TOWARDS FERTILISERS FOR IMPROVED UPTAKE BY PLANTS

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TOWARDS FERTILISERS FOR IMPROVED UPTAKE BY PLANTS

by

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SUMMARY.

Meeting human needs within the ecological limits of our planet calls for continuous reflection on and redesigning of our agricultural practices. Several transformations that drastically changed the course of agriculture have been realised over the past century including dramatic increases in yields, reduced labour requirement, optimised use efficiency of inputs and chain logistics, and spatial integration of agricultural and natural functions within the landscape, caused by driving forces such as growing ecological insights, technological innovations and societal change.

The discovery and use of mineral fertilisers has been one of the driving forces for increased crop yields and agricultural productivity. These benefits come however at an environmental cost and have not yet been effectively used to lift many poor farmers out of poverty. Any imbalanced composition of nutrients contained in fertilisers could also cause reduced nutritional quality of crop produce. Agronomic practices to apply existing fertilisers at the right time, the right place, in the right amount, and of the right composition can improve the use efficiency of fertilisers. Yet, the overall progress to reduce the negative side effects is insufficient for the desired transformation in agriculture. There have been no fundamental reflections about the role and functioning of mineral fertilisers over the past four decades or more, and little investment is made in mineral fertiliser research and development.

It is for this reason that the Virtual Fertilizer Research Centre was established to foster the creation of the next generation of fertilisers and production technologies in order to help feed the world's growing population and provide sustainable increases in global food production. The centre is virtual in the sense that it comprises the work of multiple research institutions around the world, cooperating to advance a unified research agenda.

It is proposed in this paper to more deliberately adopt knowledge of plant physiological processes, including the diversity of mineral nutrient uptake mechanisms, their translocation and metabolism as an entry point in identifying the composition, amount, and timing of nutrients to meet plant physiological needs for improved instantaneous uptake. In addition to the root, efforts should be redoubled with several other avenues, which as of now are at best haphazard, for the delivery of nutrients to the plant. The current surge in nanotechnology could for instance be leveraged to produce or deliver fertilisers in nanoparticle forms. Furthermore, ecological processes including interactions and symbioses with micro-organisms could be exploited to enhance nutrient uptake.

This paper reflects on current fertilisers and proposed research and development avenues to arrive at novel fertilisers or delivery mechanism that can leapfrog agro-technical and socio-economic developments. In addition to R&D efforts on fertiliser development, a global dialogue and the engagement of actors from sectors other than the traditional agricultural and environmental sectors will be needed. Given the link between plant fertilisation and nutrition and human nutrition, and the role as input factor in raising agricultural productivity, such actors would include those from the health and medical sector, the food industry, and development organisations.

CONTENTS

Keywords: innovative fertilisers, health and nutrition, poverty alleviation, sustainable food security, global change.

1. INTRODUCTION.

By 2050, rising human population and income levels are expected to increase global food demand by 70%, which for developing countries is projected at 100% (FAO, 2011a). This scenario calls for a substantial increase in food production to ensure sustainable food security, which is often associated with the intensive use of farm inputs - water and land - along with external inputs such as fertilisers (Tilman *et al.*, 2011). Intensification of production to increase crop yield on limited arable land is clearly important in securing adequate food supply; the important role that fertilisers play in this is undeniable. Global agriculture has become steadily more dependent on synthetic nitrogenous compounds, without the applications of which we would not be able to produce roughly half of today's world food (Erisman *et al.*, 2008). The projected consumption of nitrogen (N) fertilisers is likely to change from the current 105 Mt (million tonnes) in 2010 to 80-180 Mt by 2050, while phosphate (P_2O_5) consumption could change from the current 40 Mt to 35-70 Mt (Sutton *et al.,* 2013). Current potash (K_2O) consumption approximating 29 Mt may increase by 1 to 2% per year, reaching about 32 Mt in 2015 (Zörb *et al.*, 2014; FAO, 2011b). These estimations depend on factors such as food demand, improvements in nutrient uptake efficiency, production of biofuels and efficiency of nutrient recycling (Cordell *et al.,* 2009; Heffer, 2008).

Currently, emphasis is placed on agronomic research to improve the use efficiency of existing fertilisers through the 4R Nutrient Stewardship principles; i.e. the use of the fertiliser from the Right source, at the Right rate and at the Right time, with the Right placement (IPNI, 2014). Different agronomic strategies are followed to implement the 4R strategies, including precision application, deep placement and row application. Also, measures such as coating of fertilisers for slow release to prevent losses and to better tune the timing and availability of nutrients to the plant, are among other strategies (e.g. Chien *et al.*, 2009). Incorporated in the broader Integrated Soil Fertility Management (ISFM) approach, these agronomic practices may indeed lead to gains, indications of which are reported for China (Zhenling Cui *et al.*, 2013). The global use of fertilisers is highly unbalanced, with adequate or over-fertilisation in North America, Western Europe, China and India, and underutilisation in Africa, Eurasia and parts of Latin America (National Geographic, 2013). It has been estimated that the over-fertilisation with N in China, which is in the order of 11.8 Mt, could potentially double yields if used on the 174 million ha of cropland in sub-Saharan Africa (Ju *et al.*, 2009; Twomlow *et al.*, 2010).

In addition to regional over- or under-utilisation of fertilisers, there is often an imbalance in the ratio of nutrients supply. Data for Africa, for instance, put the total N consumption at nearly 2.8 Mt in 2005, representing an increase of 150% from 1975. Within the same period, total phosphorus (P) consumption was only about 96 kt, representing an increase of only 16% (Peñuelas *et al.*, 2012, 2013). This situation is sharply different from that in industrialised countries where both N and P supplies are balanced, or where soil P capital has been built up over time to offset any under supply (Van der Velde *et al.*, 2014).

Yet, even under the most efficient agro-production systems that are highly knowledge intensive, the apparent nutrient recovery efficiency of the macro elements N, P and K, may range from only 20% to about 80% (e.g. Baligar *et al.*, 2001). Nitrogen is lost to the environment as a greenhouse gas, causing climate change; as leachate in water, causing eutrophication; or as accumulates in the soil. The latter may cause loss in soil microbial community structure and function, including those related to crop nutrition, such as the inhibition of the activity of amidase, an enzyme involved in the transport of fixed N from bacteroides to plant cells (Dick, 1992; McLaughlin and Mineau *et al.,* 1995; Abdelrahman *et al.,* 1991). The requirement for fertilisers, either as organic or inorganic nutrients to ensure food security while preventing adverse environmental side effects, has received much attention over the past three to four decades, but much still needs to be accomplished as overall progress appears insufficient to make desired changes toward a sustainable production base. This calls for new impetus on fertilisers and fertilisation technologies to leapfrog development.

This paper will, therefore, revisit fertilisers and fertilisation technologies and their functioning, by taking basic physico-chemical, biological and ecological processes as a starting point and reflecting on the global implications and fertilisation strategies to propose avenues for arriving at innovative fertilisers or delivery strategies. With this, the paper sets the stage for the R&D strategy, as pursued by the Virtual Fertilizer Research Centre (VFRC), to foster the creation of the next generation of fertilisers and production technologies to help feed the world's growing population sustainably.

2. PLANT NUTRIENT REQUIREMENTS.

For normal growth, plants require 14 nutrient elements in different amounts (Table 1). Other mineral elements, though not essential for plant growth, but which could be beneficial, include cobalt, selenium and sodium. Humans require some additional minerals through intake from food, including meat and dairy products and water. Table 1 also presents the amounts of each of the essential nutrients required for growth for a generic plant, as well as their levels in one ton of maize kernel. The data on maize kernel contents for nutrients other than Cl^-, Mo and Ni were averaged from a 3 year measurement from plants raised under conventional (pesticide, lime and NPK fertiliser applications) conditions (Warman and Havard, 1998). Cl^- and Mo data were obtained from the International Fertiliser Society's *World Fertilizer Use Manual*, and Ni content was from an unidentified seed source (Kohiyama *et al.*, 1992). The rhizosphere is the central environment for nutrient uptake in soil, with pH being a key factor in the process of preconditioning the rhizosphere for nutrient availability (Table 1; Lucas and Davis, 1961). Extreme pH could significantly alter nutrient bioavailability. Yet, the rhizosphere pH is itself influenced by the composition and concentration of plant root exudates – including organic acids, proteins, sugars, anions and cations – and by the diversity of rhizosphere microbial community that play a significant role in nutrient mobilisation (Marschner, 1993, 2012; Abadia *et al.*, 2002; Martineau *et al.,* 2014).

Table 1: *Plant-essential mineral elements: interaction in soil, uptake forms, and typical concentrations in plants.*

Plants need 14 nutrient elements (in addition to C, H, O):	**Animals and humans need 22 nutrient elements:**
N, P, K, Mg, Ca, S, Fe, Mn, Zn, Cu, B, Mo, Cl and Ni	N, P, K, Mg, Ca, S, Fe, Mn, Zn, Cu, Mo, Cl, Ni, Co, Na, Se, I, Cr, V, Sn, As and F

Element	**Plant conc.**[1] mg kg^{-1}	**In maize grain** g ton^{-1}	**Plant uptake form**	**Nutrient movement in soil and uptake mechanism**	**Some factors affecting availability**[1]	**Uptake interaction with:**[1]
Nitrogen (N)	15,000	23,400	NO_3^-, NH_4^+	Low and high-affinity transport proteins	Antagonism between N forms; acidic pH, alkaline pH	Cl (for NO_3^-) (other cations for NH_4^+)
Phosphorus (P)	2,000	3,700	$H_2PO_4^-$, HPO_4^{2-}	Diffusion (likely under non-deficient conditions); phosphate transport proteins under deficient conditions (low or high affinity)	Metal oxides (e.g., Fe, Al) and clay minerals; Acidic pH	Zn
Potassium (K)	10,000	12,600	Monovalent ion (K^+)	Diffusion (under non-deficient conditions); K+ transporters under limiting conditions; Proton pumps (ATPases)	Clay minerals, organic matter; Acidic pH	NH_4^+, Na^{2+} CuO/ZnO oxides reduce K uptake
Magnesium (Mg)	2,000	1,400	Mg^{2+}	Divalent metal transport proteins	Acidic pH, alkaline pH	NH_4^+, Mn
Calcium (Ca)	5,000	100	Ca^{2+}	Divalent metal transport proteins	Acidic pH, alkaline pH	NH_4^+, Cu, Zn
Sulphur (S)	1,000	1,500	SO_4^{2-}	Low and high-affinity transport proteins	Acidic pH	

Table 1 (*continued*):

Element	Plant conc.[1] mg kg^{-1}	In maize grain g ton^{-1}	Plant uptake form	Nutrient movement in soil and uptake mechanism	Some factors affecting availability[1]	Uptake interaction with:[1]
Iron (Fe)	100	175	Fe^{2+}	Reduction and transport by divalent cation transporter for dicots and non-grass monocots; chelation of trivalent Fe in grass monocots	Alkaline pH	Zn, Cu, Mg,
Manganese (Mn)	50	8.2	Mn^{2+}	Divalent cation transporter	Alkaline pH, acid pH	Zn, Fe, Mg
Zinc (Zn)	20	26.4	Zn^{2+}	Divalent cation transporter	Alkaline pH, OM, clay, phosphate	N(+), P(-),cations (e.g., Ca^{2+}), Fe, Cu
Copper (Cu)	6	4.2	CuO, Cu^{+}, Cu^{2+}	Divalent cation transporter	Cations (K, Ca, Na, Zn); alkaline pH,	cations (e.g., Ca^{2+}), Fe
Boron (B)	20	4.9	Uncharged boric acid [$B(OH)_3$]	Diffusion; channel transport; high-affinity transport proteins	Alkaline pH	pH, N, Ca
Molybdenum (Mo)	0.1	0.63	Molybdate (MoO_4^{2-})	Potentially S transporters	Fe or Al hydroxides in acid soil	Cu, Al/Fe oxides
Chloride (Cl)	100	475	Cl^{-}	Proton pumps (ATPases) in cell membrane	Fe or Al hydroxides, clay	NO_3^{-}
Nickel (Ni)	0.1	0.5	Ni^{2+}	Probably divalent metal transporters	pH	Competing divalent cations

[1] Marschner *et al*., 2012.

Table 1 further presents some of the chemical forms and mechanisms by which the nutrients are taken up by plants, factors that influence their bioavailability and their uptake interaction with other nutrients (Marschner *et al.,* 2012). Indeed, as many of the different elements are taken up in similar forms, e.g. as ions, it is important to understand the antagonistic and synergistic interactions that may occur during uptake from the soil. Antagonism occurs among most nutrients, but appears to have been more studied among the micronutrients. Collectively, the uptake of nutrient elements is directed by multiple transporters, many of which transport more than one nutrient type. For example, although the iron-regulated transporter (Irt) is induced primarily by Fe deficiency, it transports Fe, Mn, Cu, Zn and possibly other divalent cations into the plant (Sinclair and Krämer, 2002). In yeast, a model eukaryotic organism, pho84, a phosphate ion transporter also is responsive to Mn, Cu, Zn and Co (Jensen *et al.*, 2003). Thus, the potential of sharing similar uptake and transport systems by these ions results in competition among them, as suggested by several reports. For instance, Zn inhibited both the bioavailability in the rhizosphere and plant uptake of Fe and Mn by bean (Dimkpa *et al.*, 2014); Fe treatment reduced the uptake of Mn, Zn and Cu in xylem sap of barley (Alam *et al.*, 2001); and even at the level of the biological transporter, addition of Zn to a Fe-deficient system stimulated the expression of an Irt to a greater extent than Fe deficiency alone (Connolly *et al.*, 2002). Interestingly, such antagonism is not limited to soil-root uptake pathways, given that a foliar application of Fe also diminished Mn, Zn and Cu uptake in wheat (Ghasemi-Fasaei and Ronaghi, 2008). Antagonism among nutrient elements often occurs when the ratio of elements are unbalanced. It seems plausible that transporters, when presented with a mixture of nutrients composed of ions that they transport, would preferentially transport more of the more abundant nutrient. This could result in inhibition in the uptake of the less abundant minerals, as observed in *Arabidopsis* for Mn vs. Fe, and in bean for Zn vs. Fe and Mn (Yang *et al.*, 2008; Dimkpa *et al.*, 2014).

Similar to antagonistic interactions among nutrient elements, synergism in nutrient uptake also has been demonstrated. Riedell (2010) reported the enhanced accumulation of Ca and Mn with N-fertiliser application in maize plants, which for Mn occurred over the plant's life cycle, while Ca uptake was enhanced at tasselling. Also, synergism between P and Mn, as well as between K and Mn, and Mg and Ca, was observed in barley with increasing P application (Matula, 1992). Antagonism or synergism among nutrients clearly demonstrates how fertiliser formulations of specific nutrient composition can influence the overall nutrition of plants.

3. FERTILISERS AND THEIR GLOBAL ROLE.

The role of fertilisers is generally related to increased food production and the attendant environmental consequences of its use. Here, we revisit the role of fertilisers for their relevance to nutrition and health (Graham *et al.*, 2012); a production factor to prevent people spiralling into poverty, a means to lift poor farmers out of poverty, as well as a catalyst for change in overall agricultural development.

3.1. Food production.

Under natural conditions, plant nutrients become available through weathering of soil, releasing P, K, and other minerals. Di-nitrogen (N_2) from the air is converted through bacterial processes, as in the case of symbiosis with legumes, or through lightning; while micronutrients may be made available to plants through the metabolism of their own root exudates, through mycorrhization, and via bacterial processes such as the production of metal biochelators. Natural production of nutrients is however unable to sustain food production. The Netherlands Scientific Council for Government Policy (WRR, 1995) analysed the acreage required to feed the world to be five to six times larger under organic than integrated agriculture with the judicious use of N and other fertilisers. Nitrogen fixation rates of legumes range from 1-3 kg N ha^{-1} d^{-1} (e.g., Giller, 2001) under optimal growth conditions, i.e., with sufficient availability of water and other nutrients, primarily P and Mo. With a growth period of 100 days in temperate regions, a maximum amount of 300 kg ha^{-1} of N could be fixed, supplying two consecutive cereal crops, on average, 100 kg N ha^{-1} $year^{-1}$, over the three year rotational period. With half of this amount taken up by the plant, assuming N recovery of 50%, maximum yields of 2.5–3 tonnes grains ha^{-1} can be attained, compared to over 10 tonnes under integrated conditions.

In most parts of the world, however, plant growth is heavily hampered by lack of soil nutrients (e.g. McCown *et al.,* 1992; Giller *et al.,* 2006; Twomlow *et al.*, 2010), more severely so than by lack of rainfall, even in semi-arid regions where, at first glance, water availability would be considered as the main limiting factor. Nutrient-limited yields are approximate 1–2 tons ha^{-1} in the Sahelian region, while the total amount of rainwater would allow yield levels up to 4-5 tons (e.g. Bindraban *et al.*, 1999, 2000). Therefore, the use of mineral fertilisers is essential to realise optimal plant growth rates and yield levels, whereas non-use of mineral fertilisers could result in dramatic expansion of the agricultural area beyond available lands suitable for agriculture. Indeed, fertilisers have been recognised as an important input for closing crop yield gaps (Mueller *et al.*, 2012).

3.2. Farm livelihood and poverty.

Conversely, insufficient use of fertilisers causes the 'mining' of soil nutrients, leading to the deterioration of the production base (Stoorvogel *et al.*, 1993; Bindraban *et al.*, 2012) and driving poor farmers unable to acquire inputs further into poverty. Under marginal and low production conditions, ecological benefits cannot be exploited, and production risks through the use of fertilisers tends to be higher (Cooper *et al.,* 2008; Twomlow *et al.,* 2008), which further constrains incentives to use fertilisers. In some instance, the timely application of fertilisers, or in split doses, may incur opportunity costs as farmers can generate higher off-farm income for their labour, leaving their farms after planting and basal application of fertilisers and returning for harvesting only, as in the case of rice cultivation in Asian countries where women would take on seasonal weeding. Such socio-economic drivers are very location- and system-specific. The countries with the lowest levels of mineral fertiliser use also have the lowest levels of agricultural productivity and the highest levels of hunger.

3.3. Human health and micronutrients.

Apart from over 800 million people being food-insecure in terms of insufficient caloric intake, malnutrition, or hidden hunger, affects the lives of about 2 billion people globally. Malnutrition results in stunted growth and reduced cognitive abilities, with long term negative effects on livelihoods due to loss of physical and intellectual capacity (Stein, 2010). Although Fe and Zn are among the most notorious, other micronutrients such as Cu, Mo and B also are insufficiently consumed. The application only of the macronutrients N, P and K for decades may have caused human-induced deficiency in soil micronutrients, with yield responses up to 50% or more found with application of micronutrient fertilisers. There is also evidence that soils that are non-responsive to NPK fertilisation on the African continent may inherently lack micronutrients, the addition of which gives higher yield responses (Voortman *et al.*, 2014 in prep). Importantly, there is evidence that the overall nutrient content of food crops has been declining with increasing yield levels from NPK fertilisation (e.g. Fan *et al.*, 2008; Sinclair and Rufty, 2012).

3.4. Environment.

Fertilisers are also essential in minimising the use of land and water resources; production ecology principles suggest that most production resources are used more efficiently under improved conditions of resource endowment (De Wit, 1992). This implies that it is essential to consider the availability of individual production factors like water and nutrients, as well as their interactions that result in 'ecological synergy'. The use efficiency of water, for instance, increases at higher yield levels (Rockström, 2003). Bindraban *et al.* (2008) show that improvements of an entire package of agronomic practices and crop genetics also increase N use efficiency over time, while integrated approaches have been shown to result in high production systems that are most effective in resource use efficiency (e.g., de Ridder and van Keulen 1990; Glendining *et al.*, 2009).

Fertilisers, therefore, play a major role in human livelihood as well as in the environment. Nitrogen and P use have, together, been recognised as one of the nine global drivers of change that pushes the earth from its stable state of the Holocene into the Anthropocene (Rockström *et al.*, 2009) with unforeseen consequences for life on earth. The use of N exceeds the planetary boundary when global change is triggered, while P is reaching that boundary. But fertilisers have implications that reach much farther and also affect other global change drivers (Conijn *et al.*, 2013). Loss of biodiversity may result from acidification of terrestrial ecosystems and eutrophication of coastal and freshwater systems because of fertiliser use. However, favourable feedbacks on biodiversity may also occur due to less clearing of natural land for agriculture because of higher yields on existing agricultural lands with judicious use of fertilisers. But then, energy use for N fertiliser production contributes to CO_2 emission, while soils fertilised with N emit increased quantities of the potent greenhouse gas, nitrous oxide (N_2O), accounting for three quarters of all global N_2O emissions. Other fertiliser-related losses occurring through indirect processes in agriculture include methane (CH_4) as in rice cultivation and enteric fermentation in ruminants (Snyder *et al.*, 2009). These and other compounds contribute directly or indirectly to climate change, stratospheric ozone depletion, ocean acidification and atmospheric aerosol loading. The strong ecological interaction between water and nutrients implies a strong relationship between fertiliser and freshwater use for agricultural production (e.g. Rockström, 2003). Furthermore, impurities in fertilisers such as cadmium (Cd) in phosphate rock and derived fertilisers contribute to chemical pollution.

3.5. Energy requirement.

The production of fertilisers is energy intensive, accounting in 2001 for about 1% or approximately 3660 PJ of global energy demand. About three quarters was needed for N fertilisers of about 80 Mt in 2001. The increasing energy efficiency in the production process was shown not to be able to offset the increase in total demand for fertilisers, leading to a further increase in energy requirements for fertiliser production (Ramirez and Worrell, 2006). The total energy for the annual production of ammonia of about 160 Mt in 2010 equals 90 million cars in terms of energy use, about one tenth of the world's car fleet (Razon, 2014). Worrell *et al.* (1994) had already assessed that increasing the use efficiency of the applied fertilisers in the agricultural field could reduce overall energy requirement by up to 44% or more. These findings suggest that most gains are to be expected from raising uptake efficiency by crop plants than by further improving the industrial production processes.

3.6. Agricultural development.

The above sections may be perceived as alarming, and with daunting challenges ahead regarding fertilisers and their use. However, the perceptions are reinforced by analyses that extrapolate past trends to assess future developments. Bindraban and Rabbinge (2012) show that agricultural development throughout history has seen forward leaps. These leaps cause sudden changes in productivity, efficiency and efficacy, discontinuing the past trends, leading to transformations in agricultural production and the food chain, and in societal demands. One such mega trend is the sudden increase in annual yield for wheat in Europe in the 1950s, and of rice in the 1960s, in Asia. Extrapolations on the wheat yield increase of 15 $kg^{-1}ha^{-1}y^{-1}$ in the Netherlands prior to the 1950s would project yields at less than 4 t ha^{-1} in the year 2000. It had however exceeded 8 t ha^{-1} in that year and pushes to over 9.5 tons today, because annual yield increase jumped from about 80 kg^{-1} ha^{-1} y^{-1} during 1950-1975 to 160 $kg^{-1}ha^{-1}y^{-1}$ after 1975. Rice yield increase of about 2.5 $kg^{-1}ha^{-1}y^{-1}$ up to 1965 suddenly jumped to 130 $kg^{-1}ha^{-1}y^{-1}$ in Indonesia, due to the introduction of a range of agronomic practices and institutional support. The shift from habits and skills to science-based agronomic practices helped to further increase use efficiency of inputs and drastically reduced labour requirements. The integration of multiple objectives in agricultural practices (e.g. Vereijken, 2002) has resulted in integrated land use planning to further optimise input use and outputs therefrom, to meet environmental targets such as limits set to leachate of nitrate. Improvements in tracking and tracing in food chains has reduced losses on both inputs and outputs. The six 'megatrends' identified by Bindraban and Rabbinge (2012) have, arguably, resulted from driving forces such as growing insights, technological innovations and societal change.

Wide gaps between current and attainable crop yields and low use efficiencies of farm inputs at field scale provide ample opportunity for new quantum leaps toward an evergreen revolution. In addition, the ability to process massive amounts of data allows integral analysis for tuning resource use at regional scales, such as an integral river basin, which also provides scope for collective management of resources and associated risk sharing (Kauffman *et al.*, 2014). Production systems are, therefore, the result of the interplay between biophysical, socio-economic, institutional and cultural factors (Dixon *et al.*, 2001). After neglecting agriculture for the last two to three decades of the previous century, its role in overall development, food security, poverty alleviation and environmental stewardship has recently been revitalised (World Bank, 2007). Fertilisers, by nature, can make a significant contribution to leapfrog agro-ecological as well as socio-economic development and catalyse the next mega-trend in agricultural development.

3.7. Prospects.

Fertilisers, as a fundamental intervention in biology and ecology and with that in multiple drivers of global ecological, agricultural and economic development, have a significant contribution to make towards sustainable provision of sufficient and high quality food, while also contributing to poverty reduction and the maintenance of vital ecosystems. Increasing fertiliser use efficiency is the end result of the interplay between agro-technological adjustment of the use of current fertilisers, ecological literacy and the socio-economic reality of farmers. Policy measures have to be put in place to stimulate physical availability, economic accessibility and knowledge exchange through extension under low agro-ecological production conditions, and to curtail any excessive use within environmental boundary conditions for intensive farm practices.

While better governance and agronomic management of current fertiliser use can resolve part of the problem, there are clear opportunities to seek new, more effective fertilisers and technologies to leapfrog these constraints. Despite the low use efficiency of fertilisers and adverse side effects of both over and under use, fertiliser research has largely been neglected for more than four decades, wherein no fundamental game-changing fertiliser products and technologies have been introduced during the past 40 years. Fuglie *et al.* (2011) estimated that the fertiliser industry invests 0.1-0.2% of its revenue in research and development, compared with about 10% and 15-20% by the seed and pharmaceutical sectors, respectively, in developing new varieties and seeds, and new medications. The fertiliser sector can clearly benefit from the multi-functionalities of fertilisers, i.e. supporting food production to help ensure food security, reducing hidden hunger by improving food produce quality, contributing to reducing environmental pressures and fulfilling its role as an efficient and economically viable production factor to lift poor farmers out of poverty. It is for these reasons that the International Fertilizer Development Center (IFDC) established the Virtual Fertilizer Research Center (VFRC) in the year 2012, to engage with multiple research institutions around the world, and cooperating to advance a unified research agenda for arriving at tangible innovative fertilisers to leapfrog agro-technical, socio-economic and institutional hurdles.

4. THE VFRC COCKPIT ON REVISITING FERTILISERS.

The nutrients required by plants are naturally present in soils. However those required in significant quantity – the macronutrients - are rarely present in sufficient amounts to allow crop plants fully to express their yield potentials. Similarly there are many soils in which the content of some micronutrients required by plants are insufficient or unavailable. The function of fertilisers, mineral or organic, is to remove the limitation to yield (or quality) which would otherwise be imposed by the nutrient shortage or unavailability.

In achieving the aim of fertiliser use for increasing the growth of agricultural crop plants, we desire that ideally the nutrients end up in the targeted plant only. However, mineral nutrients administered for crop fertilisation do not all end up in the plant and 20 to 80% may be lost to the environment or temporarily accumulate in the soil (e.g. Sebilo *et al.*, 2013).

The current total food production of about 4,000 billion tons of grain equivalents (Bindraban *et al.*, 2010) contains approximately 60 Mt of reactive N, given grain-N content of 1.5% (see also e.g. Dawson and Hilton, 2011); a comparable amount of K (or 72 Mt K_2O), and about one-fifteenth of P (or 9 Mt P_2O_5) (e.g. Smit *et al.*, 2009). Annual inputs of over 105 Mt of N, 29 Mt of K_2O and 40 Mt of P_2O_5 lead to potential build-up of nutrients in air, water and soil. Under these scenarios, recycling of nutrients back into agricultural fields is essential to curtail environmental side effects, theoretically reducing the conversion of new inert nutrients into reactive nutrients. This implies that by increasing the use of recycled nutrients, food production can be increased while reducing the production of mineral fertilisers to levels for compensating losses due to leakages only. Kalimuthu *et al.* (2014) quantified that about 51% of the P in waste was recycled to reach agricultural soils or the food and feed industry in France. They state that options exist for further improving P recycling from wastes currently produced, but that these appear to be less promising for economising these P resources for P fertilisers than scenarios based on reduced food waste or redesigned agricultural systems. In any case, whether reactive nutrients are obtained from newly mined resources or from recycled material, their uptake by crop plants should be as instantaneous as possible.

The VFRC has, therefore, been established with the aim of catalysing the development of prototypes of novel fertilisers and their application technologies. For developing game-changing fertilisers and technologies, a focus from current physical and chemical processes in the production of fertilisers to integration with more profound understanding of biological and ecological processes is needed. The VFRC has developed a comprehensive research agenda, comprising the components described in this chapter, that will evolve in discussions with scientists and actors in the virtual worldwide network.

4.1. Assessments and diagnostics.

Keeping in view the potentially vast impacts of fertilisers on food, poverty and the environment, VFRC has outlined a quantitative analytical framework to assess the impact of fertiliser interventions on the ecological drivers of planetary change (Conijn *et al.*, 2013), with the aim of raising societal awareness on the urgent need for fertiliser innovations.

One approach in the 4R Nutrient Stewardship could be to target the allocation of fertiliser types to soil types and weather conditions that could be identified with generic crop and soil modelling approaches. Systematic analysis of agro-ecosystems, with crop models as one of the tools, has allowed deeper understanding of the production, ecological processes and functioning of these system (Van Ittersum and Rabbinge, 1997). With wheat yields at about 3 tons ha^{-1} in the 1960s in the Netherlands, De Wit (1992) showed that yields could reach 10 tons ha^{-1}, well beyond mainstream insights, and revealed that nutrients, rather than water, were limiting yields more severely in the Sahelian region. These findings have governed agricultural investments in developed nations, with current average wheat yield in the Netherlands of over 9.5 tons ha^{-1}. Crop modelling is being used to identify fertiliser requirements to attain desired yield levels, but the poor resolution of soil data (e.g. Leenaars, 2013) and the complex interactions among the 14 plant nutrients (and other production factors) may allow identification of macro nutrients requirements, but not of meso- and micro-nutrients. Little or no responses to macro-nutrient application could be expected from, for instance, the 'unresponsive' soils in parts of Africa that may not be traced by the generic approach. Complementing this approach with geo-spatial analysis based on soil testing and agronomic fertiliser trials would allow analysing the direct relation between soil properties and the real effect of nutrients on yield under certain management practices. This integrated approach is recommended by the VFRC, and its development is currently underway.

Soil and plant diagnostic tools should become an integral part of fine-tuning fertiliser use to soil type and as guide to producers, traders and users, for targeting the most relevant fertiliser types to their region and production system in order to maximise plant uptake while minimising environmental losses. However, while many claims are made about new devices that quickly measure soil properties, interpretation may appear cumbersome as soil properties can be measured in different ways and the relevance of the data is likely to be crop- and environment -specific. This calls for harmonisation and standardisation of data and methodologies. Also, quick methods for the assessment of nutrient contents of fertilisers are essential to prevent adulteration.

4.2. Plant physiology and metabolic pathways.

Plants take up, transport, allocate and assign nutrients in different ways to different organs. The extent to which these roles are achieved depends on environmental conditions, crop developmental stage, and plant health status. Whereas plants elaborate a variety of mechanisms for the uptake of different elements from soil or aerially, such knowledge has not adequately been applied in increasing our understanding of the acquisition of nutrients by different food crops to enable targeted and plant-specific fertiliser strategies. A better knowledge of nutrient biochemical pathways in plants could help target the delivery of nutrients to where most required, and could, for instance, facilitate further development of effective foliar fertilisers as an alternative uptake mechanism (Voogt *et al.*, 2013). In addition, understanding the ability of plants to increase their nutrient storage capacity could help to increase uptake, yield and food quality (Sinclair and Rufty, 2012). Conventionally, nutrient elements are taken up as charged ions, implying that active transportation by proteins is required to move them across the root cell membrane. For example, N is taken up by plants in two forms, NO_3^- or NH_4^+ (Table 1; Masclaux-Daubresse *et al.*, 2010). However, the metabolism of these two forms of N by the plant is quite dissimilar: a portion of NO_3^- is transported to the leaves, where it is reduced to NH_4^+ and then reacts with sugars to generate nucleic acids, amino acids, and other building blocks, whereas NH_4^+ is directly metabolised, mainly in the roots, perhaps due to its lower mobility. Considering that sugars are produced in the leaves and have to be delivered to the root, the form of N applied to crops could cause a differential response in the plant under certain environmental conditions (see for e.g., Moritsugu *et al.,* 1983). In high-temperature agro-ecological conditions, leaf sugar would be metabolised at a faster rate due to temperature-induced increase in respiration, resulting in less sugar being availed the root for conversion into derived products. Under such conditions, N-fertiliser primarily based on NH_4^+ may not support plant growth to the desired extent. Accordingly, leafy vegetables may benefit more from NO_3^--N than NH_4^+-N fertiliser application, since the former would be transported to the leaves where the sugar is metabolised. On the other hand, at low temperatures where sugars are more readily available to the root, coupled with reduced transport of NO_3^-, NH_4^+ might be the preferred N-fertiliser.

As indicated previously, the role of micronutrients in influencing plant growth and yield, even in the presence of adequate N, P and K is becoming clearer, as more studies are conducted in this area. The uptake of some ionic micronutrients from the soil is preceded by their biological conversion to forms amenable for root uptake. With Fe, for example, the conversion of Fe^{3+} to Fe^{2+} is performed by members of a metal reductase enzyme family. This enzyme family is embedded in the root plasma membrane of dicotyledonous (e.g., bean) and non-grass monocotyledonous plants (e.g. banana), where the reduction activity takes place (Norvell *et al.*, 1993; Robinson *et al.*, 1999). In contrast, roots of grass monocots such as rice exude phytosiderophores into the rhizosphere to scavenge for Fe^{3+}; the scavenged Fe is taken up in the siderophores as a complex and then reduced internally (Schaaf *et al.*, 2004). Although both the reductase and phytosiderophore systems are induced in response to Fe deficiency, they also respond to other metals such as Mn, Zn and Cu (Schaaf *et al.*, 2004; Johnson and Barton, 2007), demonstrating the non-specificity and potential competition among micronutrients in these processes. However, current fertiliser formulations with micronutrients involve their amendment into the main NPK fertilisers, with little, if any, concern about the fate of competing micronutrients in the formulations. Given the role of micronutrients in crop yield and quality, the extent to which specific plant physiology influences the use efficiency of micronutrient fertiliser formulations deserves continuous research.

In contrast to the uptake of micronutrients as ions, recent studies from environmental nanoscience demonstrate that significant amounts of uncharged metallic particles of micronutrients also are capable of being absorbed by certain plants and transported to the aerial parts when presented through the soil (Miralles *et al.*, 2012; Gardea-Torredey *et al.*, 2014). For example, Cu presented as CuO nanoparticles was taken up by wheat and maize plants in the particulate form (Dimkpa *et al.*, 2012a, 2013; Wang *et al.,* 2012a). Similarly, the presence of Fe nanoparticles also have been observed in plants exposed to particulate Fe (Ghafariyan *et al.*, 2013). Interestingly, the same crop could differentially absorb different nutrient elements provided to it in particulate forms in the root, as observed in wheat for CuO vs. ZnO nanoparticles: Cu existed in wheat shoot mainly as CuO particles, while Zn presented as ZnO particles was found as Zn-phosphate in these plants (Dimkpa *et al.*, 2012a, 2013). This suggests that the ZnO particles dissolved in the rhizosphere and are initially absorbed by the plant as Zn^{2+}, prior to their complexation with organic phosphate molecules inside the plant. Given these contradictions, and the possibility that particulate forms of nutrients could be mobilised and remobilised via the xylem and phloem respectively (Wang *et al.,* 2012a), elucidating the mechanisms involved in the plant transport of nutrient elements in particulate forms and their conversion into plant-usable forms *in planta* could provide a promising delivery pathway for micronutrient delivery as nanoparticles, or the packaging of nutrients in general in nanoparticle encapsulations that are also capable of being taken up intact by plants (Derosa *et al.*, 2010; Gogos *et al.*, 2012; Zhang *et al.,* 2012).

Clearly, the root physiologies surrounding nutrient accumulation permit their uptake from root in forms other than just ions. One interesting observation from comparing plant responses to nutrients presented in ionic vs. particulate forms is that when applied at the same concentration at relatively high doses, the concentration at which toxicity occurs is lower with ions than with particles, depending on the nutrient (Dimkpa *et al.*, 2012a, and unpublished data). This is perhaps because the ions are readily available to the roots and could rapidly reach undesirable doses, subject to interactions with soil factors. The exposure to the particles, however, is more regulated by the slow release of the functional ions from the particles, whether taken up directly or dissolving to ions prior to uptake. A modern effective fertiliser program would require a better understanding of which crops absorb which nutrients in which form, and whether there are dramatic differences in the amount of nutrients accumulated by crop plants from the different forms in which the nutrient elements could be presented to them.

4.3. Soil-plant relations.

Soil properties dictate to a very large degree the responses of crops to nutrient elements. The pH of a soil, for example, can determine the extent to which a nutrient is available to plants (Marschner, 2012). Change in pH induced by a fertiliser treatment could also complicate the situation: the alkaline nature of urea fertilisers could impede the solubility and, therefore, availability of Zn amended to it (Milani *et al.*, 2012); NH_4^+-based fertilisers could acidify the soil due to proton release, thereby affecting P availability. Yet, in many agro-ecosystems, different fertilisers are applied to soil by farmers without proper consideration of soil pH and effects on nutrient availability. Plants can adapt to soil properties in order to enhance their ability to dissolve and take up nutrients from the soil. These adaptations may feature anatomical, morphological or physiological characteristics in specific environments such as nutrient poor soils (e.g. Aerts, 1999). Morphologically, roots may have developed high competitive ability for nutrient uptake, for example through extensive rooting systems. Physiological responses such as a large internal nutrient pool, low nutrient content in plant tissue, enhanced remobilisation within plants, and low rates of nutrient loss have been reported. Anatomical features in roots or leaves may assist in facilitating nutrient uptake and transport. Other plants have evolved to live in symbiosis with fungi and bacteria, or excrete organic acids in order to increase soil nutrient uptake. Yet, knowledge about these mechanisms is fragmented, with varying claims about their effectiveness being found in laboratory and greenhouse experiments. The ultimate applicability under field conditions is less apparent, yet with substantial potential to enhance nutrient uptake.

Soils, whether poor or fertile, often contain more nutrients than required for crop annual uptake, but that are chemically fixed. For example, due to its strong reaction with soil and subsequent lack of mobility, especially in the acidic soils of the tropics and subtropics, P is limited in bioavailability in about 30–40% of the world's arable land (Runge-Metzger, 1995; Sanchez *et al.*, 1997). K has similar fixation and mobility characteristics as P in soil (Zörb *et al.*, 2014). Extensive root systems such as longer roots, more lateral roots and more root hairs are essential to gain access to these nutrients which are not readily available (Hammond *et al.*, 2009; Zhu and Lynch, 2004; Ma *et al.*, 2013). Smit *et al.* (2013) discuss that enhancing early root growth could stimulate uptake of P, as young roots have high uptake capacity. In addition to P, NH_4^+, as well as a few other nutrient elements including Zn, K, and Na (as chloride salts) induce changes in root architecture, leading to an enhanced ability to accumulate not just the nutrient in question, but also others (Potters *et al.,* 2007 and references therein; Ma *et al.*, 2013; Stewart *et al.*, personal communication). Thus, the modification of root architecture by certain nutrient elements could have a profound influence on the overall plant nutritional status. This effect can be significant when fertilisation strategies apply these nutrients in a way that boosts early changes in root architecture, thus stimulating the early growth of the plants. However more systematic studies that directly link nutrient element-induced changes in root architecture to the overall enhancement of plant growth nutrition are needed to draw stronger conclusions; initial benefits may not necessarily translate into higher yields.

4.4. Trait identification.

Plant breeding so far has emphasised increase in yield potential, primarily of the major grains, and has evolved to breeding for resistance against pests and diseases, as well as tolerance to drought. However, little direct attention has been paid to breeding for nutrient uptake and utilisation. Knowledge about plant traits and our improved understanding of plant mechanisms to adapt to fertilisers will inform breeders, while more effective fertiliser delivery systems can be devised for agronomists. More recently, increasing attention is being paid to nutrient breeding, such as increased Fe (Sperotto *et al.,* 2012), and Zn (Mabesa *et al.*, 2013) content in rice.

4.5. Recycled fertilisers.

Once nutrients are taken up by plants and consumed by humans and animals, the waste ends up in the environment. Recycling of nutrients from waste water, manure and offal reduces overall losses and helps to recapture nutrients for plant uptake. Such organic fertilisers contain macro- and micro-nutrients, which may provide added value compared with standard mineral fertilisers. Shahbaz *et al.* (2014) for instance, show that bioslurry helps to double N uptake in Okra at similar rates of N application. They associate this finding to favourable conditioning of soil characteristics by the bioslurry such as those related to microbial activity that reduces N losses. These workers did not, however, discuss the role of the micronutrients contained in the bioslurry that also might have contributed to the increased N uptake (e.g. Oprica *et al.*, 2014). In contrast, Islam (2006) reports only small yield effects of bioslurry amendment.

Despite the potential benefits, organic fertilisers may be unbalanced in terms of relative availability of nutrients, as well as having potentially harmful components such as bacteria or fungi, or even toxic levels of (micro) nutrients or heavy metals. Alvarenga *et al.* (2007) evaluated the chemical and ecotoxicological characteristics of biodegradable organic residues for application to agricultural land and did find direct and indirect eco-toxic effects. Protocols are being develop to ensure the usefulness of organic

fertilisers (Mukome *et al.*, 2013), and for testing of fractioning methods for obtaining correct information regarding nutrients in different forms of organic waste, including composts, slurries, sludges, and digestates, such as for P and its solubility in the presence of other micro-nutrients (Garcia-Albacete *et al.*, 2012). No doubt, proper processing and sound experimentation to disentangle the many factors affecting plant growth are essential to demonstrate the value of organic fertilisers. Given the many components in an organic fertiliser source, an assessment of the impact of recycled fertilisers on plant growth may fall short in terms of sound experimentation of the precise factor contributing to the crop performance; for example, with control treatments being zero nutrient treatments, or incomparable controls like NPK applications not including micronutrients (e.g. Jha *et al.*, 2011). Protocols for sound scientific scrutiny of the increasing number of new fertilisers entering the market, including foliar fertilisers (e.g. Oprica *et al.*, 2014), are generally not available.

4.6. Fertiliser production processes.

Fertiliser production and use has centred on the macro-nutrients N, P and K, often in solid forms, as they are needed in the largest quantities and often provide immediate yield responses. As a result, although required in lower amounts, soils may have become depleted of micronutrients, when not replenished. Yields may decline and produce quality reduce (e.g. Monasterio and Graham, 2000), potentially leading to malnutrition from consumption of such produce. Insights into the mineral fertiliser interventions for specific agro-ecosystems to increase crop yield, food quality and human health will guide the development of specific micronutrient-containing fertilisers.

The majority of fertilisers are produced from large scale mining operations and industrial plants. Increasingly however, nutrients emitted into the environment are being captured and recycled back into agricultural use. Ideally, whether from mineral fertilisers or obtained from recycled material, the nutrients they contain should be taken up as rapidly as possible by crop plants. Accordingly, biological insights should guide the process of developing novel fertilisers and delivery mechanisms.

4.7. Application methods.

Administering fertilisers following the 4R approach may cause increased labour requirements and so be unsuitable for specific farm operations. Minimising labour requirements calls for the design of affordable applicators, such as for the efficient and effective deep placement of Urea Super Granules (USG) in rice cultivation (Kapoor *et al.*, 2008). Applicator design (e.g. Bautista *et al.*, 2001) should also consider anticipated transformations in agro-ecosystems, such as the dry land cultivation of rice (Bindraban *et al.*, 2006).

4.8. Claims.

Many individuals and companies claim to have developed fertiliser compositions, additives, coatings and biological agents that improve nutrient uptake and plant growth. Often, however, the validity of such claims is not verified by external assessments. The complexity of plant-nutrient uptake processes could, for instance, cause products to be effective only under specific crop and environmental conditions. Importantly, as the mechanism causing positive crop responses from such products under the prevailing crop and environmental conditions may be undetermined, their impact under other conditions may be unpredictable. Normative research that sets standards and protocols for scientific scrutiny and evaluations to unravel the functioning mechanisms ought to guide the currently mostly unregulated entrance of fertiliser products to the market.

5. TUNING FERTILISERS AND FERTILISER TECHNOLOGIES TO FARM PRACTICES.

Leveraging knowledge gained from different individual studies, an opportunity arises for the tuning of fertiliser technologies to become better aligned with an understanding of plant and soil processes and be specific to agro-ecosystems, in contrast to the current practice of largely using fertilisers which may be generic for most crops and soils. In the following sections, we highlight a number of interventions which could facilitate the attainment of an integrated crop fertilisation program.

5.1. Seed nutrient content.

For starters, guaranteeing good crop performance begins with seed selection. In particular, the nutrient contents of a seed may be crucial to the performance of the ensuing plant when soil nutrients are in limited supply. Brodrick *et al.* (1995) emphasised the need for conducting nutrient analysis of seed batches prior to sowing. They showed that Mo was a limiting factor in N_2 fixation in soils in Eastern and Southern Africa, and that sowing bean seeds with sufficient Mo contents in soil with low Mo prevented the production of Mo-deficient seeds until the 4th growth cycle. Therefore, the question arises whether a role in plant performance of nutrients carried over in seeds could be facilitated by spraying maturing fruits or seeds with specific nutrients prior to harvest, to help boost the nutrient content for the next growth cycle. Indeed, there is evidence that certain nutrients might be required to facilitate seed germination. In a 5-day germination study with rapeseed, seeds with low S, Mg and Ca had germination failure, while seeds which took more than 3 days to germinate had B deficiency (Eggert and von Wirén, 2013). The finding for S, for example, is hardly surprising, it being a component of the early-required amino acids, cysteine and methionine, involved in antioxidant regulation and synthesis of hormones, DNA and proteins (Rajjou *et al.*, 2012). Related to this is the boosting of early plant development which is demonstrated in the early application of DAP which helped in timely root development and subsequent enhancement of overall plant growth when the plants were later fertilised with otherwise unreactive phosphate rock, compared with continued DAP application (IFDC, ongoing studies).

5.2. Seed coating.

Following harvest, seeds can be coated with specific nutrients prior to next sowing. In principle, coating seeds with nutrients permits the emerging radicle to make early contact with nutrients being released from the coating formulation on the seed surface. While further research might be necessary in this area, there is a strong prospect for coating of seeds with 'germination-boosting' nutrients to provide the impetus needed to establish early plant vigour as demonstrated in a few studies. For example, Nijënstein (unpublished report) showed coating rye grass seeds with nutrients increased lateral root formation within the first 15 day of sowing, compared to plants from uncoated seeds. In that study, seed coating with N alone demonstrated greater efficacy than when combined with P, although coating with P enhanced P uptake by the plant. Similarly, Wiatrak (2013) demonstrated for wheat that seed coating with a mixed formulation of Cu, Zn and Mn (at 65, 395 and 530 ml kg^{-1} seed) significantly increased plant biomass and grain yield, as well as plant N and P contents. However, no effect of the seed coating treatment was observed in Cu, Mn and Zn contents. At higher (395 and 530 mg kg^{-1} seed) nutrient concentrations, coating of the seed also resulted in reduced N, P and Cu uptake. Contrary to these results, Scott *et al.* (1987) report that the emergence of wheat, but not oat, was reduced by P coating, whereas coating with urea reduced the emergence of both plants, more so of wheat. Similarly, barley seeds coated with P had delayed germination but increased chlorophyll content, as well as seed formation (Zelonka *et al.*, 2005). Collectively, these contrasting data suggest that the nutrient specificity of seed coating formulations needs to be determined for different crops, and the initial seed lot nutrient content, prior to widespread adoption of fertiliser technology based on seed coating.

5.3. Foliar fertilisers.

It is known that nutrient-limiting processes such as antagonism among nutrients, extreme pH, and other complex chemistries occur mainly in the soil, although there is evidence that antagonism between nutrients also could occur in plants (Ghasemi-Fasaei and Ronaghi, 2008). Circumventing the soil and applying nutrients through aerial plant parts can be a complementary fertilisation strategy, with the potential to address the restricted availability through the root. No doubt, uptake of nutrients applied from the shoot could be affected by surface tension of the suspension or solution, leaf cuticular morphology, age of leaf, and environmental vagaries associated with the operations of the stomata (Fenández and Ebert, 2005). Ideally, nutrient elements involved in shoot-specific processes such as Mg, Mn and Fe in chlorophyll biosynthesis and photosynthesis would be good nutrient candidates for foliar fertilisation. As reviewed by Fenández and Ebert (2005), foliar application of Fe fertilisers is being used to mitigate chlorosis in crop plants. In addition foliar application could increase the seed content of the nutrient, ultimately enhancing crop nutritional quality (Wang *et al.*, 2012b). While much is known for foliar application with Fe, the wide scale application of other nutrients and ultimate integration of foliar strategies into current farming practices would require more in-depth research to obtain reliable and reproducible application regimes and crop responses specific to each nutrient and their combinations.

An additional benefit may be achieved by exploiting synergistic effects. In a comprehensive pot experiment with two controls without and with basal NPK application, Oprica *et al.* (2014) showed that foliar application of a mix of N, P, K, Fe, Cu and Mn enhances nutrient content in leaves and seeds of maize and sunflower while increasing yield by 50% over the basal application of NPK alone. It is likely that the availability of micronutrients in the foliar fertiliser formulation may also have stimulated the uptake efficiency of the soil-applied NPK.

5.4. Beneficial micro-organisms.

Besides the well-documented role of N-fixation by symbiotic (e.g. *Rhizobia)* and free-living (e.g. *Azotobacter* and *Azospirillum* spp.) diazotrophs, soil microbes contribute to the nutrition of plants through various other processes. *Bacillus subtilis* can acidify the root environment, potentially helping to increase the solubility of fixed nutrients (Zhang *et al.*, 2009). *Pseudomonads, streptomycetes* and *Bacilli* serve as bio-fertilisers, producing phytohormones, siderophores and other growth-inducing compounds (Bulgarelli *et al.*, 2013). Yet, other soil microbes function as biological control agents that negate the effects of pathogenic organisms, improving plant fitness, including fitness for nutrient assimilation. For example, Prasanna *et al.* (2013) found that inoculating tomato with the biocontrol cyanobacterium, *Anabaena variabilis,* when the plants are exposed to the plant pathogen *Fusarium oxysporium* resulted in increased plant growth, yield, shoot P and Zn contents, and correlated with increased activity of pathogen defence enzymes and, ultimately, to reduced mortality of the plants. These findings demonstrate how soil micro-organisms could contribute to enhancing plant resistance through improved nutrient uptake. The degree of involvement of soil microorganisms in plant nutrition is reported in the review of Koele *et al.* (2013), who discuss the role of these organisms in helping plants to better scavenge several nutrients from the soil and reduce the effects of hazards such as drought or toxicity against heavy metals. Therefore, maintaining a diverse population of rhizosphere microorganisms by adequate management may be beneficial in the long run. The strong and multiple interactions imply, however, that the beneficial processes could be highly specific regarding plant species, soil, micro-organism and nutrients.

A role for bacteria, mainly of the *Bacillus, Pseudomonas* and *Penicillium* genera, as well as arbuscular mycorrhizal fungi (AMF) in nutrient acquisition is further demonstrated in their ability to solubilise P from both inorganic and organic sources. Phosphate-solubilising microbes perform this function by exuding organic acids such as citrate, acetate, succinate and gluconate, as well as by the enzymatic activities of phosphatases and phytases (Bulgarelli *et al.*, 2013; Koele *et al.*, 2013). This role could prove significant in an integrated fertiliser intervention, given the importance of P in the establishment of early plant

vigour and the finite reserves of this resource. It is estimated that less than 5% of the soil P is available to plants (Bulgarelli *et al.*, 2013); formulations of these microbes, or of organic acids that they produce, could be prepared and used as soil amendments specifically in soils with low P availability. Such formulations could contribute in the recycling of P fixed in soil from fertiliser treatments, thus reducing the entry of new P into the fertiliser system. Moreover, as P has been shown to increase the proliferation of root hairs, the effect on root density in turn could contribute in the better mining and uptake of other nutrients. In this regard AMF, as part of the root system, are more extensive in nature and could explore spaces not reached by roots to exploit P for plant use.

Away from the rhizosphere, microbes also are internally associated with plants (endophytic), or exist on the shoot surface (phyllospheric). Like their rhizosphere counterparts, both endosphere and phyllosphere bacteria are involved in biocontrol activities; however the potential involvement of endophytes or phyllosphere bacteria in plant nutrient acquisition is not as well resolved. Indeed, some of the rhizosphere bacteria involved in nutrient acquisition such as *Rhizobium* and *Azospirillum* are unable to establish on leaves (Lindow and Brandl, 2003), hence the potential to fix N directly from the air is negated, even with their possession of mechanisms to circumvent excess oxygen that interferes with N-fixation. Nonetheless, root endophytes could contribute to plant nutrition of other minerals. For example *Bacillus* sp B55 enhances S content in tobacco (*Nicotiana attenuata*) seedlings under S-deficient conditions (Meldau *et al.*, 2013). Not only does this strain reduce organic S, but it also exudes the volatile, plant-assimilable S compound, dimethyl disulfide (DMDS). The S is then incorporated into any number of S-containing compounds, amino acids and other S-related metabolisms such as chlorophyll or in the electron transport chain. Meldau and co-workers (2013) argued that the energy saved by not reducing inorganic S contributes to the promotion of plant growth in B55-inoculated plants. For practical applications, considering that DMDS is an organic and thus biodegradable compound, could it, or the bacteria producing it, form a component of S nutrition in fertiliser formulations for S-deficient soils? The phyllospheric cynobacteria (*Scytonema javanicum* and *S. hofmanni*; Freiberg, 1998), impact N cycle by their ability to fix N or convert NH_3 to NH_4^+ on leaf surfaces (Freiberg, 1998; Papen *et al.*, 2002). Again, given that certain above-ground microbes could contribute to plant nutrition, the question arises whether this function could be purposely exploited in modern fertiliser interventions by specifically inoculating leaves with formulations containing such microbes. In fact, earlier studies conducted in India in this area demonstrated an increase in wheat and rice dry biomass and grain weight following foliar treatment with a formulation of phyllosphere-dwelling N fixers (Sengupta and Sen 1979; Sengupta *et al.,* 1981).

Currently, different microbial inoculants are being commercially formulated for use in plant growth. Also, there are indications that they could be integrated into chemical fertilisers, which could potentially reduce mineral nutrient inputs (O'Reilly, personal communication). Nevertheless, the beneficial impact of currently available inoculants seems to vary greatly due to the complexity of the interactions, as well as potential issues with the stability of the inoculants over time, and under different climatic conditions. Moreover, many of the commercially available products may lack rigorous scientific evidence explaining their impact, warranting continued systematic research to clarify these controversies.

5.5. Nanotechnology in fertiliser development.

Nanotechnology, perhaps, holds a strong promise to influence current fertiliser status, given the dramatic effects shown by nanoscale materials in food and agriculture. Nanomaterials, having sizes in the 1-100 nm range, are highly reactive due to their small size and large surface area, compared to bulk materials. In 2006, more than $50 billion dollars of nano-enabled products were sold globally (Jusko, 2007). More recently in 2013, the Project on Emerging Nanotechnologies reports that as of March 2011, some 1300 products now contain nanomaterials (http://www.nanotechproject.org). Thus, it is anticipated that before long the fertiliser industry will fully join in the nanotechnology revolution. Indeed, available evidence indicates that the chemical and physical attributes of nanomaterials can be exploited to achieve useful benefits in crop fertilisation (DeRosa *et al.*, 2010; Ghormade *et al.*, 2010; Gogos *et al.*, 2012). Different kinds of nanomaterials, including those manufactured from elements not classified as nutrients (e.g., titanium, silicon) have been demonstrated to enhance the growth of crop plants (Zheng *et al.*, 2005; Yang *et al.*, 2007; Larue *et al.*, 2012; Siddique *et al.,* 2014). Nanoforms of micronutrients such as Zn, Fe and Mn have been demonstrated as being able to improve crop growth or the nutritional quality of these elements, sometimes to a greater extent than the ionic nutrient (Alidoust and Isoda, 2013; Pradhan *et al.*, 2013; Zhao *et al.*, 2013).

Thus, the development of ‘nanofertilisers' could be a promising technology. Through nanotechnology, micronutrients can be delivered in nanoparticulate forms so that they provide a continuous source of the ions as they dissolve in the rhizosphere or *in planta*. Similarly, current fertilisers can be packaged into forms that enhance their solubility and accessibility in the rhizosphere or in the plant tissue by encapsulating the nutrients in biodegradable nanopolymers that sense nutrient deficiency cues such as root exudate production or pH, releasing their nutrient contents for plant uptake in sync with the plant's need. Beyond single nutrients, composite nanoparticles of different but compatible nutrients also can be delivered into plant tissues via soil or foliar application, where they slowly dissolve to release ions for plant assimilation, triggered by specific environmental signals.

However, despite its immense benefits, nanotechnology also comes with risks, given the undesirable effects it could have on non-target organisms, including plants and plant-associated soil microbes (Dimkpa *et al.*, 2012b; Dimkpa, 2014; Gardea-Torresdey *et al.*, 2014). Accordingly, any large-scale adoption of nanotechnology for agricultural purposes must be preceded by rigorous research to provide a better understanding of its agro-ecological ramifications, including the plant-specificity of the activity of the different nanomaterials, as well as any potential biotoxicity. Fortunately, such research endeavours are ongoing in many centres globally, funded by government agencies such as USDA, EPA and their EU and Asian equivalents, as indicated by funding agency disclosures in the published literature.

5.6. Fertigation.

Delivery of nutrients through irrigation is yet another strategy that can be fully integrated into fertiliser regimes, to tune appropriate application rates and timing to crop demand. Fertigation has been shown to be economically viable in horticultural field crops and to provide high uptake efficiencies (e.g. Yasuor *et al.*, 2013) and fruit orchards. Further control of nutrient supply is practiced in soilless cultivation in greenhouses, where uptake efficiencies are extremely high, but may not reach 100% due, perhaps, to poor water quality with high sodium content (Van Os, 1999).

5.7. Crops and crop cycle.

A better understanding of the biological mechanisms surrounding plant nutrition may permit the identification of a range of nutrient delivery strategies that ensure not just instantaneous uptake by plants, but also the administration of the relevant nutrient. In addition to soil application, whether broadcast, placed or timed, fertilisation strategies can be better integrated to include management of seed nutrient content, seed coating, and foliar application. Throughout the crop cycle these different strategies can be exploited, as illustrated in Figure 1. Antagonistic soil-plant-microbe-nutrient relations could benefit by exploiting synergism while by-passing antagonism by combining different approaches.

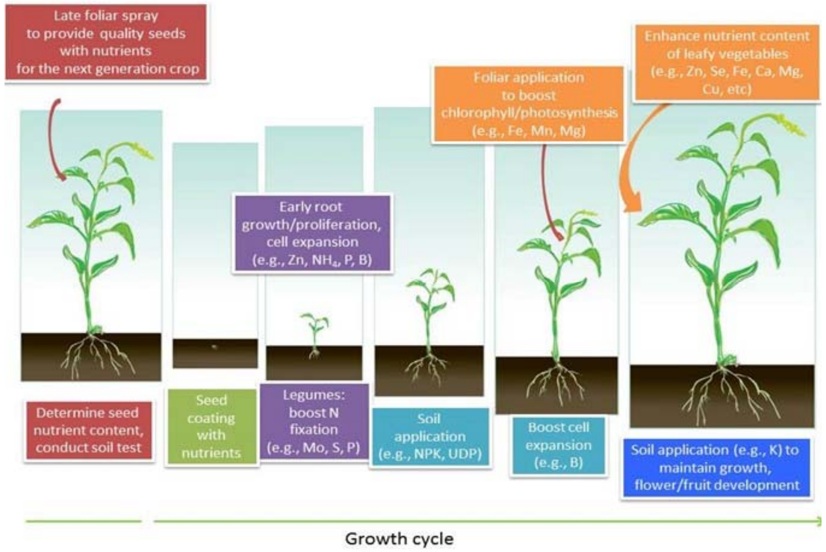

Figure 1. *Different fertilisation strategies throughout the crop cycle.*

Fertilisation strategies should also assume a more crop-specific approach. Foliar fertilisation may directly affect the yield and quality of leafy vegetables. Yet this pathway may be less effective in cereals if foliar-applied nutrients were less mobile and assimilated in leaf tissues rather than being translocated to the grains. Similarly, specific nutrient mixtures may be needed to enhance nodulation in legume crops. Insight in the requirement of nutrients during the plant's life may allow 'uploading' of rice seedlings with micronutrients for instance in the seedbeds, some of which might be sufficient for the rest of their growth cycle.

6. REVISITING FERTILISERS AND FERTILISATION TECHNOLOGIES.

While fertilisers are essential to secure sufficient food, the associated adverse environmental implications and the fact that they have not yet been effectively used to lift many poor farmers out of poverty or to help to defeat malnutrition urges the revisiting of the fertilisation process. The low uptake efficiencies and losses incurred when fertilisers are applied to agricultural crops provide a great opportunity for improvement. This gap between intended functionalities and actual impacts may arise because some chemists, chemical engineers and industrial processing technologists, following laws of physical and chemical processes, have little input from knowledge of plant physiology. No doubt, fertiliser products have to meet a range of physical and chemical property standards that primarily facilitate the industrial production processes, easy handling during transportation and mechanical application. Much of the recent increase in the production of urea as an N fertiliser has been related to an availability of local natural gas rather than to a local demand for N. The Haber-Bosch process in which inert N_2 is converted into reactive N celebrated its centennial anniversary in 2013, however there has been little conceptual change made to this ancient process, and derived fertiliser products such as urea are highly concentrated in order to reduce transport costs. Similarly, P, K and other fertilisers obtained from capital intensive mining are handled as bulk commodities that are marketed in large volumes to recover capital and operational costs. A renewed impetus is needed to arrive at novel ways of packaging and delivering nutrients to plants, based on a better integration of the plant physiological processes related to the different modes of nutrient uptake, transport and metabolism, in sync with timing and quantities of nutrient required for the physiological growth processes. In addition, the wealth of knowledge being gained from i) edaphic and soil ecological processes such as interactions among nutrients, ii) interaction between plants and micro-organisms and between nutrients and soil water – that determine nutrient solubility and availability, iii) alternative nutrient uptake forms (e.g. nano), and iv) alternative routes of plant nutrients uptake and delivery should be leveraged in developing integrated fertiliser strategies that better address the plant's need. This renewal from our understanding of plant-soil-microbes-water-nutrient processes will guide the pathway in the search for fertiliser products that deliver nutrients that can be available immediately to plants. The uptake efficiency and efficacy of such novel fertilisers can further be optimised through ISFM approaches to account for cropping system dynamics and through spatial-temporal tuning of activities, such as within watersheds.

A research protocol to tune nutrient delivery to plant's need, therefore, ought to include the following five considerations: composition, packaging, application, crop and ecosystem, coined by the VFRC as the Fertilizer Tech 5. A revisit in fertiliser research is needed to move from a mainly 'lifeless' physico-chemical process, to a 'living' biological process whereby biologists, in an interactive process, work with chemists in formulating and packaging the nutrients to meet specific crop requirements. The array of packaging and delivery mechanisms could exploit synergistic processes while by-passing antagonism such as the use of micronutrients to enhance the process of uptake of macronutrients. Macronutrients, even in poor soils, may be sufficiently present in the soil but not exploitable by crops because of limited root capacity, which could be increased through micronutrients, even with foliar application. This approach will set the stage for moving away from the current practice of largely using bulk fertilisers that are generic for most crops and soils, to highly specific and targeted quantities of fertilisers better aligned with specific plant, soil and ecological processes.

There is ample evidence that food quality can be improved through the application of the right composition of nutrients, but this opportunity to help fight malnutrition has yet to be extensively exploited. Exploiting the ecological synergies among nutrients will pave the path for improved nutritional quality of crop produce as well. The array of alternative delivery mechanisms may entail adjustments of farm practices. Yet, such fertiliser products could be easily integrated in current practices or might even reduce input costs and increase farm produce and income. Foliar fertilisers could be sprayed along with current applications of other agro-chemicals. Fertilisers packaged in tablets, much like dishwasher tablets, would contain the right composition of micronutrients in right quantities for one application per knapsack, easing application practices. Nutrient-coated seeds may not significantly affect existing farm practices. Labour requirements such as that for weeding, may even be reduced up to 15 to 25%, as is being observed with the deep placement of USG at 7 to 10 cm below the soil surface in rice, compared with broadcast application of prilled urea (IFDC, 2010).

Recapturing of nutrients either directly lost from the field or after consumption by humans and animals has to become a much more integral part of fertiliser production. Recycling nutrient fertilisers should not only be encouraged because of the finite nature of mined nutrients but as an essential strategy for reducing the amount of new inert nutrients converted into reactive nutrients and released into the environment. Normative research including setting clear standards and protocols will be required to unravel the functionality, efficiency and efficacy of recycled nutrient products and to arrive at packaging and delivery strategies for instantaneous uptake and use. Pursuing these different avenues to increase the prompt uptake of nutrients by crop plants and to recycle nutrients implies that increasing global food production may require the use of less rather than more mineral nutrients, globally. However, mineral fertiliser use should still be increased in continents that currently underutilise them.

This transformation from bulk to targeted fertilisers calls for a transition by the fertiliser industry. Transitions result from the interplay between different drivers and actors. While these may emerge spontaneously or unexpectedly due to sudden events, the governing processes of change can support a more gradual transformation. Valuable lessons could be learned from developments in pesticides over the past decades that moved from toxic, persistent chemicals towards targeted, systemic bio-pesticides based on understanding of the relevant biological processes. Research by the public and private sector, along with interventions by governments and concerns expressed by NGOs, all have contributed to the change, as was the involvement of actors in the production and distribution chain in multi-stakeholder platforms (Barzman and Dachbrodt-Saaydehb, 2011). Processes of change may be catalysed also by entrepreneurs, certainly if changing the course of the mainstream enterprises would require major industrial and business adjustments, including forward or backward integration. In this regard, the VFRC is currently painting a landscape of actors influencing the current industry and identifying actors from other disciplines, such as the health and medical sector and environmental and development organisations, that could catalyse the process of change.

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