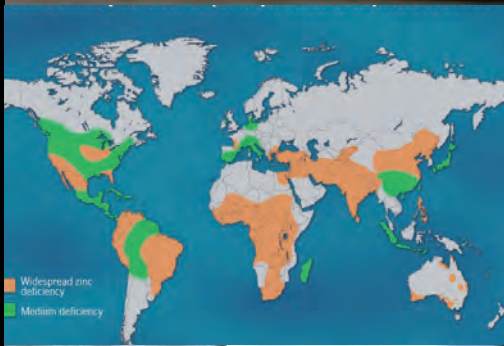


Schaarste van micronutriënten in bodem, voedsel en minerale voorraden

Achtergrondrapporten

- I. *Micronutrients in agriculture and the world food system*
- II. Suppletie van micronutriënten vanuit de mijnbouw
- III. Micronutriënten in de landbouw en beschikbaarheid in de bodem



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Toelichting bij de foto's op de omslag

Op de voorkant van linksboven met de klok mee:

- Bietenblad met zinktekort
- Rammelsbergmijn nabij Goslar in de Harz, Duitsland. Belangrijke producten waren zilver-erts, koper en lood. De mijn is gesloten in 1988.
- Runderen met koperdeficiëntie
- Kopermijn in Arizona
- Bijvoeding van schapen met mineralen inclusief micronutriënten
- Gebieden in de wereld waar zinkdeficiënties in belangrijke gewassen voorkomen.

Op de achterkant:

- Baby met zinkdeficiëntie

Schaarste van micronutriënten in bodem, voedsel en minerale voorraden

Urgentie en opties voor beleid

Achtergrondrapporten

I	R.L. Voortman (2012) Micronutrients in agriculture and the world food system – future scarcity and implications Centre for World Food Studies (SOW-VU), Vrije Universiteit, Amsterdam	blz 1
II	T. Bastein en T. van Bree (2012) Suppletie van micronutriënten vanuit de mijnbouw TNO, Delft	61
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Achtergrondrapporten bij:

Udo de Haes, H.A., R.L. Voortman, T. Bastein, D.W. Bussink, C.W. Rougoor,
W.J. van der Weijden (2012) **Schaarste van micronutriënten in bodem,
voedsel en minerale voorraden. Urgentie en opties voor beleid**
Platform Landbouw, Innovatie & Samenleving, juni 2012

Micronutrients in agriculture and the world food system

Future scarcity and implications

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1 Introduction

One of the problems Humanity is facing is how to produce sufficient good quality food for a growing population at affordable prices. The world population is still to increase by about 35 percent, to peak at about 9.5 billion around 2050. Furthermore, rising incomes in developing countries are expected to increase demand for livestock products and, consequently, for animal feeds as well. To meet the increased demand for food and feed, agricultural production will have to be stepped up, including roughly an increase of 70% of agricultural production by 2050 (Bruinsma, 2009). Meat and milk production are projected to double by 2050 (Steinfeld et al., 2006). Producing the food for the global population, by itself, may already seem a formidable task ahead. However, the world food system is not a stand-alone issue as it has many ramifications into other global issues such as climate change/greenhouse gas emissions, energy scarcity/biofuel production, scarcity of land and inputs (e.g. water, phosphorus), and last but not least biodiversity. As will be shown, there are intricate ‘linkages of sustainability’ (various authors in Graedel and Van der Voet, 2010) between these issues that need to be considered jointly so as to develop a proper perspective on the *problematique* at hand.

Naturally, agricultural production can be increased either through area expansion or through improved yields per hectare or both. The option of area expansion raises the question if there is sufficient land available that is suitable enough to allow agriculture so as to satisfy the area expansion requirements for crops, feeds and biofuels combined. Indeed, there is evidence to suggest that currently unused land has greater, and sometimes overruling, constraints for agricultural production (e.g. Young, 1999). Moreover, annually productive land is lost to urbanization, erosion and salinization. At the same time, clearing naturally vegetated land for cultivation obviously reduces biodiversity, but also inevitably results in greenhouse gas emissions (carbon, nitrogen) into the atmosphere, the magnitude of which depends on vegetation and soil characteristics. In case of biofuel crops, intended to be a low carbon energy source to displace fossil fuels, land clearing in fact causes that a carbon-debt is incurred to the extent that it may take many years to compensate for the effect of land clearing (Fargione et al., 2008; Tilman et al., 2009).

The higher crop yield pathway usually is based on increased use of inputs like water and fertilizers, but also here there are complicating issues of scarcity, environmental issues and sustainability. Fresh water is an important production factor in agriculture as about 70% of the fresh water on earth is used by it. Water is also becoming increasingly scarce (e.g. Rijsberman, 2006), while desalination of seawater is technically possible, but energy intensive, resulting in greenhouse gas emissions. Fertilizer application is one of the main vehicles to improve crop yields, but the known reserves of for instance phosphate rock are also limited (Cordell et al., 2009; Smit et al., 2009; Udo de Haes et al., 2009). Moreover, high nitrogen fertilizer doses inevitably lead to emissions of nitrous oxides, a powerful greenhouse gas (Crutzen et al., 2007). Furthermore, high doses of nitrogen and phosphorus are also likely to increase pollution of surface and ground waters, as well as coastal zones (hypoxia). In addition to the impact of arable farming, the expansion of the livestock sector may equally be expected to increase greenhouse gas emissions. Currently, this sector is already responsible for 18 percent of global emissions, notably methane (Steinfeld et al., 2006). From the point of view of greenhouse gas emissions, ideally no additional land would be cleared from vegetation and high production levels would be achieved with lower greenhouse gas emissions and pollution. This amounts to developing an entirely new agricultural technology, notably where fertilizer use is concerned. Also in

the livestock sector low-carbon technologies have to be developed, if emissions are to be minimized. Clearly, combining the production of sufficient food and energy for a growing and more affluent global population in a low-carbon manner seems a daunting challenge, unless new agricultural technologies can be developed that pave the way.

Further adding to the concern are a number of uncertainties around the future world food system. It is for instance highly uncertain what greenhouse gas induced climate change will imply for crop yield potentials and global agricultural production. Also the outcome of potential competition for land and inputs between food and biofuel production is uncertain. What will it imply for food and fuel prices and consequently accessibility of food for the poor? The recent price volatility of cereals and food riots due to higher prices may be taken as a notification of what may happen in the future. Furthermore, what will humanity have to face when the integrity of the biosphere is seriously disturbed? Unfortunately, the answers to these questions will remain highly uncertain.

Above we have seen that even basic production factors such as land, water and fertilizers may increasingly constrain the possibilities to produce the growing global food and energy requirements. At the same time though, the opportunities for improved efficiencies in agricultural production seem amply available. For instance, the current phosphorus use efficiency in agriculture is still very low (10-30%), thus leaving room for substantial improvement. It has also been suggested that sizeable improvements in crop productivity are possible based on the current water availability (Rockström et al., 2007). Improved technologies, therefore, can possibly also counteract on the scarcities of these production factors.

The preceding paragraphs have shown that the world food system is only one of a number of issues of global concern that are interlinked in a complex system with forward and backward loops between them and that must be looked into in its entirety where sustainability is concerned (various authors in Graedel and van der Voet, 2010). A large body of literature deals with the above-described land-food-feed-fuel-inputs-biodiversity nexus, though usually with only parts thereof. Remarkably, to date, imminent metal scarcities and how these could possibly affect agriculture, the world food system and human health are practically never considered. As will be shown, this constitutes a serious omission.

A number of metals are essential micronutrients for crops and humans. They are required in minor quantities only, but if present at deficient levels within plants and humans, disease and poor growth will follow, and ultimately death. Conversely, if soils are deficient in a certain micronutrient, its application as fertilizer will improve crop health, increase crop yields and ameliorate food quality for humans, thus in turn reducing human disease and even death toll. Current use of micronutrient fertilizers is low though. The fertilizers now applied to crops mostly contain N, P and K, and for the micronutrients crops rely on the amounts naturally available in the soil (and manure, if applied). Long duration cropping with high yields, therefore, inevitably results in micronutrient deficiency and, consequently, lower crop yields. Indeed, stagnating and even declining yields in the Green Revolution areas of India are attributed to unbalanced fertilization with N, P and K, resulting in micronutrient deficiencies (M.V. Singh, 2009). At the same time, it has been argued that for instance in Africa, currently unused land is likely to suffer from micronutrient deficiencies (Voortman et al., 2000; Voortman, 2010). Metal micronutrients thus may prove essential to sustain land productivity in cultivated land and they may be

instrumental in opening up new land. As such, these micronutrients may prove crucial to achieve the goal to produce sufficient food of good quality as well as energy for the global population.

Although, metal micronutrients potentially can contribute significantly to increase and sustain global food production, the point is that most of these mined metals are used for non-agricultural applications. Even for these purposes alone, a number of the micronutrients such as copper and zinc are generally expected to become scarce in a not too distant future. Opinion varies on how severe metal scarcity will be, what impact it will have on society and how humanity will cope with it (Gordon et al., 2006). However, whether optimist or pessimist, most authors agree that metals such as copper and zinc will indeed in a foreseeable future become scarce and/or expensive (e.g. McKinsey, 2011; Price, Waterhouse, Coopers, 2011). This report, therefore, considers potential scarcity of metals specifically in relation to agriculture, human nutrition and the world food system with emphasis on potential societal impacts and possible coping mechanisms. Copper and zinc are mostly used as examples. In an annex to this report attention is given to selenium. Selenium is essential for cattle and for humans, but not for plants. Given the extensive deficiencies of selenium in the food supply for both cattle and man and given the fact that we can regard selenium as representative for the important micronutrients which are essential for cattle and man but not for plants, selenium will be dealt with in an annex to this report.

The report proceeds as follows. Section 2 gives an overview which elements are essential, and discusses what essentiality of mineral nutrient entails together with the symptoms and diseases related to micronutrient deficiencies in plants and humans. Section 3 presents the quantitative mineral nutrient requirements of plants and humans. Section 4 deals with the currently known spatial extent of soil micronutrient deficiencies and how this translates into human deficiencies. It also presents an example of the global disease burden resulting from human micronutrient deficiencies. In section 5, first a brief overview is presented of currently known reserves of mineral nutrients. In conjunction some cautionary remarks are made on the quality of the available data on the reserves of mineable metal ores. What follows is an approximation of micronutrient requirements in agriculture and cautionary remarks to suggest that biofuel crops are likely to compete with food crops for nutrient inputs. Next to mining operations, soils themselves can be an important source of micronutrients. Section 6, therefore quantifies the total amounts of micronutrient present in the soil and the proportion thereof that can be taken up by plants. The gap between the two appears to be very large, thus suggesting that possibly with improved technologies a greater part of the nutrients present in the soil can be exploited. Time and again this report emphasizes guiding principles for the nature of future agricultural activities, notably the requirements for efficient nutrient use. These principles are further developed in section 7 on the basis of theoretical considerations in combination with the realities of the ecological diversity of soils, as expressed in soil chemical properties, so as to define what mineral scarcity is likely to imply for the agriculture of the future. It is further shown with examples that current fertilizer practice is remotely distant from what the guiding principles would require. Finally, this defines an extensive in-depth research agenda. Section 8 presents the conclusions. In any case, coping with mineral scarcity in agriculture, human nutrition and the global food system is a major task ahead.

2 The essentiality of mineral nutrients and plant and human deficiency symptoms

An array of mineral nutrients is essential for growth, functioning and health of plants, animals and human beings (see Table 1). This section describes, by means of examples, what the function of copper and zinc is in the growth and functioning of plants and humans, and what disease symptoms develop in case of deficiency.

Generally speaking, if the level of uptake of a particular element is insufficient in humans, it causes retardation of growth and development and, depending on the deficient element and the severity of the deficiency, particular disease symptoms may develop, including in some cases even mental retardation. Consumption of too high levels of essential mineral nutrients equally affects growth and health (toxicity). In essence, to lead a healthy and productive life, humans need a balanced supply of essential mineral nutrients (stoichiometric requirement). The same applies to plants, and when uptake of one or more nutrients from the soil is restricted, their physiology is equally disturbed, nutrient-specific diseases develop and ultimately the plant may die or reproduction may be affected. In the case of crops this results in lower economically useful yields. Human nutrient deficiencies and toxicities essentially result from soil nutrient deficiencies and toxicities, since most human food directly or indirectly derives from plants grown in soils. In the following we mainly consider nutrient deficiencies, notably regarding copper and zinc.

In plants, copper, among others, is involved in photosynthesis, production of protein and the development of reproductive organs such as flowers and seeds. Plants differ very much in their sensitivity to Cu deficiency, which finds expression in stunted growth, distortion of young leaves, necrosis of the apical meristem and bleaching of young leaves called 'white tip'. Zinc, among others, is involved in many enzymatic reactions, carbohydrate metabolism, maintenance of integrity of biomembranes and protein synthesis. Zinc deficient plants have low rates of protein synthesis and consequently the protein content of edible crop parts is low. Visible symptoms of Zn deficiency in plants are stunted growth due to shortening of internodes, drastic decreases of leaf size, die-back of apices and leaf chlorosis (Marschner, 1995).

In humans, copper is a critical functional component of many enzyme reactions. Copper containing enzymes are, among others, involved in energy production (ATP synthesis), iron metabolism involved in red blood cell formation, brain function, neurotransmitter synthesis, immune system integrity, antioxidant functions and regulation of gene expression. Clinically evident copper deficiency is rather uncommon, but it may cause anemia, low numbers of white blood cells (increased susceptibility to infection), abnormalities of bone development, loss of pigmentation and generally impaired growth. Mild copper deficiency lowers resistance to infections, and causes reproductive problems, general fatigue and impaired brain function (e.g. Linus Pauling Institute, 2011).

Zinc in humans is involved in neurotransmission and also has a catalytic and structural role in enzyme reactions (various sources quoted in Alloway, 2009). Zinc is further an element in

Table 1. Essential mineral nutrients in plant and human nutrition.

Nutrient	Plants ¹⁾	Humans ²⁾	Nutrient	Plants ¹⁾	Humans ²⁾
Nitrogen	+	+	Zinc	+	+
Potassium	+	+	Aluminium	±	-
Calcium	+	+	Chlorine	±	+
Magnesium	+	+	Cobalt	±	+
Phosphorus	+	+	Nickel	±	(+)
Sulphur	+	+	Selenium	±	+
Boron	+	-	Silicon	±	+
Copper	+	+	Sodium	±	+
Iron	+	+	Chromium	-	+
Manganese	+	+	Iodine	-	+
Molybdenum	+	+			

¹⁾ ‘+’:essential; ‘-’: not required; ‘±’ :essentiality not established, but considered beneficial

²⁾ ‘+’:essential; ‘-’: not required; ‘(+)’ : essentiality not established, but possibly required

Source: Nubé and Voortman, 2006; based on Marschner 1995; Garrow et al, 2000; Wiseman, 2002.

protein molecules involved in DNA replication. Zinc deficiency, among others, causes growth retardation, delayed sexual maturation, increased infection susceptibility, immune system deficiencies, skin rashes and chronic diarrhea. Mild Zinc deficiency is particularly common in children in developing countries and contributes to impaired physical and neuropsychological development and increased susceptibility to life-threatening infections (e.g. Linus Pauling Institute, 2011).

The examples of copper and zinc clearly demonstrate what essentiality entails and what deficient plant uptake and human ingestion of essential mineral nutrients may cause. All other essential mineral nutrients in Table 1 perform many functions, which are equally essential for the physiological functioning of plants, animals and humans. There is no substitute for these mineral nutrients that are essential for life on earth, because these nutrients cannot be synthesized by plants.

3 Mineral nutrient requirements of plants and humans

Although the nutrients mentioned in the previous section are all essential, they are required in different amounts for plant and human physiology to function properly. Each species, and in crops even each variety, has its own specific stoichiometric requirements: i.e. the relative quantities of nutrients present in the various tissues. It is, therefore, difficult to present precise figures, but even so, some broad generalizations on the quantity of essential mineral nutrients required can be made. These are briefly presented in this section.

In the case of the plant regnum, but mainly based on agronomic and crop physiological research (e.g. Marschner, 1995), commonly a distinction is made between macro-, meso- and micronutrients, which obviously implies that plant requirements are high, medium and low respectively (Table 2). To grow properly, plants need relatively large amounts of nitrogen and potassium. The plant's requirements for calcium, magnesium, phosphorus and sulphur are generally lower, hence the term meso-nutrient. In this context, it is relevant to mention that phosphorus is often considered a macronutrient, notably in the agronomic literature. However, because the phosphorus content of plants is often similar or even lower than Ca, Mg and S, it seems more appropriate to classify P as a mesonutrient. Finally, micronutrients, also called trace elements, indeed are required in very low amounts, or traces, and yet they are essential. Table 3 provides a generic quantification for these nutrient groupings in terms of plant nutrient content. These figures are not necessarily representative for the relative nutrient contents of the edible parts of crops due to specialized functions of particular plant tissues and the implied elemental requirements (e.g. the concentration of chlorophyll in leaves).

The three groups of plant nutrients considered and the differences in amounts required also have agronomic implications. If an essential plant nutrient is seriously deficient in the soil, then the application of the element concerned is expected to increase yields. The yield increments on the basis of per kilogramme applied nutrient are then likely to be highest in the case of micronutrients (Table 2). In addition to that, it is commonly observed in the agronomic literature that the application of micronutrients has a residual yield increasing effect in the following years. However, this should not come as a surprise, because the ratio of application dose and plant requirements is usually higher in micronutrients than in macronutrients. Such practices reflect the difficulties of spreading very thinly the minor amounts of nutrients required.

Human requirements for the essential macro- and mesonutrients for plants are also far higher than the trace elements. However, as might be expected, based on physiologic and, subsequently, stoichiometric requirements the ratios between nutrients are to some extent different (Table 3). A major difference is that sodium and chlorine that are possibly beneficial for plants only, are essential for animals and humans and required in relative large amounts, if compared to trace elements. One may also observe that the Ca and P content in humans is far higher than in plants. This is mainly due to the accumulation of these elements in the bone tissue of the skeleton. The figures for Ca and P, if compared to those of other elements, are therefore not representative for daily intake requirements. Yet another major difference between plants and animals is that the latter require organic micronutrients, such

Table 2. Plant mineral nutrients classified on the basis of the amounts required by plants, the yield increase per kg in case of strong deficiency and residual effect duration.*

Nutrient group	Elements	Δ Yield per kg	Residual effect
Macronutrients	N, K	Low	Short-medium
Mesonutrients	Ca, Mg, P, S	Medium	Medium (-long)
Micronutrients	B, Cu, Fe, Mn, Mo, Zn	High	Long
Accessory?	Al, Cl, Co, Na, Ni, Se, Si	??	??

*Requirements differ with species and plant parts that form the economic yield

Table 3. Generic nutrient content of plants and humans as percentages of dry weight (Sources: Markert (1992) for plants; human micronutrients from Iyengar (1998, except molybdenum); others: compilation of various internet sources).

Nutrient	Plants	Humans	Nutrient	Plants	Humans
Nitrogen	2.5	9	Zinc	0.005	0.003
Potassium	1.9	0.75	Aluminium	0.008	0.0001
Calcium	1.0	4.2	Chlorine	0.2	0.45
Magnesium	0.2	0.15	Cobalt	0.00002	0.000002
Phosphorus	0.2	3.3	Nickel	0.00015	0.000007
Sulphur	0.3	0.75	Selenium	0.000002	0.00002
Boron	0.004	0.00002	Silicon	0.1	0.0036
Copper	0.001	0.0002	Sodium	0.015	0.45
Iron	0.015	0.007	Chromium	0.00015	0.000001
Manganese	0.02	0.000016	Iodine	0.0003	0.00002
Molybdenum	0.00005	0.000039			

*The nutrient content of whole plants is not necessarily representative for the harvested or consumed part.

as vitamins, which they are unable to synthesize themselves. However, organic micronutrients are beyond the scope of this report, since it considers only essential mineral nutrients.

In sum, the availability of mineral nutrients in the soil, in proportions that match the stoichiometric requirements of crop plants, and how this transmits to human nutrition, is crucial for sustaining the world food system and humanity at large, through the effect these essential nutrients can have on crop yields and nutritional quality of food.

4 Soil and human micronutrient deficiencies and associated disease burden

In the previous sections it has been observed that human growth is retarded and diseases develop if food uptake fails to meet the stoichiometric requirements of essential mineral nutrients. This section assesses the prevalence of micronutrient deficiencies (with emphasis on zinc, and to a lesser degree on copper) in soils, plants and humans at local, national and global scales. First, the soil conditions that frequently lead to copper and zinc deficiency are summarized. Second, by means of example, the direct relationship of soil nutrient deficiency (selenium) and certain diseases is presented. Third, the spatial extent of soil micronutrient deficiencies is exposed using the examples of two large and populous countries: India and China. What follows shows, at more local scales, how severe and widespread human micronutrient deficiencies can be, if soils are deficient or diets are highly monotonous or both. Then, with global data, the spatial coincidence of soil zinc deficiency, human deficiency and the prevalence of stunting are established. Finally, the disease burden and death toll of zinc and iron deficiency is presented for major regions of the world.

Soil types and micro-nutrient deficiency occurrences

Generally, micronutrient deficiencies can be of natural origin if the original parent material, in which soils have developed, was low in the micronutrient concerned. Human-induced deficiencies occur, when land is frequently used for cropping and micronutrients are not replenished (nutrient mining). Particular soil types, though, are more prone to deficiencies, because of the inherent properties they possess. For instance, soil conditions that most commonly give rise to zinc and copper deficiencies include one or more of the following conditions:

- low total zinc/copper content (such as sandy soils with low contents of organic matter)
- alkaline pH
- high calcium carbonate content (calcareous soils)
- very low pH, highly weathered parent materials (e.g. acid tropical soils)
- peat and muck (organic soils)
- high phosphate status (natural or due to fertilizer application)

Zinc deficiency may also occur under the following conditions:

- high salt concentrations (saline soils)
- prolonged waterlogging or flooding (paddy rice soils)
- high magnesium concentrations (in the soil and in irrigation water).

Copper deficiency can further occur when molybdenum content of soils is high (Sources IDA, 1988; IZA, 2011).

Soil micronutrient deficiency and the occurrence of human disease

Although possibly instrumental for tackling human micronutrient deficiencies, very little systematic research has been undertaken to establish the relationship between soil nutrient deficiencies and the prevalence of disease. In fact, systematic soil sampling and analysis of their micronutrient levels is a rarity rather than rule. An exceptional case is the nationwide study in China of the relationship between soil selenium levels and particular diseases (Tan, 2004, quoted in Yang et al., 2007). Selenium is not an essential micronutrient for plants, but it has been classified under the group of beneficial elements.

However, selenium is an essential micronutrient in human nutrition, and there are two well-defined disorders that are caused by or at least associated with selenium deficiency: Keshan disease and Kaschin-Beck disease. Keshan disease occurs mainly in children and women of child-bearing age, and impairs cardiac functioning. Kaschin-Beck disease is an osteo-arthropathy, causing deformity of joints (Tan et al., 2002). Figures 1 and 2 show the strong geographical linkages between soil selenium deficiency and the occurrence of human selenium deficiency as expressed in disease prevalence. For Chinese circumstances, the areas where these diseases occur have low population densities. In the past, people possibly stayed clear of areas with overt disease symptoms due to micronutrient deficiencies. The phenomenon that historically people have avoided areas with micronutrient deficiencies has also been observed in Africa (Voortman and Spiers, 2010). The China case study thus shows that the occurrence of human micronutrient deficiencies can be directly linked to soil conditions if knowledge on micronutrient deficiencies is available in combination with overt disease symptoms. Often though soil micronutrient levels are not known and clinical symptoms may not be as obviously expressed. Nevertheless, as we will see later, micronutrient deficiencies may be widespread, and severe to the extent that the functioning of humans is impaired.

Soil micronutrient deficiencies; the cases of India and China

Numerous publications have reported soil micronutrient deficiencies worldwide, but these also usually refer to spot observations, without an indication for what larger areas they are applicable (e.g. Sillanpää, 1982). Estimates of the spatial extent of micronutrient deficiencies for large areas that are clearly data-driven are available for India and China. These data are based on soil sample analysis and use earlier established threshold levels to establish deficiency/sufficiency on the basis of absolute levels of available plant nutrients present in the soil. In both countries micronutrient deficiencies occur widespread. Figure 3 shows the percentage of soils that are zinc deficient in India by administrative divisions. Zinc deficiencies have been established for 49% of the farmland (Singh 2011). In India, furthermore Boron, Molybdenum, Manganese and Iron deficiencies were 33, 13, 12, and 5 percent of farmland respectively, not mutually exclusive (see Table 4). Moreover, sulphur deficiencies occur in 46 percent of the Indian farmland (A.K. Singh, 2011). Copper deficiencies have only recently surfaced in India and are estimated to exist in 3% of the farmland. In India micronutrient deficiencies have successively become evident since 1960, when the Green Revolution started, and are attributed to unbalanced nutrient application, focusing on N, P and K only (Singh, 2008; A.K. Singh, 2011; M.V. Singh, 2011).

For China, zinc levels by natural units are presented in Figure 4. In the early nineties 51.1 percent of China's farmland was deficient in zinc (Lin and Li, 1997 quoted in Zou et al., 2008). Boron, molybdenum, manganese and iron deficiencies were 34.5, 46.8, 21.3, and 5.0 percent of farmland, respectively, not mutually exclusive (Lin and Li, 1997 quoted in Zou et al., 2008). In China the extent of copper deficiency was 6.9% of farmland (see Table 4). It particularly occurs in the southern parts of the country where zinc levels are high. This coincidence may be an expression of the well-known Cu-Zn antagonism, whereby high zinc levels inhibit the uptake of copper by plants, and vice-versa.

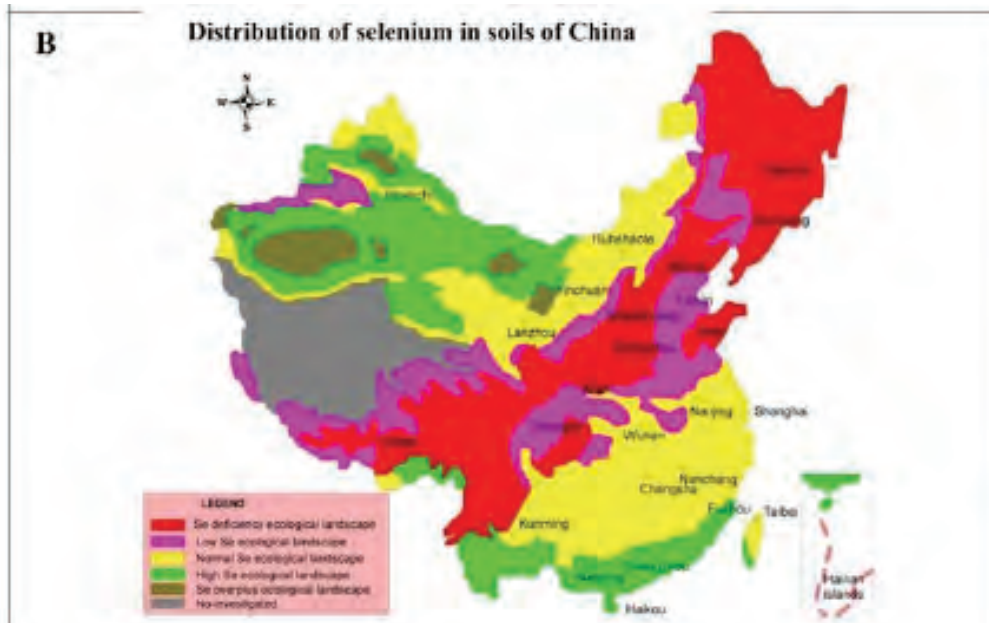


Figure 1. Grades of selenium present in China soils; reddish colors are low (Source Tan, 2004).

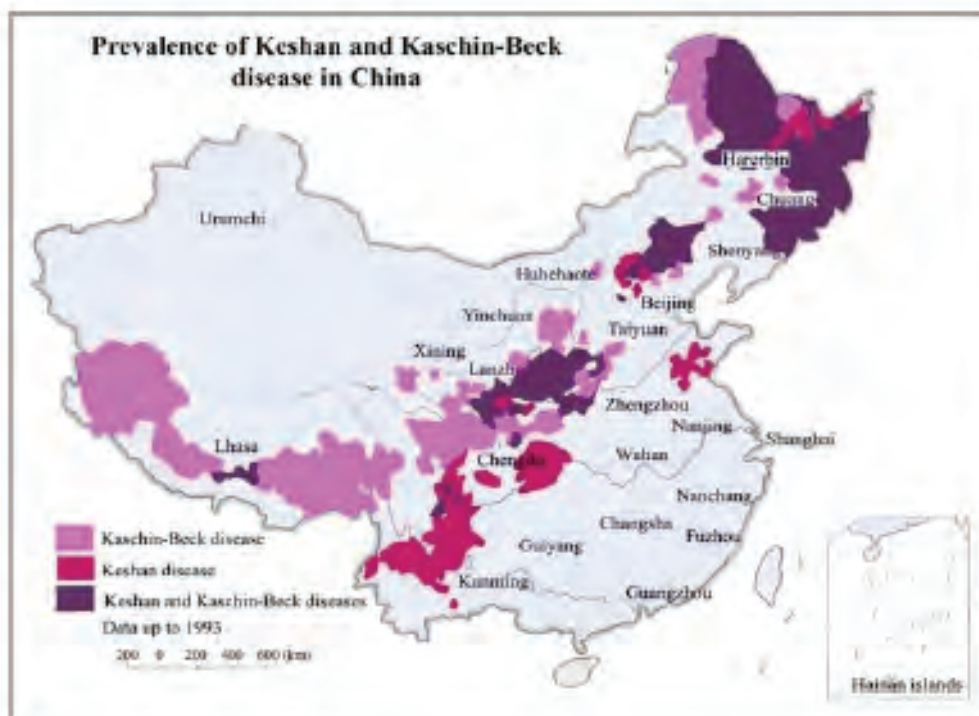


Figure 2. Prevalence of Keshan and Kaschin-Beck disease (and combinations) in China (source Tan, 2004).

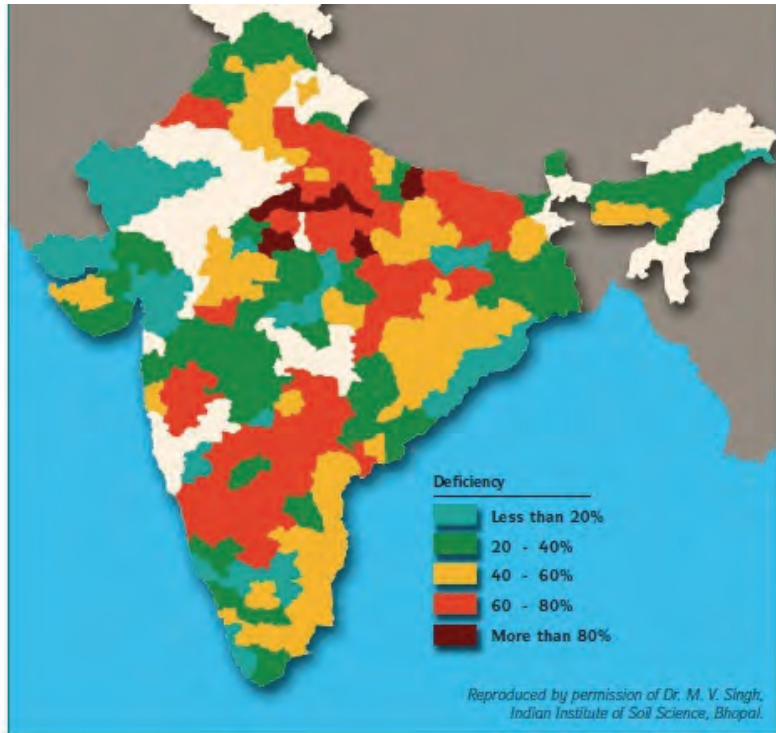


Figure 3. Percentage of farm land with zinc deficiency in India (source: Alloway, 2008).

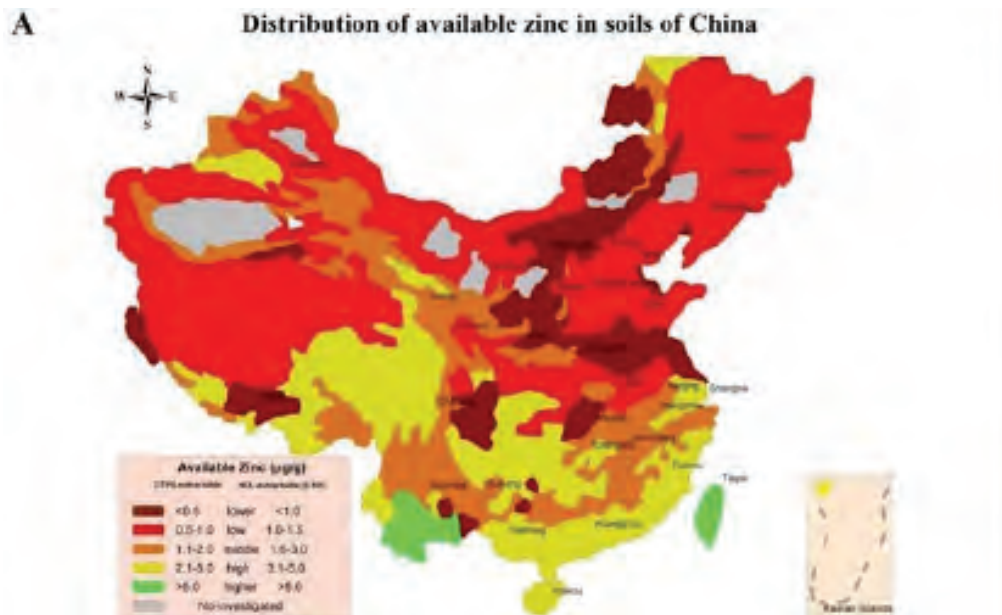


Figure 4. Grades of zinc present in China soils; red and dark red is low (Source: Yang et al., 2007, based on Liu, 1994).

Table 4. Micronutrient deficiencies in India and China as % of the farm land (For sources see text).

Micronutrient	India (%)	China (%)
Boron	33	34.5
Iron	5	5.0
Copper	3	6.9
Manganese	12	21.3
Molybdenum	13	46.8
Zinc	49	51.1
Sulphur	46	?

Other sources indicate 30% copper and 40% iron for China.

It is unclear whether the relative minor extent of iron and copper deficiency are reliable estimates, since other sources suggest deficiency levels of about 40 and 30 percent, respectively (Yang et al., based on Liu, 1991, 1993 and 1994). In any case, in China various micronutrient deficiencies occur on a very significant portion of its farmland. Although not reported as such, the large-scale micronutrient deficiencies in China are probably also induced by the Green Revolution technology and, because the data quoted are relatively old, the situation may have worsened ever since.

Other countries with a large proportion of zinc deficient arable land are Turkey, Iran and Pakistan with 50, 60 and 70 percent, respectively. Most of the Cerrado region of Brazil also appears to be zinc deficient (various sources quoted in Alloway, 2009). Spot-wise micronutrient deficiencies have been recorded widespread in Sub-Sahara Africa (Sillanpää, 1982; Kang and Osiname, 1985; Davies 1997), but systematic analysis based on soil chemical analysis as in India and China is lacking. When specifically researched, micronutrients often have given large yield increases: zinc in Ghana, Malawi, Nigeria and Zimbabwe (Abunyewa and Mercer-Quarshie, 2004; Wendt and Rijpma, 1997; Kayode and Agboola, 1985; Rodel and Hopley, 1973), copper in Nigeria and Tanzania (Ojeniyi and Kayode, 1993; Lisuma et al, 2006), boron in Malawi and Zimbabwe (Wendt and Rijpma, 1997; Rodel and Hopley, 1973) and iron in Nigeria (Kayode and Agboola, 1985). Targeted research is likely to reveal widespread micronutrient deficiencies in Sub-Sahara Africa as well, among others due to the nature of the soil parent material (Voortman et al., 2003)

In sum, India and China are large countries and together harbor about 1/3 of the global population. Both countries have further in common that a large amount of research is dedicated to soil micronutrient deficiencies. This research reveals that a broad spectrum of micronutrients can be deficient and some of these at very extensive scales. In both countries Zinc deficiency occurs in about 50 percent of the farmland and boron deficiency is present in 30 percent. Moreover, in China molybdenum deficiency affects almost 50 percent of the farmland. Although India and China cannot be held representative for the rest of the world, the data presented must be taken as a sign of how extensive and serious soil micronutrient deficiencies can be. In the case of zinc, this is confirmed by data from Turkey, Iran and Pakistan. Zinc and other micronutrient deficiencies have also been recorded widely across Sub-Sahara Africa.

Human micronutrient deficiencies

There are two common ways of assessing human micronutrient deficiencies. First, the food intake can be recorded and, in combination with the mineral content of the different foods, the intake of the various mineral nutrients can be calculated. Since analysis of food is time consuming and costly, mostly standard food tables are used for this purpose, which makes the method less precise. A second method is the analysis of blood serum for the various mineral nutrients. For each element specifically deficiency/sufficiency can be assessed while using earlier established threshold levels. Although this method fairly precisely measures conditions inside the human body, it is usually not implemented at large scales. Serum-based micronutrient studies, therefore, are mostly of a local nature. An exception is again China where estimates of human zinc deficiency at national level are available. It appears that about 60 percent of the rural population of China suffers from sub-clinical zinc deficiency (various sources quoted in Yang et al., 2007). More recently such figures have been confirmed through consumption data: insufficient zinc intake was observed in 2/3rds of the people below age 17 in Jiangsu province (Qin et al., 2009). Extensive soil zinc deficiency in China thus coincides with widespread human zinc deficiency.

To illustrate how serious micronutrient deficiencies can be, some spot-wise data will be presented for India and Africa. For instance in Haryana, India, serum-based analysis in pregnant women revealed multiple micronutrient deficiencies: serum levels for Zn, Fe and Cu were too low in 73.5, 73.4 and 2.7 percent, respectively (Pathak et al., 2004). It must be observed though that serum analysis of pregnant women is likely to overestimate the percentages of deficiencies of the population at large. In Burkina Faso it was established that 72 percent of children were zinc deficient (Müller et al., 2003). South African primary school children were zinc deficient in 46 percent of the cases (Samuel et al., 2010). Large food intake studies in Rwanda, Uganda and Tanzania, revealed at the level of households 87, 80 and 56 percent iron deficiency and 54, 50 and 26 percent zinc deficiency, respectively in these three countries (Ecker et al., 2010). These deficiencies reflect a common phenomenon in Africa where diets are very monotonous and heavily relying on locally produced staple foods. Because of such prevailing situations, one may suspect widespread occurrences of micronutrient disorders in Sub-Saharan Africa. *In sum*, nationwide data for China and spot-wise data from India and Sub-Saharan Africa show that large portions of rural populations may be affected by micronutrient deficiencies and frequently this refers even to multiple essential mineral nutrients.

Worldwide soil and human zinc deficiency and prevalence of human stunting

The cases of India and China have shown how widespread soil zinc deficiency can be. More local studies have also revealed the occurrence of broad-based human micronutrient deficiencies, notably in developing countries. At the global scale only for zinc there is a spatially explicit representation of its deficiency in soils with some reliability as depicted in Figure 5 (Alloway, 2008). The map is a heroic attempt to present the extent of Zn deficiencies worldwide. Zinc deficiencies in India and China are well represented in the map and the less extensive zinc deficiency in Southern China is also present. Extensive zinc deficiencies in Turkey, Iran and Pakistan are also shown up in the map and areas with zinc deficiency in Australia reflect Australian research (Holloway et al., 2008). Zones with widespread zinc deficiency in the USA are equally well represented (ILZRO, 1975). Particularly in the case of Africa the reliability may be questioned, since little systematic work has been done on micronutrient deficiencies. However, as earlier

indicated, when explicitly tested, zinc deficiency surfaced most frequently. So, although the sources used are not mentioned, for the map scale concerned the information seems sufficiently reliable, certainly while the category ‘widespread deficiency’ does not imply that all soils in the areas concerned are zinc deficient.

A human zinc deficiency risk in children under 5 years is depicted in Figure 6. The high-risk areas practically all coincide with areas showing soil zinc deficiency. The countries involved are mainly developing countries. It also appears that human zinc deficiency risks are lower in developed countries, even where soils are zinc deficient (e.g. USA, Europe). This is likely due to the fact that in developed countries the food eaten is more varied and of different geographic origin, while also including animal-based products. Remarkably, the risks of human zinc deficiency are medium in China and some Latin American countries, while soil zinc deficiency is widespread. In the case of China this contradicts local sources of information on the prevalence of human zinc deficiency.

Human zinc deficiency is frequently linked to the prevalence of stunting for which spatially explicit actually measured global data are available. Recording child age, height and weight on a sample basis is standardly conducted in all countries under the umbrella of the WHO. Data on the prevalence of stunting is based on the height for age ratio for children under 5 years of age. A child is considered stunted if the score is below minus two standard deviations from the median value of a global reference population as specified in the WHO child growth standards. From the outset it must be doubted if stunting can substitute for zinc deficiency, even though it is well known that low zinc intake results in growth retardation in humans (and plants). Since only the measurement of height is used and many other variables can contribute to stunting it supposedly is more of a synoptic indicator, signalling chronic under-nutrition. However, the data are quantitative and zinc deficiency is likely to be involved in stunting. Indeed, the coincidence of zinc deficiency (Figure 6) and stunting (Figure 7) is striking.

From Figure 7 we can further observe that practically all high-income countries have a low percentage of stunting incidences, which is coincident with absence of human zinc deficiency, even when soil zinc deficiency is present as for instance is the case in the USA (Figure 5). Very high levels of stunting occur mainly in Sub-Saharan Africa and South and South-East Asia¹ with a spatial coincidence of soil zinc deficiency (Figure 5) and associated human deficiency symptoms (Table 5). Relatively high stunting levels further occur in some isolated pockets.

¹ In this context it is relevant to mention that adult people of South Asian descent possibly have a predisposition for a low Body Mass Index (Nubé, 2008). Whether or not this would also imply high stunting incidences in children is uncertain. Anyway, low birth weights according to UNICEF (2006) in South Asia occur in 31 percent as opposed to 14 percent in Sub-Saharan Africa.

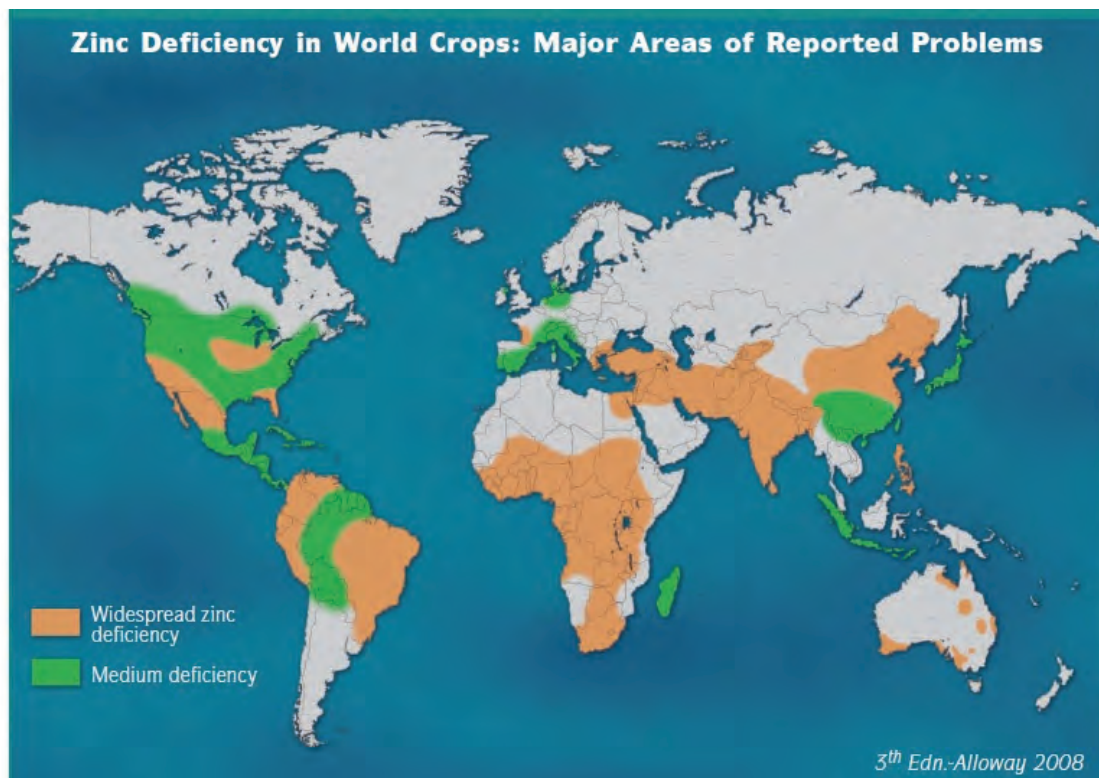


Figure 5. Global areas with soil zinc deficiencies (Source: Alloway, 2008).

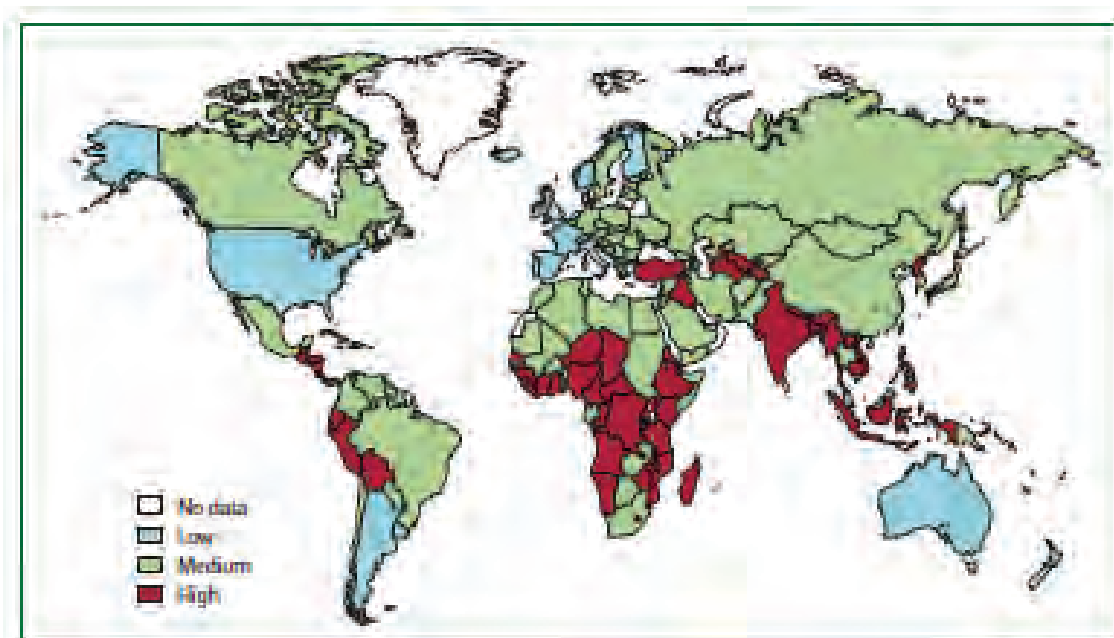


Figure 6. National risk of zinc deficiency in children under 5 years (source: Black et al., 2008).

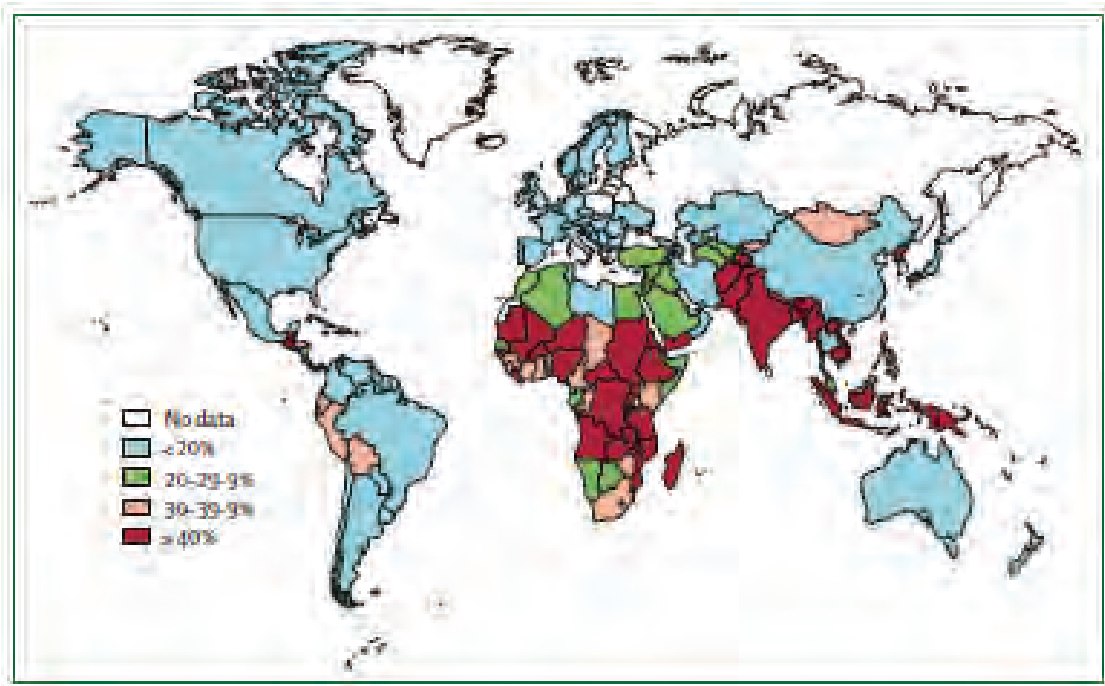


Figure 7. Prevalence of stunting in children under 5 years (source: Black et al., 2008).

Table 5. Estimated prevalence of iron and zinc deficiencies and annual death tolls for under 5 age children by geographic region (Source: Caulfield et al., 2006).

Region	Iron deficiency Anemia (%)	Zinc Deficiency (%)	Deaths Iron (thousands)	Deaths Zinc (thousands)
East Asia and the Pacific	40	7	18	15
Eastern Europe and Central Asia	22	10	3	4
Latin America and the Caribbean	46	33	10	15
Middle East and North Africa	63	46	10	94
South Asia	76	79	66	252
Sub-Saharan Africa	60	50	21	400
High-income countries	7	5	6	0

China and parts of South America again deviate from this pattern: soil zinc deficiencies occur widespread while stunting levels are low. Yet, as earlier observed, human zinc deficiency is widespread in China (Yang et al., 2007) and sizeable in Latin America (Caulfield et al., 2006). It thus appears that in low-income countries soil zinc deficiencies generally translate in human deficiencies, while high stunting prevalence rates practically always coincide with soil zinc deficiencies, but zinc deficiency does not necessarily always lead to stunting.

More quantitative data on the prevalence and impact of zinc deficiency is only available in tabular form for broad regions of the world. Table 5 presents data on the incidence of Fe and Zn deficiency in under 5 years old children and the resulting annual death toll (Source: Caulfield et al., 2006). The data are mere estimates and though obtained using a consistent methodology, they can be considered as plausible orders of magnitude only. Table 5 first of all confirms that micronutrient deficiency prevalence is low only in high-income countries. Human zinc deficiencies are particularly frequent in South Asia

and Africa, but it also occurs extensively in the Middle East and North Africa and with considerable incidence in Latin America and the Caribbean as well. The latter two observations to some extent confirm the earlier reported soil zinc deficiencies. However, the coincidence of soil and human deficiencies as reported for China is not evident in the data for East Asia. Letting prevail the Chinese national data on sub-clinical zinc deficiency, and while excluding high-income countries, the areas with high incidence of human zinc deficiency thus do correspond with the areas of soil zinc deficiency (Figure 5). The death tolls due to zinc deficiency are particularly large in South Asia and Sub-Saharan Africa. The total number of deaths amounts to about 800,000 per year, an order of magnitude similar to malaria victims. The extent of iron deficiency anemia is in general even greater than zinc deficiency, but the number of deaths is often far less. The set of maps, and the quantitative data on zinc deficiency presented here, thus indicate that human micronutrient deficiencies appear to be a typical condition of many developing countries and result regionally in a very high disease and death burden.

Summing up and outlook

The previous paragraphs have shown that sometimes there is an evident relationship between low soil micronutrient levels and certain diseases: the case of Selenium in China, and the case of zinc in developing countries in general. For other micronutrients such straightforward linkages have not been encountered. Next, it could be assessed how widespread soil deficiencies for a number of essential plant nutrients are, using the examples of India and China. Thereafter, the severity of human micronutrient deficiencies was shown with examples from China, India and Sub-Saharan Africa. Lastly, the coincidence of soil zinc deficiency, human zinc deficiency and stunting of children has been analyzed at the global scale. It appeared that such relationships do not exist in high-income countries, but in developing and emerging countries soil zinc deficiencies commonly translate in human zinc deficiencies and stunting, but not always so. Furthermore the magnitude of the disease burden of zinc deficiency has been discussed. Disease and death rates are particularly large in Sub-Saharan Africa, South Asia, North Africa and the Middle East, at some distance followed by South America and the Caribbean. Human zinc deficiencies, and more generally malnutrition are thus concentrated in low-income countries. It reflects a monotonous staple food diet with low micronutrient densities, obtained from zinc deficient soils. As such human micronutrient deficiencies are not only a result of under-development, but also a cause, since the diseases deriving from it, impair the working capacity or even may result in mental retardation.

Although the problem at hand may seem immense in terms of severity of human suffering and its spatial extent, the solution is relatively simple and straightforward, at least theoretically. Micronutrients can be applied as fertilizers to deficient soils. In the absence of other major soil constraints, theoretically this will raise both crop yields and micronutrient densities of food. Higher yields can liberate land and labour for diversification towards vegetables, fruits, fuel and livestock, thus producing a win-win situation, as it increases food availability and improves dietary quality. However, there are some constraints as well. First it must be known which soils are deficient for which nutrients. Moreover, nutrients in the soil interact where uptake by plants is concerned and soil biota can play a role in plant nutrition as well. Therefore, micronutrient application technologies have to be developed that are effective given the total chemical and biotic constellation of soils. Both issues are knowledge intensive. Lastly, in cases such as copper and zinc, alternative uses have to be weighed. For instance, is copper to be used for mobile phones from which it can be recycled or for a dissipative use such as applying it to land as

fertilizer, where recycling is only possible to a limited extent. These issues will be further elaborated in following sections.

5 Available mineral resources and requirements of the world food system

Essential micronutrients can be applied to soils if these are deficient with the objective to increase crop yields and improve the quality of human nutrition. The quality of ingested food can obviously also be improved by food fortification or supplementation, but it is generally expected that food-based approaches through the crop medium ensure greater bioavailability and consequently absorption in the human body (Nubé and Voortman 2011). Moreover, by using these more artificial methods, the advantages of increased crop yields and global food production would be forgone. The most indicated source of micronutrients to be applied in agriculture are pure nutrients as obtained from metal mining operations. However, most metals are currently by and large used for other purposes than agriculture (e.g. metal industry, construction, electrical applications, and automotive industry). Metal use in agriculture thus would be a competing use. This section, therefore, first briefly summarizes known available metal reserves in ore deposits and current consumption levels (mainly outside agriculture) to assess how strong competition between different uses possibly will be. Second, the requirements for essential mineral nutrients in global agriculture will be estimated. Although metals are also required for agricultural inputs such as pesticides and feed supplementation in livestock systems, this section will concentrate on fertilizers, since these will be the most demanding use. The nutrient requirements are discussed separately for the world food system and for the purpose of growing biofuels, because between these two uses there will be competing claims for land, but also inputs such as plant nutrients. This section concludes with a discussion of sustainability issues in relation to micronutrient use in global agriculture.

Mineable reserves, annual consumption and estimated duration of availability

Occurrences of mineral deposits are classified on the basis of whether they have actually been established or not (geological assurance) and the likely economic viability of exploitation. *Reserves* consist of the category of identified resources (measured, indicated and inferred), which are considered economically exploitable with current technologies at current price levels and available data on these reserves will be used in the following.

The data used to assess the known mineable reserves derive from the US Geological Survey (USGS, 2011), generally considered the most comprehensive source of information (e.g. Diederer, 2010). Table 6 presents for a number of essential plant nutrients the reserves, the reserve base (for definition see observations with Table 6), annual production/consumption and the years left of reserves at current consumption levels (please note that quantities are expressed in different units). Nitrogen is an essential nutrient but not included in Table 6 since it is not mined and derives from atmospheric sources in which it is amply available. Reserves of mineable Ca and S are not given, but these are very large and set no limitation. Reserves of phosphate are based on IFDC (2010) as endorsed by USGS (2010). However, reserves of phosphate rock include large quantities in China that are suspected to be low-grade ore (i.e. have a low percentage of P_2O_5). Indeed, at current levels of use, the high-grade P reserves would be exhausted already by 2014 (Zhang et al. 1985, quoted in Ma et al., 2011). Cobalt is not considered as an essential plant nutrient and yet included in Table 6, as it is essential in animal and human nutrition and is also required for biological nitrogen fixation by legumes.

Table 6. Mineral nutrient resources: reserves, consumption and years left at current consumption levels in 2010.

Element	Formula	Unit	Reserve	Reserve Base 2008	Production 2010	Years left on reserve
Macro-meso-nutrients:						
Phosphate rock	variable	1000 tons	65,000,000	50,000,000	176,000	369
Potash	K ₂ O	1000 tons	9,500,000	17,000,000	33,000	287
Magnesium	Mg	1000 tons	2,400,000	3,600,000	5,580	430
Micronutrients:						
Boron	B ₂ O ₃	1000 tons	210,000	410,000	3,500	60
Cobalt	Co	1 ton	7,300,000	13,000,000	88,000	83
Copper	Cu	1000 tons	630,000	940,000	16,200	39
Iron	Fe	million tons	180,000	370,000	2,400	75
Manganese	Mn	1000 tons	630,000	5,200,000	13,000	48
Molybdenum	Mo	1 ton	9,800,000	19,000,000	134,000	41
Zinc	Zn	1000 tons	250,000	460,000	12,000	21
Possibly essential:						
Nickel	Ni	1 ton	76,000,000	140,000,000	1,550,000	49

Source: USGS, 2011.

Observations regarding Table 6:

- Reserves are identified and considered economically exploitable with current technologies and price levels
- Reserve bases are expected resources and those identified but not economically exploitable with current technologies and price levels. Figures for the reserve base were discontinued after 2008 because the data are ‘not current enough to support defensible reserve base estimates’.
- Reserves of essential mineral nutrients Ca and S not given but these are very large
- Reserves of phosphate rock are larger than the reserve base due to among others a revision by IFDC (2010) that was endorsed by USGS (2011). The reserve base was not revised. Instead the much less certain resources were estimated at 290 billion tons (IFDC, 2000). Reserves and reserve base of Phosphate rock include large quantities in China that are suspected to be low grade ore i.e. have a low percentage of P₂O₅.
- Cobalt is not considered as an essential plant nutrient, but is essential in animal nutrition and is also required for biological nitrogen fixation by legumes.
- Reserves of iron refer to crude ore, production refers to usable ore but it includes figures for crude ore in the case of China.

Table 6 and Figure 8 represent a mere static evaluation only of demand and supply of mineral nutrients. It calculates the number of years that currently known reserves can produce the current use levels. The picture emanating from this static evaluation is that P, K and Mg reserves are sufficient for a number of centuries, while the lifetime of virtually all micronutrient sources is less than 100 years. Most critical are zinc, copper and molybdenum with 21, 39 and 41 years of reserve life left, respectively. Assuming an annual increase in demand gives lower figures of course (e.g. Diederer, 2010), but a more dynamic approach would also have to consider developments in technology, including mining. The results show that, under static assumptions, scarcity of a number of essential mineral nutrients is imminent in the foreseeable future, suggesting that stiff competition for alternative uses may be expected and, consequently, that prices may increase.

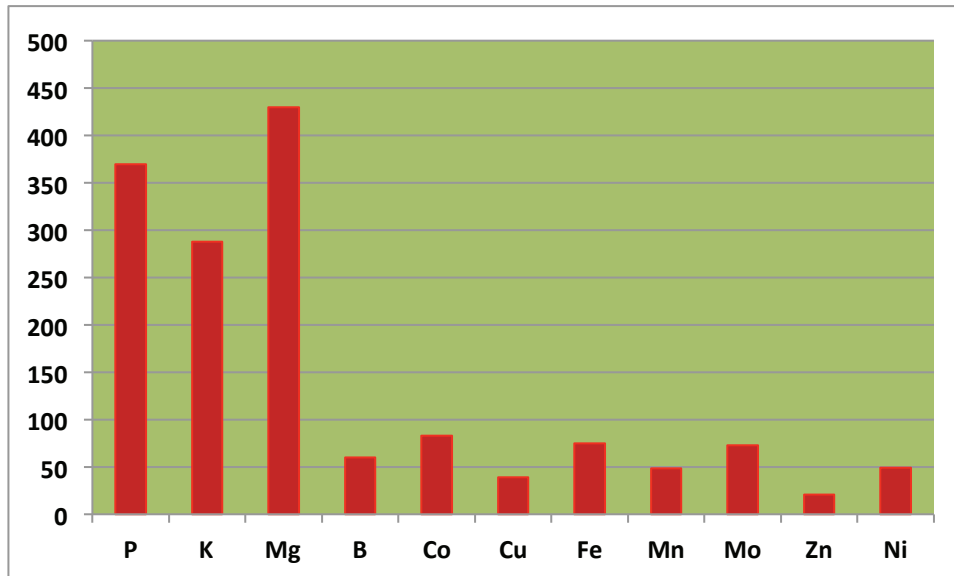


Figure 8. Number of years of supply for essential mineral nutrients (vertical axis) based on current reserves and consumption levels (data source: USGS, 2011).

Although simple calculations, from the outset it must be emphasized that the above outcomes are prone to error due to inherent problems in the data (e.g. Rosenau-Tornow et al., 2009). First, the use of terminology for classifying resource categories such as reserves is inconsistent among countries and companies and lack transparency (IFDC, 2010; Gordon et al., 2007). Second, mineral inventory determination entails great inherent uncertainties due to interpretation of a limited number of observations (poor sampling) and probabilistic estimation, but often based on wide variations in (sometimes inappropriate) methodologies (e.g. Morley et al., 1999; Dominy et al., 2004; Emery et al., 2006; Singer, 2010). Third, the figures are compiled by USGS while using government sources, individual companies and ‘independent’ sources. There are various reasons of a strategic nature why governments and companies would over- or under-report. For instance companies may under-report with the objective to maintain high price levels. On the other hand they may over-report in order to avoid interference of politicians in the production process on the basis of the notion of scarcity. Bleischwitz (2006), in the case of oil, indeed suggests that figures are deliberately manipulated. More generally, the figures may be unreliable because governments consider them as strategic information as well. And lastly, it has been observed that the ‘the USGS Minerals Information Team activities are less robust than they might be’ (NRC, 2008). Yet, there is no choice other than to use the USGS data, as these are the only comprehensive source of information (pers. comm., Prof. Peter van Straaten).

Despite these data problems, it is clear though that, even at current use levels only, metals such as copper and zinc will become scarce and expensive, and would eventually be entirely in use for non-agricultural purposes in the near future, unless appreciable new exploitable reserves will be located. Obviously existing reserves are likely to increase through mineral exploration. Higher metal prices may also make it possible to mine ore deposits currently considered uneconomical, thus adding to mineable reserves. In addition, mineable reserves may also be increased due to technological developments in mining and beneficiation, which, for instance, would allow to use lower grades of ore, or whereby mining under difficult conditions would become technically feasible (e.g. ocean floors).

Essential mineral nutrients in the global food system

Essential mineral nutrients are widely used in agriculture as fertilizers to food, feed, oil and fiber crops. Geographically though, there is great variation in the intensity of fertilizer use. High-dose fertilizers are commonly used in high-income countries, but also in emerging economies like China, while in Sub-Sahara Africa fertilizer inputs are negligible. The elements used as fertilizer are mainly N, P and K, but the fertilizer types used may also contain some essential micronutrients as ‘impurities’. This micronutrient content varies strongly with the type of fertilizer and the origin and nature of the source material. In the absence of fertilizer use, as in Africa, crops rely for their growth on native levels of all macro-, meso- and micronutrients as present in the soil being cultivated. Transporting crop yields (and residues) away from the field then leaves the soil impoverished in terms of the entire spectrum of essential nutrients (nutrient mining). By contrast, for instance in the intensive agriculture of China, large doses of nitrogen and phosphorus are usually applied. Notably phosphate fertilizers may include some other essential mineral nutrients as impurities. Otherwise, the crops draw on non-NP nutrients as present in the soil (or manure, if applied). These will have to be replaced eventually in order to sustain high yields. Indeed, as earlier indicated, increasingly micronutrient deficiencies are observed in South and East Asia, notably of zinc, but also of S, Fe, Mn, B, Mo and Cu (Singh, 2011). Sustaining yields in this case thus requires application of these essential micronutrients as fertilizers. In the African case though, the first objective would be to improve crop yields and the empirical evidence suggests that, next to macronutrients, micronutrients may well play a key-role in this respect (Voortman, 2010; Chapter 2).

To obtain an impression of the requirements we make simple on the back of an envelope calculations. Suppose that half of the present crop and pastureland is zinc deficient (source: FAO) and requires an application of 10 kg of zinc per hectare. Whereas total crop and pastureland is about 5 billion hectares² such corrective applications would amount to 25 million tons of zinc or about twice the current annual production. Maintenance fertilization with zinc at crop yields of 5 ton/ha thereafter would be 0.15 kg per year for all land, totaling 750 thousand tons, or 6% of the current annual primary production of zinc. By itself these figures appear modest, but they must be applied annually for ever and spreading zinc very thinly over arable land is a very dissipative use of a scarce resource. The current reserves of zinc, if applied in the described manner in agriculture only, would last for 330 years provided crop residues are left in the field. The latter is unlikely to occur, but if used as animal feed, removal of crop residues can be partly compensated through manure application.

In sum, new land taken into use usually has particular soil fertility problems, cultivation without fertilizer use leads to nutrient mining, while fertilizer application on intensively cultivated land is unbalanced in regard of the stoichiometric requirements of plants. Thus, under virtually all conditions micronutrients will have to be applied to sustain crop yields. The annual amounts of for instance zinc fertilizer to be applied at the global level may seem modest, but these amounts have to be applied perpetually, while at the same time representing a very dissipative use of a scarce resource. Moreover, all the currently mined micronutrients are practically in total used for non-agricultural purposes

² This figure possibly overestimates intensively used land as the FAO category pastures apparently also includes rangelands.

and such uses are likely to continue and further expand. The use of nutrients in agriculture thus will have to face stiff competition with other uses indeed and is likely to result in either lower land productivity or higher food prices. No matter what the outcome, there will be impacts on the world food system, which are difficult to quantify as yet.

*Nutrient requirements and biofuel production*³

The interest in the production of biofuels is driven by the expected scarcity of liquid fuels, and also because it is seen as a possible pathway to arrive at a low-carbon economy. Moreover, biofuel production could reduce the dependency of industrialized countries on a few oil-rich countries (geopolitics). From the outset it is natural to suspect that biofuel production will compete with food and feed crops for land, and also for inorganic fertilizers. However, this is point of intensive discussion in the literature and some sources mistakenly suggest that biofuels can be grown sustainably on marginal lands without fertilizer inputs. These discrepancies, therefore, require clarification.

The advocates of biofuels tend to concede that current first generation bio-fuels indeed do compete with food and feed for land and inputs. But, they expect technological change in bio-fuel production using so-called second generation feed stocks. Such technologies would make it possible to harvest and use biomass, ranging from desert shrubs, to tall savannah grasses and tropical forests, from land unsuitable to grow food and feed crops. The impression is created that in this way competition for land and mineral inputs can be avoided. However, this may be the case for instance in remote areas where small scale bio-fuel production takes place to satisfy local demand and where rest products, containing the essential mineral nutrients, are also locally re-cycled. However, large-scale bio-fuel production has particular requirements. To be effective as little as possible energy should be used in producing and processing the bio-fuel. To achieve the required efficiency, large volumes of biomass need to be produced in the proximity of a biofuel production plant, so as to ensure the minimization of energy losses for instance in transportation of the feed stock. This principle is precisely the reason why ethanol production from sugarcane in Brazil is particularly efficient. Obviously, the production of biomass with large yields in short distances requires good soils and fertilizer inputs. Therefore, large-scale bio-fuel production, no matter what feedstock is used, can be expected to compete for land, labour and inputs such as inorganic fertilizers.

With respect to harvesting biomass from marginal land, first of all it must be considered that net primary production is usually lower under such conditions. It is therefore unlikely that the above requirement for short distances between processing plant and location of feedstock production can be met. Moreover, also on marginal land the principles of production ecology apply: without replacing the nutrients exported from the land with the feedstock, yields will inevitably decline over time. In fact, being marginal is likely to imply that greater quantities of fertilizers are needed or a broader spectrum of essential nutrients, so as to ensure high yields.

With respect to nutrient cycling, however, there may be some promising opportunities in the case of large scale bio-fuel production with high yields from good soils, again provided some requirements are met. In essence the bio-fuel product consists of carbohydrates only. Therefore, the rest product, containing essential mineral nutrients can be used to replenish soil fertility on the harvested land, thus closing the nutrient cycle.

³ Largely based on Keyzer et al., 2009.

However, such options are viable only, if processing the crop residues and transportation of nutrients back to the fields do not compromise the balance of energy produced and used. In the case of large-scale biofuel production on marginal land such possibilities are less evident, since the larger distances involved imply that the redistribution of nutrients will earlier compromise the balance of energy gains and expenses. A potential solution could consist of mobile processing plants, whereby rather than the feedstock, the fuel is transported, while nutrients can be immediately locally re-cycled. Such technologies are currently not even envisaged.

In sum, large scale CO₂-efficient biofuel production, whether based on crops or second generation feedstocks, while using currently envisaged technologies, will inevitably lead to competition for land and inputs, including inorganic fertilizers. Biofuel production on marginal lands will also inevitably require fertilizer nutrients. Nutrient neutral biofuel production seems a useful option on fertile soils, but its feasibility still needs to be verified.

Summary and outlook

This section merely reported on known mineable reserves of metals and the requirements in the world food (and energy) system. With respect to mineable reserves, the reliability of data is in question, but accepting this as a fact of live, suggests that mineral reserves for quite a number of essential nutrients will be depleted within a number of decades, at least while using the static fixed-stock approach assessment. At the same time, mere population growth and increasing affluence will dramatically increase metal requirements, unless we accept a lower per capita metal intensity. Remarkably, the potential impact of an imminent metal scarcity, resulting in high fertilizer prices, on the world food system is rarely considered. High micronutrient prices obviously are likely to result in higher food prices, while at the same time, cash-constrained poor farmers may not even avail of the resources to afford micronutrient fertilizers. Admittedly, this section has also shown that addressing soil micronutrient deficiencies followed by maintenance micronutrient applications does require quantities of metals that are not extravagant, yet they are sizeable. The dissipative use of metals in the world food system will have to compete with more conventional applications in more concentrated forms that offer greater opportunities for recycling. Thus, if metals are to be used as fertilizers to sustain the world food system, then from the outset this defines the guiding principle that the fertilizer technologies that have to be developed are highly efficient in raising crop yields and global agricultural production. These issues will be addressed in the following sections.

6 Nutrients in soils and their management

Earlier it has been observed that the application of essential mineral nutrients to soils used for cropping may increase yields and improve the quality of the food produced, in case such nutrients are present at deficient levels in the soil. However, the previous section has shown that the quantities of these nutrients required to correct all deficiencies in the global agricultural lands are sizeable, while at the same time mineable source materials may become scarce and also have competing uses. The high prices of nutrients that may follow from this situation possibly result in non-application, thus compromising global food production or, alternatively will lead to food price increases. Therefore, this section explores alternative nutrient sources, notably those already present in soils and how these possibly can be managed more effectively. These nutrients in soils occur in different forms, some of which are available to plants, while others are not. Generic figures on both will be used to calculate how long cropping can be sustained on these bases and what the potential use duration could be if agricultural technologies were to be developed that close the gap between plant-available and unavailable nutrients as present in the soil. However, nutrient availability for plants is not only determined by the absolute level of a certain nutrient in the soil itself. Other factors and processes are also involved, such as nutrient interactions and the functioning of soil biota. These will be briefly summarized so as to end up with some guiding principles for research aiming at increased availability of plant nutrients already present in the soil.

Sources of nutrients, the factors of soil formation and human influences.

To begin with, human land use obviously can affect the nutrient content of soils in many ways, either coincidentally or purposely. Losses may be incurred through volatilization (for instance at ploughing, as is the case for nitrogen) or when crops are removed from the field without returns of fertilizer, manure or biomass (nutrient mining). Human induced erosion can also cause large losses of nutrients where fertile land is concerned. On the other hand, soil nutrient levels may be increased by cultivating nitrogen-fixing legumes. Large-scale increases of nutrient levels, notably of N and P, obviously derive from the systematic and frequent use of inorganic fertilizers and manures at high doses. Such practices though, in turn may lead to losses again, resulting in eutrophication of surface water and pollution of groundwater. It proves difficult to generalize on the outcome of human influences on soil-nutrient content as they are highly site and management specific. However, in the case of developing countries, human influences frequently result in mere slight modifications of the natural conditions. The following paragraph, therefore, briefly summarizes the natural sources of soil nutrients and the processes that alter their levels as present in soils, thus providing the context for the remainder of this section.

Soils obviously are the primary source of essential mineral nutrients for plants, including for crops. The levels of essential plant nutrients in the soil vary with the content in the original soil parent material (e.g. Mitchell 1972), soil formation processes and land use history. The main natural source of essential soil nutrients on Earth is the weathering of soil parent rock by which nutrients become available for plants from the resulting soil. This process is ongoing as long as weatherable minerals are present in the rooting zone of the soil. The type and amount of essential plant nutrients that become available in this way, is closely related to the mineralogy of the parent rock concerned. Other sources of nutrients are biological nitrogen fixation and atmospheric deposition. On the other hand, nutrients may be lost from the soil under high rainfall conditions, or with less rain but

longer exposure (soil age), through leaching and subsequent discharge to rivers. Because leaching rates differ with the nutrient concerned, over time, with increasing soil age, the nutrient stoichiometry of the soil may be altered. Essentially the natural soil stoichiometry is determined by the factors of the equation of soil formation (Jenny, 1941) with the most prominent role for soil parent material, followed by the joint effect of soil age, relief and climate (leaching), the effect of each of which is difficult to single out (Voortman, 2011). These variables and processes involved in soil formation govern the ecological diversity of soils, the patterns of distribution of natural vegetation as related to ecosystem functioning, as well as the inherent primary production potentials and land suitability for crops.

Total plant nutrient supplies in agricultural soils from natural sources

The total level of chemical elements present in the soil, deriving from natural sources, at any one site, obviously varies in dependence of the interaction of the earlier mentioned factors of soil formation. For our purpose, therefore, a generic approach must be used, while the analysis is also restricted to copper and zinc (for an overview of all nutrients see Table 7). The average abundance of Cu and Zn in the earth's crust as measured in rock exposures is 28 and 67 ppm, respectively (e.g. Rudnick and Gao, 2003). It is unclear how these figures have been arrived at, given the fact that the elemental content naturally varies with rock lithology (e.g. Yaroshevskii, 2007), which in large parts is not even exposed. Nevertheless, many sources present figures that are remarkably similar, albeit with some spread in the case of copper.

Clearly, surface soils are unlikely to neatly reflect the average mineral content of the rock from which they derive. Yet, a quick perusal of the literature confirms the order of magnitude. Using the above figures, while assuming a soil bulk density of 1.2, shows that the 20 and 50 cm of topsoil would contain about 70 and 175 kg of Cu, respectively. Copper removal by crops is estimated at 0.005 kg per ton yield only. Thus, provided that all the copper in the in the upper 50 cm of soil could be accessed by crops, an annual crop, yielding 5 tons, could be sustained for 6720 years, that is, if crop residues were to be incorporated in the soil. For zinc the 20 and 50 cm of topsoil would contain 160 and 400 kg, respectively. Zinc removal by crops is larger than copper and estimated at 0.03 kg per ton yield. Using the same assumptions implies that, on the basis of the total zinc levels present in the soil, a 5 ton annual crop could be sustained for 2680 years. Under more modest assumptions, where only the nutrients in the top 20 cm can be assessed, the total elemental content under the same other assumptions would still suffice for 2700 and 1070 years for copper and zinc, respectively. Clearly the assumptions used, notably the point that all of a nutrients present in the soil could be accessed and used up by plants, are unrealistic (as will be discussed in the following paragraphs). Nevertheless, these calculations show that the minor requirements for micronutrients of crops, in combination with large reservoirs present in the soil, potentially could support high crop yields for quite an extended period of time.

Table 7. Presence of elements in the earth's crust (source: Rudnick and Gao, 2003; (o) is: expressed as oxide).

Nutrient	ppm	Nutrient	ppm
Phosphorus (o)	1500	Cobalt	17
Potassium (o)	28000	Chromium	92
Sodium (o)	32700	Boron	17
Calcium (o)	35900	Molybdenum	1.1
Magnesium(o)	24800	Nickel	47
Sulphur	621	Aluminium (o)	15400
Manganese (o)	1000	Chlorine	370
Iron (o)	50400	Iodine	1.4
Zinc	67	Silicon (o)	666200
Copper	28	Selenium	0.09

Available plant nutrient supplies in agricultural soils from natural sources

Although informative by themselves, the calculated figures in the previous paragraph on how long the total elemental content of soils could possibly sustain the production of crops are misleading, simply because the assumptions used are not supported with currently available knowledge. The total elemental content of soils consists for each nutrient of the sum of different forms (chemical bonds), present in different pools (e.g. in soil water, organically bound, adsorbed to clay particles). Usually the largest portion of this total soil content of a particular nutrient is not available for plant uptake, that is with currently available technology. In soil chemistry, therefore, different analyses are made to establish total and available nutrient levels. The total elemental content is established with very aggressive reagents, while for available nutrients weaker reagents are used, which extract only the more loosely bonded portion of the total nutrients present. The latter methods have been developed empirically: when values obtained are low, crops usually respond to addition of the nutrient concerned, and when the values are high there is usually no yield increase.

Table 8 presents 'available' values for P, Cu, Zn and Fe for topsoils and subsoils of the Angonia district in NW Mozambique (Voortman and Spiers, unpublished). This district combines an exceptional diversity of parent materials with a large variation in climatic conditions, thus resulting in a wide variety of entirely different soils. Moreover, the data reflect truly natural conditions, since the soil samples were taken in 1978 when there was little industrial activity in the neighbourhood (little atmospheric deposition) and fertilizers had not been used yet. The data first of all confirm the very large variation of native available nutrient levels (the minimum and maximum values in Table 8). cursory analysis of the literature has shown that the order of magnitude of means and ranges in this district, are in accordance with observations made elsewhere. Table 9 uses these average values for available Cu and Zn (of Angonia) in combination with the earlier presented generic total elemental values (Table 7) to compare how long crop production could be sustained (on the basis of the earlier made assumptions).

Table 8. Available P, Cu, Zn and Fe in the topsoil and subsoil of soils in Angonia district, Mozambique (values in ppm; topsoil 0-20 cm, subsoil 20-50 cm; tr = traces or practically 0) (Source: Voortman and Spiers, unpublished data).

Variable	N	Mean	Std Dev	Minimum	Maximum
P (topsoil)	115	21.7	23.7	tr	109.00
Cu (topsoil)	114	1.5	1.1	0.08	6.24
Zn (topsoil)	114	1.0	0.5	0.22	2.84
Fe (topsoil)	114	2.2	1.3	0.70	6.40
P (subsoil)	111	11.5	27.7	tr	192.00
Cu (subsoil)	111	1.3	1.3	0.04	7.96
Zn (subsoil)	111	0.6	0.3	0.16	2.00
Fe (subsoil)	111	1.1	1.1	0.30	9.00

Table 9. Total and available soil nutrients and resulting years of nutrient supply.*

Category	Copper	Zinc
Total elemental content (generic)	28	67
Topsoil available nutrients (Angonia)	1.5	1.0
Subsoil available nutrients (Angonia)	1.3	0.6
Years of supply: Total elements	6720	2680
Years of supply: Available nutrients	276	30

*Assumptions: rooting depth is 50 cm; all nutrients can be accessed and used; annual yield 5 tonnes; crop residues are incorporated; per ton harvest: 0.005 kg Cu and 0.03 kg of Zn; soil bulk density 1.2

The data in Table 9 are an example of the generally very large difference between total elemental content and plant-available nutrients in soils. The resulting tremendous gap in terms of years that cultivation could be sustained suggests an alternative for the application of mined micronutrients in case these become scarce and/or expensive. The data indicate that land productivity can possibly be maintained on the basis of nutrients already present in the soil, provided that nutrient management technologies can be developed that close the gap between total and available plant nutrients in the soil. Achieving this, is a major scientific challenge ahead, but must be seen as a mechanism of buying time only.

Soil factors affecting plant availability

Thusfar, for the sake of simplicity, while dealing with plant nutrition, only absolute levels of essential mineral nutrients in the soil have been considered. However, actual uptake of nutrients is not only governed by the absolute level of individual available nutrients present themselves. Indeed, the relationship between actual plant nutrient uptake and soil chemistry is considerably more complex. For instance, the uptake of a particular nutrient is also influenced by the levels of other nutrients present in the soil. Such relationships may be synergetic as well as antagonistic. A well-known antagonism is that high P levels in the soil induce a Zn deficiency, and vice-versa. Plant nutrition/uptake studies could account for such interactions by using the ratios between individual nutrients in the analyses. To date, however, little is known on how such ratios need to be interpreted in the multi-dimensional space of the levels of all the essential nutrients present in the soil simultaneously (its stoichiometry). Adequate knowledge, yet to be developed, would, based on these mechanisms, allow manipulating the availability of one nutrient through the application of another. For instance, there is indeed evidence that calcium application can improve availability and uptake of micronutrients (e.g. Sanik et al., 1952). Thus,

potentially the plant availability of scarce and expensive nutrients, rather than by applying these themselves, could be improved through application of less scarce and cheaper elements such as calcium, magnesium and sulphur.

Next to interactions among available nutrients in the soil, actual nutrient uptake possibilities for plants are also influenced by the size and nature of the various pools in which individual elements are present in the soil. It may be suspected that, through equilibria between the different pools, some of the available pool withdrawn by crops will be replaced from other pools. However, long-term dedicated research to assess this possibility is scarce and inconclusive. Asymptotic decreases of available plant nutrients in the soil have been observed under continuous cropping (Ma, 2009), but some of these results can also readily be described as linear decreases. In any case, these findings suggest that replacement rates of available nutrients which are removed by crops from stronger bonded pools, is very modest, at most. Clearly, the interactions between the different nutrient pools, the mechanisms involved in these equilibria, and how these can be influenced so as to increase the plant-availability, requires major scientific attention if the gap between total element content and plant-available nutrients in soils is to be closed.

Apart from nutrient stocks and chemical processes in the soil, nutrient availability for higher plants can also be influenced by soil biota. For instance, crops may obtain scarce nutrients through a mutualistic relationship with mycorrhizae (soil fungi) whereby the higher plant supplies the fungus with assimilates in return. These fungi have access to a larger volume of soil than plant roots do and can also take up nutrients from pools that are unavailable to higher plants. The extent to which these soil fungi can transfer nutrients, however, also depends on the chemical composition of the soil medium. For instance, to function properly these mycorrhizae require calcium and copper (Lévy et al., 2004; Hagerberg et al., 2011; see also: Jarstfer et al, 1998). Hence, inorganic fertilizers may be used to promote such mutualistic mechanisms and to increase the transfer of nutrients from the soil to higher plants. Of particular importance in this case is calcium, as it is amply available on earth, while it enhances mycorrhiza functioning and improves micronutrient uptake directly. On the other hand though, fertilizer applications may also affect prevalence and functioning of mycorrhizae: the application of N or P frequently reduces the abundance and activity of the fungi (e.g. Mäder et al., 2000). Both mechanisms call for combined nutrient and mycorrhizae research under real (non-laboratory) conditions. However, mycorrhizae research is difficult under field conditions. Current scientific knowledge, therefore, is insufficient to allow generalized quantitative statements on their possible beneficial effects on plant growth and the role mycorrhizae play in nutrient cycling, perhaps with the exception of the effects of calcium. This situation thus defines a spearhead research agenda with the objective to develop biota-based technologies to improve availability of nutrients already present in the soil.

Beyond mycorrhizae, there is additional great wealth of life in the soil, where, in fact most of the biodiversity on earth exists. This includes, among others, bacteria, protozoa, nematodes, mites, collembola's, earthworms, termites etc. All these interact with each other, with soil chemical properties and also with higher plants such as crops notably in the crop rhizosphere. For several species (-groups), such as growth enhancing bacteria, it has also been established that they influence the rate of growth of higher plants. However, generally speaking very little is known on the functioning of biota in the rhizosphere, let alone on how their functioning relates to the total soil chemical constellation and the availability of nutrients to higher plants. In short, 'we (...) have an

extraordinary ignorance about how best we can manipulate it (the rhizosphere functioning to our advantage' (Hinsiger et al, 2009: see also Andrén et al., 2008 and Fierer et al., 2009). These observations obviously further add to the research agenda of the future.

Assessment

Soils naturally vary in their contents of individual essential plant nutrients due to the impact of the factors of soil formation, in turn being subject to nutrient management in agriculture. Invariably though, there is a very large gap between the total amount present in the soil and the part that is available for plant uptake. Narrowing this gap, by increasing the proportion of nutrients that is available, could be an important step to maintain land productivity under conditions of scarcity of mineable essential mineral nutrients. But this calls for novel technologies of nutrient management in agriculture. Four possible pathways have been discussed, two of which are mainly of a chemical nature (referring to manipulation of nutrient pools as well as nutrient interactions) and two are soil biota-based (use and manipulation of mycorrhizae and other soil biota), while combinations are likely to be most beneficial. Guiding principles for such technologies are that they use minimal amounts of nutrients that are likely to become scarce, and that non-scarce nutrients are used wherever possible. Such practices should liberate deficient and non-available forms of nutrients so as to maximize crop growth and to optimize the nutritional value of food. At the same time though, they should prevent nutrient losses through luxury uptake by crops and losses through leaching of nutrients from the root zone. Research to develop such innovative agricultural technologies and land management principles amounts to an entirely novel avenue in scientific discourse.

7 Nutrient use efficiency in agriculture; theory and practice

Because essential mineral nutrients are likely to become scarce and more expensive it is relevant in this context to verify how nutrient applications can be minimized while maintaining high productivity levels. To this effect the underlying basic principles of fertilizer application and their implications will be discussed. Thereafter, current practice will be described and the extent to which the basic fertilizer principles are actually applied in the field, while using examples from Africa and China. By means of examples some implications will be shown notably on how the application of N and P induces Cu and Zn deficiencies, thus actually increasing the need for application of Cu and Zn, rather than minimizing requirements.

Fertilizer principles; theoretical considerations

The first principle in fertilizer use is Liebig's law of the minimum (Figure 9). This illustration of the principles involved is obviously an oversimplification, given the many interactions between nutrients and biota that may occur in actual soils. Nevertheless, it illustrates very well the principles involved. The basic principle is that the ceiling of attainable crop yield is determined by the most limiting nutrient. Application of that nutrient then brings certain yield improvement until another nutrient becomes limiting. Applying a combination of the most limiting nutrients will thus give a substantial yield improvement. Clearly application of non-limiting nutrients is wasteful and represents an unnecessary drain of scarce resources. Efficient nutrient use therefore requires application of the most limiting ones only.

The second principle refers to decreasing marginal returns (Figure 10). The principle implies that, if a nutrient is deficient, at low levels of application one kg extra of fertilizer will give a high return in terms of kgs of the crop product. These per each extra kg returns gradually decline with increasing the dose of fertilizer applied until an extra kg has zero effect, whereafter yields may actually decline. Thus to obtain maximum returns to fertilizer, small doses are preferable. Such small doses of the most limiting nutrients are not only likely to be the most economical but also maximize kg product per kg fertilizer used. A constraint of this approach may be that, in aggregate, it will produce insufficient food to satisfy the requirements of the global population. Or more precisely, it may make the use of nutrients more efficient, but will not allow a larger food production.

The third fertilizer principle refers to interactions between nutrients. Figure 11 shows the stylized overall picture of the N-dependent response to P. At low N there is a greater response to P if compared to medium N levels. At high N levels there is hardly response to P and yields soon even decline (Source: Voortman and Brouwer, 2003). Further investigations have led to a hypothesis on the various interactions among plant nutrients in the soil as shown in Figure 12 (Source: Voortman and Spiers, 2010). The figure implies that copper, iron and zinc are mutually antagonistic where uptake by plants is concerned. Phosphorus is mutually antagonistic with these three micronutrients. The equilibria are further conditioned by the ratios of cations (Ca/Mg, Mg/K and (Ca+Mg)/K), which themselves reflect antagonisms between the cations. Overall these interactions are being shaped by the total amount of exchangeable bases (TEB), soil texture and Al levels. This hypothetical model still needs to be further completed with other micronutrients and interactions involved. Furthermore, the modification of nutrient interactions by soil biota such as mycorrhizae has yet to be further investigated so as to the entire picture in the right perspective.



Figure 9. Liebig's law: crop yield is determined by the most limiting nutrient.

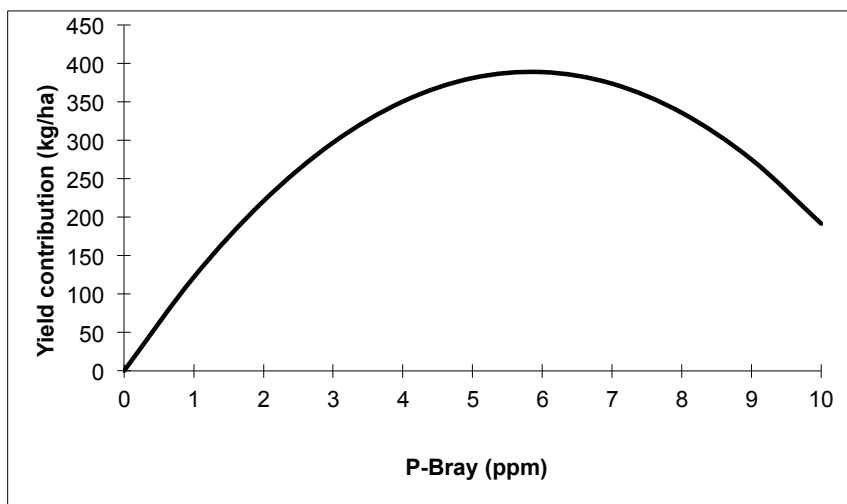


Figure 10. Stylized yield response to P for current range of P-Bray (Source: Voortman and Brouwer, 2003).

Fertilizer principles; practical implications

The above fertilizer principles one and three imply that to achieve the desired effective yield improvement, the fertilizer technologies to be applied have to be finely tuned to local soil chemistry conditions. The main constraint for such developments is that it is knowledge intensive. To illustrate this point we consider data about on velvet bean, a nitrogen fixing legume, as researched in Zimbabwe (Table 10). Without P fertilizer the yield varies from 317 to 7240 kg.

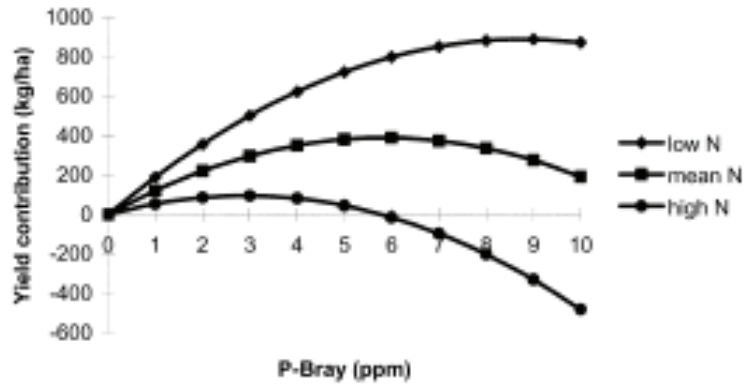


Figure 11. N-dependent yield response to P-Bray (Source: Voortman and Brouwer, 2003).

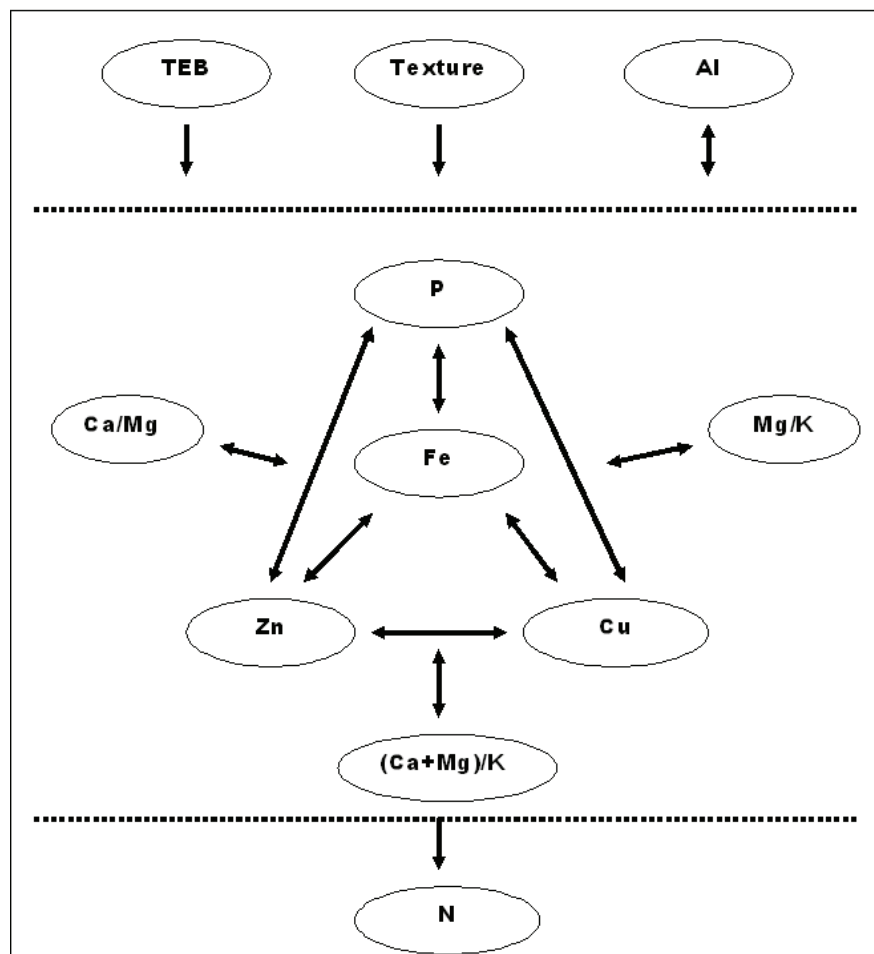


Figure 12: Schematic diagram of interactions between soil chemical properties in relation to plant nutrition, representing the key ecological factors governing the ecological diversity of soils, patterns of distribution of vegetation types and determining land use potentials. (Source: Voortman and Spiers, 2010).

Table 10. Biomass production (kg/ha, dry mass) by velvet bean with and without P and yield increase/decrease due to P application ($\Delta\%$), on exhausted sandy soils in six smallholder communal areas in northern Zimbabwe, 1996/97 season (Source: Hikwa et al., 1998).

Communal Area (Site)	- P	+ P	$\Delta\%$
Mangwende (1)	317	318	0.3
Zvimba (1)	1260	2410	91.3
Zvimba (2)	1620	850	-47.5
Chiduku (1)	1865	1757	-5.8
Gokwe South (1)	1916	2368	23.6
Gokwe South (2)	1964	1826	-7.0
Chiduku (2)	2703	4538	67.9
Chihota (2)	3405	4275	25.6
Mangwende (2)	5250	5351	1.9
Chihota (1)	5290	10665	101.6
Nyazura (2)	6610	6490	-1.8
Nyazura (1)	7240	8020	10.8

Such variation is clear evidence of the great variety of natural conditions. Even within the same small area (Mangwende), yields vary from 317 to 5250 kg. It shows that such natural conditions vary at very local scales. With P applied, we first of all note that the response to fertilizer is also highly variable and that in most cases yields either increase very marginally or even decrease. It implies that P is not deficient or in relation to other nutrients already is present in excess, respectively. Differences in response to fertilizer are also very locally determined: where unfertilized yields are rather similar, the response may vary from 90 percent positive to almost 50 percent negative (Zvimba). So indeed, due to very locally determined soil variability both unfertilized yields and yield response to the same fertilizer dose can vary dramatically. Therefore, fertilizer types and doses have to vary with the spatial variation existing in the chemical constellation of soils. To achieve this is a very knowledge intensive trajectory indeed. This trajectory, based on the use of local knowledge and the use of bio-indication, is beyond the scope of this paper, but for Africa this has been developed in Voortman and Spiers (2010, Chapter 6).

Actual fertilizer practice; the cases of Africa and China

The previous paragraphs have developed the theoretical basis of efficient fertilizer technologies in relation to the spatial diversity of soils and it has been concluded that fertilizer technologies need to vary according to the local soil chemical properties. Here actual practice will be discussed taking two widely differing examples: first Sub-Sahara Africa where hardly any fertilizers are being used and then China where ample use of fertilizers is being made.

Africa

Although hardly any fertilizer is used in Africa, there has been a considerable amount of fertilizer research and most countries have fertilizer recommendations. Individual African countries usually have a single pan-territorial or so-called blanket fertilizer recommendation. These recommended technologies are frequently similar to those that were successful in the Green Revolution in Asia. The actual amounts may vary, but they mostly prescribe large doses. With respect to the nutrient mix, these technologies

are usually restricted to macro- and mesonutrients, most commonly N and P, and sometimes K, is also included. For instance, in Malawi 90 kg N and 40 kg P per hectare per year are recommended (Snapp et al., 2003) and the current fertilizer recommendation in Zimbabwe consists of 120 kg N, 30 kg P, and 25 kg K per ha per year (Zingore et al., 2007). These technologies are usually derived from theoretically calculated climatic yield potentials based on climatic parameters and the amount of nutrients that would then be removed from the land. They do not reflect local soil conditions. So, contrary to the above defined fertilizer principles, the doses are large, they are not fine tuned to local soil conditions and they only consider a very restricted choice of essential plant nutrients.

Most agronomic experiments apply similar mixes of plant nutrients and doses. There is much research to show that such technologies, based on a very restricted choice of essential plant nutrients, frequently indeed give little response or have even negative effects (e.g. Smaling and Janssen, 1993; Mbagwu et al., 1984; Wopereis et al., 2006; Szilas et al., 2007; see also Table 10). Moreover, at high doses the phenomenon of decreasing marginal returns is often confirmed. A telling example showing that high doses can even be detrimental to crop yield and fertilizer efficiency in Africa comes from Zimbabwe. Experimental research has shown that at application rates lower than 20 kg of N per hectare, each kilo of N could produce 80 kg of maize, falling rapidly with increasing doses to minus 5 kg maize per kg of N at application rates higher than 90 kg ha⁻¹ (Kamanga et al., 2001). Recently, it has been further confirmed that high fertilizer doses are more generally very inefficient in Zimbabwe (Zingore et al., 2007). Similar observations have been made with respect to P in the savannah soils in Nigeria (Ayodela and Agboola, 1982; Uyovbisere and Lombin, 1991; Sanginga et al., 2000; Kogbe and Adediran, 2003). These four papers are consistent in their observations that, at application rates of more than about 20 kg P per hectare, there is either no further response to P or yields actually decline rapidly. Also elsewhere research has concluded that recommended fertilizer doses can be reduced so as to enhance efficiency and reduce costs (Wendt and Jones, 1997; Nwoke et al., 2004).

The recommended fertilizer technologies, therefore, may not only be inappropriate for the soils to which they are applied in terms of nutrient composition, but also the recommended high doses can be extremely inefficient due to the effect of decreasing marginal returns. The confirmation of the basic principle of decreasing marginal returns obviously is good news for cash-constrained farmers. It implies that if N or P would indeed be deficient, they can obtain substantial yield improvement with small amounts of fertilizer, so as to ensure profitability. However, it is remarkable that, although on theoretical and empirical grounds, decreasing marginal returns are to be expected, the amount of research that experiments with optimal, modest fertilizer doses is quite limited and certainly does not find expression in the promoted fertilizer recommendations.

In sum, commonly recommended and experimented fertilizer technologies may well be inefficient and consequently not profitable, because of the restrictive choice of essential plant nutrients applied and, in addition, because of the high doses used. Not surprisingly, poor profitability of blanket fertilizer applications are no isolated cases.

Asia and China

Up to the early 1960's, before the so-called Green Revolution, inorganic fertilizer use in Asia was very modest. Thereafter, crop yields of rice, wheat and maize could be substantially increased, largely based on the use of N and P fertilizer and improved crop

varieties, which are responsive to these inputs. With the proceeding Green Revolution the use of fertilizer has dramatically increased. However, currently there is an evident fatigue in productivity gains in the countries concerned such as India and China (Kesavan and Swaminathan, 2008). Indeed, many long-term experiments show that crop yields stagnate and frequently even decline (e.g. Ladha et al., 2003; Aggarwal et al., 2004; Biswas and Benbi, 1997; Tirol-Padre and Ladha, 2006). Although the data vary, the use of mineral N and P is becoming increasingly inefficient. For instance, it is reported that of the N applied in irrigated rice systems in Asia only 31 % is harvested with the crop (Cassman et al., 2002), compared with an optimal recovery in the order of 70-80%. More recently, this order of magnitude was confirmed (20-30%) by Ju et al. (2009). The most recent report arrives at an average 16-18 percent of on-farm N recovery in intensive wheat-maize systems (Cui et al., 2010).

Regression analysis on annual N use and food production in China also suggests that nitrogen use is becoming rapidly less efficient (Zhu and Chen, 2002). Countrywide in China the use of nitrogen fertilizer amounts to almost 50 million tons. Of this total amount only 4.4 million ton is reported to reach households included in food, while 23 million tons is lost to the atmosphere and 20 million tons to ground and surface water (Ma et al., 2009). The N use inefficiency thus leads to very high greenhouse gas emissions (as N_2O and NH_3), increased levels of N in groundwater and frequent occurrences of algal blooms in lakes and red tides in estuaries (Zhu and Chen, 2002; Ju et al., 2009). At the same time, soils suffer from acidification (Wang et al., 2010; Guo et al., 2010). Cassman et al. (1998) suggest that one of the reasons for farmers to use high N doses is that recommended levels do not take into account the N levels present in the soil which can be high particularly under flooded rice. They also do not account for the very high N deposition rates in China, which even approach up to 100 kg/ha (Cui et al., 2010).

Hence, current practice is a certain recipe for inefficiency of the use of mineral fertilizer, which is confirmed by a broad spectrum of data. Xie et al. (2007) for instance report an extreme case whereby farmers apply 200 kg N per ha per year to rice, while achieving a yield increase of 300 kg rice only (not significantly different from the control) and their general conclusion is that N doses can be reduced with 45% without affecting yields. This is confirmed by Ju et al. (2009), who suggest that annual N applications of 550-600 kg/ha in double cropping systems can be reduced by 30-60 percent without significant reduction of yield.

The high inefficiencies though do not entirely derive from not accounting for local environmental conditions. First of all, fertilizer is cheap as it is subsidized by the Chinese government (production and transport), but it also appears that farmers are urged to use fertilizers by local officials who take kickbacks from fertilizer sales (Hvistendahl, 2010). In any case, N fertilizer use efficiency in China (and other Asian Green Revolution countries) is very low and as China alone produces 38% of the global anthropogenic N (2005), this must obviously be of worldwide concern (Cui et al., 2010).

With respect to phosphorus the use efficiency in Asia appears even worse. The highest efficiency of P use (that is the fraction which is included in the crop) is around 30 percent, but it can be even as low as 10% (Blake et al., 2000; Baligar et al., 2001), while the average recovery is estimated at 50%. Other assessment methods in China suggest that P use efficiencies on average are 36, 5 and 7% for crop production, animal production and the whole food chain, respectively (Ma et al., 2009). Further studies suggest that in wheat,

rice and maize production only 3.2, 2.6 and 0.9% of the applied P fertilizer ends up being consumed by humans, respectively (Ma et al., 2011). Global studies confirm China to be the largest single areal extent of the lowest P use efficiency class (Macdonald et al., 2011). The inefficiency of P fertilizer use also results in high P accumulation in soil (P is less mobile than N). The study of Ma et al. (2011) calculates accumulation levels of 29.4, 13.6 and 21.3 kg/ha per year for wheat, rice and maize production, respectively. High P accumulation is also observed elsewhere in Asia. For instance in 20 year experiment with rice-wheat in the Indo-Gangetic plain a three-fold increase of available soil P was observed (Kumar and Yadav, 2001). A large scale sampling of soils in South Korea shows that in about 30 years Available P increased 2.5 times on lowland paddy soils and 5-fold on upland soils (Joh and Koh, 2004), leading to luxury uptake of phosphorus, lower yield due to micronutrient deficiencies, in combination resulting in low food quality.

The high rates of soil P accumulation then brings us back to the micronutrients, since, as earlier observed, high soil P causes that the uptake by plants of micronutrients such as Cu and Zn is impeded. High P fertilizer applications may not only decrease the efficiency of P use, but may also be one of the reasons for the earlier reported widespread micronutrient deficiencies in the Asian Green Revolution areas. Indeed in the Indo-Gangetic plains micronutrients apparently start to appear and Zinc deficiency is notably widespread (Aggarwal et al., 2004; Pingali and Shah, 2001). Biswas and Benbi (1997) also show in long-term experiments that high yields could be maintained only with the application of Zn or farmyard manure, which obviously contains micronutrients. Chaudhary and Narwal (2005) indeed demonstrate that continuous application of farmyard manure increases available levels of Zn, Fe, Mn and Cu in the soil. The observed inefficiency of P is obviously already of serious concern by itself, because the mineable reserves are finite. But intoxicating the soil with a scarce resource (P) thus has the effect of causing soil deficiencies of even scarcer resources

Too high levels of available soil P levels will not only negatively affect crop yields, but also the quality of food. Application of P fertilizer generally increases the phytate content in the crop and phytate is a nutrient binder. It plays an important role in seed germination but cannot be digested by mono-gastric animals such as pigs, chickens and humans. Consequently most of the P present in phytate is after animal or human consumption directly excreted. Moreover, phytate inhibits the uptake of Zn and thus it can cause Zn deficiency even though Zn may be sufficiently present in the food. Indeed, human micronutrient deficiencies are widespread in China and rapidly increasing. Sub-clinical Zn deficiency is in the order of 50-60% among the Chinese population (Yang et al., 2007). Continued application of high doses of P fertilizer is, therefore, a certain recipe for lower food quality and further increasing zinc deficiencies in humans.

In sum, current fertilizer practice in China is remotely distant from the above-presented theoretical principles that define fertilizer efficiency. These practices are a cause of very extensive and serious environmental problems and a source of very high greenhouse gas emissions, but not only so. Crop yields are also stagnating or even declining and the quality of food in terms of micronutrient content is decreasing. Continued overdosing with P is a certain recipe for lower yields and poor quality food, and inevitably will require that scarce metals have to be used in dissipative ways, whereby recycling options are limited. At the same time, the use of metals in agriculture will have to compete with applications in other sectors such as technology

Assessment

Inevitably inorganic fertilizers will have to be used in agriculture to sustain the high yields needed to produce the food for a growing and more affluent global population. However, fertilizers such as N and P need to be employed more efficiently for a number of reasons. The large doses commonly used are the cause of surface, ground water and coastal zone pollution and N overuse in particular is a source of greenhouse gas emissions. Moreover, inefficient fertilizer use makes food unnecessarily more costly, while at the same time it diminishes the quality of food, notably in the case of P over-use. The lavish application of N and P should not, and cannot, be copied in the case of micronutrients, since these are far more scarce, while currently also having their main application outside agriculture. Nevertheless, to produce the required food efficiently, will inevitably call for considering essential mineral nutrients beyond N and P, including scarce metal elements, even though their application in agriculture is of a dissipative nature.

8 Concluding remarks

This report has set out to sketch that humanity is faced with a number of global problems that are intricately linked. The issues involved, first of all, include rising food and feed demand due to population growth and expected greater affluence. Other concerns, among others, are climate change due to greenhouse gas emissions, energy scarcity, competition for good land and inputs between food and biofuel production, scarcity of land, water and fertilizer inputs (phosphorus), extensive pollution of ground and surface water due to fertilizer use, and the integrity of the biosphere (biodiversity). The complex linkages and interactions between these global problems are such that solving one issue can cause another problem to increase in magnitude. Disregarding this interconnectedness in a partial analysis frequently results in optimistic findings, but a broader approach commonly reveals that humanity is facing a daunting challenge. The question is not if we can produce the food, feed and fiber for a growing and more affluent global population, but if we can do so with modest fertilizer doses, with low greenhouse gas emissions, with low water consumption, with little ground and surface water pollution, while simultaneously producing sizeable quantities of biofuels and while maintaining the ecosystem services of the biosphere. This certainly is not an easy task.

It has further been emphasized that the literature gives hardly any attention to the potential impacts of metal scarcity on agricultural production and the global food system. That metals such as copper and zinc may become scarce in the foreseeable future is well established on the basis of currently known mineable reserves, consumption levels and expected demand growth. The future role of these metals in the global food chain and growing demand deriving there from is usually neglected. A number of metals are essential micronutrients for plants, animals and humans, or in short for life on earth. They are needed in small amounts only, but deficiency, whether in plants, animals or humans, inevitably leads to growth retardation, disease or even death, depending on the severity of the deficiency. The essentiality of these metals for life entails that they cannot be substituted by other elements. If micronutrients are deficiently present in the soil, their application in agriculture will raise crop yields, while simultaneously improving nutritional quality (micronutrient densities). Consequently, metal micronutrients may prove crucial to sustain the global food system.

Micronutrient scarcities add to the problem of scarcity of macro- and meso-nutrients such as N, P and K at some time to come, whereby mineable P and K may become depleted and N be too expensive/energy intensive to produce. The difference between the scarcities for instance between P and micronutrients is that currently mined P is almost exclusively used in agriculture, while the micronutrients are by and large used for non-agricultural purposes (construction, industry, etc.). Another dissimilarity is that the known reserves of the micronutrients, if compared to those of P, are much smaller: in the order of a few decades rather than a few centuries. In combination, both differences suggest that scarcity of micronutrients may be expected much sooner as well as being severe to the extent of precluding their use in agriculture.

The above indicative number of years that reserves of copper and zinc (a few decades) will be able to cover demand are calculated on the static fixed-stock assumption, which is a rather pessimistic method of analysis. Clearly, more resources will be found, prices may increase with the result that mining lower grade ore or ores difficult to mine become economical, substitution may take place and recycling may become attractive. But

how far this optimism of the opportunity cost paradigm can carry on is, obviously, also uncertain. Moreover, externalities of mining operations are currently not reflected in the prices of minerals: pollution of air, water and soil, biodiversity. Furthermore, water and energy use in mining is expected to grow exponentially, and both are likely to become scarce and expensive as well. Also here partial analyses may prove to be too optimistic. In any case, this issue is beyond the scope of this report and is considered elsewhere (Bastein and Van Bree, 2012). Nevertheless, the quotes on mineral scarcity in Text box 1 provide an informative sample of current diverse opinion. It can be concluded though, that metal scarcity will become real in a not too distant future, but it is difficult, if not impossible, to quantify the time left before scarcity is real and how severe its impact will be.

Even without an impending scarcity of metals, there is reason enough to pay attention to them within the context of agriculture and the global food system. Currently, the use of metals as micronutrients in crop production and animal husbandry is very limited. Their use in agriculture is likely to increase drastically for various reasons and, unlike for non-agricultural uses, in plant, animal and human nutrition these essential micronutrients cannot be substituted for. The increased use of micronutrients is dictated by the present very unbalanced nutrient applications in high-input agriculture, being usually restricted to N and P, and in lesser extent to K. Such practices will not go unpunished as is currently evident from crop yield trends in the Asian Green Revolution areas, where about 50 percent of the arable land is considered zinc deficient. The extent of zinc deficiency is also large in Sub-Saharan Africa, where hardly any fertilizers are used, thus suggesting widespread natural soil micronutrient deficiencies. Here, crop yield response to promoted fertilizer technologies frequently remains low, causing non-adoption, precisely because the micronutrient deficiencies are not addressed.

The use of micronutrients in agriculture is all the more important because of the widespread and increasing occurrence of human micronutrient deficiencies, which result in human disease and a global death toll of a similar magnitude as malaria, mainly in developing countries. In short, micronutrients are likely to play a crucial role in the sustainable production of sufficient good quality food in the future. This report further has established that the quantities of micronutrients required to sustain the world food system on an annual basis are modest if compared with contemporary other applications, but because of the essentially of these elements for life on earth they will have to be applied everlastingly.

The increasing and perpetual requirements for micronutrients in the world food system obviously calls for substitution and recycling where other uses are concerned, as well as the development of technologies to do so effectively (including water and energy use). Whereas, using metals as fertilizers constitutes a dissipative use, also in agriculture they must be applied such that a maximum yield response and optimum food quality is achieved. This calls for fertilizer technologies that, in terms of dose and composition, are finely tuned to local soil chemical conditions.

Text Box 1: Quotes on mineral scarcities

- ‘To some extent one may say that the difference in approach between the fixed stock and the opportunity cost paradigm represents the difference between technological pessimism versus technological optimism’ (Foran and Poldy, 2001).
- ‘the optimists, like the pessimists, have not provided adequate data to support their position, although history is on the sides of the optimists’ (Willet, 2002).
- ‘Depletion raises the specter of a world where resources are too costly to use rather than a world with no resources’ (Tilton, 2002).
- ‘The future course of copper prices is impossible to predict with any accuracy given the great uncertainties’ (Tilton and Lagos, 2007).
- ‘We do not and indeed cannot know whether it will be possible in practice to overcome any resource constraint’ (Neumayer, 2000).
- ‘To conclude that there is no reason whatsoever to worry is tantamount to committing the same mistake the pessimists are often guilty of- that is the mistake of extrapolating past trends’ (Neumayer, 2000).
- ‘Scarcities affect each other’ and ‘we know too little about the quantitative impact of scarcities on each other’ (Anonymous, 2009).
- ‘Exploration of new locations and technological innovation in mining and extraction has kept the available and known material reserves on par with the increase of demand. Will this continue in the 21st century as well? It is difficult to predict a century ahead, but looking at a number of developments, we are afraid the answer is: no (Wouters and Bol, 2009).
- ‘The stakes are too high to gamble on timely and adequate future technological breakthroughs to solve our problems’ (Diederer, 2009).
- The question is: ‘How best to prepare for increasing scarcities in the world’ (Anonymous, 2009).
- ‘The careful stewardship of available resources represents a task for the future’ (Angerer et al., 2009).

A basic requirement hereto is the development of knowledge on what governs the spatial diversity of soils, what are the operating mechanism in ecological functioning involved, how is this expressed in soil stoichiometry, and what does this imply for fertilizer doses and composition requirements and the yield response that follows. This is knowledge intensive. Hitherto, agronomic research has been of a trial and error nature and, consequently, this practice has to be changed towards building up a coherent and comprehensive analytical framework and knowledge on the operating mechanisms involved where soil stoichiometry and yield response to fertilizer is concerned. Furthermore, research attention, while using a similar analytical framework including the functioning of soil biota, will have to be directed to the issue of closing the gap between the nutrient pools of total elemental content and the part thereof that is available for plant uptake. Together, this defines a large well-founded and well-targeted research agenda developed on the basis of a coherent set of guiding principles: a formidable task ahead indeed.

Finally, the uncertainty associated with data on metal resources present in the mantle of the earth, on their location, and whether they can be economically mined at acceptable environmental costs, calls for attentive preparedness, that includes monitoring of mineral prospection results, actual development of demand and supply and future

projections thereof. And, as earlier mentioned, attentive preparedness obviously further includes the development of novel agricultural technologies, that are less dependent on conventionally mined sources of metals, so as to enable mitigation of potential negative impacts of metal scarcity on agricultural production and the world food system.

Annex 1: Selenium

Selenium is an essential mineral nutrient for animals and humans. It is not established as being essential for plants, but it possibly is beneficial (Marschner, 1995).

Human deficiencies

Human selenium deficiency is an important health problem globally, with prevalence estimates in 0.5-1.0 billion people. This estimate does not include the number of people that consume insufficient selenium for optimal protection against cancer, cardiovascular diseases and severe infectious diseases, including HIV (Haug et al., 2007). Selenium deficiency is the cause of the well-known Keshan disease and Kashin Beck disease. Keshan is endemic cardiomyopathy (hart disease) most frequently observed in children and women at childbearing age in China. Kashin-Beck is an endemic osteoarthropathy (stunting of feet and hands causing deformity of joints). It occurs in Siberia, China, North Korea and possibly in parts of Africa (Fordyce, 2005).

Increasing evidence becomes available that selenium is involved in other aspects of human health. Links have been established between selenium deficiency and iodine deficiency disorders (goiter and cretinism) that still need further investigation. There is evidence to suggest that increased selenium intake provides protection against cancer and it is implicated in cardio-vascular health. A further role is suspected in human reproduction and protection against viral attacks, including HIV/aids (Rayman, 2000, 2002; Kupka et al., 2004). Selenium deficiency has also been linked to human muscular dystrophy (which is common in selenium deficient livestock). Finally, a comprehensive review on selenium and breastfeeding suggests that worldwide for about 30% of women the selenium concentrations in breastmilk are inadequate for satisfying the selenium requirements of their breastfed children (Zachara and Pilecki, 2000; Dorea, 2002). Another important observation is that human selenium intakes are decreasing rather sharply in developed countries: by 1/3 in 25 years in the UK (Jackson et al., 2003). The margin between selenium deficiency and toxicity is rather narrow, but overt human toxicity problems are rare.

Animal deficiencies

Selenium deficiency in animals is very common and widespread across the globe (Oldfield, 1999). Selenium deficiency causes white muscle disease, a degeneration of muscles, generally decreasing mobility and if the heart or lungs are affected death may follow. Animals on a deficient diet during gestation may produce offspring that is equally deficient and the newborns may be dead or very weak and die within days. Selenium deficiency further depresses the response of the immune system. In chicken, deficiency may lead to massive hemorrhages beneath the skin. Low selenium pastures are more generally associated with 'ill thrift': subclinical growth deficits or rapid weight loss. Toxicity most frequently occurs on seleniferous soils. Acute toxicity is rare since animals tend to avoid plants that accumulate selenium. Chronic selenium intoxication leads to two diseases known as alkali disease and blind staggers in grazing animals. Both cause poor performance of animals and can lead to death.

Selenium in soils and agriculture

Although not essential, plants do not avail of mechanisms that preclude selenium to enter the plant, and plant selenium content varies with the level of soil selenium and the total soil chemical constellation. Consequently, selenium application to agricultural land

can be used to increase its content in animal feed and human food (various sources quoted in Nube and Voortman, 2011). Because selenium is not essential for plants, such practices will not increase crop yield. Although selenium is ubiquitous in soils, its density is generally very low, but also showing large differences even at short distances. Selenium can be present in soils as elemental selenium, as selenide, selenite, or selenate, or as organically bound selenium, and of these different forms, selenate is most mobile and best taken up by plants. Other factors affecting selenium uptake by plants are the degree of sandiness of soils, and also the pH, with more selenium being available at higher pH (Lyons et al, 2003, 2005; Wang et al., 2005). Furthermore, both iron and sulphur have a negative effect on soil selenium availability. In fact, it has been suggested that increased sulphur concentrations in soils, resulting from high global levels of fossil fuel burning and related emission of sulphur, are partially responsible for globally decreasing levels of selenium availability (Lyons et al, 2003). Selenium may also become toxic and the particular feature of selenium is that the difference between deficient and toxic levels is smallest of all micronutrients. Selenium application to cropland is therefore frequently controlled by environmental regulations. The same applies to animal feed supplements, but this can easily be circumvented by obtaining a veterinary prescription.

The literature sources on soil selenium content do vary, but the figure in the earlier presented Table 11 can be considered representative: 0.09 ppm and for ease of calculation we use 0.1 ppm. Under natural conditions the level of selenium in soils may vary from traces (practically nil) in low-selenium soils to over 150 ppm in seleniferous soils. Using the average figure on soil selenium content (and the same assumption as for zinc and copper) implies that the total amount of selenium in the top 20 cm and top 50 cm is 0.24 kg and 0.60 kg, respectively. Of this total amount, about 2% is present in plant-available forms or about 5 and 12 grams per ha, respectively. At on average 0.02 ppm selenium, plant content is very low, and using the same assumptions as used for copper and zinc, crop removal per hectare would amount to 0.1 gram per year. Table 11 gives the time duration that soil selenium content could sustain such a level of removals under hypothetical conditions. These calculations assume:

- that selenium is equally distributed across world cropland,
- that all the selenium present in the soil can be taken up by plants (which is contrary to experience),
- that plants can fully exploit the soil up to 50 cm depth (which is frequently not the case in crop plants), and
- that only 5 tons of crop product is removed from the field per year per ha (which in developed countries is by far surpassed).

Table 11: The time duration of soil supply of selenium to crops dependent on assumptions on soil depth and total and available soil selenium content.

Soil depth (cm)	Total Se (g/ha)	Duration (years)	Available Se (g)	Duration (years)
20	240	2400	5	50
50	600	6000	12	120

Selenium resources

Selenium does not occur in ores of sufficient densities to warrant specific mining for it. The main source is that it is a byproduct in the process of refining copper. Further, high levels of selenium occur in some coal deposits and black shales, but the extraction technology is still too expensive. Some phosphate rock deposits also contain appreciable amounts of selenium. The 2011 global reserves of selenium amount 93,000 metric tons, of which 2/3 are concentrated four countries: Chile, Russia, Peru and the United States. Refinery production with 70% was concentrated in Germany, Japan and Belgium (but according to USGS data are poor). In 2008 the reserve base was about double the amount of the reserves: 170,000 versus 82,000 metric tons. Annual consumption in 2011 was 2000 metric tons. Hence the reserve/consumption ratio suggests that at current consumption levels current reserves will be depleted in about 42 years. If all agricultural land would annually receive a maintenance application of 0.1 gram of selenium, this would amount in total to 500 metric tons, or 25% of current annual production. In Finland standard practice is to add 10 mg Se per kg of fertilizer: at 200 kg fertilizer per hectare, this would amount to 2 grams per hectare. If this were to be copied worldwide, it would amount to 10,000 metric tons or five times the annual production. Experiments in Brasil were conducted at even 10 and 20 grams per hectare (Cerqueira Luz et al., 2010). Both observations suggest that in case of suspected deficiency, the dosage applied is obviously substantially larger than maintenance applications. We do not know what percentage of agricultural land is selenium deficient, however.

Selenium is commonly used as feed additive in animal husbandry. In 2003 the livestock population of cattle, buffalo, sheep and goats was about 2 billion of an assumed 400 kg cattle equivalent. Recommended supplements are in the order of 1 mg per 100 kg per day. If the entire world livestock would be supplemented this would take 3000 metric tons per year, 1.5 times the current annual production. Of course this would imply that part of the land would have no need to be fertilized, since manure application would do the job.

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Suppletie van micronutriënten uit de mijnbouw

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1 Introductie

Het Platform Landbouw, Innovatie & Samenleving (adviesorgaan op het gebied van landbouw voor het ministerie van EL&I) vraagt zich af *of er sprake is, nu of in de toekomst, van mogelijke schaarste van micronutriënten en wat de consequenties daarvan zijn voor de landbouw en de voedselvoorziening* (vrij naar de website www.platformlis.nl).

Uiteindelijk gaat het daarbij om de vraag in hoeverre tekorten van micronutriënten in de landbouw kunnen worden weggenomen door suppletie van deze nutriënten.

Om deze vraag te kunnen beantwoorden is een beeld van de aanbod- en de vraagzijde nodig. In deze bijdrage zal worden ingegaan op de supply-zijde van de (minerale) micronutriënten die enerzijds van belang zijn voor de landbouw en waarvan anderzijds kan worden vermoed dat op termijn schaarste zou kunnen ontstaan (met als gevolg leveringsproblemen, dan wel hoge prijsvolatiliteit). De beschouwing richt zich daarbij hoofdzakelijk op de elementen koper (Cu) en zink (Zn).

2 Mineraalschaarste

2.1 Reserves: een statische of dynamische grootheid?

Schaarste is op zich een economisch fenomeen waar prijsvorming in onze samenleving mede op gebaseerd is: schaarste aan goederen en diensten veroorzaken een hogere prijs en daardoor aan de ene kant een rem op consumptie en aan de andere kant stimulans voor een innovatieve zoektocht naar alternatieven om het gebruik van het schaarse goed te verminderen, en naar nieuwe bronnen (bijvoorbeeld andere, diepere mijnen, of mineraalwinning op zee). Als maat voor schaarste wordt in bepaalde bronnen de verhouding tussen de huidige productie en de huidige (bekende) reserves genomen (het 'statische' wereldbeeld). Dit verhoudingsgetal is echter vanwege de dynamiek in de mijnbouwwereld niet maatgevend voor het aantal jaren totdat een materiaal 'op' is.

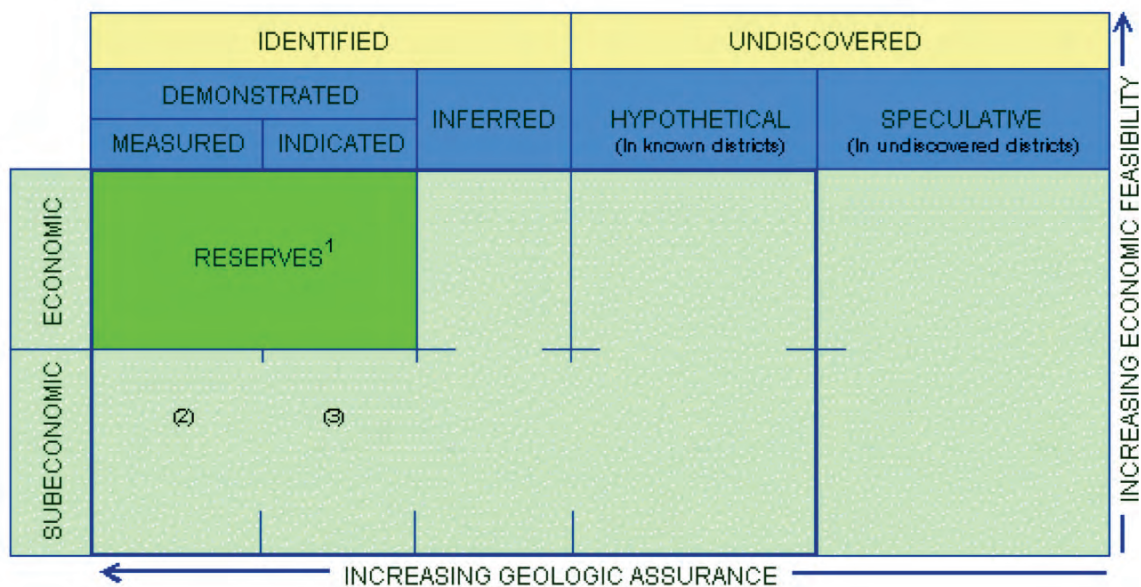
De aardkorst bevat onnoemelijke hoeveelheden mineralen: het is echter de vraag wat op een gegeven moment economisch en (dus ook) technologisch haalbaar is om te winnen. De inschatting en rapportage van de hoeveelheid aanwezige en winbare ertsen wordt over het algemeen aan de hand van onderstaand schema weergegeven (zie Figuur 1). Hierin is de 'reserve' dat deel van de totale 'resources' dat geologisch gedemonstreerd is en dat –op het moment van rapportage- commercieel te winnen is. Afhankelijk dus van de economische, politieke en technologische randvoorwaarden kan de reserve van grootte veranderen. De resources zijn de geïdentificeerde (i.e. geologisch vastgestelde) mineraalbronnen, die van economisch belang kunnen worden als de omstandigheden veranderen en die in principe in voldoende hoeveelheid en concentratie voorkomen om technologisch gewonnen te kunnen worden (en dan 'gepromoveerd' worden tot 'reserves'.)

De 'hypothetical' en 'speculative' voorraden bevatten geschatte hoeveelheden die nog te weinig onderzocht zijn om het economisch potentieel ervan in te kunnen schatten.

Rapportages zijn gebaseerd op de 'reserves'. De meest uitgebreide bron van (openbare) informatie is de US Geological Survey (USGS).⁴

Een statisch grondstofbeeld, waarbij uitputting kan worden verondersteld op basis van de reserves en de jaarlijkse gewonnen hoeveelheid, doet dus geen recht aan het dynamisch karakter van de inschatting van winbare grondstofvoorraden. Sterker nog, mijnbouwbedrijven zullen geen acties ondernemen om reserves te vergroten boven een (R/P)waarde van 30-40 jaar. Exploratie is een uiterst kostbare aangelegenheid, en een eventueel succes, en dus verlenging van de productiehoeveelheden tot boven de 40 jaar vertegenwoordigt geen extra 'shareholders value' voor de betrokken bedrijven. Dat geeft dus een rem op de ontwikkeling van de reserves: daarmee kunnen formele reserves op niveau blijven terwijl toch aanzienlijke productie plaatsvindt.

⁴ Alle relevante informatie is te vinden in de zgn. USGS Mineral Commodity Summaries die jaarlijks een update krijgen.



Figuur 1. Een overzicht van de terminologie met betrekking tot de schaarste van mineralen (bron: http://pubs.usgs.gov/bul/b1450b/1450_F1.gif).

Het gaat echter ook te ver om bij een risico-inschatting over het ontstaan van mineraalschaarste de grootte van de huidige reserves niet mee te nemen. Zo zal een absoluut kleine reserve niet snel kunnen groeien als nieuwe technologieën daar bijvoorbeeld om vragen. Alleen al omdat het enorme investeringen (en lange lead times) vergt om nieuwe mijnbouwprojecten tot ontwikkeling te brengen. Verder zal bij lagere R/P-verhoudingen meer en sneller exploratie-activiteit moeten plaatsvinden. Kortom, de R/P-verhouding vertegenwoordigt geen realistisch beeld van de snelheid van uitputting, maar vertegenwoordigt wel een sterke indicator van kwetsbaarheden.

2.2 Wat maakt mineraalschaarste zo urgent?

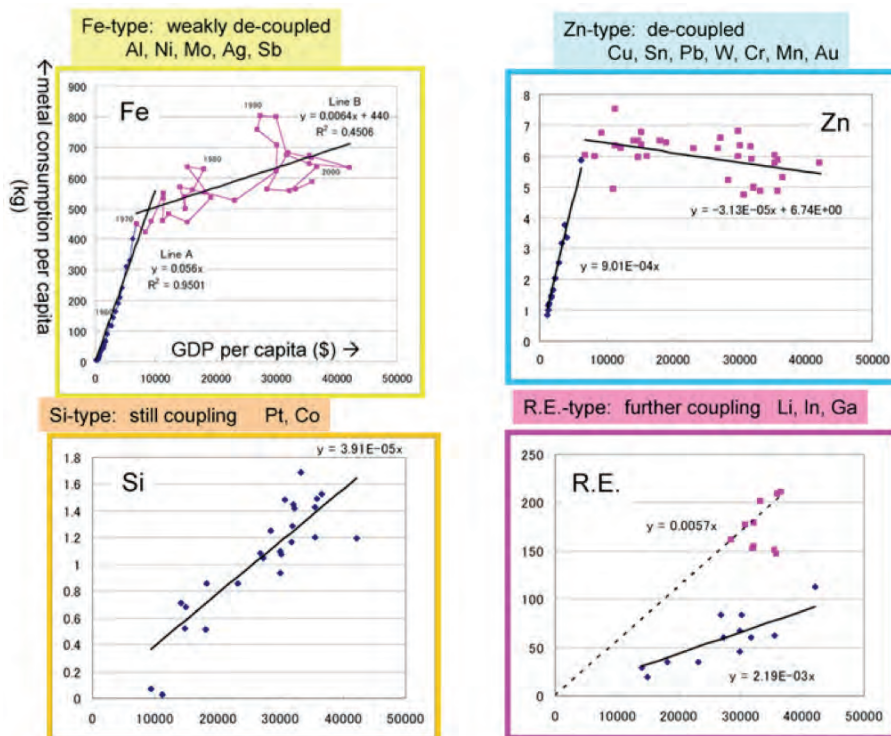
Anders wordt het als schaarste het gevolg is van uitputting (en dus verarming) van bronnen. In die zin is mineraalschaarste een deelprobleem van een breder uitputtingsprobleem dat in 1972 zo treffend werd weergegeven in (de 1^e editie van) “Limits to Growth”⁵. Een groeiende wereldbevolking en een wereldwijd groeiende welvaart zorgen voor sterke druk op veel van onze bronnen (mineralen, energie, water, land, voedsel) op hetzelfde moment. Deze lock-in effecten veroorzaken tal van niet-lineaire afhankelijkheden, die tot grote druk op de beschikbaarheid (en dus op de prijs) zullen leiden. Om minerale mijnbouw als voorbeeld te nemen: mijnbouw vergt grote hoeveelheden (zoet) water en energie (voor transport en tal van refining-stappen in de eerste fasen van het proces); die hoeveelheden nemen drastisch toe naarmate de ertsgraad lager wordt. Deze set van onderlinge relaties wordt uitgewerkt in het boek *Linkages of Sustainability* (Graedel en Van der Voet, 2010), waarin o.a. wordt ingeschat dat het risico bestaat dat in 2040 tot 40% van het wereldwijde energieverbruik ingezet zal moeten worden om in onze behoefte aan mineralen te voorzien. Dergelijke inschattingen geven al aan dat op termijn een enorme druk zal ontstaan op prijs en beschikbaarheid van minerale

⁵ De meest recente editie is: *Limits to Growth, the 30-year update* door Donella en Dennis Meadows en Jorgen Randers uit 2004.

grondstoffen. Die druk kan (voor geselecteerde groepen mineralen) nog worden vergroot door:

- Explosieve vraaggroei als gevolg van nieuwe technologie (zoals bijvoorbeeld t.b.v. de energietransitie): het gebruik van elementen uit de reeks van zeldzame aardmetalen en materialen als indium en gallium stijgen de laatste jaren sterk door de introductie van iPads, plasmaschermen, LED-verlichting, PC's en windturbines; dit aspect wordt nog versterkt door de lead times (5-10 jaar) voor het ontdekken en in gebruik nemen van nieuwe mijnbouwlocaties (nog afgezien van de enorme investeringskosten daarvoor).
- Het geologische feit dat veel van de 'exotische' elementen als (ppm-)bijproduct van andere metalen worden gewonnen en dus geen zelfstandige marktdynamiek kennen (voorbeeld: cadmium en indium als bijproducten van zinkwinning).
- Geopolitieke ontwikkelingen: economisch winbare ertsen liggen niet homogeen verspreid over de wereld: landen als China, Zuid-Afrika, Brazilië, Kazachstan en Australië zijn grootmachten op mineraalgebied en kunnen het bezit van ertsen strategisch inzetten. Het tijdelijk blokkeren van zeldzame-aarde-export aan Japan door China in het najaar van 2010 is daar een sprekend voorbeeld van.

Overigens is de groei van de consumptie voor bepaalde grondstoffen *ontkoppeld* van groei in welvaart, m.n. door efficiency-maatregelen. Deze trend is o.a. zichtbaar voor koper en zink (zie Figuur 2).



Figuur 2. Verschillende maten van ontkoppeling van de vraag naar grondstoffen en de groei van de welvaart (bron: T.E. Graedel en E. van der Voet, editors, *Linkages of Sustainability*, MIT Press, 2010).

Samenvattend, zonder te kunnen spreken over het 'opraken van metalen', is er alle reden over de brede linie een opwaartse druk op de prijzen te verwachten tezamen met een toenemende leveringonzekerheid. En dus is het zaak met grote waakzaamheid te kijken

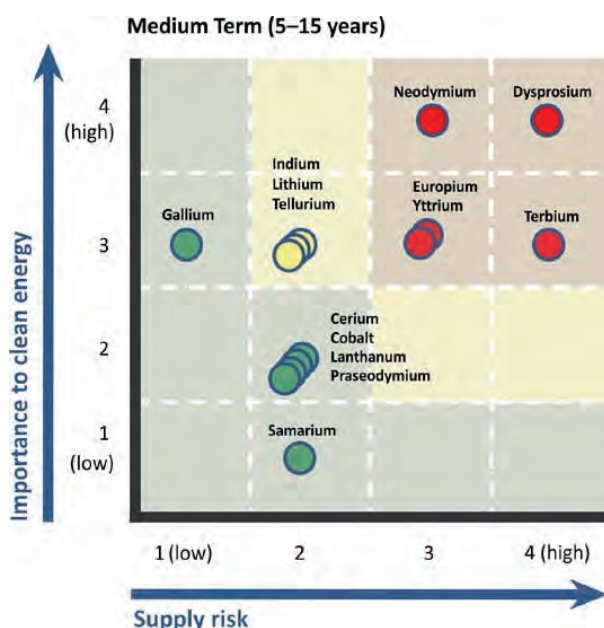
naar de ontwikkelingen op dit gebied, de gevolgen daarvan in de eigen waardeketen, en alternatieve strategieën te ontwerpen.

2.3 Wat zijn de kritieke mineralen?

De zorg om voldoende, betrouwbare en betaalbare toevoer van mineralen, leidt wereldwijd (en dan natuurlijk m.n. in sterk geïndustrialiseerde landen) tot activiteiten die variëren van risicoanalyse tot strategische voorraadvorming, een actievere rol op diplomatiek vlak en het inzetten op het zoeken naar vervanging, het versterken van recycling en het nadenken over fiscaal beleid dat consumptie moet remmen.

Voor die risicoanalyse hebben verschillende instanties prioriteitenlijsten gemaakt van ‘critical materials’. Prioriteit wordt i.h.a. langs twee assen bepaald: één as geeft dan de mate van leveringonzekerheid aan (reservehoeveelheid, landafhankelijkheid, druk van concurrerende technologie), de andere as gaat in op het belang van het materiaal vanuit het oogpunt van de belanghebbende (economisch belang voor de EU, relevantie voor energietransitie voor JRC-IE en US-DoE, militair belang voor US-DoD). In figuren 3 en 4 zijn de hoofdresultaten gegeven van risicoanalyses van resp. de EU (RMI, 2010)⁶ en het US-DoE⁷ (US Department of Energy, 2010).

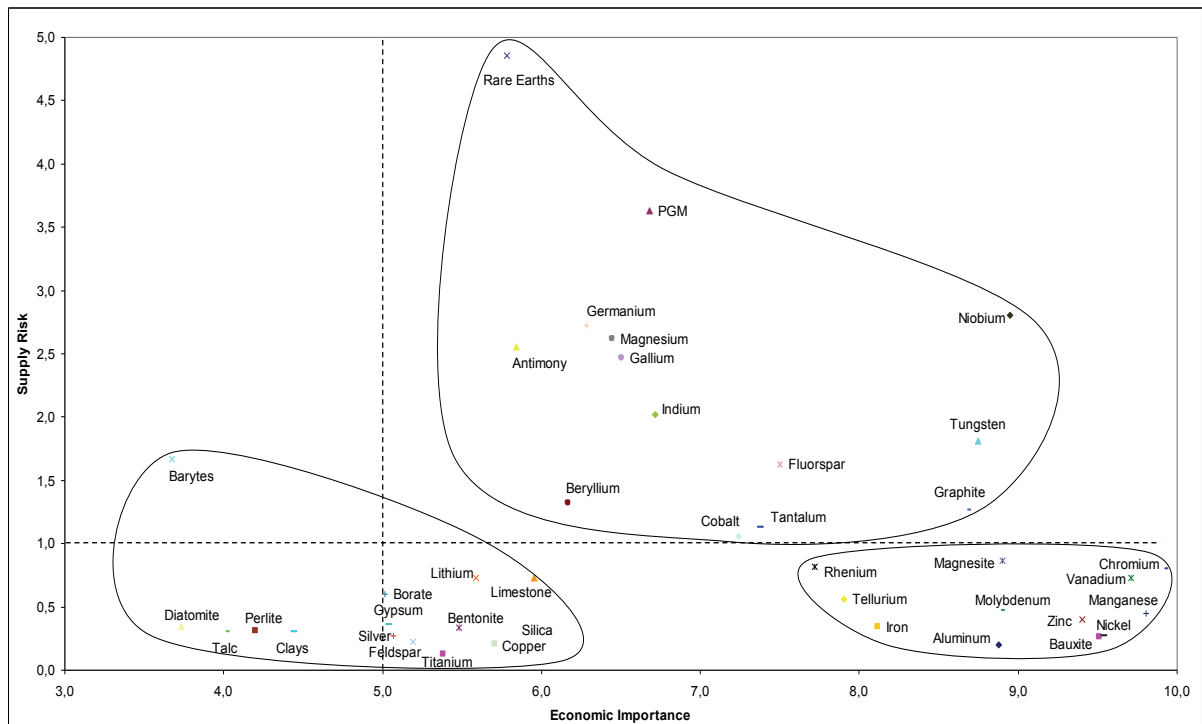
De meeste prioriteit krijgen wereldwijd de zeldzame aardmetalen (REM of REE), de platina-groep-metalen (PGM), indium, germanium, gallium, niobium, wolfram, antimoon, magnesium.



Figuur 3. Kritieke mineralen, vanuit oogpunt van duurzame energie (bron: US Department of Energy, 2010).

⁶ Het rapport van de Ad-hoc working group van het Raw Materials Initiative RMI verscheen in juli 2010

⁷ In december 2010 verscheen deze risico-analyse van de DoE; beide rapporten zijn te downloaden.



Figuur 4. Kritieke mineralen vanuit oogpunt van economisch belang (bron: RMI, 2010).

In deze lijsten ontbreken koper en zink als prioriteitsmaterialen. In het rapport van het Raw Materials Initiative⁸ worden ze meegenomen als te onderzoeken materialen, maar de ‘supply-risk’ wordt zo laag ingeschat dat het geen prioriteitsgebieden worden. Wel wordt erkend dat het om economisch uiterst belangrijke materialen gaat. En daarbij past de kanttekening dat het Raw Materials Initiative een tijdshorizon van 10 jaar heeft genomen. Het Amerikaanse Ministerie van Defensie houdt een aantal materialen ‘in stock’. Dit zijn Beryllium, Tantaal, Niobium, PGM, Iridium, Tin, Zink, Thorium, Wolfram en Kobalt. Zink is nog ‘in stock’ maar wordt inmiddels niet meer als kritiek, noch strategisch beschouwd, en de voorraad wordt dus actief afgebouwd.

⁸ Site: http://ec.europa.eu/enterprise/policies/raw-materials/critical/index_en.htm; hierin verwijzingen naar relevante documenten

3 Koper: aanbod, vraag, ontwikkelingen

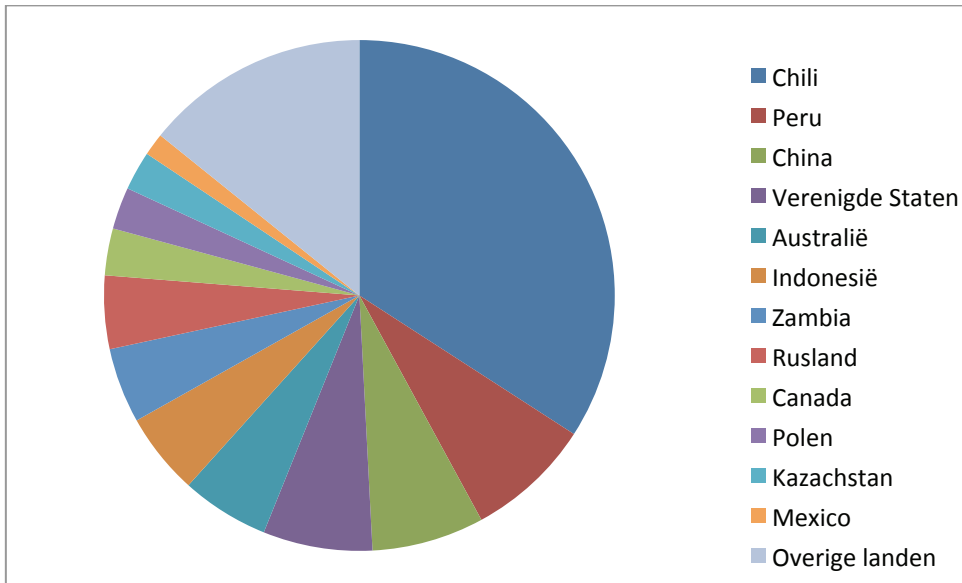
3.1 Aanbod: Voorraden, Jaarlijkse productie en productielocaties

In de onderstaande tabel worden de bekende reserves, en productiecijfers van koper weergegeven.⁹ Met ‘reserves’ wordt hier bedoeld de hoeveelheid bewezen voorraden die onder de huidige omstandigheden (economie, technologie) economisch winbaar zijn. De P/R-verhouding (productie over reserve) voor koper schommelt (al jaren) tussen de 30 en 40 jaar (op dit moment 39 jaar), onafhankelijk van de hoogte van de productie. Er lijkt geen jaarlijkse uitgebreide studie aan deze cijfers vooraf te gaan, maar eerder een inschatting en opgave van mijnbouwbedrijven en producerende landen. De verdeling van de kopermijnbouwproductie over landen is weergegeven in Figuur 5, de verdeling van de raffinagecapaciteit in Figuur 6.

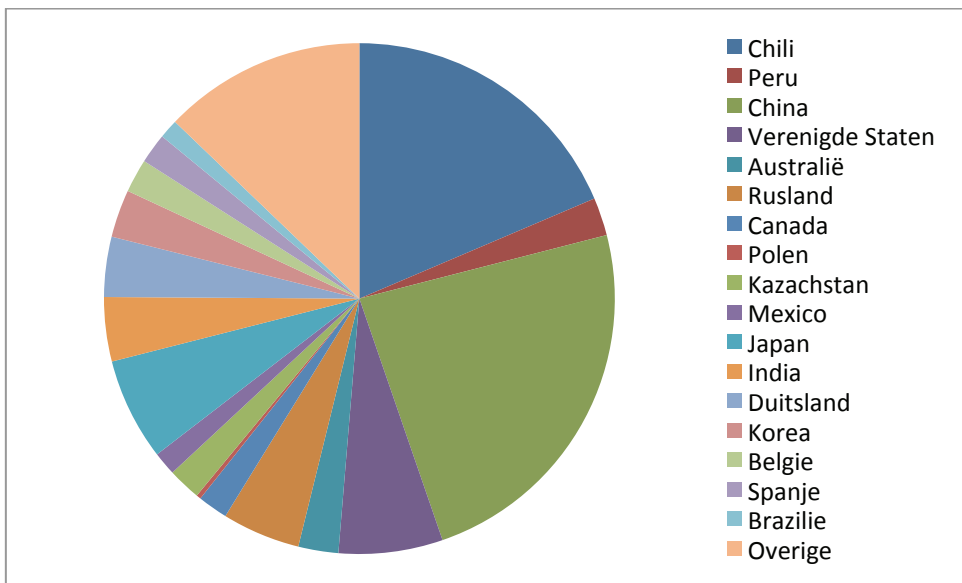
Tabel 1. Reserves en productiecijfers voor koper (bron: USGS Mineral commodity summaries, January 2011 (<http://minerals.usgs.gov/minerals/pubs/commodity/>)).

	Reserves (ton)	Mijnbouw 2010 (ton/jaar)	Refining (ton/jaar)
Chili	150.000	5.520	3272
Peru	90.000	1.285	423
China	30.000	1.150	4175
Verenigde Staten	35.000	1.120	1160
Australië	80.000	900	446
Indonesië	30.000	840	
Zambia	20.000	770	
Rusland	30.000	750	870
Canada	8.000	480	336
Polen	26.000	430	50
Kazachstan	18.000	400	368
Mexico	38.000	230	261
Japan			1140
India			715
Duitsland			669
Korea			532
België			374
Spanje			335
Brazilië			213
Overige landen	80.000	2.300	2259
Totaal	630.000	16.200	18400

⁹ Tenzij anders vermeld zijn de gegevens afkomstig over reserves en productiehoeveelheden afkomstig van de USGS Mineral Information website: <http://minerals.usgs.gov/minerals/pubs/commodity/>



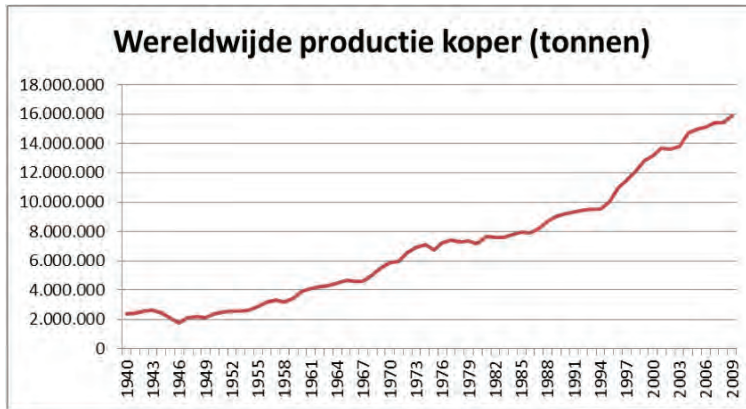
Figuur 5. verdeling kopermijnbouwproductie (bron: USGS Mineral Commodities 2010).



Figuur 6. Verdeling Koperraffinage (bron: USGS).

Naast de zogeheten ‘inferred’ bronnen (o.a. in Chili), worden nog veel toekomstige ‘undiscovered’ reserves verondersteld op de zeebodem (in massieve sulfides) (zie Figuur 1).

De wereldwijde productie van koper neemt al jaren gestaag toe (zie Figuur 7); een relatieve ont koppeling in de reeds geïndustrialiseerde wereld, wordt meer dan gecompenseerd door een toename aan wereldbevolking en welvaart.

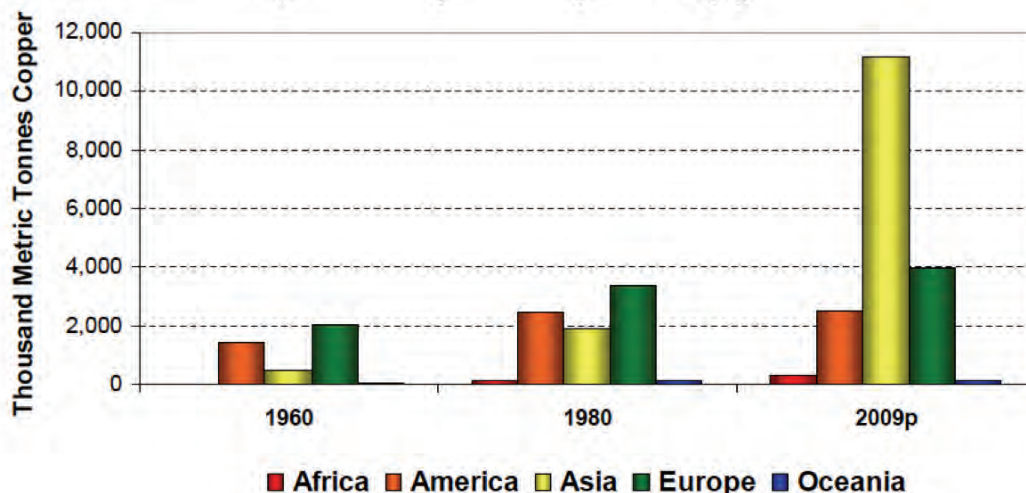


Figuur 7. Wereldwijde productie van koper 1940-2009 (bron: USGS).

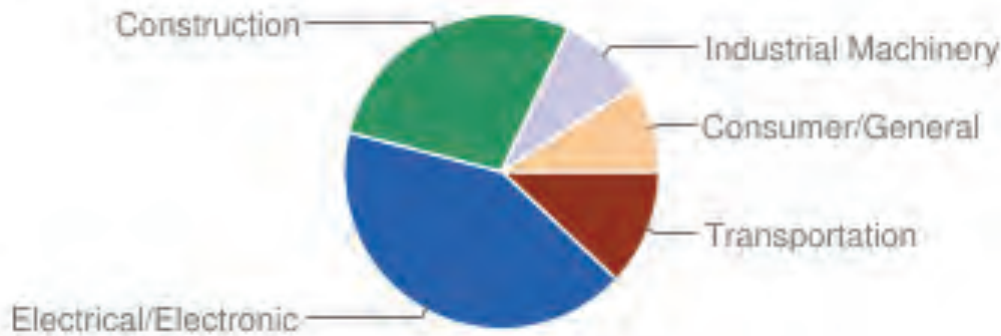
Zowel de primaire winning als de verwerking van erts vindt plaats in een groot aantal landen. Daarbij zijn de grootste mijnbouwlanden niet noodzakelijkerwijs de grootste verwerkers van kopererts. Zo is opvallend dat Chili de grootste mijnbouwlocatie is, maar China de belangrijkste speler als het gaat om de verdere verwerking. Marktverstoring zoals in het geval van zeldzame aarden het geval is (meer dan 95% van de productie en verwerking vindt in China plaats), is in het geval van koper dan ook niet aan de orde. Dit is ook aanleiding geweest voor de opstellers van het rapport van de Raw Materials Initiative de ‘supply risk’ van koper zodanig laag in te schatten dat koper – voor de komende 10 jaar - niet in de ‘gevaarzone’ van kritieke materialen terecht komt.

3.2 Vraag: Gebruik en applicaties van koper

Gedurende de laatste 30 jaar is de koperconsumptie sterk gegroeid en dan vooral in Azië.



Figuur 8. Gebruik van geraffineerd koper per regio voor 1960, 1980 en voorlopige cijfers ('preliminary') voor 2009 (bron: International Copper Study Group, 2010).



Figuur 9. Belangrijkste toepassingen van koper (bron: International Copper Study Group).

De huidige verdeling van het kopergebruik is in bovenstaande figuur weergegeven. Wat opvalt aan de gebruiksverdeling, is dat naast het dominante gebruik in het vervoeren van elektriciteit, koper grootschalig wordt ingezet in de constructiewereld (buizen, verwarming, ventilatie, maar ook in aanzienlijke mate als constructiemateriaal zelf). Zonder op details in te gaan, spreekt het -gezien deze applicaties- vanzelf dat toenemende prijzen van koper een range aan alternatieve oplossingen met zich mee zal brengen.

3.3 Ontwikkelingen

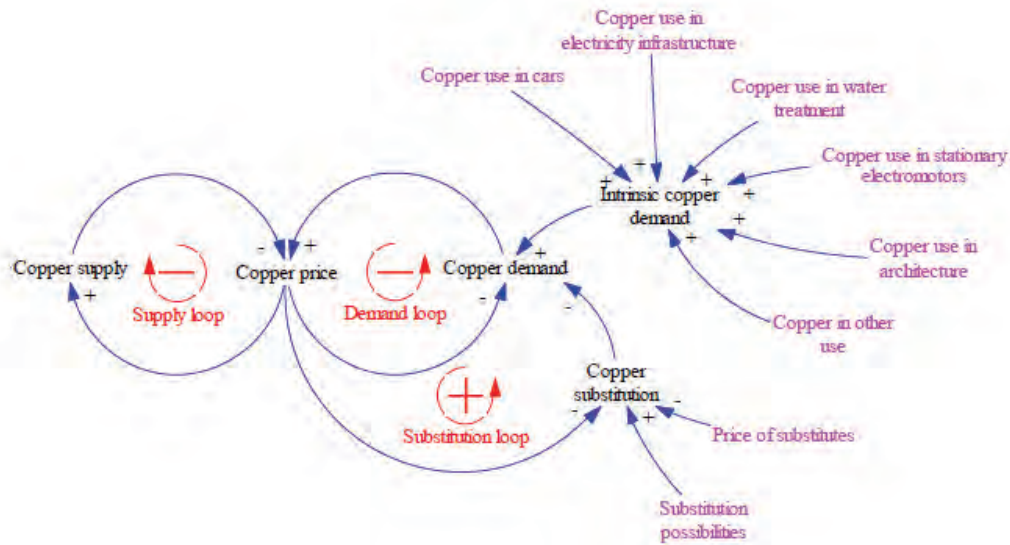
3.3.1 Toch koperschaarste?

Alhoewel koper door zowel de US-DoE als door het RMI niet als kritisch wordt bestempeld, ligt wel voor de hand dat het gebruik van koper zal toenemen naarmate onze energievoorziening (inclusief automobilititeit) meer gebaseerd zal zijn op elektriciteit. Kleijn en Van der Voet (2010) geven aan dat er stevige knelpunten zijn te verwachten in de koper-supply (in 2050) als een groot deel van de elektriciteitsbehoefte uit de Sahara zou moeten komen via koperkabels (energieopwekking uit Concentrated Solar Power CSP). Deze belemmeringen zijn zo groot dat of deze projecten niet op deze schaal van start kunnen gaan, of goede alternatieven (via bijvoorbeeld aluminiumgeleiding) voorhanden moeten zijn.

Fraunhofer ISI schat in dat in 2030 (t.o.v. 2006) een verdrievoudiging plaatsvindt van de koperbehoefte voor enkele specifieke technologieën (m.n. industriële elektromotoren, en motoren t.b.v. elektrische auto's), waardoor de totale druk op koper en de behoefte om alternatieven (Aluminium Core Steel Reinforced kabels, plastic leidingen voor water, glasfibers voor dataverkeer) te zoeken sterk zal toenemen (Angerer et al., 2009). Deze enorme behoeftetoename zal niet noodzakelijkerwijs plaatsvinden, omdat markt- en prijsbewegingen dit beïnvloeden. Systeemdynamische modellering kan worden ingezet om in niet-lineaire systemen met grote onzekerheden een beeld te creëren van mogelijke toekomstscenario's (en de invloed van ingrepen daarop). Een recente studie van Auping (TU Delft, 2011) richt zich op het kopersysteem. Het uitgangspunt staat gegeven in onderstaande figuur.

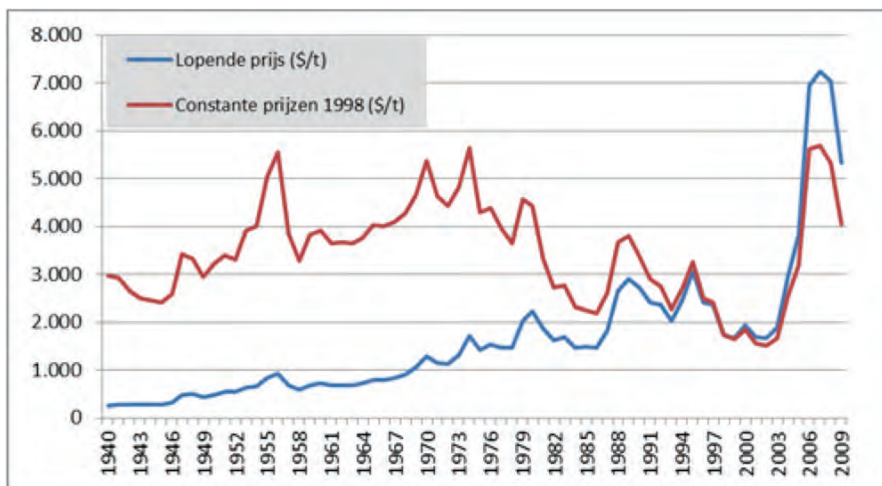
De belangrijkste bevindingen uit deze SD-studie voor de lange termijn zijn:

- Koperprijzen blijven enorm volatiel, als gevolg van een onbalans tussen vraag en aanbod, lange lead times voor nieuwe mijnbouw (en overige infrastructuur) en de 'concurrentie' met reële substituten;
- De kopervraag blijft geleidelijk afnemen door de toename van de kosten (vanwege afname van de ertsgraad) en de te verwachten stabielere prijs van substituten.

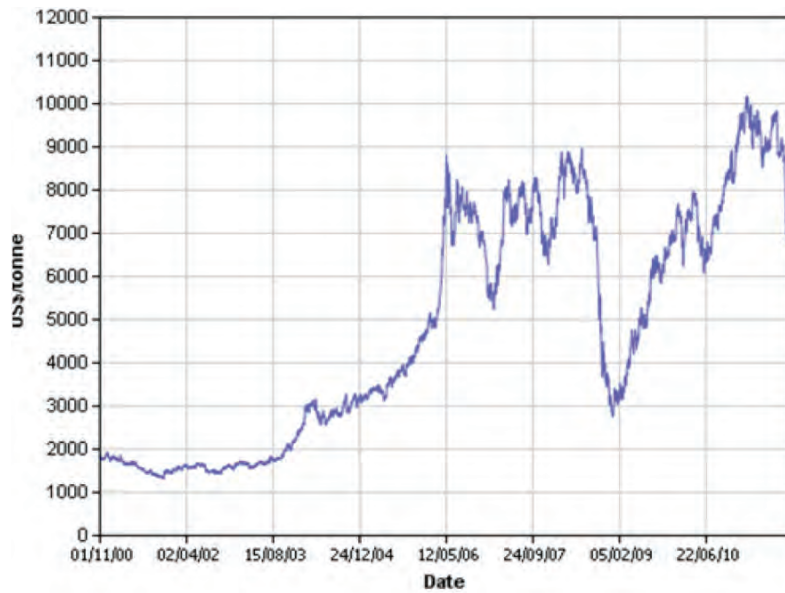


Figuur 10. Het kopersysteem (bron: Auping, 2011).

Dat een hoge volatiliteit niet alleen in de toekomst is te verwachten maar ook nu al van toepassing is, blijkt uit Figuren 11 en 12.



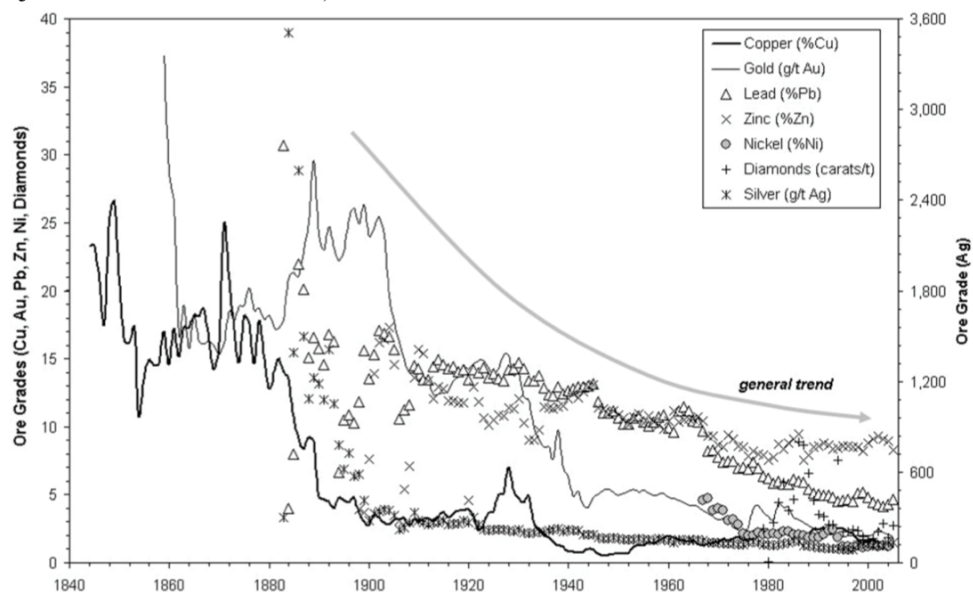
Figuur 11. Lange-termijn prijsontwikkeling van koper 1940-2009 (bron: USGS).



Figuur 12. Recente prijsontwikkeling van koper (US\$ per ton) (bron: London Metals Exchange (November 2011)).

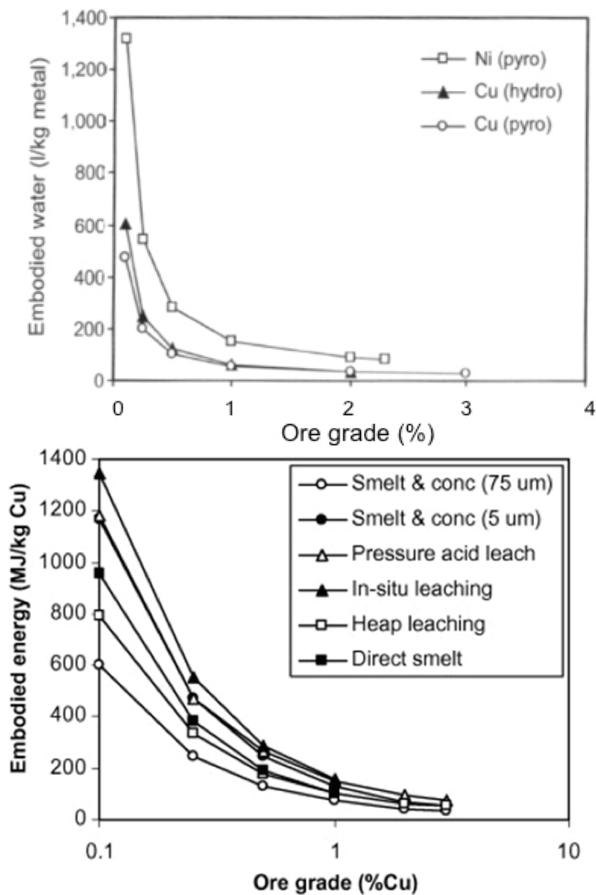
3.3.2 Afnemende ertsgraad en toenemende energiekosten

Door de jaren heen, neemt de ertsgraad van verschillende mineralen af (zie figuur 13) (zie bijvoorbeeld Mudd, 2009).



Figuur 13. Afname ertsgraad van een aantal mineralen (bron: Mudd, 2009).

Met name voor koper zijn de consequenties hiervan goed gedocumenteerd. Figuur 14 laat zien dat bij een lagere ertsgraad de benodigde hoeveelheid energie en water voor (koper)mijnbouw veel hoger is (zie Norgate, 2010).



Figuur 14. Benodigde hoeveelheid water en energie voor de kopermijnbouw in afhankelijkheid van de ertsgraad (bron: Norgate, 2010).

Omdat de druk op betaalbare energie en zoet water (en daarmee de kosten) aanzienlijk kunnen stijgen in de komende decennia, is het afnemen van de ertsgraad een risicofactor die tot sterke prijsstijgingen kan leiden. Dit zijn prijsstijgingen die los staan van toename in gebruik als gevolg van groei in bevolking en welvaart.

4 Zink: aanbod, vraag, ontwikkelingen

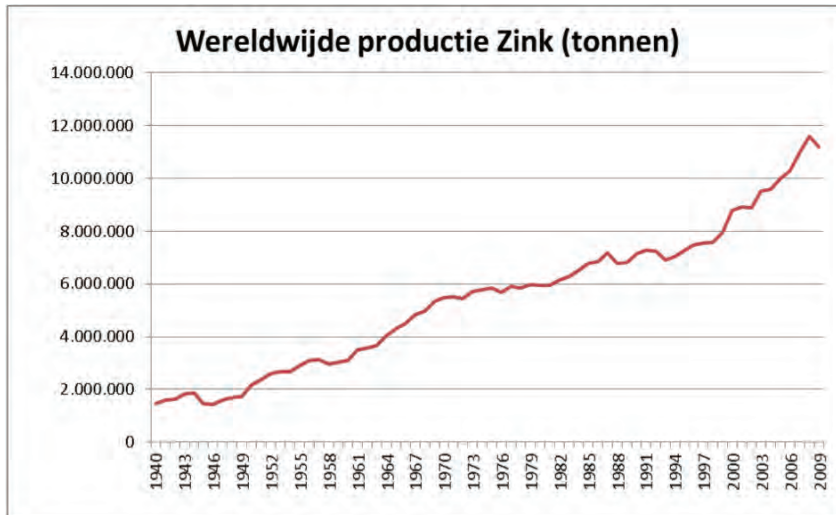
4.1 Aanbod: voorraden, jaarlijkse productie en productielocaties

Tabel 2. Reserves en productiecijfers voor zink in 2010 (bron: USGS Mineral commodity summaries, January 2011 (<http://minerals.usgs.gov/minerals/pubs/commodity/>)).

Zinkproductie (x1000 ton)	Reserves (ton)	Mijnproductie (ton per jaar)	Smeltercapaciteit (ton per jaar)
China	42.000	3.500	4.360
Overige landen	62.000	1.580	2.418
Peru	23.000	1.520	-
Australië	53.000	1.450	531
India	11.000	750	582
Verenigde Staten	12.000	720	203
Canada	6.000	670	686
Mexico	15.000	550	300
Kazachstan	16.000	480	329
Bolivia	6.000	430	-
Ierland	2.000	350	-
Japan	-	-	643
Korea	-	-	623
Spanje	-	-	501
Rusland	-	-	225
Wereld Totaal	250.000	12.000	11.400

De R/P-verhouding (reserves/productie) voor zink liggen hiermee op ongeveer 21 jaar, aanzienlijk korter dan voor koper (tussen de 30 en 40 jaar).

Evenals bij koper zijn veel landen betrokken bij de mijnbouw van zink. Dat betekent dat de leveringszekerheid van zink niet de inzet van geopolitiek zal komen. Dit geldt in iets mindere mate ook voor de smelter-capaciteit: ook die is aanwezig in veel landen (overigens betekent dit ook dat infrastructuur en kennis in meer landen aanwezig is), alhoewel China duidelijk een belangrijke speler is op deze markt (bijna 40% van het wereldtotaal).



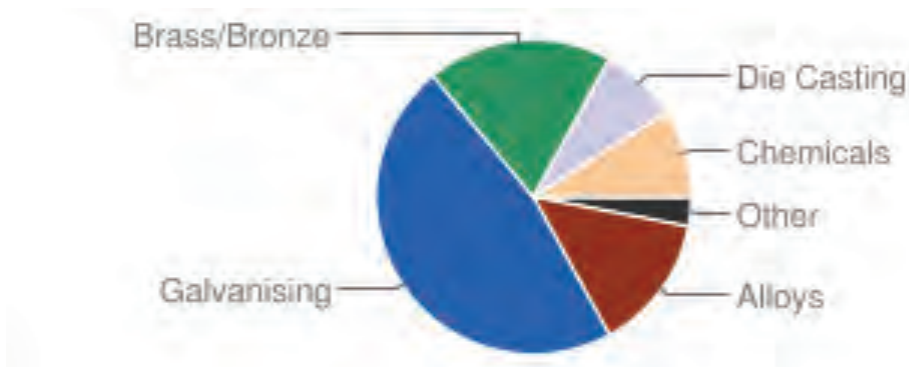
Figuur 15. Wereldwijde productie van zink (bron: USGS).

De productiegroei in het geval van zink is vergelijkbaar met die van koper: een gestage groei, die het gevolg is van ontwikkelingen in een zich ontwikkelende wereld met een groeiende wereldbevolking.

Met name de verdeling over een groot aantal producerende landen, was ook (net als in het geval van koper) in het Raw Materials Initiative rapport aanleiding om zink (alhoewel het economisch belang groter werd ingeschat dan voor koper) niet op te nemen in de lijst van kritieke grondstoffen.

4.2 Vraag: huidig gebruik

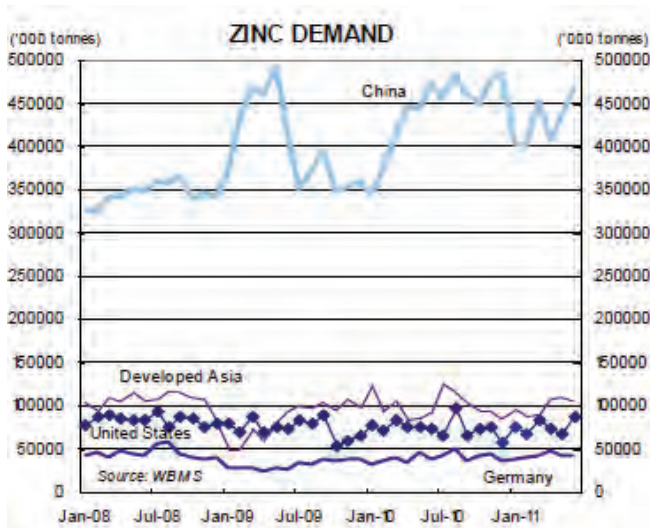
De belangrijkste Industriële zinktoepassingen, liggen in de metallurgische wereld.



Figuur 16. Belangrijkste toepassingen van koper (bron: International Lead and Zinc Study Group).

Volgens de USGS wordt zink stof (*zinc compounds en dust*) hoofdzakelijk gebruikt in de landbouw, verf- en rubberindustrie.

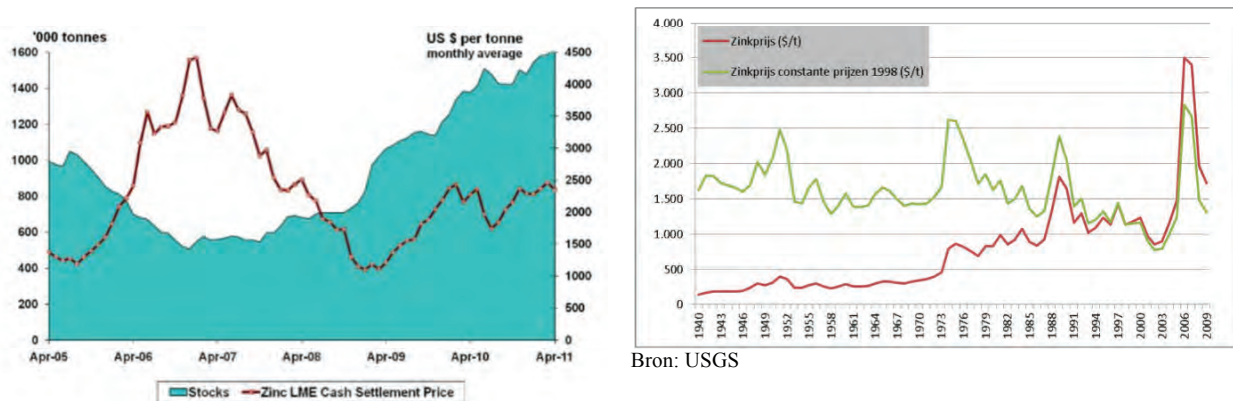
De coatingtoepassingen maken zink populair: het levert een uiterst lange en onderhoudsvriendelijke levensduur op. Daarmee zijn er wel alternatieven te bedenken (zowel metallurgische, als op basis van verf en plastic coating), maar de alternatieven zijn (vanzelfsprekend) duurder.



Figuur 17. De vraag naar zink (in 1000 ton per jaar) in een aantal landen (bron: Citi Group Global Markets, 2011).

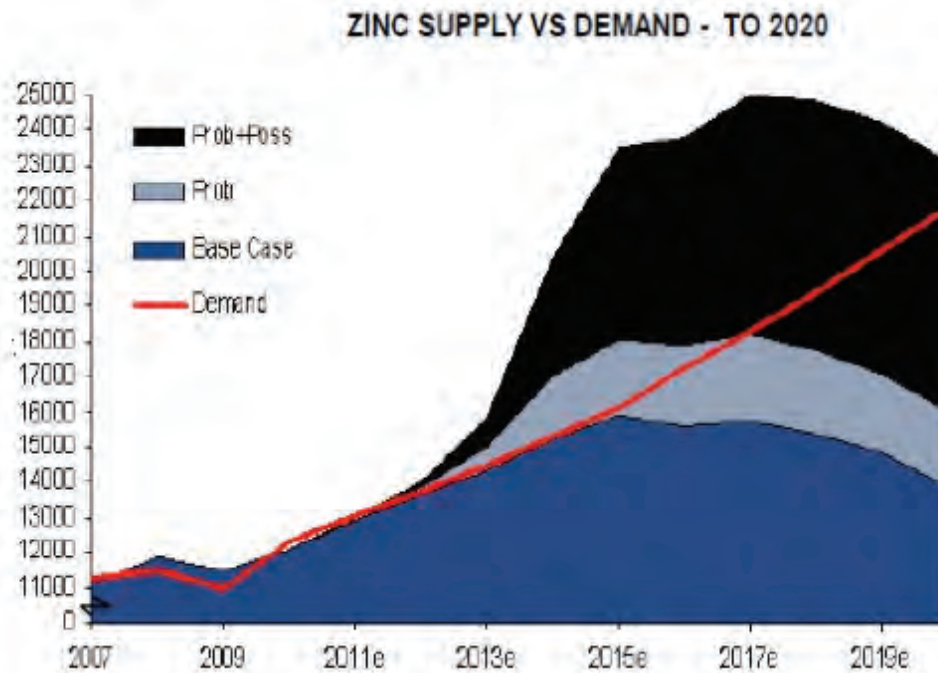
De wereldwijd toenemende welvaart leidt tot een groeiende behoefte aan metalen en dus aan corrosiebescherming. Uit bovenstaande figuur blijkt dat China een enorm belangrijke positie inneemt als consument van zink. Anders dan in het geval van koper, wordt voor zink geen additionele stijging van de vraag verwacht als gevolg van toepassingen in nieuwe technologie.

4.3 Ontwikkelingen: prijzen zink en toekomstverwachting



Figuur 18. Recente en lange termijn prijsontwikkeling van zink (in US\$ per ton) (bron: International Lead and Zinc study group).

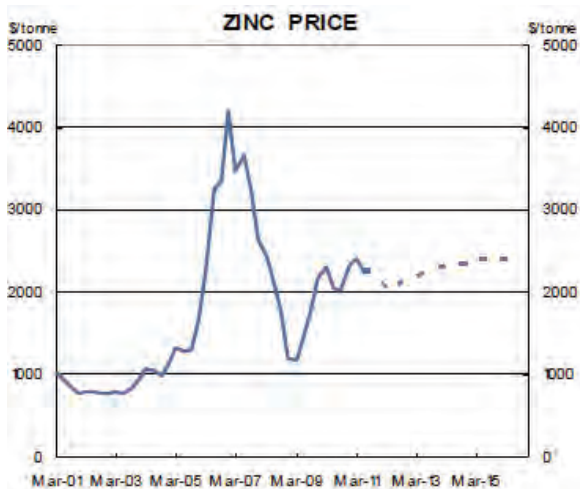
Ondanks het niet-kritieke karakter van het zink-systeem, schommelt de prijs op vergelijkbare wijze als die van koper. Zowel qua marktdynamiek, als qua complexiteit m.b.t. het opzetten van nieuwe mijnbouwexploitaties spelen dezelfde fenomenen, die dus ook hier tot een aanzienlijke marktvolatiliteit leiden.



Figuur 19. Feitelijke vraag en aanbod (tot 2011) en verwachte totale vraag naar zink (rode lijn) tegenover verschillende scenario's voor het totale aanbod van zink (Bron: Citigroup Global markets, 2011).

De verwachting is dat het aanbod van zink tot ca. 2017 groter zal zijn dan de vraag (zie Figuur 19).

Gezien de toenemende vraag, met name in grootverbruiker China, wordt voor de nabije toekomst een continue – maar in feite toch nog beperkte - stijging van de prijs voorzien in de ordegrrootte van \$300 van het huidige niveau (zie Figuur 20).



Figuur 20. Recent prijsontwikkeling van zink (bron: Citi Group Global markets 2011).

5 Andere bronnen: recycling en micronutriënten uit afvalwater?

Alhoewel in de komende jaren geen fysieke schaarste is te verwachten op het gebied van de hier behandelde micronutriënten koper en zink, is het goed te kijken of andere bronnen in aanmerking komen voor suppletie van deze nutriënten.

Op dit moment worden zowel koper als zink intensief gerecycled: tussen de 30 en 50% van ingezette koper en zink is afkomstig uit secundaire stromen (NB: van veel van de kritieke high-tech-metalen wordt minder dan 1% teruggewonnen via recycling, soms door ontbreken van beschikbare technologie, vaker nog door het ontbreken van een economisch rendabele logistiek, aangezien deze materialen slechts in kleine concentraties in high-tech-applicaties voorkomen).

Omdat micronutriënten in landbouwgewassen en dus voedsel voorkomen, zal een groot gedeelte van deze nutriënten weer in effluenten en in mest terecht komen. Tabel 3 geeft de samenstelling van het droge-as aan (dat na verbranding van RWZI-slib ontstaat). Hieruit blijkt o.a. dat in verbrand slib-as ongeveer 2,5 g/kg zink in slib-as en 1 g/kg koper in slib-as aanwezig is in deze as. Vergeleken met zelfs de armste mijnbouwoperaties, zijn dit echter nog steeds lage concentraties. De armste koper-mijnbouw vindt momenteel plaats op een concentratie van 0,3 – 0,5% koper in erts (d.w.z. 3 – 5 g/kg koper in erts). Dit bevindt zich (zo wordt aangenomen) dicht bij de mineralogische barrière, die aangeeft beneden welk gehalte het bovenmatig veel energie kost om economisch verantwoord mijnbouw te kunnen plegen. Naar analogie, lijkt het niet haalbaar om zuiver koper en zink uit verbrand slib-as te isoleren. Wellicht is een inzet in minder zuivere vorm te overwegen, alhoewel contaminatie met andere (zware) metalen daar een probleem zou kunnen vormen.

Tabel 3. Gehalten van mineralen in verbrand slib-as in mg/kg droge stof van slibverwerking Noord-Brabant (bron: SNB/Unie van Waterschappen, 2011).

Maandmonsters (o.b.v. mengmonsters, analyse met ICP na HF-ontsluiting)		gemiddelde									
eenheid	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	
CaCO ₃	g/kg d.s.	geen data			30	39	56	38	30	43	25
Cd	mg/kg d.s.	3,4	3,8	3,2	3,8	4,1	3,8	3,5	3,0	3,6	3,4
Cr	mg/kg d.s.	100	104	106	118	143	106	113	108	116	113
Cu	mg/kg d.s.	914	882	884	888	1177	1083	1049	1048	1075	1131
Ni	mg/kg d.s.	220	198	205	86	74	63	71	70	65	67
Pb	mg/kg d.s.	58	58	57	261	297	264	279	267	282	280
Zn	mg/kg d.s.	2205	2173	2439	2262	2453	2183	2200	2258	2217	2350
As	mg/kg d.s.	15	15	18	24	21	23	24	22	22	22
Mo	mg/kg d.s.	19	18	21	27	28	27	28	29	24	27
Sb	mg/kg d.s.	5	5	8	9	13	23	28	18	17	19
Hg	mg/kg d.s.	0,07	0,07	0,09	0,1	0,1	0,1	0,1	0,1	0,1	0,1
Ca	g/kg d.s.				155	152	152	137	137	140	139
Al	g/kg d.s.				57	55	55	47	51	49	52
Fe	g/kg d.s.				99	95	88	85	77	82	78
S	g/kg d.s.				21	19	22	19	17	19	19
P	g/kg d.s.				85	83	84	78	79	84	91
deeltjesgrootte x10	um				7	8	10	6	7	7	8
deeltjesgrootte x50	um				70	75	87	69	71	77	78
deeltjesgrootte x90	um				315	325	450	331	317	346	338
VMD	um				118	123	164	122	119	131	129

Herberekening naar andere voorstelling

6 De status van enkele andere micronutriënten: B, Mn, Se, Mo

Naast koper en zink spelen enkele andere mineralen ook een belangrijke rol als micronutriënt. De situatie m.b.t. deze mineralen is op hoofdlijnen gegeven in Tabel 4.

Tabel 4. Reserves, productiecijfers en toepassingen voor een aantal andere micronutriënten (bron voor R, P en R/P: USGS Minerals Information, 2011 (<http://minerals.usgs.gov/minerals/pubs/commodity/>)).

Stof	R (ton)	P (ton per jaar)	R/P ¹⁰ (jaar)	Aandelen in productie	Toepassingen	Opmerkingen
B (boor)	210.000	3.500	60	>75% Turkije, Chili, Argentinië	Chemie (bleek), glas	Geen recycling, maar substituten mogelijk
Mn (mangaan)	630.000	13.000	48	50% uit Z-Afrika, Chili, China	Staal- en Al-legeringen	Diepzeemijnbouw? Geen substituten bekend
Mo (molybdeen)	9.800.000	234.000	42	>75% uit US, China, Chili	legeringen	Substitutie mogelijk, met andere 'schaarse' metalen
Se (seleen)	88.000	2.260	39	Bijproduct van koper; >75% uit Duitsland, Japan, Canada	Glas, electronica, PV	Prijzen stijgen, substituten mogelijk

Op seleen na, worden deze grondstoffen ook genoemd in het RMI: er wordt een wezenlijk economisch belang aan gegeven, maar de 'supply risk' wordt ook hier niet hoog ingeschat, waardoor deze materialen niet onder de meest kritieke grondstoffen worden geschaard.

Ook in vergelijking met de uitgebreider besproken micronutriënten koper en zink, valt op dat de R/P-verhoudingen gunstig afsteken. Schaarste valt niet op kortere termijn te verwachten dan voor koper en zink. Ook niet bij seleen, alhoewel dat als bijproduct wordt gewonnen: de koperproductie zal immers ook toenemen, zodat de potentie voor seleenwinning navenant zal toenemen.

Overige nutriënten waarvoor de minerale voorraadsituatie in kaart kan worden gebracht zijn: kalium, calcium, magnesium, zwavel en ijzer. Gegevens over deze mineralen worden gegeven in de bijlage.

¹⁰ USGS Minerals Information 2011

7 Conclusies

De aandacht voor krapte op de mineralenmarkt zal de komende jaren toenemen. De aandacht zal daarbij voornamelijk uitgaan naar een set kritieke mineralen, zoals die (o.a.) door de EU is vastgesteld.

Koper en zink worden gezien als belangrijke materialen voor de economie van de EU, maar niet als metalen waarvoor (binnen de gekozen tijdshorizon van 10 jaar) een groot risico voor leveringsonderbreking bestaat, deels omdat de grondstofwinning niet gedomineerd wordt door een beperkt aantal landen. Daarmee kan gesteld worden dat deze twee metalen de komende decennia niet in absolute zin ‘opraken’ of schaars worden. Alhoewel we aannemelijk hebben gemaakt dat statische R/P (reserve/productie)-verhoudingen geen realistisch beeld geven van de concreet te verwachten grondstoffenproblematiek, geeft de R/P-verhouding wel een beeld van de mate waarin zorgen omtrent grondstoffen toenemen, en waarin actie (o.a. nieuwe mijnbouwactiviteiten) zou moeten plaatsvinden. In die zin is de huidige situatie m.b.t. zink (een R/P-verhouding van ongeveer 20) zorgwekkender dan die voor koper en enkele overige in dit stuk besproken micronutriënten. Disclaimer daarbij is wel dat hier altijd wordt uitgegaan van de publieke informatie die door de USGS ter beschikking wordt gesteld. Er wordt –ook in Europees verband– hard gewerkt aan het opzetten van meer informatiebronnen. Het huidige beeld voor koper zou in de nabije toekomst zorgelijker kunnen worden, omdat de behoefte aan koper in de komende decennia sterk (i.e. sterker dan op basis van toenemende bevolking en welvaart is te veronderstellen) zou kunnen toenemen door een toenemend belang van elektrificatie. Door deze toenemende vraag, maar ook door de karakteristieken van de mijnbouw- en mineralenmarkt is volatiliteit en prijsstijging op de metaal (koper en zink) markt van blijvende aard. De kwetsbaarheid daarvan zal voor verschillende markten anders uitpakken: dat zal afhangen van de prijselasticiteit van die markten, oftewel de heftigheid waarmee de vraag reageert op prijsveranderingen. De hoogte van prijsstijgingen wordt hierbij vooral bepaald door het aandeel dat de metalen hebben in de totale kostprijs van een eindproduct. Zo kan bijvoorbeeld berekend worden dat de kostprijs van een zgn. flat panel display (waarde ongeveer 600EUR) slechts met 0,2% zou stijgen indien de prijs van het hiervoor benodigde indium zou verdubbelen (in dit voorbeeld komt de waarde van het LCD-scherm dan op 601,20 euro). Hoe deze verhoudingen in de landbouwwereld uitpakken, is in het kader van deze bijdrage niet nader bekeken.

Alhoewel uit de deze stukken blijkt dat er geen onmiddellijk tekort dreigt aan de besproken micronutriënten, is zorg op zijn plaats. Net als in het geval van fosfaat gaat het bij micronutriënten om materialen die –anders dan bij diverse industriële toepassingen– een niet-vervangbare rol hebben voor het leven op aarde. Dat prijsvolatiliteit en prijsstijgingen aan de orde van de dag zullen blijven is welhaast zeker. De mate waarin dit bepalend is voor de landbouwsector zal enerzijds afhangen van de concrete bijdrage van de micronutriënten in (landbouw)opbrengsten en anderzijds van de draagkracht van de individuele boer, die in verschillende delen van de wereld verschillend zal kunnen uitpakken.

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Bijlage : Samenvatting risicogegevens micronutriënten

Tabel 5: Risicogegevens voor de belangrijkste micronutriënten (bron voor R, P en R/P: USGS). In deze tabel is ook een aantal materialen opgenomen dat niet tot de micronutriënten behoort, maar wel tot de essentiële voedingsstoffen.

	Reserve (ton)	Productie (ton / jaar)	R/P (jaar)	Bijproduct?	Geografische Concentratie? ¹¹	Substituten beschikbaar?	Supply Risk ¹²
N	Ruim beschikbaar (uit de lucht)	131.000	n.a.	Nee	Laag	Nee	
P (fosfaat erts)	65.000.000	176.000	370	Nee	67% van productie in 3 landen, 77% van voorraad in Marokko	Nee	
Cu	630.000	16.200	39	Nee	Laag	Deels	0,2
Zn	250.000	12.000	21	Nee	Laag	Moeilijk	0,4
Mn	630.000	13.000	48	Nee	Laag	Nee	0,4
Mo	9.800.000	234.000	42	Nee	Hoog	Ja, maar door andere kritieke mineralen	0,5
B	210.000	3.500	60	Nee	Hoog	Ja	0,6
Se	88.000	2.260	39	Ja	Hoog	Ja	
Fe	180.000.000	2.400.000	75	Nee	Laag	-	
K	9.500.000	33.000	288	Nee	Laag	-	-
Ca (als 'lime')	Ruim beschikbaar	310.000		-	Laag	-	-
Mg	2.400.000	5.580	430	Nee	Hoog	Ja	2,6 ¹³
S	Afkomstig uit minerale olie: ruim beschikbaar	68.000	n.a.	-	Laag	-	-
Na	Ruim beschikbaar	n.a.	n.a.	-	laag		

Micronutriënten in de landbouw en beschikbaarheid in de bodem - Focus op koper en zink

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1. Introductie

Micronutriënten (spooorelementen) als B, Mo, Cu, Zn, Fe en Ni zijn essentieel voor een goede groei van gewassen en dieren. Gehalten in de bodem en daarmee in planten zijn van nature vaak te laag voor een optimale gewasgroei en/of dierprestatie. Wereldwijd komt een tekort aan Zn maar ook Cu dan ook vaak voor (Voortman, 2011). Bemesting is noodzakelijk om tekorten bij gewassen op te heffen. Resultaten uit Turkije laten zien dat dit kan leiden tot spectaculaire opbrengststijgingen (tot wel 600%) in Zn-deficiënte gebieden (Cakmak et al., 1996). Dit heeft daar geleid tot een sterk stijgend gebruik van Zn-houdende meststoffen. Anderzijds wordt in India verwacht dat de problematiek met betrekking tot Zn-tekorten verscherpt (Singh, 2011).

Tegelijkertijd is het van belang om efficiënt met micronutriënten om te gaan, omdat deze schaars en relatief duur zijn en nog duurder zullen worden. De wereldvoorraden van bijvoorbeeld winbaar koper en zink zijn zeer beperkt (Bastein, 2011). Anderzijds kan overmatig gebruik leiden tot milieuproblemen. In Nederland wordt vooral op de veehouderijbedrijven van de zware metalen Cu en Zn meer aangevoerd dan dat er met het gewas wordt afgevoerd. Dit leidt tot ophoping en/of extra uit- en afspoeling naar het oppervlaktewater.

Om efficiënt met spooorelementen om te kunnen gaan dient enerzijds bekend te zijn welke factoren de beschikbaarheid van spooorelementen in de bodem beïnvloeden en anderzijds dient bekend te zijn wat de gewas- en dierbehoefte is. In deze bijdrage wordt vooral ingegaan op bodemprocessen en de rol van grondonderzoek om de beschikbaarheid van spooorelementen voor gewassen te duiden.

2. Gewas- en dierbehoefte en overschotten in Nederland

2.1. Gewas- en dierbehoefte

Gewassen verschillen in hun behoefte aan Cu en Zn. In Tabel 4 is voor een aantal gewassen weergegeven of ze een hoge of lage gewasbehoefte aan deze elementen hebben en op welke processen in de plant Cu en Zn invloed hebben. In Nederland is de voorziening van gewassen met Cu en Zn in het algemeen goed door het gebruik van dierlijke mest dat relatief hoge gehalten aan Cu en Zn bevat.

Cu en Zn zijn essentieel voor een goede diergezondheid en dierprestatie (Tabel 4). De behoefte van dieren aan Cu en Zn hangt af van de diersoort, leeftijd en productiedoel. In Tabel 2 is globaal weergegeven welke ranges in behoefte-normen van ruwvoer gehanteerd worden voor melkvee en varkens (EU 2003a; EU2003b, COMV, 2005; Jacela et al., 2010). Met bemesting kunnen deze gehalten in gewassen voor ruwvoer in principe ongeveer gerealiseerd worden, maar in de praktijk is de opname meestal lager (zie Tabel 1), terwijl gehalten van boven de 10 mg Cu per kg ds voer via bemesting niet te realiseren zijn. Veelal wordt daarom extra Cu en Zn toegevoegd aan krachtvoerders en worden er mineraalconcentraten toegevoegd aan ruwvoer, te meer daar voldoende Cu en Zn verondersteld wordt positief te werken op de diergezondheid en het weerstandsvermogen.

Tabel 1. Het gemiddelde Cu- en Zn-gehalte en de 95% range van enkele belangrijke ruwvoerders.

Ruwvoeder	Cu-gehalte (95%-range)	Zn-gehalte (95%-range)
Weidegras	9 (5 - 13)*	..
kuilgras	8 (5 -11,5	..
snijmaiskuil	4 (2 – 6)	35 (20-50)

Tabel 2. De behoefte aan Cu en Zn uitdrukt in mg per kg droog voer.

Diersoort	Cu	Zn
Melkvee*	8-12	25-50
Varkens	5-10	50-125

* In Nederland worden voor droogstaand melkvee en jongvee beduidend hogere normen aangehouden

2.2. Cu- en Zn-overschotten

Uit een inventarisatie van Den Boer et al. (2007) op 25 melkveehouderijbedrijven in Drenthe bleek dat de Cu- en Zn-voorziening regelmatig het dubbele of meer bedroeg van wat vanuit veevoedingstechnisch oogpunt nodig is. Dit resulteerde gemiddeld over de bedrijven in positieve Cu- en Zn-balans van respectievelijk 184g Cu/ha en 304 g Zn/ha. Bovendien was de variatie tussen bedrijven zeer groot. Indien op de bedrijven Cu-houdende voetbaden werden gebruikt kon het Cu-overschot oplopen tot 1 kg/ha. Op nationaal niveau is het Cu en Zn in mengvoerders de belangrijkste bron van toevoer (via dierlijke mest) naar landbouwpercelen (Jongbloed en Römken, 2009) en bedroeg voor Nederland als geheel het overschot respectievelijk ongeveer 400 en 1100 ton Cu en Zn per jaar.

Door een aangepast management en aanpassingen in de minerale samenstelling van voedermiddelen zijn Cu- en Zn-overschotten drastisch te verkleinen (Den Boer et al., 2007;

Vliet et al., 2009), mits erfbetreiders hun adviezen naar de agrarisch ondernemer met betrekking tot de spoorelement voorziening op elkaar afstemmen. Naar verwachting zal dit leiden tot lagere gehalten in de mest. In combinatie met een lagere mestgift per ha als gevolg van het vigerende N- en P-beleid zal de aanvoer naar landbouwpercelen naar verwachting voldoende afnemen. Voor een adequate voorziening van gewassen met Cu en Zn wordt het dan belangrijker om via grondonderzoek te kunnen voorspellen hoeveel Cu en Zn beschikbaar kan komen door nalevering uit de bodem en welke factoren hierop van invloed zijn. Dan kan beter onderkend worden of er bemesting nodig is en zo ja, welk type meststof of welke toedieningstechniek het beste gebruikt kan worden Dit is des te belangrijker voor gebieden waarbij de voorziening met Cu en Zn marginaal (zoals in de tropen, Zuidoost Azië) is.

3. Spooreslementen in de bodem: factoren die van invloed zijn op beschikbaarheid

3.1. Vormen

Spooreslementen zijn in verschillende vormen in de bodem aanwezig, zowel in de vaste als in de opgeloste fase. De vier belangrijkste vormen zijn:

- als vrij anion/kation in de bodemoplossing;
- gecomplexeerd met anorganische/organische bestanddelen in de bodemoplossing; en
- geadsorbeerd aan metaal(hydr)oxiden, organische stof en/of kleimineralen; en
- in bodemmineralen

Er is een groot verschil tussen de totaalgehalten aan (spoor)elementen in de bodem (Tabel 3) en de concentratie in de bodemoplossing.

Tabel 3. Totaalgehalten aan Cu en Zn die wereldwijd in de bodem worden aangetroffen en de concentratie ervan in de bodemoplossing, uitgedrukt als totaalconcentratie in de bodemoplossing. Data uit Mengel & Kirkby (1987) en Kabata-Pendias & Pendias (2001).

Element	totaalgehalte, mg kg ⁻¹	concentratie in bodemoplossing, mg kg ⁻¹
Koper	1 – 140	0,0018 – 0,135
Zink	3,5 – 770	0,021 – 0,570

Over het algemeen komt een groot deel van de voorraad aan Cu en Zn voor in mineralen in de bodem, waaruit deze vrij kunnen komen door verwerking. Doorgaans is dit een zeer langzaam proces en zal zeer weinig bijdragen aan de beschikbaarheid van het spooreslement voor een gewas binnen een groeiseizoen.

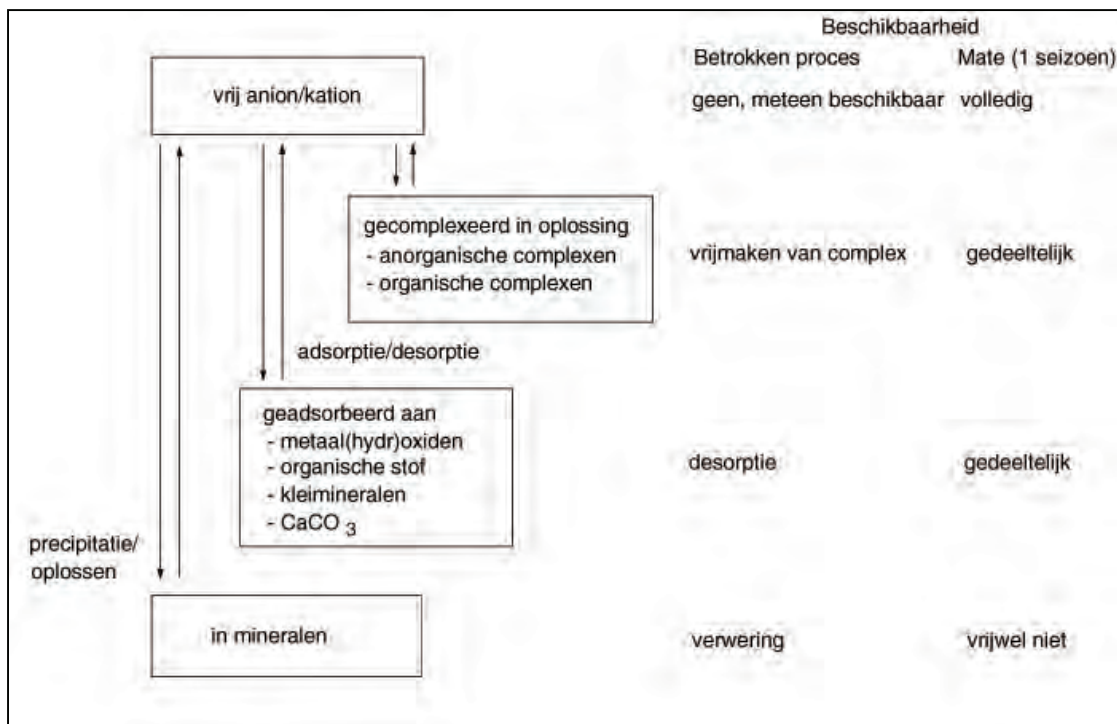
Voor spooreslementen geldt dat alleen de vrije vorm in oplossing (het Cu²⁺, Zn²⁺ ion), opneembaar is voor de plant en dus chemisch gezien beschikbaar is. Dit is slechts een fractie van het totaal (Tabel 3).

Tussen de concentratie van het vrije ion in oplossing en de andere vormen van het element in de bodem bestaat een chemisch evenwicht. De ligging van dat evenwicht wordt bepaald door de affiniteit van de chemische reacties. Een daling van de concentratie van het vrije element in oplossing leidt tot een verschuiving van het evenwicht, waardoor een deel van het spooreslement vanuit de gecomplexeerde of geadsorbeerde fase wordt vrijgemaakt en in oplossing komt. Deze nalevering buffert de concentratie van het vrije spooreslement in oplossing zoals schematisch is weergegeven in Figuur 1.

Complexering in oplossing met anorganische/organische complexvormers speelt een rol bij Cu en Zn en wordt beïnvloed door de pH. Anorganische complexvormers zijn onder andere chloride (Cu en Zn), sulfaat (Zn) en carbonaat (Zn). Daarnaast kunnen Cu en Zn in oplossing gecomplexeerd zijn met opgeloste organische stof (Ashley, 1996). Gecomplexeerd Cu en Zn is niet direct beschikbaar voor opname. Het moet eerst worden vrijgemaakt van het complex.

Wel verhoogt complexering de mobiliteit van Cu en Zn in de bodemoplossing, waardoor de gewasopname kan toenemen.

Het adsorptiecomplex is de belangrijkste micronutriënten-buffer in de bodem en daarmee de belangrijkste bron van opname door de plant. Geadsorbeerd aan bodembestanddelen (klei, organische stof, metaal(hydr)oxiden, kalk) moeten Cu en Zn eerst worden gedesorbeerd alvorens ze opneembaar zijn voor de plant. Wanneer de adsorptie toeneemt, is de evenwichtsconcentratie van het sporelement in oplossing lager en is het sporelement dus minder beschikbaar voor opname. Heel weinig organische stof en kleimineralen is ongunstig, want dan spoelen nutriënten snel uit; een heel hoog gehalte aan klei, ijzeroxiden en organische stof is ook weer niet gunstig, want dan neemt de beschikbaarheid van de nutriënten relatief weer af, omdat zoveel geadsorbeerd wordt.



Figuur 1. Schema van de belangrijkste bodemfracties waarin hoofd- en sporelementen aanwezig zijn. De processen die van invloed zijn op het beschikbaar komen van een bepaalde fractie en de mate waarin de verschillende fracties kunnen vrijkomen voor opname binnen een groeiseizoen zijn aangegeven.

3.2. Factoren die de beschikbaarheid beïnvloeden

De factoren die de adsorptie en resorptie bepalen, en daarmee de mate waarin Cu en Zn beschikbaar zijn, zijn onder andere:

- pH;
- vochtgehalte;
- temperatuur; en
- interacties met andere elementen.

Adsorptie/desorptieprocessen zijn sterk pH-afhankelijk. Bij adsorptie aan metaal(hydr)oxiden en kleimineralen leidt een verhoging van de pH tot een hogere adsorptie van Cu en Zn,

waardoor de beschikbaarheid afneemt. De Cu en Zn-concentratie in de bodemoplossing nemen in 100-voud af per eenheid dat de pH toeneemt. Hierdoor neemt ook de opname van Cu en Zn door de plant sterk af bij verhoging van de pH. Op kalkgronden zonder bemesting zal daardoor vaak een Zn tekort optreden.

Het vochtgehalte van de bodem dient voldoende te zijn voor nutriëntentransport. Met de aanvoer van water naar de wortels worden immers ook spoorelementen, die zich in de bodemoplossing bevinden, meegevoerd. Onder droge omstandigheden zijn nutriëntengehalten in gewassen dan meestal ook duidelijk lager. Een goede vochtvoorziening kan ertoe leiden dat bij een relatief lage beschikbaarheid toch voldoende Cu en Zn wordt opgenomen.

Voor de meeste elementen geldt dat afname van de temperatuur leidt tot afname van de opname van nutriënten.

Wat de interactie met andere elementen betreft wordt de opname van Cu sterk beperkt door andere divalente kationen, vooral Zn^{2+} . Een overmaat Zn kan leiden tot een Cu-tekort. Cu en N vertonen sterke positieve interacties. Meer N verhoogt de opname van Cu en dat geldt ook omgekeerd. Toediening van relatief grote hoeveelheden N- en P-meststoffen kunnen door stimulering van de groei leiden tot Cu-gebrek bij planten die in gronden groeien met lage Cu-gehalten. Cu en P zijn antagonisten. Verhoging van de hoeveelheid P in de bodem leidt door competitie om adsorptieplekken op de organische stof, tot vermindering van de hoeveelheid geadsorbeerd Cu in de bodem. Op korte termijn leidt dit tot toename van beschikbaarheid van Cu. Op lange termijn leidt dit echter, door afname van de geadsorbeerde Cu-ionen die een soort voorraad vormen, tot Cu-gebrek. Anderzijds zijn planten met P-gebrek vatbaar voor Cu-toxiciteit. Cu-toxiciteit kan leiden tot Fe-gebrek in planten: Cu en Fe zijn antagonisten.

Zn vertoont interacties met vele elementen: Zn-P, Zn-N, Zn-K, Zn-Mn, Zn-Fe en Zn-Cu (Moraghan & Mascagni, 1991). De interactie met P is bekend. Hoge P-giften kunnen leiden tot het ontstaan van Zn-tekort en daardoor tot een opbrengstderving i.p.v. een opbrengststijging. Doordat meer P wordt opgenomen versnelt de groei van de spruit en dit leidt tot 'verdunning' van de Zn-concentratie in het gewas en daardoor tot Zn-gebrek. Daarnaast neemt de Zn-oplosbaarheid in de bodem af bij verhoging van P-concentraties in bodemoplossing. Gewassen met tekort aan Zn kunnen hoge P-gehalten hebben. Het komt voor dat ogenschijnlijke Zn-gebreksverschijnselen, in werkelijkheid P-toxiciteitsverschijnselen zijn.

3.3. De rol van de plant

Niet alleen de zojuist genoemde factoren beïnvloeden de beschikbaarheid van spoorelementen voor de planten, maar planten kunnen zelf ook een actieve rol spelen in de opname. Plantenwortels kunnen de chemische omstandigheden in de nabijheid van de wortel (rhizosfeer) sterk beïnvloeden door een verandering in de pH. Deze verandering van pH hangt samen met het opnamemechanisme van kationen en anionen. Opname van kationen is gekoppeld aan afgifte van H^+ en opname van anionen aan een netto afgifte van OH^- . Wanneer de opnamebalans van (kationen-anionen) negatief is (d.w.z. wanneer netto meer anionen worden opgenomen), wat doorgaans het geval is wanneer N als nitraat wordt opgenomen, stijgt de pH in de rhizosfeer. Als N overwegend wordt opgenomen als ammonium, of bij planten met symbiotische stikstofbinding, is de opnamebalans van (kationen-anionen) positief en daalt de pH in de rhizosfeer (Aquilar & Van Diest, 1981;

Gahoonia et al., 1992; Thomson et al., 1993). Door een verandering van de pH in de rhizosfeer verandert ook de beschikbaarheid van spoorelementen. Bijvoorbeeld een pH-stijging in de rhizosfeer zorgt voor een verminderde beschikbaarheid van Cu en Zn. Dit betekent dus dat de vorm waarin N wordt opgenomen een belangrijke rol speelt bij de opname van mineralen.

Plantenwortels scheiden diverse organische verbindingen uit, bijvoorbeeld suikers, enzymen, organische zuren, en in bijzondere gevallen phytosideroforen: stoffen die zorgen dat bepaalde elementen gemakkelijker opgenomen kunnen worden. De uitscheiding van organische zuren uit de wortels van sommige plantensoorten kan sterk toenemen door fosfaatgebrek, waardoor meer P kan worden opgenomen. De capaciteit van wortels om phytosideroforen uit te scheiden verschilt sterk tussen plantensoorten en tussen rassen van een soort (Römheld & Marschner, 1990; Marschner, 1995).

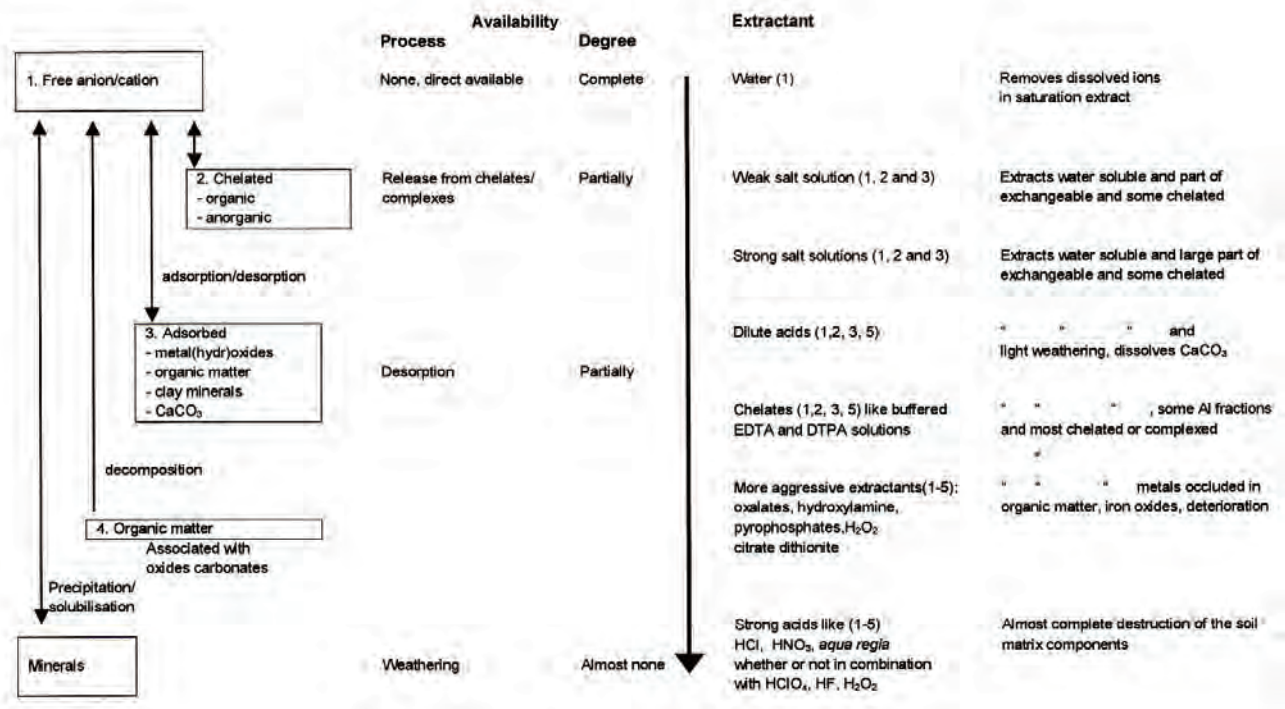
In Tabel 4 zijn enkele van invloed zijnde factoren op de beschikbaarheid in beknopte vorm weergegeven.

4. Grondonderzoek als indicator voor de beschikbaarheid in de bodem

4.1. Bepaling van de beschikbaarheid met achtergronden

De ontwikkeling van grondonderzoeksmethodieken kwam in de twintiger jaren van de vorige eeuw op gang en werd sterk geïntensiveerd na 1945. De ontwikkelde technieken zijn vooral gebaseerd op “trial and error” onderzoek (Van Erp en Van Beusichem, 1998). Diverse extractiemiddelen zijn in het verleden getest om vast te stellen of ze agressief genoeg waren om met de toen beschikbare analytische technieken verschillen in extraheerbaar nutriëntgehalte tussen gronden vast te stellen. Deze verschillen zijn vervolgens gerelateerd aan opbrengst- en respons proeven op bemesting. Deze correlatieve benadering heeft ertoe geleid dat elk land en/of regio zo’n beetje zijn eigen extractie methodiek heeft, hetgeen resulteert in tientallen verschillende methodieken (Jones 1998, Bussink & Temminghoff 2004) met hun eigen waarderingssystematiek. Dit bemoeilijkt het uitwisselen van bodemanalyse gegevens en bijbehorende adviezen tussen regio’s.

In Nederland werd tot voor kort 0,43 M salpeterzuur en 0,4 M azijnzuur als extractiemiddel gebruikt om respectievelijk Cu en Zn te bepalen. De destijds afgeleide relaties tussen de hoeveelheid geëxtraheerd en gewasrespons verklaren vaak niet meer 25%.



Figuur 2. Belangrijkste fracties van sporelementen in de bodem, processen van invloed op het beschikbaar komen van bepaalde fractie, mate waarin de verschillende fracties kunnen vrijkomen voor opname binnen een groeiseizoen en type extractiemiddel dat van invloed is op het vrij maken van micronutriënten uit een bepaalde fractie. Het is slechts een grove indicatie van wat de belangrijkste fracties zijn die micronutriënten vrij maken voor de bodemplossing (Bussink & Temminghoff, 2004).

Met de komst van nieuwe analysetechnieken in de afgelopen decennia (ICP, ICP-MS) kunnen tot meer dan 1000 keer lagere gehalten worden gemeten (Bussink & Temminghoff, 2004). Dat biedt de mogelijkheid om met zwakkere extractiemiddelen te gaan werken die beter het wortelmilieu weerspiegelen.

In zijn algemeenheid dient een goed extractiemiddel informatie te geven over:

- de hoeveelheid die direct beschikbaar is in de bodem (intensiteit); en
- de hoeveelheid die gemakkelijk in oplossing kan komen om de door de plant opgenomen hoeveelheid te vervangen (capaciteit of hoeveelheid).

Voor een optimale gewasgroei c.q. het realiseren van een bepaald gewenst gehalte in het gewas, dienen de nutriëntconcentraties in de bodemoplossing boven een bepaalde waarde te blijven. Een groeiend gewas zal eerst de direct beschikbare hoeveelheid opnemen. Het gehalte in de bodemoplossing zal daardoor dalen. Vervolgens bepaalt de hoeveelheid die gemakkelijk in oplossing kan gaan of een zekere minimumconcentratie in de bodemoplossing gehandhaafd kan blijven om zo optimale gewasgroei of een gewenst gehalte in het gewas te realiseren. Bemesting is nodig indien dit niet het geval is. Dit concept is uitstekend beschreven door Mengel & Kirkby (1987). Echter wanneer er maar één extract wordt gebruikt per element is het minder goed mogelijk om onderscheid te maken tussen intensiteit en capaciteit. Het resultaat kan zijn dat de correlatie coëfficiënt tussen gewasrespons en grondanalyseresultaat relatief laag is. Twee typen extractie, één voor intensiteit en één voor capaciteit is in principe een betere benadering maar duurder en daardoor nu niet gebruikelijk.

4.2. Ontwikkelingsperspectief en behoefte naar bepaling beschikbaarheid in grond

De afgelopen decennia is detectielimiet voor het meten van sporelementen enorm omlaag gegaan (Bussink & Temminghoff, 2004). Daardoor kan van diverse agressieve extractiemiddelen geswitcht worden naar één zwak extractant (bijvoorbeeld met 0,01 M CaCl_2). Deze weerspiegelt beter wat er werkelijk beschikbaar is (de intensiteitsbepaling). Bovendien maakt dit het mogelijk om recht te doen aan het feit dat de gewasrespons voor een element niet alleen afhankelijk is van het betreffende element, maar ook van de overige elementen in de bodemoplossing en de vaste fase van de bodem (klei, zand, oxiden en organische stof) die bijvoorbeeld bepaald kan worden met spectroscopische technieken (zie verderop). Zogenaamde multi-nutriënt gebaseerde bemestingsadviezen (het advies voor bijv. Cu is niet alleen afhankelijk van de Cu-toestand, maar ook van de Zn- en P-toestand) worden daarmee in principe mogelijk. De beoordeling van sporelement beschikbaarheid voor het gewas kan daarmee belangrijk worden verbeterd. Bijkomend voordeel is dat voor veel sporelementen minder gewasonderzoek nodig is om vast te stellen of sporelement niveaus adequaat, te laag of te hoog zijn. Immers er kan beter worden voorspeld welk gehalte aan sporelementen in het gewas te verwachten is.

In het fysisch-chemisch grondonderzoek zijn de afgelopen decennia nieuwe inzichten ontstaan in het begrijpen van bodemchemische processen en hoe deze processen ingrijpen op de beschikbaarheid van (spoor)elementen. Dit betekent het met behulp van modellen toepassen van kennis over de nalevercapaciteit van de vaste fase (ad- en desorptiegedrag van klei, oxiden en organische stof en het complexatiegedrag van in de bodemoplossing aanwezige (an)organische liganden), in de evaluatie van het grondanalyse resultaat. Uit werk van Wageningen Universiteit blijkt dat het gedrag van diverse zware metalen (waaronder Cu

en Zn) inmiddels goed te beschrijven is. Temminghoff et al. (1998) kon voor Cu een directe relatie ontwikkelen tussen het extractie resultaat met 0.01 M CaCl₂ en het adsorptie/desorptie gedrag van de vaste fase. Bovendien gaf dit een beter verband met de opname door gras dan extractie met 0,43 M HNO₃ extractie. McLaren et al. (1987) vond een goede relatie tussen 0,01 M CaCl₂ extractie en gewasopname voor Co, in het bijzonder wanneer rekening wordt gehouden met de pH.

Het bovenstaande betekent dat indien de samenstelling van de vaste fase bekend is en de concentratie aan (spoor)elementen met een zwak extractant is bepaald, dat het dan mogelijk is om de beschikbaarheid van een sporelement voor gewasopname nauwkeuriger en op meer fundamentele grondslag te voorspellen. Bijkomend voordeel is dat in principe ook aangegeven kan worden in welke vorm een nutriënt het beste toegediend kan worden, hoe het ruimtelijk verdeeld dient te worden (bijvoorbeeld breedwerpig toedienen versus plaatsing) en of bemesting van de bodem wel de beste strategie is of dat tijdig met bladbemesting dient te worden begonnen.

Het vaststellen van de compositie van de vaste fase kan relatief duur zijn, maar is slechts iedere 5-10 jaar nodig. Bovendien zijn goedkope technieken in opkomst. Niet invasieve technieken zoals nabij infrarood spectroscopie (NIR) of mid infrarood spectroscopie (MIR) hebben een groot potentieel. Chang et al. (2001) heeft 33 chemische, fysische en biologische parameters van 802 grondmonsters getest afkomstig uit 4 gebieden van de VS. Zij lieten zien dat totaal C, totaal N, CEC (kationenuitwisselingscapaciteit), zand en silt hoeveelheid relatief nauwkeurig voorspeld konden worden. Recentelijk bevestigde Brown et al. (2006) deze bevindingen. In Nederland heeft Blgg AgroXpertus enkele jaren geleden nabij infrarood spectroscopie (NIR) recentelijk voor grondonderzoek geïntroduceerd. In Australië wordt MIR al langer toegepast in routinematig grondonderzoek. Daarbij worden onder andere klei, zand, silt, totaal C, CEC en de kationencompositie van de CEC gemeten.

Recentelijk is een onderzoek gestart om voortbouwend op basis van de zojuist genoemde kennis te komen tot een nieuwe waarderingssystematiek voor sporelementbeschikbaarheid in gronden. Deze is niet alleen in Nederland maar in principe ook internationaal inzetbaar. Ook voor ontwikkelingslanden lijkt dit de gewenste oplossingsrichting, daarbij gebruik makend van een zwak multinutriënt extractiemiddel en het vaststellen van de samenstelling van de vaste fase (spectroscopisch of via een agressieve extractie) met daaraan geadsorbeerde sporelementen.

4.3. Gewasonderzoek in relatie tot grondonderzoek

Een duidelijk gebrek aan sporelementen kan veelal visueel worden onderkend. Situaties met een beperkt tekort (tot 10%) zijn visueel vaak lastig te onderkennen. Gewasonderzoek kan dan uitkomst bieden en op basis daarvan kunnen er maatregelen worden genomen via bladbemesting om een tekort op te heffen. Echter een eventuele achterstand/opbrengstderving door een tekort kan niet meer ongedaan worden gemaakt. Ook is op basis van gewasonderzoek lastiger vast te stellen of het tekort van een bepaald nutriënt het gevolg is van tekort van dat nutriënt of het gevolg is van bijvoorbeeld een overaanbod van andere nutriënten (denk aan Zn- en P-interactie) of een te hoge pH. Meer informatie over gewasanalyse is te vinden in Reuter & Robinson (1986) en Bussink & Temminghoff (2004).

4.4. Te nemen maatregelen

Bij een tekort aan spoorelementen is niet alleen bemesting met spoorelementen nodig maar dient als eerste op basis van het grondonderzoek te worden nagegaan of bekalking nodig is om de pH op orde te brengen en om bijvoorbeeld vast te stellen of er een risico bestaat van P-geïnduceerd P-gebrek. Ook maatregelen die bijdragen aan een betere vochtvoorziening en doorwortelbaarheid van de bodem (een betere bodemstructuur) zijn van belang voor een goede nutriëntbenutting. Aansluitend dient de keus gemaakt te worden welke minerale meststof zinvol kan worden toegepast. Als Zn-meststoffen worden gebruikt, ZnO, ZnSO₄ en Zn-chelaten. Als Cu-meststoffen worden gebruikt, CuO, Cu₂O, CuSO₄ en Cu-chelaten. De werking is het hoogst bij de chelaten en het laagst bij de oxiden. Daartegenover staat dat chelaten het duurst zijn. Andere vormen komen ook voor. De eigenschappen van de grond (mate van vastlegging van) in combinatie met de kostprijs van de meststof bepalen welke meststof het beste ingezet kan worden en hoe (plaatsing bij de wortel of breedwerpige toediening). Voor situaties met een sterke vastlegging kan naast plaatsing van meststoffen of het gebruik van chelaten ook gedacht worden aan bladmeststoffen. Het toepassen van gecoat zaaizaad behoort ook tot de mogelijkheden.

Organische mest is een bron van spoorelementen, waardoor bemesting met Cu en Zn in Nederland slechts beperkt nodig is. De beperkte resultaten in de tropen geven aan dat mest vaak wel werkt (soms ook niet) maar veelal is het effect niet eenduidig alleen aan spoorelementen toe te schrijven daar met de mest ook N, P en K worden aangevoerd. Vaak wordt mest echter gedroogd en als brandstof gebruikt waardoor het niet beschikbaar is als meststof. De as zou als mest gebruikt kunnen worden maar dat wordt zelden gedaan. Het toepassen van compost is een optie. Compostering van afval wordt in ontwikkelingslanden echter weinig toegepast (Hoornweg et al., 1999).

Het toepassen van mest, compost en het laten liggen van gewasresten draagt bij aan het op peil houden en of verhogen van het organisch stofgehalte van de bodem en stimuleert het bodemleven. De natuurlijke bodemvruchtbaarheid, en als onderdeel daarvan de beschikbaarheid van spoorelementen, neemt daarmee toe.

5. Samengevat

De problematiek met spoorelementen is divers. Er zijn regio's waar ruim wordt omgegaan met spoorelementen en waaruit het oogpunt van het voorzorgsprincipe (milieu), voedselveiligheid, de toenemende schaarste aan spoorelementen efficiënter dient te worden omgegaan met spoorelementen. Anderzijds zijn er wereldwijd veel regio's waar de bodem te weinig spoorelementen bevat voor een goede gewasgroei en/of voorziening van dieren en mensen met voldoende spoorelementen.

De laatste decennia maakt kennisontwikkeling van het gedrag van spoorelementen in de bodem in combinatie met de ontwikkeling van nieuwe analytische technieken het mogelijk om de beschikbaarheid van spoorelementen in de bodem in relatie tot andere bodemparameters beter te duiden. Multi-nutriëntextractie met een zwak extractiemiddel in combinatie met een karakterisering van de vaste fase, bijvoorbeeld via spectroscopische technieken, lijkt de oplossingsrichting. Bovendien is zo een meer universele benadering mogelijk die overal inzetbaar is. Daardoor kan de regionale verscheidenheid in adviessystemen (en het daarmee gepaard gaande onderhoud) sterk verminderen. Uitontwikkeling en toepasbaar maken in operationele systemen is opgepakt maar heeft meer aandacht. Dit kan bijdragen aan meer duurzame voedselproductie en het verminderen van spoorelementengebrek in de landbouw wereldwijd. Van belang daarbij is niet alleen te kijken naar het spoorelementgebrek zelf maar ook naar achterliggende oorzaken als een te lage pH, interacties met andere nutriënten en een goede bodemstructuur.

Ook de inzet van lokale bronnen als mest, compost en gewasresten die de bodemkwaliteit verbeteren maar ook spoorelementen leveren verdient meer aandacht. In de tropen en ontwikkelingslanden zijn deze bronnen maar beperkt beschikbaar, waardoor de inzet van minerale spoorelement meststoffen nodig is. Op basis van kennis van de bodem kunnen deze meststoffen efficiënter worden ingezet, waardoor de kosten dalen en de opbrengsten stijgen.

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Tabel 4. Gewasbehoefte en functies van spoorelementen, en factoren die de beschikbaarheid van en de behoefte aan spoorelementen beïnvloeden.

Micro-nutriënt	gewasbehoefte			functies in			factoren nadelig voor beschikbaarheid	behoefte aan meststoffen	opmerkingen
	hoog	medium	laag	Plant	Dier	mens			
Cu	bieten citrus haver luzerne sla spinazie ui tarwe	bloemkool broccoli gerst klaver komkommer maïs radijs tomaten uien wortelen	asperge aardappel bonen erwten grassen	van invloed op: • reproductie, slechte vruchtzetting • chlorofyl productie	• stofwisselings -enzymen (tekort geeft slechte conditie, groei, diarree)	• nodig voor vorming van bloed, bindweefsel botvorming, goed functioneren van afweersysteem, bloedstolling	<ul style="list-style-type: none"> • hoge pH • droogte • lage os- en zeer hoge os-gehalten 	gelijkblijvend: <ul style="list-style-type: none"> • minder dierlijke mest • veehouderij veel mineralen-mengsels 	<ul style="list-style-type: none"> • verbetering grondanalyse is mogelijk • S-bemesting op maat i.v.m. nadelig effect op Cu-beschikbaarheid dier • Let op voorziening kleipercelen
Zn	bonen citrus gierst fruitbomen maïs rijst spinazie ui vlas	aardappel bieten gerst komkommer luzerne sla tomaat	asperge erwten gras granen kool wortelen	<ul style="list-style-type: none"> • vele enzymen betrokken bij synthese van aminozuren en eiwitten en vorming van groeihormoon auxine 	<ul style="list-style-type: none"> • groei-processen • celdeling • wondheling 	onderdeel van vele enzymen in lichaam <ul style="list-style-type: none"> • opbouw eiwitten • groei en vernieuwing van weefsel, • koolhydraat-stofwisseling, functioneren afweersysteem 	<ul style="list-style-type: none"> • hoge pH • hoge os-gehalten • lage temperatuur • droogte • veel fosfaat • lichte zandgronden (veel fosfaat) 	geen tot enigszins mest <ul style="list-style-type: none"> • minder dierlijke mest • minder gewas-beschermings-middelen 	<ul style="list-style-type: none"> • geen op grondonderzoek gebaseerd advies beschikbaar voor gevoelige gewassen • let op voorziening bij vollegrondsgroenteteelt



Toelichting bij de foto's op de omslag

Op de voorkant van linksboven met de klok mee:

- Bietenblad met zinktekort
- Rammelsbergmijn nabij Goslar in de Harz, Duitsland. Belangrijke producten waren zilver-erts, koper en lood. De mijn is gesloten in 1988.
- Runderen met koperdeficiëntie
- Kopermijn in Arizona
- Bijvoeding van schapen met mineralen inclusief micronutriënten
- Gebieden in de wereld waar zinkdeficiënties in belangrijke gewassen voorkomen.

Op de achterkant:

- Baby met zinkdeficiëntie