



The effects of balanced nutrient managements and nano-fertilizers effects on crop production in semi-arid areas

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Abstract

The common features of semi-arid region of West Asia and North Africa (WANA) are limited rainfall and harsh production environments. Soil of these regions are intensively tilled, they are low in organic matter content and consequently have weak structural stabilities. Furthermore water scarcity is one most limiting factor for plants growth in these areas. Although the conditions of soil and water are vastly different from place to place, all plants need permeable soils with high organic matter and sufficient concentrations of essential elements for an acceptable growth. Therefore a balanced fertilization strategy with macro and micronutrients in plant nutrition is very imperative for crop production in these areas. In this context, nano-technology can be one of the most powerful tools for improving the plant production in modern agriculture, and is estimated to become a driving economic force in the near future. It is predicted that nano-technology can boost agricultural production through the nano-formulations of agrochemicals and production of nano-fertilizers. During the last decade, some studies tried to examine the potential of nano-biotechnology to improve nutrients use efficiency and strategies that result in the design and development of efficient new nano-fertilizer delivery platforms for use at the farm level. A nano-formulated fertilizer presents unique physico-chemical properties, so that they can fulfill plant root requirements more efficiently in comparison with conventional fertilizers (in the form of salts or in bulk size). The gradual and regulated release of the nutrient could be through the process of dissolution and ion exchange reactions. Utilization of nano-fertilizers may increase solubility and dispersion of insoluble nutrients in soil, reduce nutrient immobilization (soil fixation) and increase their bio-availability. Between the nutrients the efficiency of nitrogen, phosphorus, zinc and iron are well documented in these regions. Besides, nanoparticles have unique physicochemical properties compared with bulk particles, so that their small size and propensity to cross barriers (cell wall and plasma membrane) facilitates effective absorption and their large specific surface can result in good level of interaction with intracellular structures. Consequently nano particles can be used to increase the supply of elements to plant shoots and foliage. Nano-silicon dioxide (nSiO₂) and nano-titanium dioxide (TiO₂) has exceptional optical and biological characteristics and has recently caught the attention of plant physiologists.

Keywords: beneficial nutrients, drought stress, foliar utilization, integrated application, nano-particles

Introduction

Nutrients managements through the application of fertilizer play a critical role in improvements of global food security in the past half century, especially under favorable climatic conditions (Ryan et al., 2012). Adequate and balanced plant nutrition is broad concept, involving the application of all the required elements for plant growth in accurate quantities and at the right time and is seen as having a crucial role in impressive developments in food production.

The West Asia and North Africa (WANA) region extends from Morocco in the west to Pakistan in the east and from Turkey to Ethiopia. The climate of the region is mainly Mediterranean, merging into a continental one inland and at higher elevations. Agricultural development in the WANA region is mostly influenced by arid and semi-arid climate which makes it the poorest region in the world in terms of water resources and soil condition. Although the region occupies about 14% of the total area of the world (18.5 million Km²) and supports about 10% of the world's population (almost 600 million), it possesses only about 2% of the total renewable water resources and this may affect the plant nutritional aspects (Roozitalab, 2000). Opportunities for expanding rainfed or irrigated areas in WANA are few. It is in this context that sustainable increases in rainfed agricultural productivity of grain,

pasture, forage and livestock are the key focus of ICARDA. Previous researches in semiarid region of WANA has established that multi-nutrient deficiency is the norm rather than an exception. The results of analysis of a large number of soil samples from farmers' fields in these area showed that generally the soils are low in organic matter, indicating general a high density of the soil and low physico-chemical quality of soil. Apart from deficiencies of the major nutrients nitrogen (N) and phosphorus (P), the deficiencies of secondary nutrient sulfur (S) and micronutrients especially zinc (Zn) and Iron (Fe) are widespread and indeed revealing (Rashid and Ryan, 2004; Sahrawat and Wani 2013; Sahrawat et al., 2013; Ryan, 2008). In these regions, low yield is partly due to the following factors: a) high nutrient turnover in soil-plant system coupled with low and imbalanced fertilizer use, b) deficiencies of micro and secondary nutrients, c) soil degradation due to salinization and alkalization as well as erosion, d) wide nutrient gap between nutrient demand and supply, and e) low fertilizer use efficiency (Rao and Reddy, 2010; Rayan et al., 2012). Soils of these areas often have low to medium available phosphorus (P), medium to high potassium (K), low iron (Fe), manganese (Mn) and zinc (Zn). Therefore, nutrient management is one of the important approaches in achieving high productivity of potato in this region.

However, the arid and semi-arid regions have not benefited from the "green revolution" as much as areas with acceptable soil moisture status. High yielding crop varieties express their full potential only when supplied with non-limiting amounts of water, fertilizers and usually large inputs of pesticides (FAO, 1998). In arid and semi-arid regions, crop responses to inputs such as fertilizers have generally been low and unprofitable to the farmer. Understandably, input levels remain low and yields are not increasing. The problem of increasing crop productivity in these regions is widely recognized as difficult.

Soil of these area have very low organic matter, for that reason it seems that more favorable results can be achieved by adoption of the best management practices (Janmohammadi et al., 2014). Among the agronomical practices, the advantages of application of plant residues or farmyard manure in improving the physicochemical properties of soil have been well studied. Soil of semi-arid regions are intensively tilled, they are low in organic matter content and consequently have weak structural stabilities (Shirani et al., 2002). In this area removal of straw for animal feed is common and this may indicating the importance of adding manure when straw is removed. Preservation of soil organic carbon is essential for the long-term productivity of dryland agro-ecosystems and it can improve the soil structure, water infiltration, water holding capacity, and bulk density, and it sustains microbial activity. It is has been showed that of farmyard manure can supplies all major macronutrients (N, P, K, Ca, Mg, S) essential for plant development, as well as micronutrients (Fe, Mn, Cu and Zn). Also it can sustain soil nutrient concentration and stimulate various features of soil fertility (Satyanarayana et al., 2002).

Trace elements are imperative to world agriculture and play a vital role in human health. Between the micronutrients, the deficiencies of Zinc (Zn), iron (Fe) and manganese (Mn) have become the most distinguished yield-limiting factors in semi-arid region of West Asia and North Africa (WANA) and are partly responsible for low food nutrition (Ryan, 2008). In relation to the importance of micronutrients is interesting to note that over 2 billion people across the world suffer from micronutrient deficiencies and hidden hunger (Tulchinsky, 2010). However, the availability of micronutrients is greatly depends on soil pH and high pH ties up trace elements such as iron, manganese, zinc, and others, leading to micronutrient deficiencies. Plant nutrition is a difficult subject to understand completely, partially because of the variation between different plants and even between different species or individuals of a given clone. Elements present at low levels may cause deficiency symptoms, and toxicity is possible at levels that are too high. Furthermore, deficiency of one element may present as symptoms of toxicity from another element, and vice versa. An abundance of one nutrient may cause a deficiency of another nutrient (Huner and Hopkins, 2009).

Although fertilizers have a fundamental role in improving the productivity across the spectrum of crops, the nutrient use efficiencies of conventional fertilizers is relatively low (Subramanian et al., 2015). Given the soil statues of semi-arid environments, it seems that one way of improving the low productivity of crops can be application of new generation of micronutrients fertilizers. Derosa et al. (2010) suggested that nano-fertilizers, nanoparticles based fertilizer, are one potential output that could be a major innovation for agriculture; the large surface area and small size of the nano-materials could allow for enhanced interaction and efficient uptake of nutrients for crop fertilization. This review focused on the importance of macro and micronutrients on performance of crop under semi-arid region and highlighted the balanced nutrition. Also characterizes of nano-fertilizers were compared with conventional bulk fertilizer.

Nitrogen

Establishing a benchmark for N is as important as for water. Nitrogen is very important element due it is a major component of chlorophyll, the compound by which plants use sunlight energy to produce sugars from water and carbon dioxide (i.e., photosynthesis). In plant tissue, the nitrogen content ranges from 1 and 6%. It is also a major component of amino acids, the building blocks of proteins. Without proteins, plants wither and die. Some proteins act as structural units in plant cells while others act as enzymes, making possible many of the biochemical reactions on which life is based (Marschner, 2011).

Nitrogen (N) fertilization of semiarid soil to increase shoot growth is neither widely recommended nor extensively applied. However, utilization of nitrogen fertilizer, could have an obvious and immediate impact on crop yields. Nevertheless, responses of crop in this area to N have varied considerably, often with conflicting results, which can be attributed to the seasonal rainfall and the crop rotation, which highly influence soil N availability (Ryan et al., 2010). Much can be done to increase the efficiency of N fertilizer for dryland crops with innovative placement and timing of application. For example, concentrated bands of ammonia-based fertilizer inhibit nitrification and hence denitrification and leaching. Topdressing as a tactical response to a favourable season or a forecast rain event can greatly increase yield and protein responses compared to the practice of strategic or regular application according to a blanket recommendation.

It have been reported that Nitrogen consistently increased dry matter and grain yields in either year, generally being significant up to 80 kg ha⁻¹. There were significant differences observed among varieties, as well as interactions of varieties with years. Crop N uptake varied with varieties and increased with increasing fertilizer. N Recovery was variable and generally less than 50%. For optimum level of nitrogen fertilizer it has been recommend that N fertilization of cereal in semi-arid region on shallow soils, where root growth and moisture holding capacity are limited, should be promoted. It seems that competition for applied N between root systems and the microbial populations on these low organic matter, semiarid soils may also interfere with the plant response to N (Root-Bernstein et al., 2014).

Most of the cropping in the arid and semi-arid areas continues to be under rainfed conditions, and a majority of the farmers are small farmers with meager resources. Because of the poor resource base-both physical and socioeconomic the crop yields are low and production is unstable due to variable weather conditions. Therefore there are significant interaction between soil water statues and nitrogen. The interaction between water and nitrogen was described by Van Keulen (1981) as follows: 'Growth under nitrogen deficient conditions implies a slower rate of accumulation of dry matter, which, combined with a different distribution of the material, leads to a prolonged period in which vegetation does not cover the soil completely. Under such conditions, direct soil evaporation is longer than under non-deficient conditions where a closed canopy is reached earlier. The amount of moisture available for transpiration is thus smaller under nitrogen deficient conditions. Nitrogen (N) use efficiency increases with increasing rainfall and is influenced by crop rotation. Under rainfed conditions, modest N losses by volatilization can occur. Leaching losses are usually minimal (Ryan et al., 2012).

The majority of plant-available nitrogen is in the inorganic forms NH₄⁺ and NO₃⁻ (sometimes called mineral nitrogen). Ammonium ions bind to the soil's negatively charged cation exchange complex (CEC) and behave much like other cations in the soil (Havlin et al., 2005). Nitrate ions do not bind to the soil solids because they carry negative charges, but exist dissolved in the soil water, or

precipitated as soluble salts under dry conditions. Because applied N has such a rapid and cosmetic effect on crops, some farmers are tempted to apply excess (Ryan et al., 2010). Over-fertilized crops that experience a terminal drought frequently produce lower yields, as much as 25% of a crop yielding 4 t ha⁻¹. The symptoms are early maturity, yield that is low in relation to the amount of vegetative growth and pinched grain of high protein content. The disorder has been widely recognized in Australia for a century and is known as 'haying-off'. Similar symptoms have been reported from many other dryland cropping regions.

The presumed cause of the yield decrease is reduced stored soil water at the time of flowering because of extra vegetative growth. The risk of haying-off is a major disincentive for farmers to supply sufficient N for crops to achieve their water-limited yield potential, so that, in a variable environment, crops are under fertilized in the favorable seasons. Nodulating bacteria from the family Rhizobiaceae are common in the semi-arid region but it appears that they have a smaller share in the production of nitrogen when compared with well irrigated condition. Data on the dynamics of rhizobial populations in such areas have shown that (1) the naturalized rhizobium population is very small and, by themselves, do not promote proper nodulation and, (2) the inoculant rhizobia do not persist between crops (Martins et al., 2003).

It is consistent with conclusion of (Ryan et al. 1985; Ryan et al., 2012) who stated that In contrast to other regions, non-conventional materials with various trade names, and purporting to be based on 'enzymes', 'growth regulators' and 'biofertilizer', are being marketed to some extent despite the evidence of limited effectiveness. However, application of nitrogen biofertilizers increased yield and yield components of barley under semi-arid area in west of Middle East.

It has been revealed that grain yield and biomass yield significantly increased by application of biofertilizer which account important benefit, causing decreasing in the inputs of production because of economizing much money to chemical fertilizers and increasing in yield and biological yield. Application of Supernitroplass biofertilizer with Phosphate barvar2 treatment has the highest seed yield (7.6 ton/ha) and non-application of biofertilizers treatment has the Pishtaz cultivar has the lowest seed yield (6.3 ton/ha) (Azimi et al, 2013). It seems that the efficiency of nitrogen biofertilizers strictly depended on soil and weather condition. Integrated application of biofertilizer can improve their efficiency.

Between 50 and 70% of the nitrogen applied using conventional fertilizers — plant nutrient formulations with dimensions greater than 100 nm is lost owing to leaching in the form of water soluble nitrates, emission of gaseous ammonia and nitrogen oxides, and long-term incorporation of mineral nitrogen into soil organic matter by soil microorganisms (Sekhon, 2014). Numerous attempts to increase the NUE have so far met with little success, and the time may have come to apply nanotechnology to solve some of these problems. It seems that nutrient delivery systems that exploit the nano-scale porous domains on plant surfaces can be developed. The potential use of nanotechnology to improve fertilizer formulations (DeRosa et al., 2010).

A nano-fertilizer refers to a product that delivers nutrients to crops in one of three ways. The nutrient can be encapsulated inside nano-materials such as nanotubes or nano-porous materials, coated with a thin protective polymer film, or delivered as particles or emulsions of nano-scale dimensions. Owing to a high surface area to volume ratio, the effectiveness of nano-fertilizers may surpass the most innovative polymer-coated conventional fertilizers, which have seen little improvement in the past ten years (Naderi and Danesh-Shahraki, 2013).

Phosphorous

Phosphorus is one of 17 nutrients essential for plant growth. Its functions cannot be performed by any other nutrient, and an adequate supply of P is required for optimum growth and reproduction. Phosphorus is classified as a major nutrient, meaning that it is frequently deficient for crop production and is required by crops in relatively large amounts. Phosphorus is an essential nutrient both as a part of several key plant structure compounds and as a catalysis in the conversion of numerous key biochemical reactions in plants (Barker and Pilbeam, 2015). Phosphorus is noted especially for its role in capturing and converting the sun's energy into useful plant compounds. Phosphorus is a vital component of DNA, the genetic "memory unit" of all living things. It is also a component of RNA, the compound that reads the DNA genetic code to build proteins and other compounds essential for plant structure, seed yield and genetic transfer (Marschner, 2011). The structures of both DNA and RNA are linked together by phosphorus bonds. Phosphorus is a vital component of ATP, the "energy unit" of plants. ATP forms during photosynthesis, has phosphorus in its structure, and processes from the beginning of seedling growth through to the formation of grain and maturity. This element is essential for the general health and vigor of all plants. Some specific growth factors that have been associated with phosphorus are: stimulated root development, increased stalk and stem strength, improved flower formation and seed production, more uniform and earlier crop maturity, increased nitrogen N-fixing capacity of legumes, improvements in crop quality, increased resistance to plant diseases and supports development throughout entire life cycle (Mengel and Kirkby, 2012).

Crop response to phosphorus depends on the availability of phosphorus in the soil solution and the ability of the crop to take up phosphorus. The availability of phosphorus in the soil solution has already been discussed. The ability of a plant to take up phosphorus is largely due to its root distribution relative to phosphorus location in soil (Beegle and Durst, 2002). Because phosphorus is very immobile in the soil, it does not move very far in the soil to get to the roots. Diffusion to the root is only about 1/8 of an inch per year, and relatively little phosphorus in soil is within that distance of a root. Thus, the roots must grow through the soil and basically go get the phosphorus the plant needs (Havlin et al., 2005). Therefore root growth is very important to phosphorus nutrition. Any factor that affects root growth will affect the ability of plant to explore more soil and get adequate phosphorus. Soil compaction, herbicide root injury, and insects feeding on roots can all dramatically reduce the ability of the plant to get adequate phosphorus (Fageria et al., 2010). Young seedlings can suffer from phosphorus deficiency even in soils with high available phosphorus levels because they have very limited root systems that are growing very slowly in cold, wet, early early-season soil conditions. This is why some crops respond to phosphorus applied at planting in starter fertilizers even in relatively high phosphorus soils (Beegle and Durst, 2002). The rainfall of agricultural areas of WANA varies from 300 to 700 mm. Although in absolute terms rainfall is low only in the northern half of the desert margins, the high inter-annual variability associated with erratic distribution of rainfall both in location and during the growing season, constitute major limitations for agricultural production. Continuous and intensive cropping without restoration of the soil fertility has depleted the nutrient base of most of the soils (Bationo and Kumar, 2002). Phosphorus deficiency is a major constraint to crop production in WANA region and response to N is substantial when moisture and P are non-limiting. Its application is necessary to conserve the resource base as well as to increase short-term production. It has been revealed that the major problems under semiarid condition in Northwest Pakistan are (1)

low soil moisture and (2) low soil fertility especially P unavailability (Amanullah et al., 2012). Unfortunately under semiarid condition plants are not able to get the required P (Aziz et al., 2005; Shenoy and Kalagudi, 2005) due to high soil pH and low organic matter (Iqbal et al., 2015). Deficiency of soil P is one of the important factors restricting maize growth and yield in semiarid climates (Gyaneshwar et al., 2006). Phosphorus adsorption under calcareous soils (Johnston, 2001; Ibriki et al., 2005; Zakirullah and Khalil, 2012) in semiarid condition (Hao et al., 2002; Gill et al., 2004; Aziz et al., 2005) decrease availability of P for the crop plants. Investigating proper P rates for improving crop productivity is of significant importance under semiarid climates (Amanullah et al., 2012).

The conservation of the resource base is an environmental issue and is not only a necessity for WANA region but is also a global concern. Despite widespread and acute P deficiencies in west WANA soils, very little P fertilizer is used by farmers. Plants absorb mainly inorganic phosphorus (Pi) but the organic phosphorus (Po) is also an important reservoir for plant nutrition (Suñer et al., 2014). Some soil studies have shown P deficiencies in the semiarid regions, and that extractable P content is lower due to soil pedogenetic characteristics and the agricultural history of the region. The P compounds strongly bound to soil fine fraction have been shown to be unaffected by tillage treatments (Rosell et al., 2000). Phosphorus in the coarse fraction, however, sharply decreases due to cultivation.

There are considerable interaction between P and other elements. Boulal et al. (2014) reported that phosphorus fertilization increased N and P concentrations in stems and leaves with a significant effect in the case of P concentration in leaves. However stems and leaves K concentration were not affected by phosphorus fertilization. Comparing the concentration of macronutrients in the stems and the leaves, results showed that stem N content was lower than leaves N content. Similar results were reported by Hua et al (2012). However the difference between P and K contents in the stems and the leaves depends on P fertilizer treatment. P content was similar in stems and leaves under P fertilizers plots, however without P fertilizers P content was 36% lower in the leaves compared to the stems.

Diverse group of soil microorganisms are involved in solubilizing insoluble P complexes enabling plants to easily absorb P (Tripura et al., 2005). Many kinds of soil bacteria (*Bacillus*, *Pseudomonas*, *Rhizobium*, and *Enterobacter*) and fungi (*Aspergillus* and *Penicillium*) have the skill to change insoluble form of P in the soil into soluble form through releasing organic acids such as formic acids, propionic acids, acetic acids, fumaric acids, and succinic acids (Walpolá and Yoon, 2012). The use of bio-fertilizers such as phosphate solubilizing bacteria as inoculants with the seed increases P availability and uptake by the plants because the beneficial microbes produce of organic acids which reduce soil pH (Rodríguez et al., 2006). These acids reduce the pH and bring the dissolution of bound forms of phosphate (Walpolá and Yoon, 2012). Beneficial microorganisms are important not only for the reduction of the quantity of chemical fertilizers and environment friendly (Hafeez et al., 2002) but also increased crop productivity (Afzal et al., 2005; Canbolat et al., 2006; Gyaneshwar et al., 2006; Yasmin and Bano, 2011). Because of phosphorus immobility and soil fixation, placement of fertilizer phosphorus can affect its availability to plants. Fertilizer that is broadcast and plowed down is mixed uniformly with a large amount of soil. Thus, the probability of root contact with the fertilizer is maximized. At the same time, though, added fertilizer is in greater contact with absorbing surfaces in the soil, thereby increasing phosphorus fixation. When the fertilizer is applied as a concentrated band,

contact with the soil and thus fixation is minimized (Beegle and Durst, 2002).

Sulfur

Sulfur is one of the 16 elements essential to crop production. It is typically considered a secondary macronutrient (along with calcium and magnesium), but is essential for maximum crop yield and quality. Sulfur is often ranked immediately behind nitrogen, phosphorus, and potassium in terms of importance to crop productivity (Barker and Pilbeam, 2015). Sulfur is a component of the amino acids cysteine and methionine making it essential for protein synthesis in plants. Plants contain a large variety of other organic sulfur compounds, such as glutathione, sulfolipids and secondary sulfur compounds which play an important role in physiology and protection against environmental stress and pests. Sulfur fertility has historically not been a major concern for growers on most soils, as soil organic matter, atmospheric deposition, manure application and incidental sulfur contained in fertilizers have typically supplied sufficient sulfur for crop production. However, reductions in the amount of sulfur contributed by these factors combined with increased sulfur removal with greater crop yields have made sulfur deficiencies more common (Marschner, 2011).

Sulphur (S) is an essential plant nutrient required by all crops for optimum production. Plants take up and use S in the sulphate ($\text{SO}_4\text{-S}$) form, which like nitrate ($\text{NO}_3\text{-N}$), is very mobile in the soil and is prone to leaching in wet soil conditions, particularly in sandy soils (Marschner, 2011). Sulphur deficiencies are becoming increasingly common in semi-arid region. Deficiencies can be easily corrected with fertilizers containing sulphate (Fageria et al., 2010). Generally, S is the third most limiting soil nutrient in cereal, oilseed and forage crop production in Alberta. It is third only to nitrogen (N) and phosphorus (P) in fertilizer use in semi-arid area (Havlin et al., 2005).

Several interactions exist between nutrient pools and they are usually described as nutrient “transformations” or nutrient “cycles”. The concentration of H^+ ions in the soil solution is expressed in terms of pH as a measure of potential acidity and has a pronounced effect on transformations, and therefore pool size of soil nutrients (Marschner, 2011). Environmental conditions (e.g. humid or arid climatic conditions) and cultivation techniques (e.g. paddy field cultivation) modify availability of plant nutrients directly and indirectly through altering soil pH conditions. Native chemical and mineralogical properties of soils, environmental conditions, and cultivation practices determine the pool size and extent of transformations of sulfur and chloride in soils and, therefore, their availability to plants (Kleinhenz, 1998).

Greater or smaller availability of these nutrients can exert positive or detrimental effects on plant growth and crop performance. A large proportion of the cultivated lands WANA region consist of calcareous soils. Such soils have high levels of calcium and pH that cause nutrient deficiencies. Sulfur oxidation in soils is an effective process in the reclamation of saline soils in addition to providing the sulfur needs of plants. Sulfuric acid is an appropriate substance to reduce the pH of soil and irrigation water, but since its handling needs special precautions, application of sulfur itself is recommended (Hemmaty et al., 2012). The solubilizing effect of elemental sulfur (S) on P, Fe and Zn and other micronutrients in the intimate contact with them has been demonstrated in soil. Rego et al. (2007) reported that sulfur application can improve the absorption of other nutrient in semi-arid region. They showed that applications of S, B and Zn also significantly increased the uptake of N, P, K, S, B, and Zn in the crop biomass. Results show widespread deficiencies of S, B, and

Zn under dryland agricultural conditions; results also show that the nutrient deficiencies can be diagnosed by soil testing. Janmohammadi and Sabaghnia (2016) investigated the effects of application of sulfur (0, 15, 30 kg ha⁻¹ sulfur) and three nano-chelated micronutrients (nano-Zn, nano-Fe and nano-Mn) on yield and some morphological traits of chickpea, in a semi-arid region of Iran. Day to maturity (DM), first pod height (FPH), primary branch per plants (PBP), secondary branch per plant (SBP), number of pods per plant (NPP), number of empty pod per plant (EPP), number of seeds per plant (NSP), seed yield (SY), straw yield (ST), biological yield (BY), harvest index (HI), and 1000 seed weight (TSW) significantly affect by both factors. The best performance was obtained by integrated application of 30 kg ha⁻¹ sulfur and nano-Zn.

The effect of sulfur on oil pH depends on the presence of microorganisms, particularly *Thiobacillus spp.* Applying acidifying materials such as elemental sulfur is regarded as a possible and economic way to improve nutrient availability and plant growth in calcareous and alkali soils. In this regards Hemmaty et al. (2012) reported that the highest rate of available phosphorous was obtained when 2 kg

sulfur + organic material + *Thiobacillus* bacteria was used, which was 53.9 percent more than the control treatment. However, this increase may not be attributed to the association of *Thiobacillus* with organic matter in this treatment because these bacteria are mainly obligate chemolithotrophs which use CO₂ as the major carbon source under all growth conditions and organic materials seem not to play an important role in their metabolism.

Zinc

Zinc is essential for the normal healthy growth and reproduction of plants, animals and humans and when the supply of plant-available zinc is inadequate, crop yields are reduced and the quality of crop products is frequently impaired (Barker and Pilbeam, 2015). In plants, zinc plays a key role as a structural constituent or regulatory co-factor of a wide range of different enzymes and proteins in many important biochemical pathways and these are mainly concerned with: carbohydrate metabolism, both in photosynthesis and in the conversion of sugars to starch, protein metabolism, auxin (growth regulator) metabolism, pollen formation, the maintenance of the integrity of biological membranes, the resistance to infection by certain pathogens. When the supply of zinc to the plant is inadequate, one or more of the many important physiological functions of zinc is unable to operate normally and plant growth is adversely affected (Alloway, 2008). The changes in plant physiological mechanisms brought about by a deficiency of zinc can result in the plant developing visible symptoms of stress which might include one or more of the following: stunting (reduced height), interveinal chlorosis (yellowing of the leaves between the veins), bronzing of chlorotic leaves, small and abnormally shaped leaves and/or stunting and rosetting of leaves (where the leaves form a whorl on shortened stems). These different types of symptoms vary with plant species and are usually only clearly displayed in severely deficient plants. In cases of marginal deficiency, plant yields can often be reduced by 20% or more without obvious visible symptoms. This is called 'hidden', 'latent' or 'subclinical' deficiency. Zinc-deficient soils causing hidden deficiency may remain undetected for many years unless soil or plant diagnostic tests are carried out (Barker and Pilbeam, 2015).

Responses of chickpea (*Cicer arietinum*) cultivars (Jam from Kabuli type and Pirooz from Desi type) to Biosuper (The mixture of *Azospirillum*, *Azotobacter*, *Basillus subtilis* and *Pseudomonas fluorescens*) inoculation as bio-fertilizer and micro-nutrient (FeEDDHA and ZnSO₄) fertilization were studied under semi-arid

condition of Iran (Janmohammadi et al., 2012). The best result was achieved through ZnSO₄ application concomitant with bio-fertilizer inoculation. Future more results obtained from current study indicated that Kabuli type of chickpea was more responsive than Desi type against bio-fertilizer inoculation and micro-nutrients application.

Intense temperature and low organic matter content in semi-arid region leads to poor soil fertility (Rego et al., 2003) and low nitrogen status.

Extensive studies with cereals by Cakmak (2004) in Turkey showed that the problem of Zn deficiency was widespread, with serious implications not only for crop production, but also human health. Research on Zn in forage legumes, suggest that deficiency may also be common in Syria. Low levels of soil organic matter can exacerbate the problem, as does the transition from superphosphate to more concentrated and forms, with less Zn as an incidental contaminant. Soil surveys and the use of soil information from existing data bases can help indicate areas where micronutrient deficiencies are likely to occur.

The deficient nutrient status decreases the availability of nutrient in food grain and ultimately reduces availability nutrient rich food to rural people. The reduce availability of nutrient in grain particularly micronutrient leads to increase micronutrient malnutrition. There are several approaches adopted to eliminate micronutrient malnutrition. The ferti-fortification of Zn is a promising and cost-effective measure to increase Zn concentration (agronomic bio-fortification) in cereal grain to address Zn malnutrition (Rakshit et al., 2013; Singh and Prasad, 2014). Application of nitrogen fertilizer positively affect Zn concentrations in wheat grain and also reported that change in mineral status of soil which will affect the nutrient concentration of plant (Germ et al., 2013). Kiekens (1980) also studied the adsorption of zinc on a calcareous soil and found that the reaction was not reversible due to some of the zinc being irreversibly fixed by the soil. These findings on the fixation/sorption of zinc on calcium carbonate have some important implications for the behaviour of zinc in calcareous soils. Some of the worst zinc deficiency problems in crops occur on calcareous soils in arid and semi-arid regions of the world

Iron

Iron is the most important metal and one of the major constituents of the lithosphere. Its average content of the Earth's crust is about 5%. The global terrestrial abundance of Fe is calculated to be around 4.5% and it is not considered a trace element in rocks and soils. However, Fe plays a special role in the behavior of several trace elements and is in the intermediate position between macro- and micronutrients in plants, animals, and humans (Kabata-Pendias, 2011).

The geochemistry of Fe is very complex in the terrestrial environment and is largely determined by the easy change of its state of oxidation in response to physicochemical conditions. Fe is very reactive chemically and is similar in behavior to other metals, especially to Co and Ni. Its behavior is also closely linked to the cycling of O, S, and C. In variable environmental conditions, Fe reveals various characteristics and can be siderophilic, chalcophilic, or lithophilic. In most minerals formed near the Earth's crust surface, Fe occurs as the ferric (Fe³⁺) ion, whereas in deeper rocks the ferrous (Fe²⁺) ion predominates. However, it is known to occur also at +4 and +6 oxidation states in various complexes and in specific environments. Fe is a catalyst to chlorophyll biosynthesis and acts as an oxygen carrier and aids in respiratory enzyme systems. Like Zn, Fe is not efficiently translocated within the plant, so deficiency symptoms first show up on younger leaves. The classic Fe symptom is interveinal chlorosis,

a pale green to yellow leaf with sharp distinction between green veins and yellow interveinal tissues (Monreal et al., 2015).

Under Fe limitation, plants employ a set of responses to boost Fe mobilization and uptake from soil. Fe absorption by plants is based on two strategies (Kobayashi and Nishizawa, 2012). Non-grass crops like bean use the first strategy, which is based on the reduction of Fe via the release of protons through the root membrane to acidify the surrounding environment and solubilize Fe, and also via the reduction of Fe⁺³ to Fe⁺² by ferric reductase present in root membranes, an enzyme that also catalyzes the reduction of Cu (Santi et al., 2005; Kim and Guerinot, 2007). One unit drop in pH increases the solubility of Fe by 1,000-fold. Gramineous plants use the second strategy involving the chelation of Fe by phytosiderophores (PS), such as mugineic acids, which are exuded by roots to bind Fe with high affinity for plant uptake (Conte and Walker, 2011).

Given the importance of chickpea in Mediterranean-type environment, it seems that one way of improving the low productivity of chickpea can be application of new generation of micronutrients fertilizers. Derosa et al. (2010) suggested that nano-fertilizers, nanoparticles based fertilizer, are one potential output that could be a major innovation for agriculture; the large surface area and small size of the nano-materials could allow for enhanced interaction and efficient uptake of nutrients for crop fertilization. Furthermore, nano-fertilizers could be more soluble or more reactive than bulk conventional fertilizers. Also this modern fertilizer can exactly release their active ingredients in responding to environmental triggers and biological requirements (Monreal et al., 2015). Subsequently, supply of plant nutrients as nano-sized active particles could be perhaps predicted to have a considerable effect on fertilizer efficiency and crop productivity.

Conclusions and future perspectives

The key is to combine nutrient inputs with crop management practices that increase the supply of water to the crop. The steps to maximize water use by the crop are known in principle. The long-term sustainability of many existing cropping systems in semi-arid environments is questionable because of imbalanced nutrition and water scarcity. Crop phosphorus nutrition depends on the ability of the soil to replenish the soil solution with phosphorus as the crop removes it and on the ability of the plant to produce a healthy and extensive root system that has access to the maximum amount of soil phosphorus. There are many good fertilizer sources of phosphorus, and manure is an excellent source of phosphorus for crops. Application of fertilizer and manure must be done to maximize the chemical and physical availability of the phosphorus to crops. The results of analysis of a large number of soil samples from farmers' fields in the semi-arid tropical regions of India showed that generally the soils are low in organic carbon (C), indicating general poor soil health. Apart from deficiencies of the major nutrients nitrogen (N) and phosphorus (P), the deficiencies of secondary nutrient sulfur (S) and micronutrients especially zinc (Zn) and iron (Fe) are widespread and indeed revealing. The results from a large number of on-farm follow-up trials comparing soil test-based balanced nutrition with farmers' inputs showed that balanced plant nutrient management significantly increases crop productivity and enhances grain and straw quality of crops. Evaluations showed that sulfur fertilization in calcareous and alkaline soils can significantly reduce pH and improves soil properties. In calcareous soils the intake of nutritional elements by the plant are impaired which result in the reduction of yield and productivity. Besides, the plants do not efficiently benefit from the fertilizers applied to the soil. In this study, sulfur fertilization improved soil properties and intake of the nutrients. By

amelioration of soil pH, concentration of phosphorus and iron in the soil, chlorophyll content in the leaves, the concentration of P, Fe and Zn in the leaves. Use of soluble and nano-chelated micronutrient sources is largely confined to high-value in crops. Overall, balanced nutrient management significantly increases yield of various crops compared to those with farmers' inputs in semi-arid region. Clearly, there is an opportunity for nanotechnology to have a profound impact on energy, the economy and the environment, by improving fertilizer products. New prospects for integrating nanotechnologies into fertilizers should be explored, cognizant of any potential risk to the environment or to human health.

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