from natural materials, which are urgently needed to ensure sustainable intensification of agricultural systems.

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References

Abiven, S., Schmidt, M., Lehmann, J. 2014. Biochar by design. Nat. Geosci. 7, 326–327.

Ahmad, F., Ahmad, I. and Khan, M.S. 2008. Screening of free-living rhizospheric bacteria for their multiple plant growth promoting activities. Microbiol. Res.163, 173–181.

Albareda, M., Rodríguez–Navarro, D.N., Camacho, M., Temprano, F.J. 2008. Alternatives to peat as a carrier for rhizobia inoculants: solid and liquid formulations. Soil Biol. Bioch. 40, 2771–2779.

Alipour, Z.T. 2016. The Effect of Phosphorus and Sulfur Nanofertilizers on the Growth and Nutrition of Ocimum basilicum in Response to Salt Stress. J. Chem. Health Risk. 6, 125–131.

Andrade, M.M.M., Stamford, N.P., Santos C.E.R.S., Freitas, A.D.S., Sousa, C.A., Lira, J.M.A. 2013. Effects of biofertilizer with diazotrophic bacteria and mycorrhizal fungi in soil attribute, cowpea nodulation yield and nutrient uptake in field conditions. Sci. Hortic. 162, 374–379.

Araújo, B.R., Romao, L.P.C, Doumer, M.E., Mangrich, A.S. 2017. Evaluation of the interactions between chitosan and humics in media for the controlled release of nitrogen fertilizer. J. Environ. Manage. 190, 122–131.

Ardakani, S.S., Hedari, A., Tayebi, L., Mohammadi, M. 2010. Promotion of cotton seedlings growth characteristics by development and use of new bioformulations. Int. J. Bot. 6, 95–100.

Arora, N.K., Tiwari, S., Singh, R. 2014. Comparative study of different carriers inoculated with nodule forming and free living plant growth promoting bacteria suitable for sustainable agriculture. J. Plant Path. Microb. 5, 229.

AAPFCO, 1995. Official Publication No. 48. Published by Association of American Plant Food Control Officials. Association of American Plant Food Control Officials (AAPFCO). Inc.; West Lafayette, Indiana, USA.

Aulakh, M.S., Rennie, D.A. 1987. Effect of wheat straw incorporation on denitrification of N under anaerobic and aerobic conditions. Can. J. Soil Sci. 67, 25–834.

Azeem, B., KuShaari, K., Man, Z.B., Basit, A., Thanh, T.H. 2014. Review on materials & methods to produce controlled release coated urea fertilizer. J. Control. Release. 181, 11–21.

Bahl, N., Jauhri, S. 1986. Spent compost as a carrier for bacterial inoculant production. In Proceedings of the International symposium on scientific and technological aspects of cultivating edible fungi, The Pennsylvania State University, University Park, PA. pp. 63–68.

Baishya, K. 2015. Impact of agrochemicals application on soil quality degradation—a review. In International Conference on Science Technology and Management. University of Delhi, New Delhi, pp. 778–786.

Balmford, A., Green, R.E., Scharlemann, J.P.W. 2005. Sparing land for nature: exploring the potential impact of changes in agricultural yields on the area needed for crop production. Global Change Biol. 11, 1594-1605.

Bansiwal, A.K., Rayalu, S.S., Labhasetwar, N.K., Juwarkar, A.A., Devotta, S. 2006 Surfactant-modified zeolite as a slow release fertilizer for phosphorus. J. Agric. Food. Chem. 54, 4773–4779.

Barthod, J., Rumpel, C., Paradelo, R., Dignac, M.F. 2016. The effects of worms, clay and biochar on CO_2 emissions during production and soil application of co-composts. Soil. 2, 673–683.

Barua, S., Tripathi, S., Chakraborty, A., Ghosh, S. and Chakrabarti, K. 2012. Characterization and crop production efficiency of diazotrophic bacterial isolates from coastal saline soils. Microbiol. Res. 167, 95–102.

Bashan, Y. 1998. Inoculants for plant growth promoting bacteria for use in agriculture. Adv. Biotechnol. 16, 729–770.

Bashan, Y. 1986. Alginate Beads as Synthetic Inoculant Carriers for Slow Release of Bacteria That Affect Plant Growth. Appl. Environ. Microbiol. 51(5), 1089–1098.

Bazilah, A.B.I., Sariah, M., Abidin, M.A.Z. et al. 2011. Influence of carrier materials and storage temperature on survivability of Rhizobial inoculants. Asian. J. Plant. Sci. 10, 331–337.

Bentsen, N.S., Felby, C., Thorsen, B.J. 2014. Agricultural residue production and potentials for energy and material services. Progress in Energy and Combustion Science, 40, 59-73.

Besoain, E., Sepúlveda, G. 1985. Minerales secundarios. In: Tosso, J. (Ed.), Suelos Volcanicos de Chile, Firstedition. Instituta de Investigaciones Agropecuarias. Ministerio de Agricultura, Santiago, Chile, pp. 153–214.

Bhatnagar, A., Sillanpää, M. 2010. Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment—A review. Chem. Eng. J. 157, 277–296.

Bley, H., Gianello, C., da Silva Santos, J., Roldão Selau, P.L. 2017. Nutrient Release, Plant Nutrition, and Potassium Leaching from Polymer-Coated Fertilizer. Rev. Bras. Cienc. Solo. 41:e0160142.

Borie, F., Rubio, R., Morales, A., Curaqueo, G., Cornejo, P. 2010. Arbuscular mycorrhizae in agricultural and forest ecosystems in Chile. J. Soil. Sci. Plant Nutr. 10 (3), 185–206.

Borie, F., Rubio, R., Rouanet, J.L., Morales, A., Borie, F., Rojas, C. 2006. Effects of tillage systems on soil characteristics, glomalin and mycorrhizal propagules in an Chilean Ultisol. Soil Tillage Res. 88, 253–261.

Borie, F., Rubio, R. 2003. Total and organic phosphorus in Chilean volcanic soils. Gayana Bot. 60, 69–78.

Bortolin, A., Aouada, F.A., Mattoso, L.H.C., Ribeiro, C. 2013. Nanocomposite PAAm/methyl cellulose/montmorillonite hydrogel: evidence of synergistic effects for the slow release of fertilizers. J. Agric. Food Chem. 6, 7431–7439.

Bréant, D., Jézéquel, K., Lebeau, T. 2002. Optimization of the cell release from immobilized cells of Bacillus simplex cultivated in culture media enriched with Cd2+: influence of Cd2+, inoculum size, culture medium and alginate beads characteristics. Biotechnol.Lett. 24:1237–1241.

Brisson, N., Gate, P., Gouache, D., Charmet, G., Oury, F.X., Huard, F., 2010. Why are wheat yields stagnating in Europe? A comprehensive data analysis for France. Field Crops Res. 119, 201–212.

Brühl, C., Lelieveld,J., Tost, H., Höpfner, M., Glatthor, N. 2015. Stratospheric sulfur and its implications for radiative forcing simulated by the chemistry climate model EMAC. J. Geophys. Res. Atmos. 120(5): 2103–2118.

Butzen, S. 2013. Common nitrogen fertilizers and stabilizers for corn production. Crop Insights vol. 23 no. 2. DuPont Pioneer, Johnston, Iowa.

Cai, Y., Qi, H., Liu, Y., He, X. 2016. Sorption/Desorption Behavior and Mechanism of NH_4^+ by Biochar as a Nitrogen Fertilizer Sustained-Release Material. J. Agric. Food Chem. 64 (24), 4958–4964.

Calabi-Floody, M., Rumpel, C., Velásquez, G., Violante, A., Bol, R., Condron, L.M., Mora, M.L. 2015. The Role of Nanoclays in Carbon stabilization in Andisols and Cambisols. J. Soil. Sci. Plant Nutr. 15 (3), 587–604.

Calabi-Floody, M., Velásquez, G., Gianfreda, L., Saggar, S., Bolan, N., Rumpel, C., Mora, M.L. 2012. Improving bioavailability of phosphorous from cattle dung by using phosphatase immobilized on natural clay and nanoclay. Chemophere. 89, 644–655.

Calabi-Floody, M., Bendall, J.S., Jara, A.A., Welland, M.E., Theng, B.K.G., Rumpel, C., Mora, M.L. 2011. Nanoclays from an Andisol: Extraction, properties and carbon stabilization. Geoderma. 161, 159–167.

Calabi-Floody, M., Theng, B.K.G., Reyes, P., Mora, M.L. 2009. Natural nanoclays: applications and future trends - a Chilean perspective. Clay Min. 44(16), 1–176.

Campos, D.C., Acevedo, F., Morales, E., Aravena, J., Amiard, V., Jorquera, M.A., Inostroza, N.G., Rubilar, M. 2014. Microencapsulation by spray drying of nitrogen-fi xing bacteria associated with lupin nodules. World J. Microbiol. Biotechnol. 30, 2371–2378

Cao, G. 2004. Nanostructures and Nanomaterials-Synthesis Properties and Applications, Imperial College Press, London. pp. 448.

Cassman, K.G., de Datta, S.K., Amarante, S.T., Liboon, S.P., Samson, M.I., Dizon, M.A. 1996. Long-term comparison of the agronomic efficiency and residual benefits of organic and inorganic nitrogen sources for tropical lowland rice. Exp. Agric. 32, 427–444.

Chabbi, A., Lehmann, J., Ciais, P., Loescher, H.W., Cotrufo, M.F., Don, A., SanClements, M., Schipper, L., Six, J., Smith, P., Rumpel, C. 2017. Aligning agriculture and climate policy. Nat. Clim. Change. 7, 307–309.

Chen, G., Guan, Y., Tong, L., Yan, B., Hou, L. 2015. Spatial estimation of $PM_{2.5}$ emissions from straw open burning in Tianjin from 2001 to 2012. Atmos. Environ. 122, 705–712.

Chinnamuthu, C.R., Boopathi, P.M. 2009. Nanotechnology and Agroecosystem. Madras Agric. J. 96, 17–31.

Cordell, D., White, S. 2011. Peak phosphorus: clarifying the key issues of a vigorous debate about long-term phosphorus security. Sustainability 3, 2027–2049.

Cordell, D., Drangert, J.O., White, S. 2009. The story of phosphorus: Global food security and food for thought Global Environ. Change. 19, 292–305.

Costa, M.M., Cabral-Albuquerque, E.C., Alves, T.L., Pinto, J.C., Fialho, R.L. 2013. Use of polyhydroxybutyrate and ethyl cellulose for coating of urea granules, J. Agric. Food Chem. 61(42), 9984–9991.

Crutzen, P.J., Heidt, L.E., Krasnec, J.P., Pollock, W.H., Seiler, W. 2016. Biomass Burning as a Source of Atmospheric Gases CO, H_2, N_2O, NO, CH_3Cl and COS, in: Crutzen, P.J., Brauch, H.G. (Eds.), Paul J. Crutzen: A Pioneer on Atmospheric Chemistry and Climate Change in the Anthropocene, Nobel Laureates 50, DOI 10.1007/978-3-319-27460-7.

Crutzen, P.J. 1981. Atmospheric chemical processes of the oxides of nitrogen including nitrous oxide, in Delwiche, C.C. (Ed.), Denitrification, nitrification and atmospheric nitrous oxide. John Wiley, New York, USA, pp. 17–44.

Dabin P 1980. Phosphorus deficiency in tropical soils as a constraint on agricultural output, in: Metz, J.F., Brady, N.C. (Eds.), Priorities for alleviating soil-related constraints to food production in the tropics. IRRI, Los Banos (Philippines), pp 217-233.

da Rosa, G.S., Rocha., C.d.S. 2012. Use of vinasse to produce slow-release coated urea in spouted bed. Can. J. Chem. Eng. 91, 589–597.

Dawson, C.J., Hilton, J. 2011. Fertiliser availability in a resource-limited world: Production and recycling of nitrogen and phosphorus. Food Policy 36, S14–S22.

Daza, A., Santamaria, C., Rodriguez-Navarro, D.N., Camacho, M., Orive, R., Temprano, F. 2000. Perlite as a carrier for bacterial inoculants. Soil Biol. Bioch. 32,567–572.

DeRosa, M.R., Monreal, C., Schnitzer, M., Walsh, R., Sultan, Y. 2010. Nanotechnology in fertilizers. Nat. Nanotechnol. J., 5, 91–96.

Detroit, W.J. 1988. Controlled release formulation for fertilizers. US Patent, 4789391 A.

Devassine, M., Henry, F., Guerin, P., Briand, X. 2002. Coating of fertilizers by degradable polymers. Int. J. Pharm. 242, 399–404.

Dhar, D.W., Prasanna, R., Singh, B.V. 2007. Comparative Performance of Three Carrier Based Blue Green Algal Biofertilizers for Sustainable Rice Cultivation, J. Sustain. Agric. 30, 2, 41–50.

Ding, Y., Liu, Y.X., Wu, W.X., Shi, D.Z., Yang, M., Zhong, Z.K. 2010. Evaluation of Biochar Effects on Nitrogen Retention and Leaching in Multi-Layered Soil Columns. Water Air Soil Pollut. 213, 47–55.

Donida, M.W., Rocha, S.C. 2002. Coating of urea with an aqueous polymeric suspension in a two-dimensional spouted bed. Dry. Technol. 20 (3), 685–704.

Du, C.W., Zhou, J.M., Shaviv, A. 2006. Release Characteristics of Nutrients from Polymer coated Compound Controlled Release Fertilizers. J. Polym. Environ. 14, 223–230.

Dunford, N.T., Edwards, J. 2010. Nutritional bioactive components of wheat straw as affected by genotype and environment. Bioresour. Technol. 101 (1), 422–425.

Egamberdieva, D., Adesemoye, A.O. 2016. Improvement of Crop Protection and Yield in Hostile Agroecological Conditions with PGPR-Based Biofertilizer Formulations, in: Arora, N.K., Mehnaz, S., Balestrini, R. (Eds.), Bioformulations: for Sustainable Agriculture, Springer, India, pp 199–211.

Elser, J., Bennett, E. 2011. Phosphorus cycle: A broken biogeochemical cycle. Nature. 478, 29–31.

Entry, J.A., Sojka, R.E. 2007. Matrix Based Fertilizers Reduce Nitrogen and Phosphorus Leaching in Greenhouse Column Studies. Water Air Soil Pollut. 180, 283–292.

EPA, 2007. Nanotechnology white paper. U.S. Environmental Protection Agency (EPA) Report EPA 100/B-07/001, Washington DC, USA.

Escudey, M., Galindo, G., Förter, J.E., Briceño, M., Diaz, P., Chang, A., 2001. Chemical forms of phosphorus of volcanic ash-derived soils in Chile. Commun. Soil Sci. Plan. 32, 601–616.

FAO, 2009. How to feed the world: 2050. High Expert Forum, 12-13 Oct. 2009. Food and Agriculture Organization of the United Nations (FAO). Rome. pp. 1–35.

FAO, 2001. “World Soil Resources Reports” In: Driessen, P. Deckers, J. (Eds), Lecture Notes on the Major Soils of the World. Food and Agriculture Organization of the United Nations (FAO) Rome, pp. 1–10.

Fischer, R.A., Byerlee, D., Edmeades, G.O. 2009. Can technology deliver on the yield challenge to 2050? Paper prepared for expert meeting on “How to Feed the World in 2050.” 24–26 June 2009. FAO, Rome.

Foster, A. 2013. Development of Biocompatible aptamer films as smart materials for Novel fertilizer systems. Master Thesis. Carleton University, Ottawa, Canada.

Fravel, D.R., Marois, J.J., Lumsden, R.D., Connick, W.J. 1985. Encapsulation of potential biocontrol agents in an Alginate-Clay matrix. Phytopathology. 75, 774–777.

Garay, M.R.M., Rallo, B.M., Carmona, C.R., Araya, C.J. 2009. Characterization of anatomical, chemical, and biodegradable properties of fibers from corn, wheat, and rice residues. Chil. J. Agric. Res. 69(3), 406–415.

Glaser, B., Wiedner, K., Seelig, S., Schmidt, H.P., Gerber, H. 2015. Biochar organic fertilizers from natural resources as substitute for mineral fertilizers. Agron. Sustain. Dev. 35, 667–678.

Glaser, B., Lehmann, J., Zech, W. 2002. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal—A review. Biol. Fert. Soils 35, 219–230.

Godfray, H.C.J., Beddington, J.R., Crute, I.R., Haddad, L., Lawrence, D., Muir, J.F., Pretty, J., Robinson, S., Thomas, S.M., Toulmin, C. 2010. Food security: the challenge of feeding 9 billion people. Science 327, 812-818.

Golden, B., Slaton, N., Norman, R., Gbur, E., Wilson, C. 2011. Nitrogen Release from Environmentally Smart Nitrogen Fertilizer as Influenced by Soil Series, Temperature, Moisture, and Incubation Method. Commun. Soil Sci. Plant Anal. 42(15), 1809–1824.

González, M., Cea, M., Medina, J., González, A., Diez, M.C., Cartes, P., Monreal, C., Navia, R. 2015. Evaluation of biodegradable polymers as encapsulating agents for the development of a urea controlled-release fertilizer using biochar as support material. Sci. Total Environ. 505, 446–453.

González, S., Salazar, F., Neuenschander, A., Arata, P., Tessada, R., Salas, C. and Searle, J. 2009. Resultados del sector 4: Agricultura. p. 181-209. In González, S. (Ed.) Inventarios anuales de gases de efecto invernadero de Chile. Serie Temporal 1984/2003 para Sectores No-Energía. Boletín INIA Nº 185. Instituto de Investigaciones Agropecuarias INIA, Santiago, Chile.

Grassini, P., Eskridge, K.M., Cassman, K.G. 2013. Distinguishing between yield advances and yield plateaus in historical crop production trends. Nat. Commun. 4, 2918, http://dx.doi.org/10.1038/ncomms3918.

Gruère, G.P. 2012. Implications of nanotechnology growth in food and agriculture in OECD countries. Food Policy. 37, 191–198.

Gupta, S., Agarwal, R., Mittal, S.K. 2016. Respiratory health concerns in children at some strategic locations from high PM levels during crop residue burning episodes. Atmos. Environ. 137, 127–134.

Habets, S., de Wild, P.J., Huijgen, W.J.J., van Eck, E.R.H. 2013. The influence of thermochemical treatments on the lignocellulosic structure of wheat straw as studied by natural abundance ^{13}C NMR. Bioresour. Technol. 146, 585–590.

Hale, L., Luth, M., Crowley, D. 2015. Biochar characteristics relate to its utility as an alternative soil inoculum carrier to peat and vermiculite. Soil Biol. Biochem. 81, 228–235.

Hansen, M.A.T., Ahl, L.I., Pedersen, H.L., Westereng, B., Willats, W.G.T., Jørgensen, H., Felby, C. 2014. Extractability and digestibility of plant cell wall polysaccharides during hydrothermal and enzymatic degradation of wheat straw (Triticumaestivum L.). Ind. Crops Prod. 55, 63–69.

Haygarth, P.M., Bardgett, R.D. and Condron, L.M. 2013. Phosphorus and nitrogen cycles and their management, in: Gregory P.J., Nortcliff, S. (Eds), Soil Conditions and Plant Growth. Wiley-Blackwell, pp. 132–159.

He, Z., Xia, X., Peng, S., Lumpkin, T.A. 2014. Meeting demands for increased cereal production in China. J. Cereal Sci. 59, 235–244.

Heard, J., Cavers, C., Adrian, G. 2006. Up in smoke-nutrient loss with straw burning. Better Crops. 90(3), 10–11.

Hegde, S.V., Brahmaprakash, G.P. 1992. A dry granular inoculant of Rhizobium for soil application. Plant Soil. 144(2), 309–311.

Hu, J., Guo, H., Li, J., Gan, Q., Wang, Y., Xing, B. 2016. Comparative impacts of iron oxide nanoparticles and ferric ions on the growth of Citrus maxima. Environ. Pollut. 221, 199–208.

Huang, G., Shi, J.X., Langrish, T.A.G. 2007. A new pulping process for wheat straw to reduce problems with the discharge of black liquor. Bioresour. Technol. 98, 2829–2835.

Hubbe, M., Nazhad, M., Sánchez, C. 2010. Cellulosic biomass and organic waste into high value soil amendments: A review. BioResources 5(4), 2808–2854.

Ibrahim, A.A., Jibril, B.Y. 2005. Controlled release of paraffin wax/rosin-coated fertilizers. Ind. Eng. Chem. Res. 44, 2288–2291.

IFDC, 2010. World Phosphate Rock Reserves and Resources. International Fertilizer Development Center (IFDC), Muscle Shoals, AL 35662, USA. ISBN 978-0-88090-167-3.

Islam, Md.R., Madhaiyan, M., Boruah, H.P.D., Yim, W., Lee, G., Saravanan, V.S., Fu, Q., Hu, H., Sa, T. 2009. Characterization of Plant Growth-Promoting Traits of Free-Living Diazotrophic Bacteria and Their Inoculation Effects on Growth and Nitrogen Uptake of Crop Plants. J. Microbiol. Biotechnol. 19(10), 1213–1222.

Ivanova, E., Teunou, E., Poncelet, D. 2005. Alginate based macrocapsules as inoculants carriers for production of nitrogen biofertilizers, in: Gruev, B., Nikolova, M., Donev, A.

(Eds), Proceedings of the Balkan Scientific Conference of Biology in Plovdiv (Bulgaria), pp. 90–108.

Jackson, A.M., Whipps, J.M., Lynch, J.M. 1991. Production, delivery systems, and survival in soil of four fungi with disease biocontrol potential. Enzyme Microbial. Technol. 13, 636–642.

Jarosiewicz, A., Tomaszewska, M. 2003. Controlled-release NPK fertilizer encapsulated by polymeric membranes. J. Agric. Food Chem. 51(2), 413–7.

Jiang, D., Zhuang, D., Fu, J., Huang, Y., Wen, K. 2012. Bioenergy potential from crop residues in China: Availability and distribution. Renewable Sustainable Energy. Rev. 16, 1377– 1382.

Jintakanon, N., Opaprakasit, P., Petchsuk, A., Opaprakasit, M. 2008. Controlled-release materials for fertilizer based on lactic acid polymers. Adv. Mater. Res. 55, 905–908.

Jorquera, M.J., Martínez, O.A., Marileo, L.G., Acuña, J.J., Saggar, S., Mora, M.L. 2014. Effect of nitrogen and phosphorus fertilization on the composition of rhizobacterial communities of two Chilean Andisol pastures. World J. Microbiol. Biotechnol. 30, 99–107.

Jorquera, M., Hernández, M., Rengel, Z., Marschner, P., Mora, M.L. 2008. Isolation of culturable phosphobacteria with both phytatemineralization and phosphate-solubilization activity from the rhizosphere of plants grown in a volcanic soil. Biol. Fertil. Soils. 44, 1025–1034.

Joseph, S., Graber, E.R., Chia, C., Munroe, P., Donne, S., Thomas, T., Nielsen, S., Marjo, C., Rutlidge, H., Pan, G.X., Li, L., Taylor, P., Rawal, A., Hook, J. 2013. Shifting paradigms: development of high-efficiency biochar fertilizers based on nano-structures and soluble components. Carbon Manag. 4(3), 323–343.

Kennedy, I.R., Choudhury, A.T.M.A. and Kecskés, M.L. 2004. Non-symbiotic bacterial diazotrophs in crop-farming systems: can their potential for plant growth promotion be better exploited? Soil Biol. Biochem. 36, 1229–1244.

Keyser, H.H., Somasegaran, P., Bohlool, B.B. 1993. Rhizobial ecology and technology, in: Metting, Jr. F.B. (Ed), Soil microbial ecology: applications in agricultural and environmental management. Marcel Dekker Inc NY, pp 205–226.

Khavazi, K., Rejali, F., Seguin, P., Miransari, M. 2007. Effects of carrier, sterilization method, and incubation on survival of Bradyrhizobium japonicum in soybean (Glycine max L.) inoculants. Enzyme Microb. Tech. 41, 780–784.

Kim, J., Grate, J.W., Wang, P. 2006. Nanostructures for enzyme stabilization. Chem. Eng. Sci. 61, 1017–1026.

Kim, S.Y., Kim, M., Lee, S., Lee, J., Ko, G. 2012. Survival of microorganisms on antimicrobial filters and the removal efficiency of bioaerosols in an environmental chamber. J. Microbiol. Biotechnol. 22(9), 1288–1295.

Komarneni, S. 2010. Potential of nanotechnology in environmental soil science, in: Proc. the 9th international conference of the East and Southeast Asia federation of soil science societies, pp. 16–20.

Koppmann, R., Von, C.K., Reid, J.S. 2005. A review of biomass burning emissions, Part 1: gaseous emissions of carbon monoxide, methane, volatile organic compounds and nitrogen containing compounds Atmos. Chem. Phys. 5(10), 455–516.

Kulikova, N.A., Filippova, O., Volikov, A.B., Perminova, I.V. 2016. Slow nitrogen release from humic substances modified with aminoorganosilanes. J. Soils Sediments. DOI 10.1007/s11368-016-1507-1

Kumar, B., Trivedi, P., Pandey, A. 2007. Pseudomonas corrugata: a suitable bioinoculant for maize grown under rainfed conditions of Himalayan region. Soil Biol. Biochem. 39, 3093–3100.

Ladha, J.K., Tirol-Padre, A., Reddy, C.K., Cassman, K.G., Verma, S., Powlson, D.S., van Kessel, C., Richter, D.B., Chakraborty, D., Pathak, H. 2016. Global nitrogen budgets in cereals: A 50-year assessment for maize, rice, and wheat production systems. Scientific Reports. 6(19355), DOI: 10.1038/srep19355.

Lal, R. 2006. Enhancing crop yields in the developing countries through restoration of soil organic carbon pool in agricultural lands. Land Degrad. Dev. 17, 197–209.

Lal, R. 2004. Soil carbon sequestration to mitigate climate change. Geoderma 123, 1–22.

Lal, R. 2003. Soil erosion and the global carbon budget. Environ. Int. 29(4), 437–450.

Lan, R., Liu, Y., Wang, G., Wang, T., Kan, C., Jin, Y. 2011. Experimental modeling of polymer latex spray coating for producing controlled-release urea, Particuology. 9(5), 510–516.

Lee, Y., Park, J., Ryu, C., Gang, K.S., Yang, W., Park, Y.K., Jung, J., Hyun, S. 2013. Comparison of biochar properties from biomass residues produced by slow pyrolysis at 500 °C. Bioresour. Technol. 148, 196–201.

Leggo, P.J. 2000. An investigation of plant growth in an organo–zeolitic substrate and its ecological significance. Plant Soil. 219, 135–146.

Lehmann, J., Rillig, M.C., Thies, J., Masiello, C.A., Hockaday, W.C., Crowley, D. 2011. Biochar effects on soil biota – A review. Soil Biol. Biochem. 43, 1812–1836.

Lehmann, J., Joseph, S. 2009. Biochar for environmental management: an introduction, in: Lehmann, J., Joseph, S. (Eds). Biochar for environmental management. Earthscan, London, pp. 1–12.

Lemke, R.L., Zhong, Z., Campbell, C.A. and Zentner, R. 2007. Can pulse crops play a rolein mitigating greenhouse gases from north American agriculture? Agron. J. 99, 1719–1725.

Le Quéré, C., Moriarty, R., Andrew, R.M., Canadell, J.G., Sitch, S., Korsbakken, J.I., Friedlingstein, P., Peters, G.P., Andres, R.J., Boden, T.A., Houghton, R.A., House, J.I., Keeling, R.F., Tans, P., Arneth, A., Bakker, D.C.E., Barbero, L., Bopp, L., Chang, J., Chevallier, F., Chini, L.P., Ciais, P., Fader, M., Feely, R.A., Gkritzalis, T., Harris, I., Hauck, J., Ilyina, T., Jain, A.K., Kato, E., Kitidis, V., Klein Goldewijk, K., Koven, C., Landschützer, P., Lauvset, S.K., Lefèvre, N., Lenton, A., Lima, I.D., Metzl, N., Millero, F., Munro, D.R., Murata, A., Nabel, J.E.M.S., Nakaoka, S., Nojiri, Y., O'Brien, K., Olsen, A., Ono, T., Pérez, F.F., Pfeil, B., Pierrot, D., Poulter, B., Rehder, G., Rödenbeck, C., Saito, S., Schuster, U., Schwinger, J., Séférian, R., Steinhoff, T., Stocker, B.D., Sutton, A.J., Takahashi, T., Tilbrook, B., van der Laan-Luijkx, I.T., van der Werf, G.R., van Heuven, S., Vandemark, D., Viovy, N., Wiltshire, A., Zaehle, S., Zeng, N. 2015. Global Carbon Budget 2015. Earth Syst. Sci. 7, 349–396.

Li, L.J., Wang, Y., Zhang, Q., Li, J.X., Yang, X.G., Jin, J. 2008 Wheat straw burning and its associated impacts on Beijing air quality Sci. China Series D—Earth Sci. 51, 403–414.

Li, P.P., Wang, X.J., Yuan, X.F., Wang, X.F., Cao, Y.Z. and Cui, Z.J. 2011. Screening of a Composite Microbial System and Its Characteristics of Wheat Straw Degradation. Agr. Sci. China. 10(10), 1586–1594.

Li, X., Lei, Z., Qu, J., Li, Z., Zhou, X., Zhang, Q. 2017. Synthesizing slow-release fertilizers via mechanochemical processing for potentially recycling the waste ferrous sulfate from titanium dioxide production. J. Environ. Manage. 186(1), 120–126.

Li, Z., Zhang, Y. 2010. Use of surfactant-modified zeolite to carry and slowly release sulfate. Desalin. Water Treat. 21, 73–78.

Li, Z. 2003. Use of surfactant-modified zeolite as fertilizer carriers to control nitrate release. Micropor. Mesopr. Mater. 61, 181–188.

Liang, S., Zhang, L., Xu, J. 2007. Morphology and permeability of cellulose/chitin blend membranes. J. Membr. Sci. 287 (1), 19–28.

Lipper, L., Thornton, P., Campbell, B.M., Baedeker, T., Braimoh, A., Bwalya, M., Caron, P., Cattaneo, A., Garrity, D., Henry, K., Hottle, R., Jackson, L., Jarvis, A., Kossam, F., Mann, W., McCarthy, N., Meybeck, A., Neufeldt, H., Remington, T., Sen, P.T., Sessa, R., Shula, R., Tibu, A., Torquebiau, E.F.2014. Climate-smart agriculture for food security. Nat. Clim. Change. 4, 1068–1072.

Liu, C.H., Wu, J.Y., Chang, J.S. 2008. Diffusion characteristic and controlled release of bacterial fertilizer from modified calcium alginate capsules. Bioresour. Technol. 99, 1904–1910.

Liu, J., Su, Y., Li, Q., Yue, Q., Gao, B. 2013. Preparation of wheat straw based superabsorbent resins and their applications as adsorbents for ammonium and phosphate removal. Bioresour. Technol. 143, 32–39.

Liu, R., Lal, R. 2014. Synthetic apatite nanoparticles as a phosphorus fertilizer for soybean (Glycine max). Sci. Rep. 4, 5686–5691.

Liu, X., Feng, Z., Zhang, S., Zhang, J., Xiao, Q., Wang, Y. 2006. Preparation and testing of cementing nano-subnano composites of slow-or controlled release of fertilizers. Sci. Silvae Sin. 39, 1598–1604.

Lü, S., Feng, C., Gao, C., Wang, X., Xu, X., Bai, X., Gao, N., Liu, M. 2016. Multifunctional Environmental Smart Fertilizer Based on L-Aspartic Acid for Sustained Nutrient Release. J. Agric. Food Chem. 64 (24), 4965–4974.

Luo, J., Tillman, R.W., Ball, P.R., 1999. Factors regulating denitrification in a soilunder pasture. Soil Biol. Biochem. 31, 913–927.

Ma, Z., Li, Q., Yue, Q., Gao, B., Xu, X. and Zhong, Q. 2011. Synthesis and characterization of a novel super-absorbent based on wheat straw. Bioresour. Technol. 102, 2853–2858.

Mahajan, P., Dhoke, S.K., Khanna, A.S. 2011. Effect of nano-ZnO particle suspension on growth of mung (Vigna radiata) and gram (Cicer arietinum) seedlings using plant Agar Method. J. Nanotechnol. 2011, 1–7.

Manikandan, A., Subramanian, K.S. 2014. Fabrication and characterisation of nanoporous zeolite based N fertilizer. Afr. J. Agric. Res. 9, 276–284.

Manjunatha, S.B., Biradar, D.P., Aladakatti, Y.R. 2016. Nanotechnology and its application to agriculture: A review. J. Farm. Sci. 29(1), 1–13.

Mansoori, G.A. 2005. Principles of Nanotechnology: Molecular Based-Study of Condensed Matter in Small Systems, University of Illinois at Chicago, USA, World Scientific pub. Co., pp. 360.

Marschner, P., Neumann, G., Kania, A., Weiskopf, L., Lieberei, R. 2002. Spatial and temporal dynamics of the microbial community structure in the rhizosphere of cluster roots of white lupin (Lupinus albus L.). Plant Soil. 246, 167–174.

Martínez-Viveros, O., Jorquera, M.A., Crowley, D.E., Gajardo, G., Mora, M.L. 2010. Mechanisms and practical considerations involved in plant growth promotion by rhizobacteria. J. Soil Sci. Plant Nutr. 10(3), 310–339.

Mastronardi, E., Tsae, P., Zhang, X., Monreal, C.M., DeRosa, M.C. 2015. Strategic role of nanotechnology in fertilizers: Potential and limitations, in: Rai, M., Ribeiro, C., Mattoso, L., Duran, N. (Eds.), Nanotechnologies in Food and Agriculture. Springer, pp. 25–67.

Mathews, A.S., Narine, S. 2010. Poly [N-isopropyl acrylamide]-co-polyurethane copolymers for controlled release of urea, J. Polym. Sci. A Polym. Chem. 48(15), 3236–3243.

Medina, M., Monreal, C., Chabot, D., Meier, S., González, M.E., Morales, E., Parillo, R., Borie, F., Cornejo, P. 2017. Microscopic and spectroscopic characterization of humic substances from a compost amended copper contaminated soil: main features and their potential effects on Cu immobilization. Environ. Sci. Pollut. Res. DOI 10.1007/s11356-017-8981-x.

Medina, J., Monreal, C., Barea, J.M., Arriagada, C., Borie, F., Cornejo, P. 2015. Advances in the treatment and stabilization of composted crop residues and their technological applications in agricultural, degraded and polluted soils: A review. Waste Manage. 42, 41–54.

Menezes-Blackburn, D., Jorquera, M.A., Gianfreda, L., Greiner, R.L., Mora, M.L. 2014. A novel phosphorus biofertilization strategy using cattle manure treated with phytase–nanoclay complexes. Biol. Fertil. Soils. 50, 583–592.

Menezes-Blackburn, D., Jorquera, M., Gianfreda, L., Rao, M., Greiner, R., Garrido, E., Mora, M.L. 2011. Activity stabilization of Aspergillus niger and Escherichia coli phytases immobilized on allophanic synthetic compounds and montmorillonite nanoclays. Bioresour. Technol. 102, 9360–9367.

Mishra, B.K., Dahich, S.K. 2010. Methodology of nitrogen biofertilizer production. J. Adv. Dev. Res. 1, 3–6.

Misselbrook, T.H., Menzi, H., Cordovil, C. 2012. Preface – Recycling of organic residues to agriculture: Agronomic and environmental impacts. Agric. Ecosyst. Environ. 160, 1–2.

Moelans, D., Cool, P., Baeyens, J., Vansant, E.F. 2005. Using mesoporous silica materials to immobilize biocatalysis-enzymes. Catal. Commun. 6, 307–311.

Mohanraj, J. 2013. Effect of nano-zeolite on nitrogen dynamics and green house gas emission in rice soil eco system. M. Tech. (Ag.) Thesis, TNAU, Coimbatore, India.

Mora, M.L., Cartes, P., Núñez, P., Salazar, M., Demanet, R. 2007. Movement of $NO3^-$–N and $NH4^+$–N in an Andisol and its influence on ryegrass production in a short term study. R C Suelo Nutr. Veg. 7, 46–64.

Mora, M.L., Alfaro, M.A., Jarvis, S.C., Demanet, R., Cartes, P. 2006. Soil aluminium availability in Andisols of southern Chile and its effect on forage production and animal metabolism. Soil Use Manage. 22, 95–101.

Mora, M.L., Shene, C., Violante, A., Demanet, R., Bolan, N.S. 2005. The effect of organic matter and soil chemical properties on sulfate availability in Chilean volcanic soils, in: Huang, P.M., Violante, A., Bollag, J.M., Vityakon, P. (Eds.), Soil abiotic and biotic interactions and the impact on the ecosystem and human welfare. Science Publishers, New Hampshire, pp. 223–244.

Mora, M.L., Alfaro, M., Williams, P., Stehr, W., Demanet, R. 2004. Effect of fertiliser input on soil acidification in relation to growth and chemical composition of a pasture, and animal production. RC Suelo Nutr. Veg. 4, 29–40.

Mora, M.L., Cartes, P., Demanet, R., Cornforth, I.S. 2002. Effects of lime and gypsum on pasture growth and composition on an acid Andisol in Chile, South America. Commun. Soil Sci. Plant Anal. 33, 2069–2081.

Mora, M.L., Schnettler, B., Demanet, F.R. 1999. Effect of liming and gypsum on soil chemistry, yield and mineral composition of ryegrass grown in an acidic. Commun. Soil Sci. Plant Anal. 30, 1251–1266.

Mulumba, L., Lal, R. 2008. Mulching effects on selected soil physical properties. Soil Till Res. 98(1), 106–111.

Mulder, W.J., Gosselink, R.J.A., Vingerhoeds, M.H., Harmsen, P.F.H., Eastham, D. 2011. Lignin based controlled release coatings. Ind. Crops Prod. 34(1), 915–920.

Muñoz, C., Paulino, L., Monreal, C., Zagal, E. 2010. Greenhouse gas (CO_2 and N_2O) emissions from soils: A review. Chil. J. Agric. Res. 70, 485–497.

Muresu, R., Sulas, L., Caredda, S. 2003. Legume—Rhizobium symbiosis: characteristics and prospects of inoculation. Rivoluzione Agronomica. 37, 33–45.

Murphy, J.F., Reddy, M.S., Ryu, C.M., Kloepper, J.W., Li, R. 2003. Rhizobacteria-mediated growth promotion of tomato leads to protection against Cucumber mosaic virus. Phytopathology. 93, 1301–1307.

Naiman, A.D., Latrónico, A., García de Salamone, I.E. 2009. Inoculation of wheat with Azospirillum brasilense and Pseudomonas fluorescens: Impact on the production and culturable rhizosphere microflora. Eur. J. Soil Biol. 45, 44–51.

Nair, R., Varghese, S.H., Nair, B.G., Maekawa, T., Yoshida, Y., Sakthi, D. 2010. Nanoparticulate material delivery to plants. Plant Sci. 179, 154–163.

Naisse, C., Girardin, C., Lefevre, R., Pozzi, A., Maas, R., Stark, A., Rumpel, C. 2015. Effect of physical weathering on the carbon sequestration potential of biochars and hydrochars in soil. GCB Bioenergy. 7, 488–496.

Naz, M.Y., Sulaiman, S.A. 2016. Slow release coating remedy for nitrogen loss from conventional urea: A review. J. Controlled Release. 225(10), 109–120.

Negi, Y.K., Kumar, J., Garg, S.K. 2005. Cold–tolerant fluorescent Pseudomonas isolates from Garhwal Himalayas as potential plant growth promoting and biocontrol agents in pea. Curr. Sci. 89, 2151–2156.

Ngo, P.T., Rumpel, C., Janeau, J.L., Dang, D.K., Doan, T.T., Jouquet, P. 2016. Mixing of biochar with organic amendments reduces carbon removal after field exposure under tropical conditions. Ecol. Eng. 91, 378–380.

Ngo, P.T., Rumpel, C., Doan, T.T., Henry-des-Tureaux, T., Dang, D.K., Jouquet, P. 2014. Use of organic substrates for increasing soil organic matter quality and carbon sequestration of tropical degraded soil (a 3 years mesocosms experiment). Carbon Manag. 5, 155–168.

Ni, B., Liu, M., Lu, S. 2009. Multifunctional slow-release urea fertilizer from ethylcellulose and superabsorbent coated formulations. Chem. Eng. J. 155, 892–898.

Niu, Y., Li, H. 2012. Controlled release of urea encapsulated by starch-g-poly (vinyl acetate), Ind. Eng. Chem. Res. 51 (38),12173–12177.

Núñez, P., Demanet, R., Misselbrook, T., Alfaro, M., Mora, M.L. 2010. Nitrogen losses under different cattle grazing frequencies and intensities in a volcanic soil of Southern Chile. Chil. J. Agric. Res. 70, 237–250.

Ostertag, R., DiManno, N.M. 2016. Detecting Terrestrial Nutrient Limitation: A Global Meta-Analysis of Foliar Nutrient Concentrations after Fertilization. Front. Earth. Sci. 24(23), 1–14.

Pan, I., Sen, S.K. 2013. Microbial and physico-chemical analysis of composting process of wheat straw. IJBT. 12, 120–128.

Panpatte, D.G., Jhala, Y.K., Shelat, H.N., Vyas, R.V. 2016 Nanoparticles: The Next Generation Technology for Sustainable Agriculture, in: Singh, D.P., Singh, H.B., Prabha, R. (Eds.), Microbial Inoculants in Sustainable Agricultural Productivity Vol. 2: Functional applications, Springer, India, pp. 289–300.

Panthapulakkal, S., Sain, M. 2015. The use of wheat straw fibres as reinforcements in composites, in: Faruk, O., Sain, M. (Eds.), Biofiber Reinforcements in Composite Material. Elsevier Ltd., pp. 423–453.

Park, M., Kim, C., Yang, J., Lee, H., Shin, W., Kim, S., Sa, T. 2005. Isolation and characterization of diazotrophic growth promoting bacteria from rhizosphere of agricultural crops of Korea. Microbiol. Res. 160, 127–133.

Paustian, K. Lehmann, J., Ogle, S., Reay, D., Robertson, G.P., Smith, P. 2016. Climate-smart soils. Nature. 532, 49–57.

Perez, J.J., Francois, N.J. 2016. Chitosan-starch beads prepared by ionotropic gelation as potential matrices for controlled release of fertilizers. Carbohydr. Polym. 148, 134–142.

Pingali, P.L. 2012. Green revolution: impacts, limits and the path ahead. PNAS, 109, 12302-12308.

Plaza, C., Senesi, N. 2009. The effect of organic matter amendment on native soil humic substances, in: Senesi, P.M., Huang, Xing, B. (Eds.), Biophysico-Chemical Processes Involving Natural Nonliving Organic Matter in Environmental System. IUPAC Series on Biophysico-Chemical Processes in Environmental Systems, Vol. 2. J. Wiley & Sons, Hoboken, N.J., pp. 147–181.

Pongpiachan, S., Kositanont, C., Palakun, J., Liu, S., Ho, K.F., Cao, J. 2015. Effects of day-of-week trends and vehicle types on $PM_{2.5}$-bounded carbonaceous compositions. Sci. Total Environ. 532, 484–494.

Puoci, F., Iemma, F., Spizzirri, U.G., Cirillo, G., Curcio, M., Picci, N. 2008. Polymer in agricultura: A review. Am. J. Agricult. Biol. Sci. 3(1), 299–314.

Qian, L., Hinestroza, J.P. 2004. Application of nanotechnology for high performance textiles. J. Textile Apparel Technol. Manage. 4, 1–7.

Ray, D.K., Mueller, N.D., West, P.C., Foley, J.A. 2013. Yield Trends Are Insufficient to Double Global Crop Production by 2050. PLOS ONE. 8(6), e66428.

Ray, D.K., Ramankutty, N., Mueller, N.D., West, P.C., Foley, A., 2012. Recent patterns of crop yield growth and stagnation. Nat. Commun. 3, 1293.

Riley, W.J., Ortiz-Monasterio I. and Matson, P.A. 2001. Nitrogen leaching and soil nitrate, nitrite, and ammonium levels under irrigated wheat in Northern Mexico. Nutr. Cycling Agroecosyst. 61, 223–236.

Risberg, K., Sun, L., Levén, L., Horn, S.J. and Schnürer, A. 2013. Biogas production from wheat straw and manure – Impact of pretreatment and process operating parameters. Bioresource Technology. 149, 232–237.

Roca-Pérez, L., Martínez, C., Marcilla, P., Boluda, R. 2009. Composting rice straw with sewage sludge and compost effects on the soil-plant system. Chemosphere. 75, 781-787.

Rochette, P., Angers, D.A., Chantigny, M.H., Gagnon, B. and Bertrand, N. 2008. N_2O fluxes in soils of contrasting textures fertilized with liquid and solid dairy cattle manures. Can. J. Soil Sci. 88, 175–187.

Rose, M.T., Perkins, E.L., Saha, B.K., Tang, E.C.W., Cavagnaro, T.R., Jackson, W.R., Hapgood, K., Hoadley, A.F.A., Patti, A.F. 2016. A slow release nitrogen fertilizer produced by simultaneous granulation and superheated steam drying of urea with brown coal. Chem. Biol. Technol. Agric. 3, 1–14.

Rose, R. 2002. Slow Release Fertilizers 101, in: Dumroese, R.K.; Riley, L.E.; Landis, T.D., technical coordinators. National Proceedings: Forest and Conservation Nursery Associations-1 999, 2000, and 2001. Proceedings RMRS-P-24. Ogden, UT. USDA Forest Service, Rocky Mountain Research Station, pp. 304–308.

Roy, I., Gupta, M.N. 2003. Smart polymeric materials: emerging biochemical applications.

Chem Biol. 10(12), 1161–71.

Rumpel, C., Crème, A., Ngo, P.T., Valesquez, G., Mora, ML, Chabbi, A. 2015a. The impact of grassland management on biogeochemical cycles involving carbon, nitrogen and phosphorus. Journal of Soil Science & Plant Nutrition. 15, 353–371.

Rumpel, C., Baumann, K., Remusat, L., Dignac, M.F., Barre, P., Deldicque, D., Glasser, G., Lieberwirth, I., Chabbi, A. 2015b. Nanoscale evidence of contrasted processes for root-derived organic matter stabilization by mineral interactions depending on soil depth. Soil Biology & Biochemistry 85, 82–88.

Saggar, S., Jha, N., Deslippe, J., Bolan, N.S., Luo, J., Giltrap, D.L., Kim, D.G., Zaman, M. and Tillman, R.W. 2013. Denitrification and N_2O:N_2 production in temperate grasslands: Processes, measurements, modelling and mitigating negative impacts. Science of the Total Environment. 465, 173–195.

Saggar, S., Luo, J., Giltrap, D. and Maddena, M. 2009. Nitrous oxide emissions from temperate grasslands: processes, measurements, modelling and mitigation, in: Sheldon, A.I., and E.P. Barnhart (Eds.), Nitrous oxide emissions research progress. Environmental Science, Engineering and Technology Series. Nova Science Publishers, New York, USA. pp. 1–66.

Sahu, P.K., Brahmaprakash, G.P. 2016. Formulations of Biofertilizers –Approaches and Advances, in Singh, D.P. Singh, H.B., Prabha R. (Eds.), Microbial Inoculants in Sustainable Agricultural Productivity Vol. 2: Functional Applications, Springer, pp. 179-198.

Said-Pullicino, D., Cucu, M.A., Sodano, M., Birk, J.J., Glaser, B., Celia, L. 2014. Nitrogen immobilization in paddy soils as affected by redox conditions and rice straw incorporation. Geoderma. 228–220, 44–53.

Sangeetha, D., 2012. Survival of plant growth promoting bacterial inoculants in different carrier materials. International Journal of Pharmaceutical and Biological Archive 3, 170–178.

Saranya, K., Santhana Krishnan, P., Kumutha, K., French, J. 2011. Potential for Biochar as an Alternate Carrier to Lignite for the Preparation of Biofertilizers in India. Int. Jr. of Agril., Env. and Biotech. 4(2), 167–172.

Sastry, R.K., Rashmi, H.B., Rao, N.H. 2011. Nanotechnology for enhancing food security in India. Food Policy. 36, 391–400.

Schlesinger, W.H., 1986. Changes in soil carbon storage and associated properties with disturbance and recovery, in: Trabalka, J.R., Reichle, D.E. (Eds.), The Changing Carbon Cycle: A Global Analysis. Springer-Verlag, New York, pp. 194–220.

Sekhon, B.S. 2014. Nanotechnology in agri-food production: an overview. Nanotechnol. Sci. Appl. 7, 31–53.

Selva Preetha, P., Subramanian, K.S., Sharmila Rahale, C. 2014. Sorption characteristics of nanozeolite based slow release sulphur fertilizer. Int. J. Dev. Res. 4, 225–228.

Selva Preetha, P. 2011. Nano-fertilizer formulation to achieve balanced nutrition in green gram. MSc. (Ag.) Thesis, Tamil Nadu Agricultural University, Coimbatore, India.

Senesi, N., Plaza, C. 2007. Role of humification processes in recycling organic wastes of various nature and sources as organic amendments. Clean Soil Air Water. 35(1), 26–41.

Sharpley, A.N., Meisinger, J.J., Power, J.F., Suarez, D.L. 1992. Root extraction of nutrients associated with long-term soil management. In: Hatfield, J.L., Stewart, B.A. (Eds), Limitations to Plant Root Growth. Vol.19. Adv. Soil Sci. Springer-Verlag New York, pp. 151–217.

Shaviv, A. 2005. Controlled release fertilizers, IFA International Workshop on Enhanced-

Efficiency Fertilizers, Frankfurt, International Fertilizer Industry Association, Paris, France.

Shukla, S.K., Kumar, R., Mishra, R.K., Pandey, A., Pathak, A., Zaidi, M.G.H., Sanjeev Srivastava, S.Kr., Dikshit, A. 2015. Prediction and validation of gold nanoparticles (GNPs) on plant growth promoting rhizobacteria (PGPR): a step towards development of nano-biofertilizers. Nanotechnology Reviews 4(5), 439–448.

Silva, W.O., Stamford, N.P., Silva, E.V.N., Santos, C.E.R.S., Freitas, A.D.S., Silva, M.V. 2016. The impact of biofertilizers with diazotrophic bacteria and fungi chitosan on melon characteristics and nutrient uptake as an alternative for conventional fertilizers. Sci. Hortic. 209, 236–240.

Silva, G.G.D., Couturier, M., Berrin, J.G., Buléon, A., Rouau, X. 2012. Effects of grinding processes on enzymatic degradation of wheat straw. Bioresour. Technol. 103, 192–200.

Singh, N., Agarwal, R., Awasthi, A., Gupta, P.K., Mittal, S.K., 2010. Characterization of atmospheric aerosols for organic tarry matter and combustible matter during crop residue burning and non-crop residue burning months in north-western region of India. Atmos. Environ. 44, 1292–1300.

Singh, S.K., Rai, M.K., Asthana, P., Pandey, S., Jaiswal, V.S., Jaiswal, U. 2009. Plant regeneration from alginate encapsulated shoot tips of Spilanthes acmella (L.) Murr. A medicinally important and herbal pesticidal plant species. Acta Physiol. Plant. 31, 649–653.

Smith, H., Schindler, D.W. 2009. Eutrophication science: where do we go from here? Trends Ecol. Evol. 24, 2001–2007.

Smith, P.D., Cai, M.Z., Gwary, D., Janzen, H., Kumar, P., McCarl, B., Ogle, S., O’Mara, F., Rice, C., Scholes, B., Sirotenko, O. 2007. Agriculture, in: Metz, B., Davidson, O.R., Bosch, P.R., Dave, R., Meyer, L.A. (Eds.), Climate Change 2007: Mitigation. Contribution of Working Group III To the 4th AR of IPCC. Cambridge University Press, Cambridge, UK/New York, USA, pp. 497–540. Stewart, W.M., Dibb, D.W., Johnston, A.E., Smyth, T.J. 2005. The Contribution of Commercial Fertilizer Nutrients to Food Production. Agron. J. 97, 1–6.

Smith, R.S. 1992. Legume inoculant formulation and application. Can. J. Microbiol. 38, 485–492.

Stewart, W.M., Dibb, D.W., Johnston, A.E., Smyth, T.J. 2005. The Contribution of Commercial Fertilizer Nutrients to Food Production. Agron. J. 97, 1–6.

Subramanian, K.S., Sharmila Rahale, C. 2013. Nano-fertilizers–synthesis, characterization and application, in: Adhikari, T., Kundu, S., Rao, A.S. (Eds.), Nanotechnology in soil science and plant nutrition, New India Publishing Agency, New Delhi, India, pp. 263–276.

Subramanian, K.S., Manikandan, A., Thirunavukkarasu, M., Sharmila Rahale, C. 2015. Nano-fertilizers for balanced crop nutrition, in: Rai, M., Ribeiro, C., Mattoso, L., Duran, N. Nanotechnologies in Food and Agriculture, Switzerland: Springer, pp. 69–80.

Sun, J., Peng, H., Chen, J., Wang, X., Wei, M., Li, W., Yang, L., Zhang, Q., Wang, W., Mellouki, A. 2016. An estimation of CO2 emission via agricultural crop residue open field burning in China from 1996 to 2013. J. Cleaner Prod.112 (4), 2625–2631.

Taladriz, A., Schwember, A. 2012. Cereales en las zonas centro-sur y sur de Chile ¿Qué hacer con los rastrojos?. Agronomía y Forestal. 46, 24–30.

Talebnia, F., Karakashev, D., Angelidaki, I. 2010. Production of bioethanol from wheat straw: an overview on pretreatment, hydrolysis and fermentation. Bioresour. Technol. 101(13), 4744–4753.

Tan, D.S., Jin, J.Y., Huang, S.W., Li, S.T., He, P. 2007. Effect of Long-Term Application of K Fertilizer and Wheat Straw to Soil on Crop Yield and Soil K Under Different Planting Systems. Agr. Sci. China. 6(2), 200–207.

Tao, S., Liu, J., Jin, K., Qiu, X., Zhang, Y., Ren, X., Hu, S. 2011. Preparation and characterization of triple polymer-coated controlled-release urea with water-retention property and enhanced durability. J. Appl. Polym. Sci. 120, 2103–2111.

Tarafdar, J.C., Raliya, R., Rathore, I. 2012. Microbial synthesis of phosphorus nanoparticles from Tri-calcium phosphate using Aspergillus tubingensis TFR-5. J. Bionanoscience. 6, 84–89.

Tesfay, T., Gebresamuel, G. 2016. Agronomic and economic evaluations of compound fertilizer applications under different planting methods and seed rates of tef [eragrostis tef (zucc.) Trotter] in northern Ethiopia. J. Drylands. 6(1), 409–422.

Thirunavukkarasu, M. (2014) Synthesis and evaluation of sulphur nano-fertilizers for groundnut. Ph.D. Thesis, Tamil Nadu Agricultural University, Coimbatore, India

Thompson, J.A. 1980. Production and quality control of carrier-based legume inoculants, in: Bergensen, F.J. (Ed.), Methods for Evaluating Biological Nitrogen Fixation. John Wiley & Sons Ltd, England, pp. 489–533.

Trenkel, M.E. 1997. Improving Fertilizer Use Efficiency: Controlled-Release and Stabilized Fertilizers in Agriculture," The International Fertilizer Industry Association, Paris. pp 151. International Fertilizer Industry Association (IFA). Paris, France.

Trivedi, P., Pandey, A., Palni, L.M. 2005. Carrier–based preparations of plant growth–promoting bacterial inoculants suitable for use in cooler regions. World J. Microbiol. Biotechnol. 21, 941–945

Udeigwe, T.K., Teboh, J.M., Eze, P.N., Stietiya, M.H, Kumar, V., Hendrix, J., Mascagni, H.J.Jr., Ying, T., Kandakj, T. 2015. Implications of leading crop production practices on environmental quality and human health. J. Environ. Manage. 151, 267–279.

UN, 2013. World population projected to reach 9.6 billion by 2050. United Nations (UN), Departament of Economy and social Affairs. <http://www.un.org/en/development/desa/news/population/un-report-world-population-projected-to-reach-9-6-billion-by-2050.html>(accessed 02.05.17)

USGS, 2016. Phosphate Rock. World Mine Production and Reserves. U.S. Geological Survey, Mineral Commodity Summaries (USGS). <https://minerals.usgs.gov/minerals/pubs/commodity/phosphate_rock/mcs-2016-phosp.pdf>(accessed 02.05.17)

Vadakattu, G., Paterson, J. 2006. Free-living bacteria lift soil nitrogen supply. Farming Ahead. 169, 40.

Valkama, E., Virkajärvi, P., Uusitalo, R., Ylivainio, K., Turtola, E. 2016. Meta-analysis of grass ley response to phosphorus fertilization in Finland. Grass Forage Sci. 71, 36–53.

Velásquez, G., Ngo, P.T., Rumpel, C., Calabi-Floody, M., Redel, Y., Turner, B.L., Condron, L.M., Mora, M.L. 2016. Chemical nature of residual phosphorus in Andisols. Geoderma. 271, 27–31.

Ventura, M., Alberti, G., Viger, M., Jenkins, J.R., Girardin, C., Baronti, S., Zaldei, A., Taylor, G., Rumpel, C., Miglietta, F., Tonon, G. 2015. Biochar mineralization and priming effect on SOM decomposition in two European short rotation coppices. GCB Bioenergy. 7, 1150–1160.

Veronica, N., Guru, T., Thatikunta, R., Narander Reddy, S. 2015. Role of Nano fertilizers in agricultural farming. Int. J. Environ. Sci. Technol. 1(1), 1–3.

Vistoso, E., Alfaro, M., Saggar, S., Salazar, F. 2012. Effect of nitrogen inhibitors on nitrous oxide emissions and pasture growth after an autumn application in volcanic soil. Chil. J. Agric. Res. 72(1), 133–139.

Wang, J., Liu, S., Qin, Y., Chen, X., Xing, R., Yu, H., Li, K., Li, P. 2016. Preparation and characterization of controlled-release fertilizers coated with marine polysaccharide derivatives. Chin. J. Oceanol. Limnol. http://dx.doi.org/10.1007/s00343-017-6074-9.

Wang, X., Lü, S., Gao, C., Feng, C., Xu, X., Bai, X., Gao, N., Yang, J., Liu, M., Wu, L. 2016. Recovery of Ammonium and Phosphate from Wastewater by Wheat Straw-based Amphoteric Adsorbent and Reusing as a Multifunctional Slow-Release Compound Fertilizer. ACS Sustainable Chem. Eng. 4(4), 2068–2079.

Wang, P. 2006. Nanoscale biocatalyst systems. Curr. Opin. Biotechnol. 17, 574–579.

Wei, T., Zhang, P., Wang, K., Ding, R., Yang, B., Nie, J., Jia, Z., Han, Q. 2015. Effects of Wheat Straw Incorporation on the Availability of Soil Nutrients and Enzyme Activities in Semiarid Areas. PLoS ONE 10(4), e0120994.

Wiedner, K., Rumpel, C., Pozzi, A., Maas, R., Steiner, C., Glaser, B. 2013. Chemical evaluation of chars produced by thermochemical conversion (gasification, pyrolysis and hydrothermal carbonization) of agro-industrial biomass on a commercial scale. Biomass Bioenergy 59, 264-278.

Wiedner, K., Fischer, D., Walther, S., Criscuoli, I., Favilli, F., Nelle, O., Glaser, B. 2015. Acceleration of Biochar Surface Oxidation during Composting? J. Agric. Food Chem. 63, 3830−383.

Wilson, M.A., Tran, N.H., Milev, A.S., Kannangara, G.S.K., Volk, H., Lu, G.H.M. 2008. Nanomaterials in soils. Geoderma. 146, 291–302.

Wu, L., Liu, M. 2008. Preparation and characterization of cellulose acetate-coated compound fertilizer with controlled-release and water-retention. Polym. Adv. Technol.

19, 785–792.

Wu, Z., Zhao, Y., Kaleem, I., Li, C. 2011. Preparation of calcium alginate microcapsuled microbial fertilizer coating Klebsiella oxytoca Rs–5 and its performance under salinity stress. Eur. J. Soil Biol. 47, 152–159.

Wurth, B. 2007. Emissions of engineered and unintentionally produced nanoparticles to the soil, MSc Thesis, ETH Zurich.

Xie, L., Liu, M., Ni, B., Wang, Y. 2012. New Environment-Friendly Use of wheat Straw in Slow-Release Fertilizer Formulations with the Function of Superabsorbent. Ind. Eng. Chem. Res. 51, 3855–3862.

Xie, L., Liu, M., Ni, B., Zhang, X., Wang, Y. 2011. Slow-release nitrogen and boron fertilizer from a functional superabsorbent formulation based on wheat straw and attapulgite. Chem. Eng. J. 167, 342–348.

Xu-mei, L., Zhao-bin, F., Fu-dad, Z., Shu-qing, Z., Xu-sheng, H. 2006. Preparation and testing of cementing and coating nano-subnanocomposites of slow/controlled-release fertilizer. Agric. Sci. China. 5, 700–706.

Yan, X., Yagi, K., Akiyama, H., Akimoto, H. 2005. Statistical analysis of the major variables controlling methane emission from rice fields. Global Change Biol. 11, 1131–1141.

Yang, X., Abraham, N.L., Archibald, A.T., Braesicke, P., Keeble, J., Telford, P.J., Warwick, N.J., Pyle, J.A. 2014. How sensitive is the recovery of stratospheric ozone to changes in concentrations of very short-lived bromocarbons? Atmos. Chem. Phys. 14, 10 431–10 438.

Yong, W., Jian, L., Xiaoyao, C. 2005. Biodegraded and polyurethane drape-formed urea fertilizer, J. Wuhan Univ. Technol. Mater. Sci. Ed. 20 (2), 12–14.

Zahid, M., Abbasi, M.K., Hameed, S., Rahim, N. 2015. Isolation and identification of indigenous plant growth promoting rhizobacteria from Himalayan region of Kashmir and their effect on improving growth and nutrient contents of maize (*Zea mays L.*). Front. Microbiol. 6(207), 1–10.

Zhang, J.P., Chen, H., Wang, A.Q. 2006. Study on superabsorbent composite—VII. Effects of organification of attapulgite on swelling behaviors of poly(acrylic acid-co-acrylamide)/sodium humate/organo-attapulgite composite. Polym. Adv. Technol. 17, 379–385.

Zhang, L., Liu, Y., Hao, L. 2016. Contributions of open crop straw burning emissions to $PM_{2.5}$ concentrations in China. Environ. Res. Lett. 11, 014014.

Zhang, L., Zheng, J., Chen, L., Shen, M., Zhang, X., Zhang, M., Bian, X., Zhang, J., Zhang, W. 2015. Integrative effects of soil tillage and straw management on crop yields and greenhouse gas emissions in a rice–wheat cropping system. Eur. J. Agron. 63, 47–54.

Zhang, S., Yang, Y., Gao, B., Wan, Y., Li, Y.C., Zhao, C. 2016. Bio-based Interpenetrating Network Polymer Composites from Locust Sawdust as Coating Material for Environmentally Friendly Controlled-Release Urea Fertilizers. J. Agric. Food Chem. 64 (28), 5692–700.

Zhao, L., Cao, X., Zheng, W., Scott, J.W., Sharma, B.K., Chen, X. 2016. Co-Pyrolysis of Biomass with Phosphate Fertilizers to Improve Biochar Carbon Retention, Slow Nutrient Release, and Stabilize Heavy Metals in Soil. ACS Sustainable Chem. Eng. 21, 409–414.

Table 1 Carriers and coating materials suitable for the development of smart fertilizers

Materials	Application	References
Brown coal, charcoal and biochar	*N retention*	Ding et al. (2010)
	Support material in polymer biodegradable formulations of controlled release fertilizer	González et al. (2015)
	Sustained-release fertilizer	Cai et al. (2016)
	Slow release N fertilizer	Rose et al. (2016)
	Biochar–fertilizer composite	Joseph et al. (2013)
	Inoculum carrier on PGPR bioformulations	Hale et al. (2015)
Perlite, vermiculite and bentonite, attapulgite	*In superabsorbent composites of controlled released fertilizers*	Wu and Liu (2008), Zhang et al. (2006)
	Carrier in bioformulations of bacterial inoculants	Daza et al. (2000); Khavazi et al. (2007); Ardakani et al (2010) Sangeetha (2012) Thompson (1980)
Peat	*N controlled fertilizer*	Araújo et al. (2017)
	Microbial carrier in bioformulations	Albareda et al (2008)
Alginate beads, calcium alginate gel	*Double coated control release fertilizer*	Wang et al. (2016)
	Microencapsulated bacterial fertilizer/ Encapsulation of microorganisms in Alginate-clay complexes	Trivedi et al. (2005); Wu et al. (2011) Fravel et al. (1985); Campos et al. (2014)
	Coating materials of controlled release fertilizers	
	Non environmental friendly polymers (Polyurethane, Polyacrylic acid etc)	Tao et al. (2011); Golden et al. (2011); Ibrahim and Jibril (2005) Jarosiewicz and Tomaszewska (2003); Donida and Rocha (2002)

Polymeric materials		Lan et al. (2011), da Rosa and Rocha (2012) Shaviv (2005); Rose (2002)
	Environmental friendly polymers; Syntethic (Polycaprolactone; ethyl celulose) and non-modified (Starch, agar)	Devassine et al. (2002); Niu and Li (2012); Yong et al. (2005); Mathews and Narine (2010); Jintakanon et al. (2008); Costa et al. (2013); Azeem et al. (2014)
Saw dust, locust saw dust and wood ashes	*Polymer-coated N fertilizer using bio-based polyurethane derived from liquefied locust sawdust*	Zhang et al. (2016)
	Carrier in bioformulations	Arora et al (2014)
Chitosan and Humics, Modified humic substances	*N controlled fertilizer* *Slow release N from modified humics*	Araújo et al. (2017) Kulikova et al. (2016)
	Carrier and bioprotector in bioformulations	Silva et al. (2016); Murphy et al. (2003)
Lignin, cellulosic materials, wheat bran, spent mushroom compost	*Coating in controlled release fertilizer/Pyrolized lignocellulosic material in slow-release N fertilizer*	Detroit et al. (1988); Mulder et al. (2011); Li et al. (2017)
	Carrier in blue green algal biofertilizer/ carrier of inoculant	Bahl and Jauhri (1986); Jackson et al. (1991); Dhar et al. (2007)

Table 2 Quality criteria of carriers for the development of smart fertilizers based on microbial inoculants adapted from Sahu and Brahmaprakash (2016).

Quality criteria of model carriers of Bioformulations	**References**
High water-holding and water-retention capacity and suitable for as many bacteria as possible/ Cost-effective	*Mishra and Dahich (2010)*
Free from lump-forming material/ Near sterile or easy to sterilize by autoclaving or by other methods like gamma irradiation/ Nearly neutral pH or easily adjustable and good pH buffering capacity	*Keyser et al. (1993)*
Available in adequate amounts/ Nontoxic in nature	*Bazilah et al. (2011)*
For carriers used for seed treatment, should assure the survival of the inoculants on the seed since normally seeds are not immediately sown after seed coating	*Muresu et al. (2003)*
For carriers that shall be used for seed coating, should have a good adhesion to seeds	*Hegde and Brahmaprakash (1992)*
No heat of wetting/ Easily biodegradable and nonpolluting/ Supports growth and survival of bacteria/ Amenable to nutrient supplement/ Manageable in mixing, curing, and packaging operations	*Smith (1992)*
Chemically and physically uniform	*Bashan (1998)*
The inoculant should be nontoxic, biodegradable and nonpolluting, and should minimize environmental risks such as the dispersal of cells to the atmosphere or to the ground water.	*Bashan (1998)*

Table 3. Nanofertilizers for plant nutrition. Modified from Subramanian et al. (2015)

Nutrients	Absorbent	Size	Reference
Nitrogen (N)	*Zeolite*	7-10 nm	*Mohanraj (2013)*
		20-30 nm	*Subramanian and Sharmila Rahale (2013)*
		60 nm	*Selva Preetha (2011)*
		87 nm	*Manikandan and Subramanian (2014)*
		200 nm	*Komarneni (2010)*
		420 µm	*Li et al. (2003)*
	Montmorillonite	35-45 nm	*Subramanian and Sharmila Rahale (2013)*
		50 µm	*Bortolin et al. (2013)*
	Carbon nanotubes, hydrogels, organic zeolitic complexes	40-80nm	*DeRosa et al. (2010); Liu et al. (2006); Leggo (2000); Foster (2013)*
Phosphorus (P)	*Zeolite*	25-30 nm	*Subramanian and Sharmila Rahale (2013)*
		60nm	*Selva Preetha (2011)*
		2-3µm	*Bansiwal et al. (2006)*
	Montmorillonite, bentominete and apatite	35-40nm	*Subramanian and Sharmila Rahale (2013); Liu and Lal. (2014)*
Potassium (K)	*Zeolite*	25-30 nm	*Subramanian and Sharmila Rahale (2013)*
	Montmorillonite	35-40 nm	*Subramanian and Sharmila Rahale (2013)*
NPK	*Nano-coating of sulfur layer chitosan*	78-100 nm	*Wilson et al. (2008)*
Nanocomposites	*Kaolinite*	30-80 nm	*Xu-mei et al. (2006)*
Sulfur (S)	*Zeolite*	60 nm	*Selva Preetha et al. (2014)*
		70-93nm	*Thirunavukkarasu (2014)*
		420µm	*Li and Zhang (2010)*

Zinc (Zn) iron (Fe) and Borom (B)	*Zeolite*	25–30 nm	*Subramanian and Sharmila Rahale (2013)*
		60 nm	*Selva Preetha (2011)*
		---	*Hu et al. (2016)*
	Montmorillonite	35-40 nm	*Subramanian and Sharmila Rahale (2013)*
	Nano Zn and Nano ZnO	35-20 nm	*Nair et al. (2010); Mahajan et al. (2011)*
PGPR microorganisms and biomolecules as enzymes	*Gold nanoparticles*	---	*Shukla et al. (2015)*
	Nanoclays (allophane)	100 nm	*Calabi-Floody et al. (2012, 2009); Menezes-Blackburn et al. (2011)*

Figure captions

Figure 1. Global phosphate rock reserves, data taken from US Geological Survey estimates (USGS, 2016)

Figure 2. Results from searches of the Scopus database of scientific documents (grey bars) and patents (grey lines) with the Title-abstract-keywords ‘nanotechnology AND agriculture’ (https://www.scopus.com, accessed March 24, 2017).

Figure 3. Schematic diagram of smart fertilizer effects in the soil-plant system

Figure 4. Schematic representation of smart delivery systems: a) advanced polymeric materials, degraded under external stimulus such as temperature, pH, and with water permeability to achieve a slow nutrient release; b) microorganism encapsulation