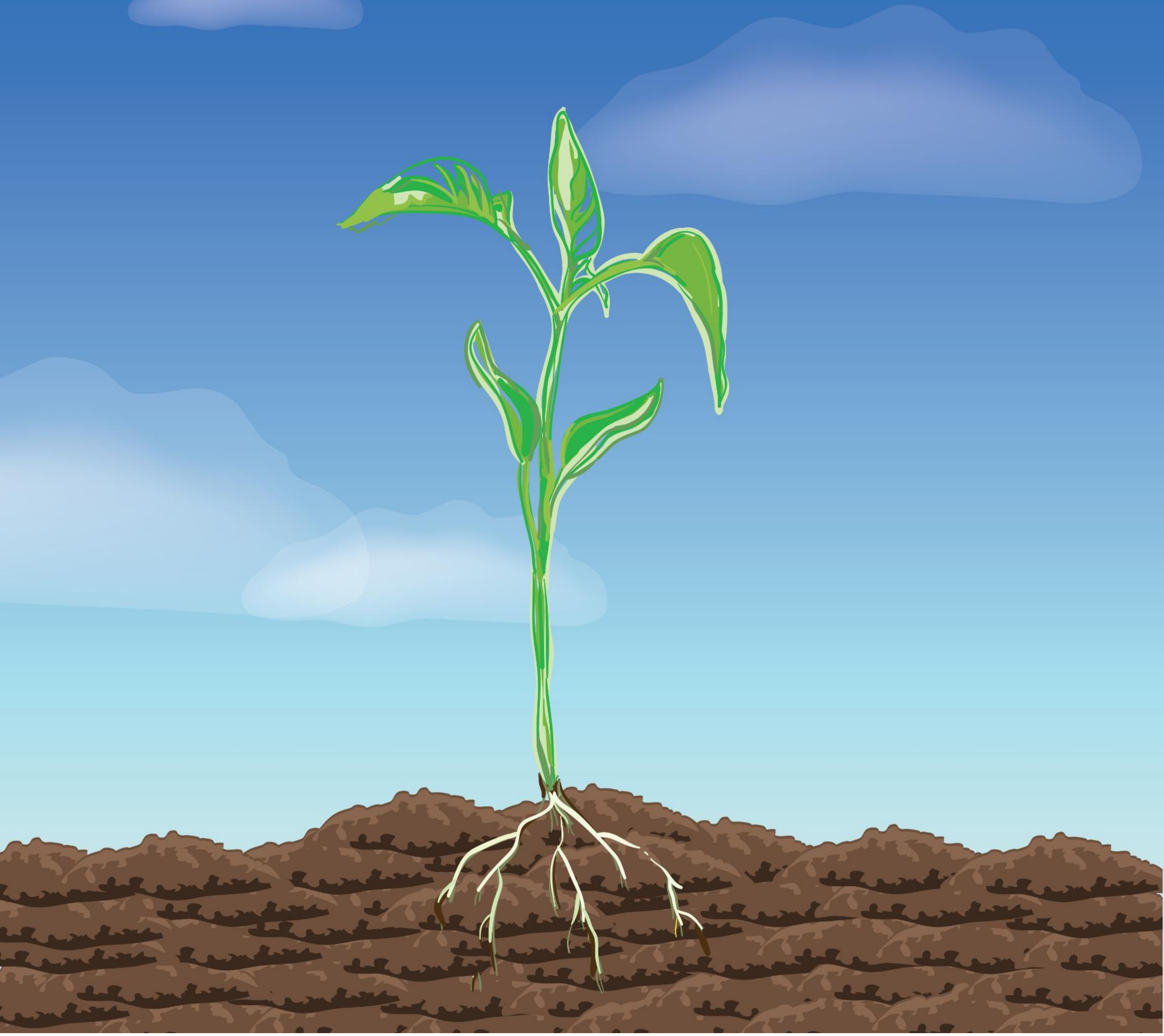
VFRC Report 2015/5

Effects of nutrient antagonism and synergism on fertilizer use efficiency



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Virtual Fertilizer Research Center

Contents

List of Acronyms and Abbreviations

IFDC	International Fertilizer Development Center
VFRC	Virtual Fertilizer Research Center
NUE	Nitrogen use efficiency (kg product/kg N). Yield increase due to N fertilizer per kg N fertilizer.

List of definitions

Macronutrients	N, K, Ca, Mg, P, S. In this report the secondary nutrients Ca, Mg, S are grouped under macro.
Micronutrients	Cl, Fe, B, Mn, Zn, Cu, Mo, Ni
Synergism	Nutrient interaction is synergistic where the yield due to the combined application of two nutrients, is more than the yield expected on the basis of the individual applications of the nutrients.
Liebig-synergism	A specific type of synergism. Typically in situations where the availability of one nutrient is limiting crop production, the addition of another nutrient shows no effect on yield, whereas addition of both nutrients shows an increased (synergistic) effect. Wallace (1990) introduced the term Liebig-synergism to describe this effect, referring to the Liebig limitation of the first nutrient.
Antagonism	Nutrient interaction is antagonistic where the yield due to the combined application of two nutrients, is less than the yield expected on the basis of the individual applications of the nutrients.
Zero-interaction	Where the yield obtained from a combination of two nutrients is equal to the yield expected on the basis of the individual application of the nutrients, the interaction is said to be zero-interaction.
Specific nutrient interactions	Process in which nutrients directly react in a chemical or biological process. In contrast to nonspecific nutrient interactions were nutrients affect each other through a series of intermediate processes (Pan, 2012).
Balanced fertilization	Supply of a combination of plant essential nutrients in line with soil reserves, the requirements and expected (or desired) yield of the crop.

Abstract

This study provides an overview of interactions between nutrients as reflected in crop yield. Based on a search-query, scientific articles were collected from which studies were selected that considered the interaction effects of specific nutrients on yield levels. Priority was given to articles in which single nutrient effects and the interaction effects on yields were studied. In total 96 articles were selected, revealing 116 interactions between all macro- and micronutrients for different agricultural crops. In 42 cases the interaction was synergistic (positive), in 17 cases the interaction was antagonistic (negative), and in 34 cases the interaction was additive (zero-interaction); the other 23 cases resulted in a non-significant (16) or a negative response (7). It is obvious that the number of studied interactions, as published in peer-review scientific articles, is low, so that it is difficult to formulate definitive conclusions. Nevertheless, some general findings include the following:

a. When the availability of two nutrients is characterized as deficient, a large increase in yield can be expected by diminishing these deficiencies.
b. For most macronutrients the mutual interactions on yield levels are synergistic.
c. Antagonistic (or negative) effects on yield levels are often found for divalent cations.

Because nutrient interactions have been studied for a limited number of crops (varieties), nutrients, soil types and climates, care must be taken to extrapolate individual results to other situations. Relating the interaction effects of nutrients on yield to universal mechanisms can be a way to increase nutrient use efficiency, especially for the group of nutrients for which the effects on yield seem rather hard to predict, such as Fe x Mn.

1 Introduction

1.1 Background

The increase in global food demand will require an increased use of natural resources such as water, land and nutrients to produce crops (Tilman et al., 2011). Three major pathways have been identified to meet this growth: decreasing the loss of production capacity, decreasing the demand of food per capita and increasing the production of food (Dogliotti et al., 2014). However, current yield trends are not sufficient to meet the forecasted demand (Ray et al., 2013). One of the factors why the potential yields are not obtained is the deficiency or imbalance of nutrients (Lobell et al., 2009). Therefore, the growth of the global food production will require more use of chemical fertilizers, and since the current environmental impact of agriculture and fertilizer use has reached its planetary boundaries (Steffen et al., 2015), it requires a greater nutrient use efficiency.

Increasing the nutrient use efficiency (and consequently yield levels) is possible in a step-by-step approach by considering all plant nutrients (not only N, P and K, but also other macronutrients and micronutrients), applying the most limiting nutrients, and applying a balanced amount of nutrients (i.e., tailored to crop needs) to get the highest yield while minimizing the loss of nutrients. This strategy implies that the dose and composition of the fertilizers are fine-tuned to local soil chemical conditions and crop requirements (Roy et al., 2006). Consideration of all nutrients is also important in high-yield agriculture as it is often assumed that interactions between nutrients become more important at higher yield levels (Tisdale et al., 1985; Aulakh and Malhi, 2005). Such nutrient interactions can be either beneficial, neutral or adverse, with respect to crop yield.

1.2 Objective

One of the targets when using fertilizers is to minimize adverse nutrient interactions (antagonism) while maximizing beneficial nutrient interactions (synergism) thereby increasing the nutrient use efficiency. The objective of this report is to provide an overview of the effects of these interactions on fertilizer use efficiencies and crop yields. This information may be the starting point for fertilizer innovations, e.g., by balancing the fertilizer composition to enhance their use efficiency.

1.3 Approach

The assessment of the occurrence of antagonism and synergism in crops was studied by posing a number of questions resulting in the following chapter outline of this report. Chapter 2 starts with a general introduction of the subject. In Section 2.2 the presence and quantitative nature of nutrient antagonism and synergism based on a literature review is given. In Section 2.3, the relationship between the uptake of micro- and macronutrients is examined. In Section 2.4, it is assessed whether there are specific mechanisms that are responsible for the interactions. Attention is given to two types of processes that are probably related to nutrient interactions: the influence of nutrient transporters (Section 2.5) and the influence on reductase enzymes and phytosiderophore production (Section 2.6). Section 2.7 explores which strategies might overcome antagonisms or stimulate synergisms. Chapter 3 provides some conclusions and identifies gaps in our knowledge, with recommendations for possible research directions to minimize antagonisms and maximize synergisms.

The activities performed in this study are an exploration of potential improvements for balanced fertilization. This may provide recommendations for research to improve the use of fertilizers for certain major crops.

1.4 Methodology

We reviewed the scientific literature on the effects of nutrients and their interactions on the yield of crops. The keywords were obtained from well-known references on mineral nutrition of plants: specifically, fertilizer technology (Mortvedt et al., 1991; Chien et al., 2009), fertilization, interactions between plant nutrients (Tisdale et al., 1985), micronutrients (Welch, 1995; Alloway, 2008) and principles of ion uptake by plants (Mengel et al., 2001; Epstein and Bloom, 2005; White, 2012), and specific fertilization of various important crop types (Fageria et al., 2011).

We searched for peer-reviewed literature investigating the effects of interactions between nutrients on yield using Scopus (Elsevier). The search-query was: ((TITLE-ABS-KEY ((nitrogen AND magnesium) OR (potassium AND iron) OR (calcium AND iron) OR (magnesium AND calcium) OR (zinc AND calcium) OR (iron AND phosphorus) OR (manganese AND potassium) OR (copper AND phosphorus) OR (nitrogen AND potassium)) AND TITLE-ABS-KEY ((potassium AND phosphorus) OR (calcium AND potassium) OR (magnesium AND phosphorus) OR (zinc AND phosphorus) OR (nitrogen AND borate) OR (potassium AND borate) OR (calcium AND manganese)))) AND (TITLE-ABS-KEY (nutrient OR fertilizer)) AND (TITLE-ABS-KEY (antagonism OR interaction OR synergism)) AND (TITLE-ABS-KEY (plant OR crop OR root OR leaves)) AND NOT (TITLE-ABS-KEY (trees OR cadmium OR toxic OR lead OR moss OR forest)) AND (LIMIT-TO (DOCTYPE, "ar")). This search produced a total of 349 publications (accessed Nov 6, 2014). The papers found using this method were selected. The references in the papers, and references to the selected papers were used for snowballing.

The papers were screened on interaction between nutrients for yield. To have a better focus on the questions from Section 1.3, the following exclusion criteria were used:

- The experimental papers that did not include original data or a statistical evaluation of the interaction were excluded[1].
- Toxicity was excluded as the main focus for this study was on the positive effects of fertilization. A large number of studies about the toxic effects of copper, zinc, and boron thus were excluded.
- In this study, no papers were searched about the variation of nutrient supply by different soils and its possible effects on nutrient interactions.

2 Results and discussion

2.1 Introduction

A balanced supply of nutrients can be important for increasing crop yield, for using fertilizers in an efficient manner, and for minimizing losses of nutrients (Fageria et al., 2011). Interactions between nutrients occur when the supply of one nutrient affects the uptake, distribution or function of another nutrient. Depending on the nutrient supply, the interaction can modify plant growth and yield. Interactions can be assessed by examining the relationship between nutrient supply and nutrient concentrations in plants, and by examining the relationship between nutrient supply and plant growth (Robson and Pitman, 1983). It has resulted in many possible relations between the supply of a nutrient and the effects on plants (Robson and Pitman, 1983; Landon, 1991) which have been discussed in detail in various reviews and textbooks (Tisdale et al., 1985; Wilkinson et al., 2000; Zhang et al., 2006; Alloway, 2008; Pan, 2012; White, 2012; Fageria et al., 2013). Knowledge of these interactions is important to understand nutrient uptake

[1] For example, a paper by R. Kumar and J.S. Bohra, 2014, "Effect of NPKS and Zn application on growth, yield, economics and quality of baby corn," *Archives of Agronomy and Soil Science,* **60,** 1193-1206, that gives a statistical description of the individual effects of S and Zn on yield of corn but not of the interaction.

processes. In many publications, the effects on concentrations, or uptake in plants, are used as the main parameter to assess the nutrient interactions (Gunes et al., 1998).

Nutrient interaction in crops is probably one of the most important factors affecting yields of annual crops (Fageria, 2014). Nutrient interactions can be studied at different scales and with different scientific interests. On the one hand, nutrient interaction at the root uptake level may be studied deterministically based on well-conditioned experiments, and on the other hand, it can be determined agronomical by studying nutrient availability and fertilizer effects on crop yield. The deterministic approach at the root interface scale is often studied in well balanced and well-conditioned circumstances, thereby eliminating external influences such as other limiting nutrients, water limitation or water excess, temperature and pH. However, it can be questioned whether these results can be directly transferred to field conditions. In contrast, data obtained from field studies to determine the agronomic nutrient interactions have the disadvantage that the external influences cannot be controlled, and thus the results at first are only valid for the circumstances they were obtained from, e.g., at given soil fertility and soil pH and a host of other confounding variables. Nutrient interaction effects as obtained from the agronomic perspective only reveal the effect on yield; it does not reveal insights about the mechanistic interactions that occur in the soil, at the soil-root interface or in the root uptake mechanism. According to Fageria (2014):

> "*Interactions occur when the supply of one nutrient affects the absorption and utilization of another nutrient […]. Nutrient interactions affect plant growth and development only when the supply of a determined nutrient is too low compared to the applied ones. In other words, yield decrease occurs only when the supply of some nutrients falls below the critical level. If the soil or growth medium has sufficient supply of other essential nutrients compared to the added one, plant growth will not be affected adversely, even though the uptake of some nutrients may decrease. Hence, plant growth or yield is considered a better criterion for evaluating nutrient interactions in crop plants.*"

The rationale for performing this study is to improve fertilization towards balanced fertilizer application and improving fertilizer efficiency. Therefore, in this study, we have selected the agronomic approach and nutrient uptake is neglected.

The effect of interactions between nutrients on yield of crops has been reviewed before for specific nutrients: for N (Aulakh and Malhi, 2005; Fageria, 2014), for K (Dibb and Thompson, 1985; Daliparthy et al., 1994), for P (Sumner and Farina, 1986), and specific for N-K interactions (Zhang et al., 2010). Pan (2012) described theoretical studies (Wallace, 1990; Rubio et al., 2003; Zinn et al., 2004) to classify nutrient interactions on the basis of quantitative descriptions of data, and models. A systematic overview of interactions between all nutrients on yield of crops has not been given yet. This is probably due to the limited number of studies (Fageria, 2001).

2.2 Synergism, zero-interaction and antagonism

This section provides a systematic assessment of the occurrence of antagonism and synergism in mineral nutrition of crops and their effects on fertilizer use. The crops and the conditions for which these interactions occur are examined, and the quantitative nature of the interaction is assessed.

Yield will be used as the main parameter to assess the nutrient interactions, which can either be positive or beneficial (synergism), negative or adverse (antagonism), zero-interaction (additive, no interaction, neutral), or partly positive (Liebig-synergism) (**Table 1; Figure 1**). Synergism refers to the response which is greater than expected from the individual responses (Tisdale et al., 1985; Wallace, 1990; Wilkinson et al., 2000; Fageria, 2001; Aulakh and Malhi, 2005; Roy et al., 2006; Fageria, 2014). The yield expected[2] (y_{ab}) on the basis of the individual responses (y_a and y_b) for the situation of zero-interaction follows from

$$\frac{y_{ab}}{y_0} = \frac{y_a}{y_0} \times \frac{y_b}{y_0} \tag{1}$$

where y_0 is the yield in the reference or control treatment. By using relative yields, it is possible to compare between different experiments, crops, fertilizers and to account for variations in the control treatments. Antagonism refers to the yield in response of two nutrients in which the combined effect is less than expected from the individual responses (Figure 1) (Sumner and Farina, 1986; Fageria, 2001; Aulakh and Malhi, 2005). This means that the actual relative yield is less than the product of the individual yield effects. Thus, even if the yield in a plot treated with nutrient a and b is higher than the plots treated with a or b, the effect is synergistic only when the yield response exceeds the expected yield on the basis of the individual responses, i.e., the actual relative yield is greater than the product of the individual yield effects (Aulakh and Malhi, 2005).

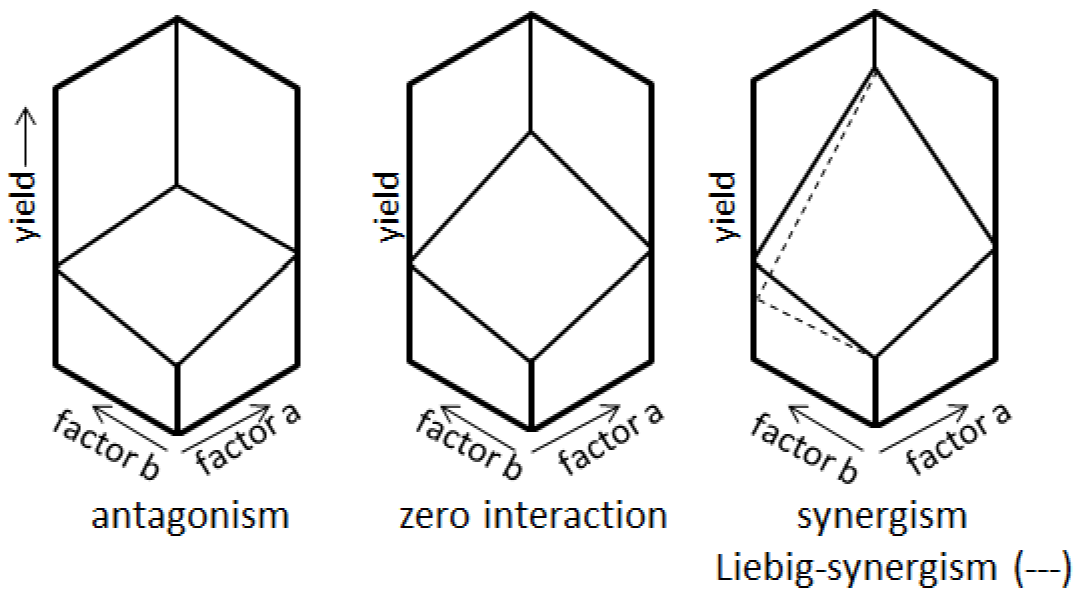


Figure 1. *Effect of the interaction of two nutrient factors on yield (after Sumner and Farina, 1986).*

[2] The expectation is based on Wallace (1990) and to our knowledge is an operational definition and is not based upon a plant physiological process.

Table 1. Definition of synergistic, antagonistic, zero-interaction and Liebig-synergism.

Interaction	Description	Evaluation
Synergism	Nutrient interaction is synergistic where the yield due to the combined application of two nutrients is more than the yield expected on the basis of the effects from the individual applications of the nutrients.	$\frac{y_{ab}}{y_0} > \frac{y_a}{y_0} \times \frac{y_b}{y_0}$
Antagonism	Nutrient interaction is antagonistic where the yield due to the combined application of two nutrients is less than the yield expected on the basis of the effects from the individual applications of the nutrients.	$\frac{y_{ab}}{y_0} < \frac{y_a}{y_0} \times \frac{y_b}{y_0}$
Zero-interaction	Where the yield obtained from a combination of two nutrients is equal to the yield expected on the basis of the individual application of the nutrients, the interaction is said to be zero-interaction.	$\frac{y_{ab}}{y_0} \approx \frac{y_a}{y_0} \times \frac{y_b}{y_0}$
Liebig-synergism	Typically in situations where the availability of one nutrient is limiting crop production, the addition of another nutrient shows no effect on yield, whereas addition of both nutrients shows an increased (synergistic) effect. Wallace (1990) introduced the term Liebig-synergism to describe this effect, referring to the Liebig limitation of the first nutrient.	$\frac{y_{ab}}{y_0} > \frac{y_a}{y_0} \times \frac{y_b}{y_0}$

In total, 116 interactions between nutrients on crop yield have been identified in 96 publications. These are provided in Appendix 1 and are discussed below to provide an overview of the interactions between nutrients. It is expected that the use of the categories synergism and antagonism is useful to describe the interaction between a pair of nutrients because it gives an indication of the yield response that might be expected from the use of fertilizers containing such nutrients. The observed interaction is, however, only valid for the circumstances under which it has been determined, as we could not disentangle the numerous confounding factors related to the agro-ecological conditions of the studies. It is not known whether it can be extrapolated to other circumstances (soils, climate and crops). Two types of studies could not be categorized according to the defined interactions: studies showing a negative effect of nutrient supply on yield and studies in which the interaction showed no effect on yield.

Synergism

An example of synergism is given in **Table 2**. In the experiment of Fageria and Oliveira (2014) a large increase in rice grain yield was obtained by using K and P. Interaction can best be determined by looking at the relative yields, i.e., relative to the yield of the control plots (Wallace, 1990). The observed effect (relative yield) of the combination of both nutrients is compared to the calculated effect obtained as the product of the individual effects (i.e., 1.1 x 1.2), and here it is greater (thus: synergism) than the product of the individual effects: 1.6 > 1.1 x 1.2.

***Table 2.** Example of synergism. The yield* is given as function of the application of nutrients.*

Rice grain yield (g plant^{-1}) at 150 kg ha^{-1} N (Fageria and Oliveira, 2014)			*Actual*	*Expected*
	100 mg kg^{-1} P	200 mg kg^{-1} P		
100 mg kg^{-1} K	10.7 (1.0)	12.3 (1.1)		
200 mg kg^{-1} K	12.6 (1.2)	16.6 (1.6)	1.6>	1.1 x 1.2=1.4

* Relative yield between parentheses.

A specific type of synergism has been defined by Wallace (1990), which he called Liebig-synergism (**Table 1**). An example has been given in **Table 3**. This interaction appears to be antagonistic at the level of no Cu application: addition of N did result in a negative effect on yield. In this case, Cu deficiency seems to limit the yield increase. When both nutrients were supplied together the yield increase was much higher than the yield due to the individual effects.

It is necessary to make the distinction between synergism and the Liebig-synergism. In the 21 studies that show a synergistic interaction, the quotient of the actual and the predicted yield increase varies between 1 and 3 (Appendix 1). When limiting factors occur and are corrected, resulting in Liebig-synergism, the response in yield is difficult to predict (Wallace, 1990). In the 21 studies that show a Liebig-synergistic interaction, the quotient of the actual and the predicted yield increase varied between 1.5 and 35, demonstrating the variation involved in Liebig-synergism. It is therefore relevant to know for which combination of nutrients such variable responses can be expected.

Table 3. *Example of a specific type of synergism: Liebig-synergism. The yield* is given as a function of the application of nutrients.*

Wheat yield (g plant^{-1}) (Wapakala, 1973)			*Actual*	*Expected*
	0 kg ha^{-1} N	44 kg ha^{-1} N		
0 kg ha^{-1} Cu	1.30 (1.0)	1.08 (0.8)		
14 kg ha^{-1} Cu	1.50 (1.2)	1.96 (1.5)	1.5 >	0.8 x 1.2=1

*Relative yield between parentheses.

Synergism was identified in 21 cases, especially between macronutrients (**Table 4**). The Liebig-synergism, in which a deficiency has to be resolved to obtain synergism, was coincidently identified also in 21 cases. Synergistic interactions are well known for N x K and N x P interactions. They are not only important for the yield but also help to explain their combined effect on root growth and the relevance for synchronized applications of N and K during the growing season (Aulakh and Malhi, 2005).

Table 4. *Interactions between nutrients that are synergistic or Liebig-synergistic. Numbers in squares refer to the number of studies of each type of interaction, totaling 42 cases.*

	K	P	S	Ca	Mg	Fe	Mn	Zn	Cu	Cl	B	Mo	Ni
N	4	3	3/2			1			3				
K		1	1		1								
P				1		1	1	2/4	1		1	1	
S											1	1	
Ca											1		
Mg						1							
Fe									1				
Mn								1	2				
Zn									1/1		1		
Cu													
Cl													
B													
Mo													

synergism
Liebig-synergism

The effect of synergism between N and other macronutrients can result in an improved nitrogen use efficiency (NUE) (kg product per kg applied N, corrected for control) (**Table 5**) as was shown by Aulakh and Malhi (2005). The advantage of such synergistic effect is that an increased NUE can be achieved with less N fertilizer when supplied in combination with another nutrient, while obtaining the same yield as compared to the application with only N. This is of major importance for fertilizer use.

Table 5. *Improved nitrogen use efficiency due to interaction with other nutrients (partly based on Aulakh and Mahli [2005])*

Crop and N Fertilization	NUE kg Grain per kg Applied N	Additional Fertilizer	NUE kg Grain per kg Applied N	Reference
Canola 120 kg N/ha	0.7	+ 60 kg S/ha	5.8	Brennan and Bolland, 2009
Wheat 80 kg N/ha	2-14.6	+ 20 kg S/ha	5.7-17.3*	Salvagiotti et al., 2009
Wheat 120 kg N/ha	20.3	+ 90 kg P/ha	25.9	Dwivedi et al., 2003
Rice 120 kg N/ha	21.6	+ 60 kg P/ha	24.6	Dwivedi et al., 2003
Corn 100 kg N/ha	8.8	+ 60 kg P/ha	13.6	Singh, 1991
Sorghum 120 kg N/ha	11.7	+ 60 kg P/ha	17.1	Roy and Wright, 1973
Sunflower 60 kg N/ha	8.8	+ 30 kg P/ha	12.6	Aulakh and Malhi, 2005
Field Pea 40 kg N/ha	10.3	+ 30 kg P/ha	15.2	Aulakh and Malhi, 2005
Soybean 80 kg N/ha	0	+ 0.4 kg Fe/ha	9	Caliskan et al., 2008
Tobacco 224 kg N/ha	0.9	+ 0.22 kg Mo/ha	3.1	Sims et al., 1975
Wheat 118-214 kg N/ha	25	+ 0.2 kg Zn/ha foliar	36	Seadh et al., 2009
Cauliflower 120 kg N/ha	68**	+ 4.2 kg Zn/ha	122**	Balyan and Dhankar, 1978

* Variation between locations; ** Fresh weight.

It is assumed that, at higher yield levels, one should consider a wider range of nutrients in fertilization, and their interactions will become more important (Tisdale et al., 1985; Aulakh and Malhi, 2005). When the crop yield reaches a plateau at a relative low yield, it may be due to the limiting supplies of another nutrient. Solving these deficiencies result in Liebig-synergism. However, some micronutrients can show synergism with macronutrients (**Table 4**). For example (**Table 6**), the addition of more Zn resulted in a higher yield of wheat on a calcareous soil, and the increase due to Zn was largest at the highest addition of macronutrients (Sakal et al., 1988). In an acid soil, Brennan (2001) showed that Zn had an effect if it was deficient, but the effect diminished when the deficiency was solved.

Table 6. *Grain yield of wheat (t ha^{-1}) as influence by NPK and Zn applications (Sakal et al., 1988)*

NPK*	0 kg Zn ha^{-1}	5 kg Zn ha^{-1}	10 kg Zn ha^{-1}
$N_0P_0K_0$	1.45	1.58	1.64
$N_{50}P_{30}K_{25}$	2.73	2.88	3.03
$N_{100}P_{60}K_{50}$	3.53	3.84	4.04

*Dose of N, P and K in terms of N, P_2O_5, K_2O in kg ha^{-1}. LSD (5%) = 0.220.

Some synergistic responses to nutrients are due to soil reactions, and the acidifying or reducing effects of one of the nutrients. A good example of this is the positive effect of NH_4 fertilizers on the yield of barley and oats in case of Mn deficiency (Petrie and Jackson, 1984) which is due to the reduction of the unavailable Mn(IV) to available Mn(II) in soil (Husted et al., 2005). Also, thiosulfate can reduce Mn(IV) in soil, and increase the Mn uptake of Mn-deficient plants (Husted et al., 2005). Hence, for all the interactions related to pH changes, due to various N-sources, the soil-reactions may have a dominating impact.

Zero Interaction

An example for zero-interaction, as shown in Figure 1 (middle panel), is given in **Table 7**. Both K and P individually improve the yield of soybean. The interaction effect in this case is predictable, as it follows from the individual effects: the relative yield increase is (about) equal to the product of the relative yield increase for the individual effects (1.5 ≈ 1.16 x 1.30). This type of interaction has been referred to as zero-interaction (Sumner and Farina, 1986; Fageria, 2001; Aulakh and Malhi, 2005): the combination of nutrients results in a yield that can be expected on the basis of the individual effects. It is worth emphasizing that zero-interaction should not to be confused with no effect of fertilizer on yield, but rather an additive effect. Zero-interaction was identified in 34 cases (**Table 8**). Identification of nutrients that show zero-interaction is important because in these cases fertilizer experiments without combinations can be extrapolated for circumstances including combinations of nutrients.

Table 7. *Example of a zero-interaction. The yield* is given as function of the application of nutrients.*

Soybean Seed Yield (t ha^{-1}) (Abbasi et al., 2012)			*Actual*	*Expected*
	28 kg ha^{-1} K	112 kg ha^{-1} K		
0 kg ha^{-1} P	1.77(1.00)	2.05 (1.16)		
60 kg ha^{-1} P	2.30 (1.30)	2.59 (1.46)	1.46 ≈	1.16 x 1.30 = 1.51

*relative yield between parentheses

Table 8. *Interactions between nutrients that show zero-interaction. Numbers in squares refer to the number of studies in which these interactions have been found, totaling 34 cases.*

	K	P	S	Ca	Mg	Fe	Mn	Zn	Cu	Cl	B	Mo	Ni
N		1	3			1	1	4	2			1	
K		1	1		3								
P			4	1			1	1	1			1	
S												1	
Ca								1			1		
Mg													
Fe								2				1	
Mn												1	
Zn													
Cu													
Cl													
B													
Mo													

zero-interaction

Antagonism

An example of antagonism, as shown in Figure 1 (left panel), is given in **Table 9**. Both Zn and Mg have a positive effect on the growth of wheat. The combined effect is, however, less than might be expected on the basis of the individual effects. Antagonism was identified in 17 cases. The quotient of the predicted and the actual yield varies between 0.3 and 0.9.

Table 9. Example of a negative interaction: antagonism. The yield is given as function of the application of nutrients.*

Wheat Shoot Biomass (g pot^{-1}) (Kumar et al., 1981)			*Actual*	*Expected*
	0 mg kg^{-1} Mg	60 mg kg^{-1} Mg		
0 mg kg^{-1} Zn	12 (1)	19 (1.6)		
20 mg kg^{-1} Zn	21 (1.7)	22 (1.9)	1.9 <	1.6 x 1.7 = 2.7

*Relative yield between parentheses.

Antagonism has been described by Robson and Pitman (1983) as two nutrients that correct the same deficiency. Such interactions appear, for example, between N and minerals that improve the symbiotic N fixation in plants (e.g., Mo, Ca or Cu) (Robson and Pitman, 1983): they both improve the N deficiency. Antagonisms are mainly detected between cations: K, Cu, Fe, Mn and Zn (**Table 10**), as will be discussed later in Section 2.5. Two exceptions that do not involve these cations are the antagonisms for Mo x P and N x S. The interaction between Mo x P, as determined by Vitoso et al. (2012) showed that both the addition of P and Mo increase the Mo uptake by white clover. The antagonism for N x S was specific for the third grass cut while the N x S interaction in the first grass cut was synergistic (Kowalenko, 2004). According to Aulakh and Malhi (2005) such seasonal variations have also been observed for the N x P interaction in pumpkin and N x K in rice. Knowledge of these antagonisms is relevant to estimate the amount of fertilizers to be used. Therefore, it is relevant to note that most of the antagonisms involve interactions between micronutrients and rarely between macronutrients (**Table 10**).

Table 10. Interactions between nutrients that are antagonistic. Numbers in squares refer to the number of studies that resulted in antagonistic interactions, totaling 17 cases.

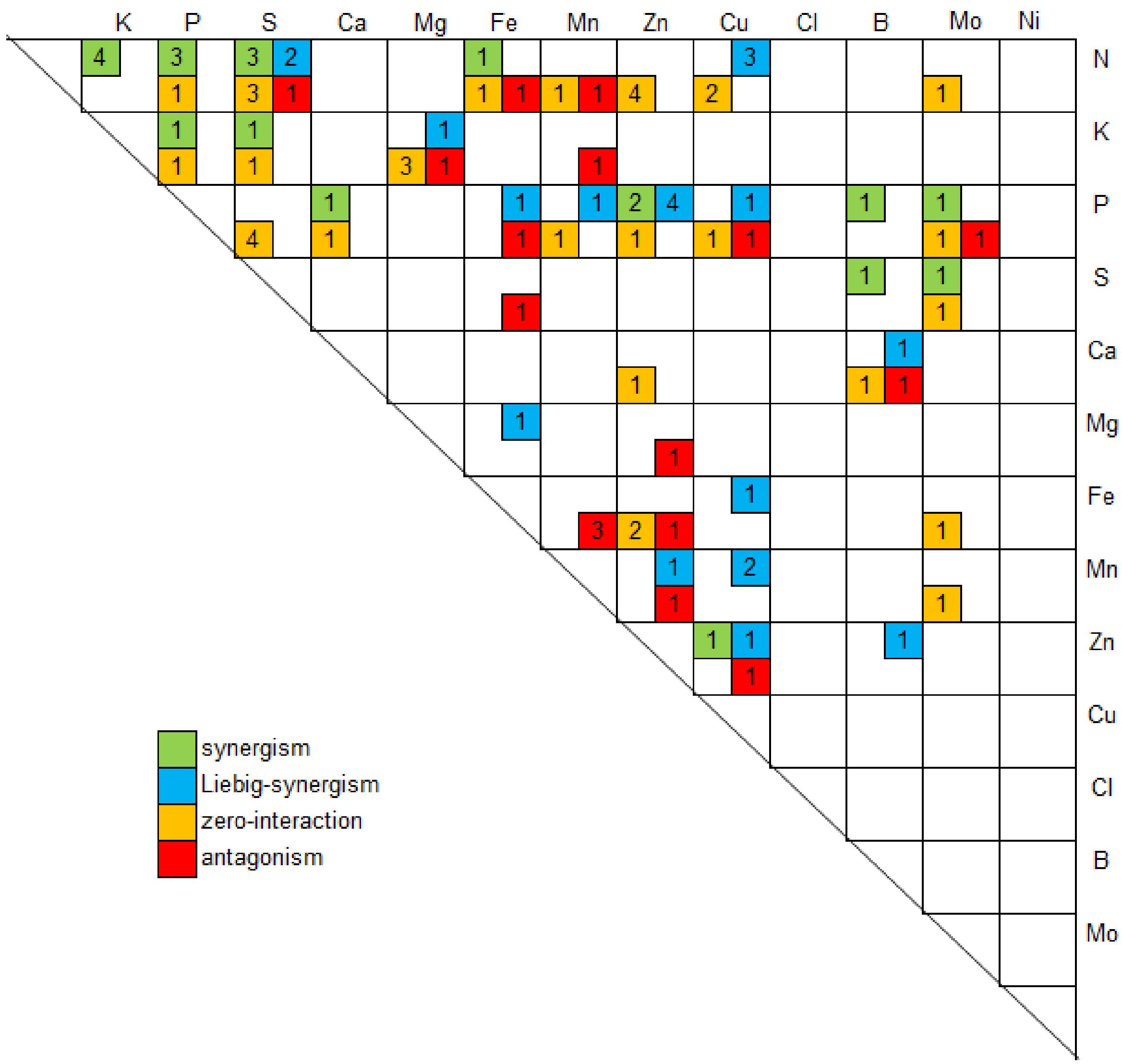
	K	P	S	Ca	Mg	Fe	Mn	Zn	Cu	Cl	B	Mo	Ni
N			1			1	1						
K					1		1						
P						1			1			1	
S						1							
Ca											1		
Mg								1					
Fe							3	1					
Mn								1					
Zn									1				
Cu													
Cl													
B													
Mo													

antagonism

For some combinations of nutrients, various types of interactions were found, such as Zn x P (synergism, Liebig-synergism, zero-interaction) (**Table 11**), showing that the type of interaction can vary. **Table 11** also shows that for a large number of nutrient combinations no interactions have been reported in the screened papers. Although some combinations of nutrients have been studied, no interactions can be determined if there is no effect on yield.

Remarkably, interactions of nutrients with Ca[3], Mg and S are rare, as was previously noted by Aulakh and Mahli (2005). No studies were found that show interactions for the cations: K x Zn, K x Cu, Fe x Ca, Mg x Ca, Mg x Cu, Ca x Cu and Mg x Mn (empty boxes in Table 11). Also no interactions were found for the micronutrients Cl and Ni.

Table 11. *Summary of all interactions reported in Table 4, Table 8 and Table 10. Numbers in squares refer to the number of studies.*



Besides interactions between nutrients that affect yield, nutrients can also have an effect on the content or uptake of other nutrients. This is relevant because human and animal nutrition is related to the nutrient content of crops. For example, the effect of K x Mg interaction has often been studied because nutrient content is relevant for animal feed. Optimal growth of ryegrass is reached at a Mg content of 1 g kg^{-1} dw (dry weight) in ryegrass (Smith et al., 1985) while lactating cows require animal feed with a Mg content of 1.6-2.4 g kg^{-1} dw (Suttle and Underwood, 2010). Supply of K has a negative effect on the Mg content of crops while the K content of crops is not affected (Bolton and Penny, 1968; Bedi and Sekhon, 1977; Ologunde and Sorensen, 1982; Ohno and Grunes, 1985), or even increased (Narwal et al.,

[3] Ca added as a soluble salt, or gypsum.

1985). High ryegrass yields, in combination with high Mg content in grass (2.5 g Mg kg^{-1} DM) are obtained in practice using a balanced fertilization of K and Mg (Reijneveld et al., 2014).

Summarizing, a systematic assessment has been performed regarding antagonism, synergism, Liebig-synergism and zero-interaction in mineral nutrition of crop plants and possible effects on fertilizer use. An integration of all results is presented in **Table 11**. It shows that, with the exception of a limited number of studies for N x S and Mg x K, interactions between macronutrients are synergistic or zero-interaction. These responses can be predicted to some degree from the individual effects of nutrients. They are of major importance for fertilizer use as can be seen from the increase of NUE in case of a more balanced use of fertilizers. On the other hand, rather unpredictable large yield responses result from solving nutrient deficiencies, Liebig-type synergisms, which in most cases involve Fe, Cu, Mn or Zn. For these cations, synergisms among each other is rare.

In most cases antagonism occurs between, or involves, one of the cations Ca, Mg, Fe, Mn, Zn or Cu. Knowledge of antagonisms is relevant to determine proper nutrient application rates. This chapter also shows that only a limited number of studies have reported interactions for each combination of nutrients (see **Table 11**, **Table 12**). Such a small number of studies does not allow for disentangling the variations due to crop species, and other variables such as soil conditions. Additionally, in some studies a negative effect of the application of nutrients on yield was found (**Table 12**). As this cannot be the intention of the use of fertilizers, these studies were assigned to a separate category. However, they can provide information about specific nutrient interactions and therefore are discussed in Section 2.4. Finally, in some studies no significant effect of nutrients on yield was obtained[4] (**Table 12**).

Table 12. *Number of interactions assessed in this report.*

Category	Number of Studies
Synergism	21
Liebig-synergism	21
Zero-interaction (additivity)	34
antagonism	17
Negative effect of nutrients on yield	7
no interaction could be detected*	16
Total number	116

* If there was no significant effect on yield, the interactions could not be categorized.

2.3 Relationship between uptake of micronutrients and application of macronutrients

In this section, the relationship between the uptake of micronutrients and the application of macronutrients are examined, and it will be identified if fertilizer strategies exist that consider both antagonism and synergism in nutrients.

Various authors have investigated if an increase in yield, especially via N fertilization, will lead to a dilution of nutrients in crops (Rengel et al., 1999). In field experiments (**Table 13**), the increased yield via N fertilizer does not lead to a significant change of the nutrient content in the grain of corn, wheat and rice. The fact that the nutrient contents or yields are not affected by N fertilizers is likely due to the adequate soil supply of these nutrients (Mg, Zn, Cu, Fe and Mn in **Table 13**). In three studies, the Zn content decreased, while in two studies, the Zn content in the grain increased.

[4] If there is no yield increase due to nutrient a or b, then no interaction can be calculated.

The use of N fertilizer increased the S content in sorghum (by 9%) (Kaufman et al., 2013), wheat (McGrath, 1985) and rice (Marr et al., 1999). The effects of yield on nutrient content are relevant for human and animal nutrition (Rengel et al., 1999). As yield increases in all cases, the uptake by crops, in grams per hectare, increases by the input of N fertilizer. Similarly, an increase in yield via various fertilizers, does not lead to large increases or decreases in nutrient concentrations in potato (White et al., 2009) or corn (Heckman et al., 2003). The content of nutrients in brown rice was not affected by S treatment for S deficient soils (Juliano et al., 1987). A decrease in Zn content of wheat grain was found in a field without Zn deficiency, as a function of P fertilizer input (Zhang et al., 2012) while an increase in the Zn content of corn was found when Zn was deficient (Friesen et al., 1980). A discussion about the complex P x Zn interactions was given by Alloway (2008).

Table 13. *Effects of macronutrient fertilizer on yield and content of micronutrients in the grain[1]. In case of a significant effect of the fertilizer on the nutrient concentration, the nutrient concentration at the lowest and highest fertilizer input is given; otherwise, the average content is given.*

Crop	Fertilizer Input Low-High (kg/ha/yr)	Yield (t/ha)	Mg (g/kg)	Zn (mg/kg)	Cu (mg/kg)	Fe (mg/kg)	Mn (mg/kg)	Reference
Brown rice [2]	0-275 N	6.8-11.6	1.5	33	3.6	26	67	(Marr et al., 1999)
Corn	0-130 N	34-42 [4]	4.6				46-63	(Riedell, 2010)
Corn	0-240 N	6.1-8.9		15-17	1.2-1.6	13-16	3.0-3.4	(Xue et al., 2014)
Corn [3,5]	0-240 N	9.5-11	1.9	18	3.6	89	45-77	(Izsáki, 2009)
Corn [5]	0-72 P	7.4-7.9	0.34	23-17	6.8-6.1	224-198	95	(Izsáki, 2014)
Corn	0-160 N	4.3-6.2	1.1	26-24	2.2		6.4	(Feil et al., 2005)
Corn (field)	0-224 N	4 -17	1.4-1.6	28	2.3-2.6	20-24	6-7	(Ciampitti and Vyn, 2013)
Dry bean (pot)	25-200 mg/kg P	1.7-7.6 [4]	1.8	27–24	5.2		17	(Fageria et al., 2012)
Sorghum	0-100 N	5.1-8.0	1.5	17	2.8	90	14	(Kaufman et al., 2013)
Winter wheat	0-300 N	5.7-9.2	1.0	27	5	35	19	(McGrath, 1985)
Winter wheat	40-160 N	4.2-5.1	1.3	24		47-56	20	(Zebarth et al., 1992)
Wheat	67-194 N	6.6-8.2		38-42	3.4-3.8	39	46-55	(Svecnjak et al., 2013)
Wheat	0-400 P	3.5-6.5		29-13	5.3-4.5	31-37	26-31	(Zhang et al., 2012)

[1] In case of bean, corn, rice and wheat, the concentrations are for the grain (dry matter) and not the whole plant. In case of brown rice, the grain without the hull.

[2] Data from the years 1992-1993.

[3] Data from the year 2001.

[4] Yield in grams per plant.

[5] Concentration in leaves.

Based on the rather constant micronutrient content, it is possible to estimate the nutrient uptake by crops from the yield. The nutrient contents in **Table 13**, however, are for the grain and not for the whole crop. Other references, as given in **Table 14**, provided the nutrient uptake by crops which, when no crop residues are left behind, is similar to the nutrient removal from the field. An extended analysis of the uptake of micronutrients in India is not used here as it did not include macronutrients (Tandon, 2009). In **Table 15**, the fertilization rates used in various studies are presented, together with the recommended fertilization rates if there is deficiency. Comparison of **Table 14** with **Table 15** shows that the fertilization rates of micronutrients are rather high compared to the annual nutrient removal, as these fertilization rates are part of a strategy in which fertilization is only performed if there are indications for deficiency (low concentrations in soil or crop, or visual symptoms). This implies that such a high dose is sufficient for several years of micronutrient availability in the root zone. Only boron is used annually, or more frequently, as it is easily leached.

Table 14. Annual nutrient uptake (kg/ha/year) for some crops.

Crop		Yield (t/ha)	N	P	K	Ca	Mg	Zn	Cu	Mn	Fe	B	Ref.
Lowland rice	straw	9.4	65	15	156	26	15	0.55	0.08	4.72	2.55	0.07	1
	grain	6.4	86	15	20	5	7	0.22	0.10	0.37	0.51	0.03	1
Upland rice	straw	6.3	56	3	150	23	13	0.16	0.04	1.32	0.65	0.05	1
	grain	4.6	70	10	56	4	5	0.14	0.06	0.28	0.12	0.03	1
Dry bean	straw	1.9	13	2	35	17	7	0.05	0.01	0.03	0.90		1
	grain	0.004	119	12	61	8	6	0.12	0.04	0.05	0.40		1
Corn	straw	11.9	72	5	153	33	21	0.18	0.05	0.45	2.05	0.10	1
	grain	8.5	127	17	34	8	9	0.19	0.01	0.08	0.21	0.04	1
Sweet corn	grain		57	10	38	2	4	0.08	0.02	0.05	0.10	0.03	2
	residue		141	15	194	23	15	0.15	0.06	0.34	0.41	0.06	2
Corn	silage	15	183	28	189	25	19	0.03	0.03	0.41	2.0		3
Grass		10	318	42	353	52	23	0.17	0.06	1.05	4.9		3

[1] Brazil (Fageria et al., 2011).

[2] Average for eight corn varieties (Heckman, 2007).

[3] Average from large number of analyses (>1,000) in the Netherlands (Evers et al., 2000).

The strategy to use micronutrients fertilizers only if there are indications for deficiency can be an effective strategy because a single addition creates a large stock in the soil, which in case of Cu, Mn, Zn, is hardly lost by leaching. This is in line with a balanced use of fertilizers in which nutrients are only applied when it affects yield favorably. Another strategy for a balanced fertilization can be an annual application of micronutrients. For example, single superphosphate in Australia contains about 600 mg Zn kg^{-1} fertilizer from rock phosphate, which according to Brennan (2001) is sufficient for wheat grain production on the long term. The use of compound NPK fertilizers containing 1% Zn is promoted in Turkey (Alloway and Cakmak, 2008). Many fertilizer blends are sold that contain micronutrients, but scientific literature on this were not found.

Table 15. Fertilization rates of micronutrients (kg/ha) for deficient situations for different countries.

Micronutrient	Fertilization Rate (kg/ha)				
	Range in various studies[1]	Netherlands[2]	Germany[3]	USA[4]	Austria[5]
B	0 – 17	0.2 – 1.5	2, 0.5*	1 – 3	0.4 – 2.5 , 0.4*
Cu	1.1 – 13.4	2.5 – 6	4, 0.5*	15	1 –10, 0.5*
Fe		not recommended			0.5 – 1.5*
Mn	3 – 40	15*	1.0*	3 – 6	10 – 20, 1.5 – 3*
Mo	0.01 – 0.5	1, 0.05*			1, 0.3*
Zn	0.6 – 17		7, 0.5*	2 – 9	5 – 10, 0.3*

* Amount for a single foliar application.

[1] Compilation of studies (Martens and Westermann, 1991).

[2] Advice in the Netherlands, application is sufficient for a period of four years (Hoeks et al., 2012).

[3] Advice in Germany, application is sufficient for a period of four years (LandwirtschaftskammerNiedersachsen, 2008).

[3] Advice in Wisconsin (Laboski and Peters).

[4] Advice in Austria (BMLFUW, 2006).

Studies about the effects of an annual fertilization with micronutrients, to compensate for the uptake by crop, are relatively rare. In a study in which the effects of P x Zn interactions on corn have been investigated over a period of 25 years in a calcareous soil (Mallarino and Webb, 1995), there was no induction of Zn deficiency by long-term high P fertilization. Based on the yield increase in this specific soil, there was zero-interaction (additive) between P and Zn. Brennan (2001) studied the effectiveness of Zn applications on the yield of wheat in sandy acidic soils. Zinc applications performed in 1983 were still effective in 1996, although the Zn application was 50% less effective after 13 years as Zn applied in 1996 (Brennan, 2001). The Zn removal from the field by wheat grain in 13 years was 7% from the applied 3 kg Zn ha^{-1}.

Summarizing, fertilizer application recommendations that considered a balanced application of nutrients have been reported, but considerations of antagonism and synergism in these studies were not found. The micronutrients content in plants have been found to remain relatively constant at increasing yield with increased application of macronutrients when sufficient micronutrients are available to the crop.

2.4 Specific mechanisms for antagonistic or synergistic responses to nutrients

In this section, we examined whether the interactions described in Section 2.2 (that is, synergism, zero-interaction and antagonism) are governed by specific processes or mechanisms.

In most cases, the authors of the studies listed in Appendix 1 did not assign specific mechanisms for the nutrient interactions. This is probably because the interactions can modify many processes in plants. Wilkinson et al. (2000) defined interactions for which no specific process can be indicated as non-specific interactions. Specific processes are for example: sorption reactions in soil, and uptake mechanism by the plant root. According to Pan (2012) non-specific interactions are typical for interactions with N (for example: N x P, N x S), as they influence all stages of plant growth. This implies that many interactions cannot be simply assigned to specific mechanisms. Therefore, attention is given to specific nutrient interactions. Specific nutrient interactions have been classified in various ways: soil, rhizosphere and plant processes (Zhang et al., 2006), and the rhizosphere processes have been classified as cation-cation, cation-anion, or anion-anion interactions (Pan, 2012). Below an attempt is made to relate the important nutrient interactions in Section 2.2 to specific mechanisms.

As mentioned, nutrients can have an effect on the uptake of another nutrient and its content in the plant. This can help to explain how the supply of one nutrient can increase the deficiency of another nutrient. As discussed by Aulakh and Mahli (2005), it has frequently been shown that the application of a nutrient results in a negative effect on crop yield when the deficiency of another nutrient is not resolved. In **Table 16**, the negative effects of nutrients on yield from Appendix 1 have been compiled, together with information from the papers about the deficiencies and the effects on nutrient contents. For example Aktas and Van Egmond (1979) found a negative yield effect of N addition to a specific soybean variety in a calcareous soil, and found a decrease of Fe content in the yield. **Table 16** shows that nutrient supply in case of deficiency for Fe, Zn, Mn or Cu often results in a decrease in yield. This decrease in yield is often related to a decrease of nutrient content if these nutrients are deficient. The antagonisms (**Table 10**), together with the negative effects of nutrients on yield (**Table 16**), are in most cases associated with the cations, Cu, Fe, Mg, Mn and Zn. The similarity between these nutrients suggests that cation-cation interactions are very relevant for interactions that influence yield. Similar uptake mechanisms and competition between the cations might explain these effects. These mechanisms will be explored in the next section.

Table 16. Negative effects of nutrient supply on crop yield

Crop	Deficiency According to Authors	Application		Type of Study*	% Yield Decrease	Effect on Nutrient Content#	Reference
Barley oats		Mn	0.01µmol/l	H	13		Pedas et al., 2011
Corn		K	22 mg/kg	G	16	-Mg	Bedi and Sekhon, 1977
Cotton		Mn	16 mg/l	H	44		Le Mare, 1977
Chickpea	Fe	Fe	2 mg/kg	G	19	-Mn	Ghasemi-Fasaei et al., 2005
Cauliflower	Cu, Mn	Cu	1 µmol/l	H	36	-Cu	Nautiyal and Chatterjee, 2002
Dwarf bean	Zn	P	200 kg/ha	G	10	-Zn	Gianquinto et al., 2000
Corn	Zn	P	80 mg/l	H	28	-Zn	Soltangheisi et al., 2014
Mustard	B	Zn	0.65 mg/l	H	72	+B	Sinha et al., 2000
Oats	Cu	N	2400 mg/kg	G	35		Dekock et al., 1971
Oats	Cu	P	1200 mg/kg	G	19		Dekock et al., 1971
Pearl millet	Zn	N	200 mg/kg	G	26	+Zn	Kumar et al., 1985
Radish		Mg	240 mg/kg	G	19		Agarwala and Mehrotra, 1984
Radish		Fe	28 mg/kg	G	41	-Mg	Agarwala and Mehrotra, 1984
Rice	Zn	Zn	64 mg/kg	G	50	-Cu	Chaudhry et al., 1973
Soybean T-203	Fe	N	250 mg/kg	G	62	-Fe	Aktas and Van Egmond, 1979
Wheat		N	180 kg/ha	F	21		Sinha et al., 1973
Wheat	Cu, Zn	Zn	65 ug/l	H	51	-Mn	Khurana and Chatterjee, 2000
Wheat	Cu	N	44 kg/ha	F	17		Wapakala, 1973
Wheat	Cu, Zn	Zn	16 mg/kg	G	89	-Cu	Chaudhry and Loneragan., 1970
Wheat	Cu, Zn	Cu	0.55 mg/l	H	42	-Mn	Khurana and Chatterjee, 2000
White lupine	Fe	Fe	8 mg/kg	G	18	-Mn	Moraghan, 1992

* F: field; G: greenhouse; H: hydroponic.

+: increase in nutrient content; -: decrease in nutrient content.

Besides nutrients interactions between cations that affect yield, there are also some cation-anion interactions that might be specific. The P x Zn interaction is probably the most discussed interaction (Alloway, 2008)[5]. As can be seen in Section 2.2 (**Table 11**) there can be various types of interactions for P x Zn. These types of interactions are relevant when Zn is almost deficient, mostly in calcareous soils, and addition of P induces Zn deficiency. To explain this, various hypotheses have been suggested, which recognize that major interactions between P and Zn occur at the plant metabolic level (Fageria, 2001). One aspect is that the control of P uptake by a plant is lost under Zn deficiency, as the expression of high/affinity P transporter proteins is linked to the Zn status of plants. This shows that complex plant-specific genetic and membrane transport is relevant for the P x Zn interaction (Huang et al., 2000; Bouain et al., 2014).

Summarizing, it is likely that processes that determine cation-cation interactions are relevant for yield of crops. In the next section, it is discussed if there is a generic mechanism responsible for these cation-cation interactions.

[5] While the mechanism for the P x Zn interaction has often been subject for research, the relevance of the interaction is also debated. Alloway (2008) stated, "High soil phosphate levels are one of the most common causes of zinc deficiency in crops encountered around the world," while Pan (2012) stated that "Direct evidence of this interaction is sparse" and "Zn responses on high P soils have not shown Zn deficiencies."

2.5 Preferential transport of nutrients

The interactions between nutrients have often been assessed by examining the relationship between nutrient supply and nutrient uptake by plants. These studies often show direct effects of other nutrients (White, 2012) which have been interpreted as competition for various uptake mechanisms. In the previous section, it was observed that cations probably show specific interactions that affect yield of crops. Interactions between cations at the root plasma membrane might be such a specific interaction. In this section, it is assessed if these cations have a common uptake mechanism.

Nutrient uptake occurs by proteins embedded in root membranes. A significant proportion (5%) of the genome encodes membrane transporters. Several plant genomes have been sequenced, specifically for rice and *Arabidopsis*. Most membrane proteins have been classified into specific gene families, sometimes on the basis of functional data but more often on the phylogenetic relationships (Maathuis, 2007). Plasma membrane transporters are proteins that catalyze the transport of nutrients across the plasma membrane. Similar cations, and similar anions compete for binding to specific carrier proteins. The uptake of cations versus anions occurs through different transport proteins (**Table 17**). Some of the identified plasma membrane transporters seem to be specific for nutrients while others are less specific. The molecular mechanism of Mg^{2+} uptake is poorly understood, and, therefore, no plasma membrane transporters for Mg are listed in **Table 17**.

Table 17. *Plasma membrane transporters for nutrients*

Plasma Membrane Transporter Families	Role for Nutrient	Reference
Ammonium transporters (AMT)	NH_4^+	1
Nitrate transporters (NRT)	NO_3^-	1
Anion channels	Cl^-	
K channels	K^+	1
Ca channels	Ca^{2+}	1
Phosphate-transporters (PhT)	$H_2PO_4^{2-}$	1
SulP	SO_4^{2-}	1
P3A-type H-ATPases	Na^+, K^+, Ca^{2+}, Zn^{2+}	1
P1B-Zn-ATPases	Zn^{2+}, Co^{2+}, Cu^{2+}	1
P2B-(Ca)-ATPases	Ca^{2+}	1
yellow-stripe1-like (YSL)	Fe^{2+}	1
natural resistant-associated macrophage (NRAMP)	Mn^{2+}, Fe^{2+}, Co^{2+}	1
Zinc (ZIP)	Zn^{2+}, Cu^{2+}, Fe^{2+}	1
Copper transporter (COPT)	Cu^{2+}	1
Borate-transporter (BOR)	$H_2BO_3^-$	2
Molybdate-transporter (MOT)	MoO_4^{2-}	2

[1] Schulz (2010).

[2] White (2012).

The transport proteins are unable to differentiate effectively between similar ions such as: potassium (K^+) and rubidium (Rb^+) (White, 2012), sulfate (SO_4^{2-}) and selenate (SeO_4^{2-}) (White et al., 2004; White et al., 2007), sulfate (SO_4^{2-}) and molybdate (MoO_4^{2-}) (Fitzpatrick et al., 2008; Shinmachi et al., 2010), phosphate (PO_4^{3-}) and arsenate (AsO_4^{3-}) (White, 2012). These examples show that the selectivity of some transport proteins in the plasma membrane of root cells is partly based on the physicochemical similarities between ions (White, 2012). In the previous section, the antagonisms between cations proved relevant for the yield of crops. Indeed some of the plasma membrane transporters families in **Table 17** are able to transport various cations. This suggests that this specific interaction, that is the competition between similar ions for to specific carrier proteins, is dominant for the interactions between cations.

Effects of interactions between these combinations of nutrients on the yield of crops have been investigated for: Mo x S (Tables 3 and 7): one study showed synergism (Sims et al., 1979), one zero-interaction (Olsen and Watanabe, 1979) and another no effect (Dhankar et al., 1996). None of the studies showed antagonism for Mo x S, probably because the nutrients contents were not deficient. These effects on crop plants suggest that competition on plasma membrane is not likely to be a major interaction between Mo x S determining yield.

Ammonium has a negative effect on K uptake via K-channels (Hoopen et al., 2010). However, K does not have the same effect on ammonium uptake via ammonium transporters (White, 2012). Literature about the effects of interaction between NH_4^+ and K^+ on the yield on crop plants is very extensive and complex, and has recently been reviewed by Zhang et al. (2010). As mentioned earlier, a positive N x K interaction has been reported in many experiments. This interaction is also dependent on the form of N, but literature is sometimes contradictory. For this report, it suffices to conclude that the N x K interaction cannot simply be explained by competition at the plasma membrane level.

To summarize, most nutrients have specific plasma membrane transporters. However, competition between divalent cations for various plasma membrane transporters is probably important. For other relevant nutrients, this specific process probably does not dominate the interaction of nutrient supply on the yield of crops.

2.6 Effect of nutrients on root reductase activity and phytosiderophore production

In this paragraph, we explored how nutrients influence the activity of the reductase enzymes and phytosiderophore[6] production in different plant species. This might be a mechanism that explains the interactions between Fe or Zn and other nutrients. Nitrogen, P and Cu have shown synergisms with Fe; Cu with P; and B with Zn (**Table 4**). The influence of macronutrients on root reductase activity and phytosiderophore production might also help to explain positive responses of crops to macronutrients in case of Fe or Zn deficiencies.

Iron deficiency by plants is caused by its low availability in soils, especially alkaline and calcareous soils. In these soils, the availability of other metallic micronutrients, specifically Zn, is also low. Plants have developed two different mechanisms to mobilize Fe in the soil to increase Fe uptake. Grasses produce phytosiderophores (plant iron carriers) (strategy II), while other plants (dicots and non-grass monocots) produce reductases capable of reduction of Fe(III) to Fe(II) that can then be taken up by plants (strategy I). Besides Fe deficiency, the release of phytosiderophores can also be induced by Zn deficiency. Phytosiderophores can also mobilize other metals (Zn, Cu) (Römheld, 1991). Iron(III)-phytosiderophores are taken up by roots via yellow stripe1 (YS1) transporters, a member of the oligopeptide transporters (Schulz, 2010). Even plants, such as peanut, that cannot produce phytosiderophores can take up iron(III)-phytosiderophores (Xiong et al., 2013), which could explain the positive effect of intercropping corn with peanut. In the case of Fe deficiency, an increased production of ferric reductase resulted in a higher yield using a genetically modified rice (Ishimaru et al., 2007).

Release of phytosiderophores is influenced by Fe and Zn nutritional status of plants (Aciksoz et al., 2011). In soil and field experiments, increases in Zn and Fe content in wheat have been documented as a function of N fertilization (Shi et al., 2010; Kutman et al., 2011). These increases in Zn and Fe can be attributed, at least partly, to a higher production of phytosiderophores due to the N supply. In hydroponic experiments it has been shown that a high N supply (Aciksoz et al., 2011), or a high S supply (Zuchi et al., 2012) can increase the production of phytosiderophores by wheat and by doing so, can increase the Fe content in a Fe-deficient wheat plant. In a pot experiment using soil, an increase of 17 to 24 mg Fe kg^{-1} was observed in brown rice as an effect of S fertilization up to 60 mg S kg^{-1} soil (Wu et al., 2014).

[6] Phytosiderophore (plant iron carrier): class of chelating compounds, common in grasses, that sequester iron.

Root ferric chelate reductase is determined by Fe-deficiency but it can also be regulated by Cu status in strawberry plants (Mukherjee et al., 2006; Pestana et al., 2013). Various Fe-reducing substances, phenolics and carboxylates, can be produced by plants to increase the Fe availability (White, 2012). Sulfur fertilization, like phytosiderophores, also revealed a positive effect on the expression of Fe^{2+} transporter (IRT1) and chelate reductase (FRO1) genes, as found in rape under Fe deficient conditions (Muneer et al., 2014). Such a synergism was not documented in an experiment with soil (**Table 4**). Antagonisms between Fe x Mn and Fe x Zn were found (**Table 10**) and might be related to ferric-chelate reductase activity, as it has been shown that the ferric-chelate reductase activity of various plants, for example, alfalfa (Barton et al., 2000), sugar beet (Chang et al., 2003), cucumber (Lucena et al., 2003), and cowpea and bean (Dimkpa et al., 2008; Dimkpa et al., 2015) can be inhibited by the high availability of metals.

Summarizing, the effects of nutrients on the reductase enzymes or phytosiderophore production which might influence the uptake of Fe, Zn, and Cu has only recently been a subject for research (Keuskamp et al., 2015).

2.7 Management strategies

In this section, potential strategies are explored by which farmers can overcome antagonisms while stimulating synergisms.

Crop plants give various opportunities to manage synergisms and antagonisms due to:
1. Different uptake routes for nutrients (leaf, roots).
2. Different nutrient requirements during the season.
3. Spatial distribution of roots in soil.
4. Effects of different plants (intercropping).
5. Specific properties of fertilizers.

According to Aulakh and Mahli (2005), the synergism among macronutrients can be exploited best by using N x P together, for example, fertilizer deep placement. The synergism between N x K can be exploited by synchronized application throughout the season. Root biomass production is relevant for a good exploitation of soil nutrients, especially in deeper soil layers, and can be influenced by fertilization and irrigation.

A combination of seed, soil or foliar applications of fertilizers has been suggested as a strategy to obtain a more efficient use of fertilizers and overcome antagonisms. This hypothesis might be valid: when nutrient combinations are antagonistic as a soil fertilizer, why not use one of them as a foliar fertilizer? Various fertilization methods are possible. Besides soil (possible for all nutrients) and foliar fertilization (possible for B, Cu, Fe, Mn, Mo, N, Ni, S, Zn), nutrients can be supplied with the seed (e.g., Mo) (Draycott and Christenson, 2003; Fageria et al., 2009) or by fertigation (which is mainly though the soil). The foliar fertilizers that can be used include the cations for which antagonisms are relevant (Sections 2.2 and 2.3).

Foliar applications are possible with nutrients soluble in water, and can often be combined with the spraying of crop protection substances (Fageria et al., 2009). An advantage of foliar nutrient application is that it can be used at a certain plant development stage. Although the response of foliar nutrient application is temporary, it can provide rapid utilization of nutrients and corrections of deficiencies. However, foliar fertilization can only be delivered using dilute solutions due to the risk of foliage burning (Tisdale et al., 1985). Therefore, foliar fertilization is mainly a supplement to soil fertilization (Fageria et al., 2009). It is widely assumed that high rates of foliar uptake only take place at relative high humidity, due to less crystallization of salt on leaves (Fageria et al., 2009), or due to more transport through the plant leaves (Fernandez and Eichert, 2009).

Foliar applications of nutrients are used for crops grown on soils that do not deliver enough nutrients, such as B, Cu, Fe, Mn, Mo and Zn on specific soils. This is highly effective if crops require only a few g ha^{-1}. In the USA the most Fe-deficient crops are soybean and high value crops, such as citrus species, and these crops receive the major portion of Fe fertilizer as foliar sprays (Alloway, 2008). In Europe most crops that need Mn are treated with foliar fertilizer (Draycott and Christenson, 2003) as this is more cost effective. Foliar fertilization in food crops may also be relevant to raise the content of nutrient in the plant products even if it does not increase the yield (Fageria et al., 2009). The efficiency of foliar application of nutrients is a complex issue, as foliar application needs a certain leaf area and is dependent on the weather (Fageria et al., 2009). In most cases, the application recommendations are lower for foliar than soil, although more applications are probably made with foliar than soil (see **Table 15**).

The efficiency of foliar fertilization versus soil fertilization is not often studied. In a comparison between Zn application on soil, with seed, foliar or a combination of methods, it was shown that the highest grain yield was found with soil, soil + foliar, or seed + foliar application methods (Yilmaz et al., 1997). A comparison of Fe application to peanut via soil and leaves showed that both were effective (Irmak et al., 2012).

Nutrient combinations that show an antagonistic response might be delivered via different routes, while synergistic response can be exploited best when added together. An example of synergism is the combination of Fe foliar fertilizer with urea, which stimulates the uptake of Fe via wheat leaf penetration (Aciksoz et al., 2014) similar to the synergism between urea and Zn or Mn in foliar fertilization (Yassen et al., 2010). Foliar fertilization of S alone did not increase soybean grain yield, while soybean responded positively if S was applied in a mixture with NPK (Garcia L and Hanway, 1976) suggesting a synergism in which nutrients have to be applied together.

Interactions between foliar and soil applied nutrients has been studied in only a few cases. On calcareous soils low in Mn, the application of Fe can result in Mn deficiency. A comparison of Fe and Mn application to bean via soil or leaves showed that both were not effective to correct Fe-induced Mn deficiency (Moosavi and Ronaghi, 2010). A similar interaction between Fe and Mn was studied on chickpea (Ghasemi-Fasaei et al., 2005) and wheat (Ghasemi-Fasaei and Ronaghi, 2008), where Mn was added to the soil and Fe was added either by soil or by leaves. The nutrient applications influenced the nutrient contents in the plants. However, the application of Mn did not have a positive effect on the yield of chickpea and wheat, and both types of Fe applications resulted in no effect on yield or even lower yields. So, the plant nutrition was not improved when both cations were applied separately via soil or via leaves. These complex responses call for further disentangling of the options for combined soil-foliar applications in exploiting synergistic and mitigating antagonistic effects among nutrients (Fageria et al., 2009; Pandey et al., 2014).

Also in some cases, intercropping nutrient-efficient plants can decrease the deficiency effects in nutrient-inefficient plants. Manganese deficiency of berseem clover in alkaline soils in NW India could be remedied by mixed cropping with other fodder crops (oats, ryegrass or raya [Mustard]), resulting in a higher Mn contents and a higher yield of berseem clover (Arneja and Sadana, 2012). This has also been observed for wheat when mixed with white lupin. Also in case of Fe-deficiency of peanut plants, mixed cropping with barley, oats and wheat was shown to increase the Fe content in peanut plants (Zuo and Zhang, 2008). Phosphorus nutrition of wheat was improved by intercropping with chickpea and lentil (Gunes et al., 2007).

Summarizing, in principle there are a number of strategies by which to overcome nutrient antagonism or stimulate synergism. The most promising route, supplying antagonistic nutrients via different routes (soil or foliage), has not been demonstrated yet. Foliar fertilization of micronutrients in combination with urea has been shown to be successful in a number of studies.

3 Summary and conclusions

Because of the projected increase in demand for food that has to be produced sustainably, there is a need to increase the fertilizer use efficiency, i.e., to obtain more yield per unit of fertilizer applied. Increasing the fertilizer use efficiency requires balanced application of fertilizers, i.e., best fertilizer formulations supplied to the plant for uptake through various organs. To achieve this, it is necessary to understand the interactions between nutrients with respect to their effects on yields and nutrient use efficiency. Such interactions can be absent (zero-interaction), positive (synergistic) or negative (antagonistic). Fertilizer formulations must take into account such positive and negative effects; or better, benefit from the positive interactions, while avoiding or mitigating negative interactions. This study provides an overview from selected peer-reviewed literature and easily accessible standard books, of available data on synergistic and antagonistic nutrient interactions as reflected in crop yield. At this stage, only quantitative yield has been considered.

Using a search query resulted in about 350 scientific research articles. In total 116 interactions between nutrients on crop yield have been identified in 96 publications: 42 synergistic (of which 21 were of the special type Liebig-synergistic), 17 antagonistic, and 34 resulted in neutral interaction. In some studies no significant (16) or difficult to explain negative results (7) were obtained. The number of reported nutrient interactions is low. However, some main findings from this review are:

- In cases where the availability of two nutrients can be characterized as deficient, increase of the availability of both nutrients often results in a large increase in yield. Identification of deficiencies and the use of optimal ratios between nutrients are therefore important in developing efficient fertilizer application schemes.
- Most macronutrients have synergistic interactions. Synergistic interactions between nutrients result in actual relative yields that are a factor 1 to 3 greater than yield predicted on the basis of individual nutrients. As macronutrients form the basis for fertilizer applications, it is worthwhile to take these synergistic interactions into account.
- Antagonisms and negative effects of nutrients are often related to the divalent cations which probably share similar uptake mechanisms. Strategies to overcome these problems might be to differentiate the fertilization of these nutrients between soil and foliar applications. This differentiation has rarely been studied for interacting nutrients.

Because nutrient interactions have been studied for a limited number of crops (varieties), nutrients, soil types and climates, care must be taken to extrapolate individual results to other conditions. Generalizing the effects of nutrient interaction on yield can be a way forward to increase the nutrient use efficiency, especially for the group of nutrients for which the effects on yield seem rather hard to predict (Ca, Fe, Mg, Mn and Zn).

The following table summarizes the results of sub-questions that were part of the study.

Question	Result
Is there a relationship between the uptake of micronutrients and the application of macronutrients?	Fertilizer application recommendations have been reported that considered a balanced application of nutrients, but considerations of antagonism and synergism in these studies were not found. The micronutrients content in plants have been found to remain relatively constant at increasing yield with increased application of macronutrients when sufficient micronutrients are available to the crop.
Are the interactions governed by specific processes or mechanisms?	It is likely that processes that determine cation-cation interactions are relevant for yield of crops. Most nutrients have specific plasma membrane transporters. Competition between divalent cations for various plasma membrane transporters is probably important. For other relevant nutrients, membrane transport may not dominate the interaction of nutrient supply on the yield of crops.
Is there an effect of nutrients on root reductase activity and phytosiderophore production?	Effects of nutrients on the reductase enzymes and phytosiderophore production can influence the uptake of Fe and Zn.
Are there any potential management strategies that can overcome antagonisms while stimulating synergisms?	In principle, there are a number of strategies to overcome antagonism or stimulate synergisms. Supplying antagonistic nutrients via soil or foliage has not been demonstrated yet. However, foliar fertilization of micronutrients in combination of urea has been shown to be successful in a number of studies.

The rationale for carrying out this study was to provide an overview of known synergisms and antagonisms between nutrients with respect to crop yield. Knowledge of these kinds of nutrient interactions can then be used to optimize fertilizer application schemes so that high yields are obtained with high nutrient use efficiencies. The ultimate amount of nutrients taken up by plants depend on a wide range of soil-, weather- and plant-related variables. The available data describing the interactions do not allow to systematically disentangle the impact of all these variables on reported yield responses to nutrient applications. Yet, the information reveals several generic principles that can be accounted for as initial steps towards more balanced application of nutrients, and to further explore the option of delivery of the nutrients to the plant through both roots and leaves. Therefore, a dual, mutually supporting, pathway of further identifying generic mechanisms of the interacting effects and empirical testing of hypothesized best balanced fertilizers is recommended to advance our insights, and to move towards short term field impact.

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Appendix I. Interactions between nutrients

Literature has been examined for studies about interactions between nutrients. Studies that determined the yield as a function of the supply of two nutrients combined or supplied separately, have been included.

The yield (y) is given for the zero treatment (y_0), for the treatment with nutrient a (y_a), nutrient b (y_b), and the combined treatment (y_{ab}). An interaction between two nutrients is synergistic when the combined effect of two nutrients on yield (y_{ab}/y_0) is greater than the product of their individual effects (y_a/y_0 x y_b/y_0). When the combined effect is less, the interaction is antagonistic. The expected yield for the combined treatment (equation 1) is calculated as proposed by Wallace (1990) as the product of the relative yields from the single effects (y_a and y_b). Zero-interaction indicates the absence of interaction ($y_{ab}/y_0 = y_a/y_0$ x y_b/y_0). A specific case of synergism has been defined by Wallace (1990) as Liebig-synergism. In this case the yield in the combined treatment (y_{ab}) is higher than any of the individual treatments (y_0, y_a or y_b) and the yield at the starting point (y_0) is limited dominantly by one nutrient. In the end point (y_{ab}) there is synergism.

Column legend

1	Number of combination of two nutrients as given in Table B	
2	Crop	
3	Treatment with nutrient a and b, given as a/b. Unit depends on the type of study. In water hydroponic studies (mg/l, mmol/l solution), pot studies (mg/kg soil) or field studies (kg/ha). Underlined is foliar application.	
4	Type of yield: mass of the shoot, grains etc.	
5	T_0	control treatment
6	y_0	yield in control treatment
7	T_a	treatment with nutrient a (for example: 10/0 is 10 and 0 kg/ha of resp. nutrient a and b).
8	y_a	yield in treatment a
9	T_b	treatment with nutrient b
10	y_b	yield in treatment b
11	T_{ab}	treatment with nutrient $a + b$
12	y_{ab}	yield in treatment in which nutrient a and b have been combined.
13	type of interaction: synergism (S), Liebig-synergism (L-S), antagonism (A), approximately zero-interaction (add.), no effect (n.e.). A negative effect, $y_0 > y_{ab}$ (neg.), is difficult to categorize.	
14	ratio	(y_{ab}/y_0) (y_a/y_0 x y_b/y_0)$^{-1}$. In case there is a positive effect on yield of treatment a+b, then synergism if the ratio >1, antagonism if ratio <1.
15	field study (F), hydroponic study (H), and greenhouse study with soils, or purified sand, in pots (G).	

In some studies, a variety of concentrations has been studied. Only one combination of two nutrients is given here. In most cases, the highest supply of nutrients was chosen, except in the case of toxic effects (if there is a yield decrease due to the addition of a single nutrient that is known to be toxic at high concentrations). In those cases, the concentrations with the highest yield have been chosen.

Some studies have given ANOVA table about the interaction and the effect of individual treatments. The type of interaction has been estimated from the ANOVA table and figures presented in these studies.
Note: ideally in nutrient interaction studies all other factors should be at an optimum level, except the nutrients under investigation (Fageria et al., 2011). This is rather difficult to comply with when studying interactions between nutrients such as iron, manganese and zinc where the availability is often determined by the soil conditions.

Table a. Effect of interactions of nutrients on yield.

Column (see explanation above the table)															
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
	crop	nutrients a/b	yield	T_0	y_0	T_a	y_a	T_b	y_b	T_{ab}	y_{ab}				
1	canola	N/K kg/ha	grain (t/ha)	0/0	0.7	138/0	0.8	0/60	0.8	138/60	1.5	S	1.6	F	(Brennan and Bolland, 2009)
1	wheat	N/K kg/ha	grain (t/ha)	0/0	1.2	138/0	1.5	0/60	1.5	138/60	2.4	S	1.3	F	(Brennan and Bolland, 2009)
1	rice	N/K mg/kg	grain (g/plant)	150/100	11	300/100	16	150/200	12.6	300/200	19	S	1.0	G	(Fageria and Oliveira, 2014)
1	oat	N/K kg/ha	grain (t/ha)	0/0		120/0		0/33		120/33		n.e.		F	(Mohr et al., 2007)
1	pineapple	N/K kg/ha	fruit (t/ha)	100/100	18	200/100	22	100/200	19	200/200	26	S	1.1	F	(Obiefuna et al., 1987)
1	maize	N/K kg/ha	grain (t/ha)	134/0	8.4	314/0	8.9	134/134	8.4	314/134	8.9	n.e		F	(Bruns and Ebelhar, 2006)
1	wheat	N/P kg/ha	grain (t/ha)	0/0	1.55	180/0	1.23	0/39	2.24	180/39	3.13	S	1.6	F	(Sinha et al., 1973)
2	sorghum	N/P kg/ha	grain (t/ha)	0/0	1.30	120/0	2.31	0/17	1.49	120/17	2.40	add	0.9	F	(Buah et al., 2012)
2	rice	N/P mg/kg	grain (g/plant)	150/100	10.7	300/100	16	150/200	12.4	300/200	19	S	1.0	G	(Fageria and Oliveira, 2014)
2	rice	K/P mg/kg	grain (g/plant)	100/100	10.7	200/100	12.6	100/200	12.4	200/200	17	S	1.1	G	(Fageria and Oliveira, 2014)
2	oat	N/P kg/ha	grain (t/ha)	0/0		120/0		0/26		120/26		n.e.		F	(Mohr et al., 2007)
3	groundnut	K/P kg/ha	pod (t/ha)	0/0		40/0		0/120		40/120		n.e.		F	(Lombin and Singh, 1986)
3	wheat	K/P kg/ha	grain (t/ha)									n.e.		F	(Touchton et al., 1980)
3	maize	K/P kg/ha	yield (t/ha)	0/0	13.5	150/0	13.7	0/45	14.7	150/45	14.8	n.e.		F	(Jakobsen, 1993)
3	soybean	K/P kg/ha	seed (t/ha)	28/0	2.8	112/0	2.9	28/60	3.0	112/60	3.8	S	1.2	F	(Jones et al., 1977)
3	soybean	K/P kg/ha	seed (t/ha)	0/0	1.8	40/0	2.1	0/120	2.3	40/120	2.6	add	1.0	F	(Abbasi et al., 2012)
4	cabbage	N/S kg/ha	crop (t/ha)	84/0	25.3	168/0	23.6	84/22	37.6	168/22	61.2	L-S	1.7	F	(Rhoads and Olson, 2001)
4	oilseed rape	N/S kg/ha	crop (t/ha)	180/0	0.4	230/0	1.1	180/10	0.4	230/10	1.7	S	1.5	F	(McGrath and Zhao, 1996)
4	teff	N/S kg/ha	grain (t/ha)	0/0	0.5	0/16	0.6	70/0	0.5	70/16	1.0	S	1.4	F	(Habtegebrial and Singh, 2006)
4	1e grass cut	N/S kg/ha	yield (t/ha)	0/0	1.4	134/0	1.8	0/12	1.7	134/12	3.2	S	1.5	F	(Kowalenko, 2004)
4	3e grass cut	N/S kg/ha	yield (t/ha)	0/0	1.1	134/0	1.5	0/12	1.8	134/12	1.2	A	0.5	F	(Kowalenko, 2004)
4	maize	N/S kg/ha	grain (t/ha)	0/0	8.2	125/0	10.3	0/15	9.0	125/15	11	add	0.9	F	(Pagani et al., 2012)
4	canola	N/S kg/ha	seed (t/ha)	0/0	0.8	252/0	2.4	0/45	0.9	252/45	2.7	add	1.0	F	(Jackson, 2000)
4	sunflower	N/S mg/l	seed (g/plant)	7/1	1.3	168/1	5.9	7/75	1.3	168/75	35.6	L-S	6	G	(Hocking et al., 1987)
4	wheat	N/S kg/ha	grain (t/ha)	25/0	2.6	105/0	3.3	25/30	2.8	105/30	3.6	add	1.0	F	(Salvagiotti et al., 2009)
5	potato	K/S mg/l	tuber (g/plant)	2/1	119	8/1	188	2/4	142	8/4	253	S	1.1	H	(Moinuddin and Umar, 2004)
5	sunnhemp	K/S kg/ha	fiber (t/ha)	0/0	0.5	60/0	0.6	0/40	0.7	60/40	0.8	add	1.0	F	(Saha et al., 2013)
6	white clover	P/S kg/ha	yield (t/ha)	0/0	1.8	80/0	3.0	0/30	4.8	80/30	7.4	add	0.9	F	(Sinclair et al., 1996)
6	grass	P/S kg/ha	yield (t/ha)	0/0	6.2	80/0	8.4	0/30	10	80/30	14	add	1.0	F	(Sinclair et al., 1996)
6	chickpea	S/P kg/ha	seed (kg/ha)	0/0	0.8	0/80	1.0	30/0	0.9	30/80	1.1	add	1.0	F	(Islam et al., 2012)
6	soybean	P/S mg/kg	grain (g/pot)	0/0	2.0	80/0	2.4	0/80	2.6	80/80	3	add	1.0	G	(Kumar and Singh, 1980)
8	oats, rape, clover											n.e.		G	(Johansson and Hahlin, 1977)
9	ryegrass	Ca/P mg/kg	yield (g/pot)	0/0	4.7	1.2/0	5.9	0/2.2	6.3	1.2/2.2	6.7	add	0.9	G	(Bailey, 1991)
9	cotton	Ca/P mg/l	dm (g/pot)	6/2	2.4	90/2	3.1	6/30	7.1	90/30	15	S	1.6	H	(Le Mare, 1977)

Column (see explanation above the table)															
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
	crop	nutrients a/b	yield	T_0	y_0	T_a	y_a	T_b	y_b	T_{ab}	y_{ab}				
12	wheat	K/Mg mg/kg	shoot (g/pot)							214/18		n.e.		G	(Ohno and Grunes, 1985)
12	corn	K/Mg kg/ha	yield (t/ha)							270/45		n.e.		F	(Rehm and Sorensen, 1985)
12	sorghum	K/Mg mg/l	shoot (g/pot)							200/50		add		H	(Ologunde and Sorensen, 1982)
12	lucerne	K/Mg mmol/l	shoot (g/pot)	0.5/0.5	10.6	4/0.5	13.8	0.5/2	10.76	4/2	12	neg.		H	(Omar and El-Kobbia, 1965)
12	corn	K/Mg mg/kg	shoot (g/pot)	0/0	20	22/0	24	0/16	22	22/16	27	add	1.0	G	(Bedi and Sekhon, 1977)
12	corn	K/Mg mg/kg	shoot (g/pot)	0/0	25	22/0	21	0/16	25	22/16	29	L-S	1.3	G	(Bedi and Sekhon, 1977)
12	Cowpea	K/Mg mg/l	shoot (g/pot)									A		H	(Narwal et al., 1985)
12	ryegrass	K/Mg kg/ha	dm (t/ha)	0/0	9	284/0		0/88		284/88	11	add		F	(Bolton and Penny, 1968)
16	soybean	N/Fe kg/ha	seed (kg/ha)	0/0	2.1	80/0	2.2	0/0.4	2.1	80/0.4	2.8	S	1.3	F	(Caliskan et al., 2008)
16	wheat	N/Fe kg/ha	grain (t/ha)	118/0	6.8	214/0	9.1	118/0.24	8.1	214/0.24	10	add	0.9	F	(Seadh et al., 2009)
16	soybean T-203	N/Fe mg/kg	dm (g/pot)	0/0	23	250/0	9	0/0.035	26	250/0.035	15	neg.		G	(Aktas and Vanegmond, 1979)
16	soybean Hawkeye	N/Fe mg/kg	dm (g/pot)	0/0	44	250/0	62	0/0.035	44	250/0.035	58	A	0.9	G	(Aktas and Vanegmond, 1979)
18	white lupine	P/Fe mg/kg	dm (g/pot)	0/0	3.9	120/0	4.2	0/8	3.22	120/8	5.2	L-S	1.5	G	(Moraghan, 1992)
18	maize	P/Zn+Fe	grain (t/ha)	0/0	4.7	150/0	4.6	0/30	5.1	150/30	4.7	neg.		F	(Nair and Babu, 1975)
18	soybean	P/Fe mmol/l	shoot (g)	0.1/0.001	4.0	2/0.001	9.5	0.1/20	5.50	2/20	11	A	0.8	H	(Rotaru and Sinclair, 2009)
19	sorghum	Fe/S mg/kg	dm (g/pot)	0/0	6.3	0/30	10	5/0	11	5/30	15	A	0.8	G	(Olsen and Watanabe, 1979)
21	radish	Mg/Fe mg/kg	dm (g/pot)	0.05/0.1	0.4	240/0.1	0.3	0.05/28	0.2	240/28	0.9	L-S	4.6	G	(Agarwala and Mehrotra, 1984)
22	barley oats	N/Mn kg/ha	grain (t/ha)	0/0	0.9	22/0	2.4	0/5.6	2.4	22/5.6	3.1	A	0.5	F	(Petrie and Jackson, 1984)
22	wheat	N/Mn kg/ha	grain (t/ha)	118/0	6.8	214/0	9.1	118/0.24	8.2	214/0.24	10.2	add	0.9	F	(Seadh et al., 2009)
23	soybean	K/Mn umol/l	dm (g/plant)	1/0	2.2	10/0	2.1	1/0.002	3.3	10/0.002	2.9	A	0.9	H	(Heenan and Campbell, 1981)
24	barley oats	P/Mn umol/l	dm. (g/pot)	3/0.0015	5.5	30/0.0015	7.4	3/0.015	4.8	30/0.015	9	L-S		H	(Pedas et al., 2011)
24	potato	P/Mn umol/l	shoot (g/pot)	32/0.05	8.5	128/0.05	11.5	32/9.5	10.0	128/9.5	14	add	1.0	H	(Barben et al., 2011)
26	cotton	Ca/Mn mg/l	dm. (g/pot)	6/0.5	7.20	90/0.5	12.5	6/16.5	4.0	90/16.5	11	neg.		H	(Le Mare, 1977)
28	maize	Fe/Mn mg/kg	dm (g/pot)	0/0	3.4	50/0	4.5	0/100	5.0	50/100	5.5	A	0.8	G	(Bansal et al., 1999)
28	chickpea	Fe/Mn mg/kg	dm (g/pot)	0/0	3.68	2/0	2.99	0/30	3.51	2/30	3	neg.		G	(Ghasemi-Fasaei et al., 2005)
28	wheat	Fe/Mn mg/kg	dm (g/pot)	0/0	3.38	8/0	3.51	0/15	3.80	8/15	3.05	neg		G	(Ghasemi-Fasaei and Ronaghi, 2008)
28	soybean	Mn/Fe umol/l	dm (g/pot)	0/0	0.95	1.8/0	1.65	0/20	1.10	1.8/20	1.6	neg.		H	(Heenan and Campbell, 1983)
28	soybean	Fe/Mn mg/kg	grain (t/ha)	0/0	2.1	50/0	3.0	0/40	3.2	50/40	3.5	A	0.76	F	(Kobraee and Shamsi, 2011)
28	dry bean	Fe/Mn mg/kg	shoot (g/pot)	0/0	3.3	8/0	3.4	0/30	3.6	8/30	3.4	n.e.		G	(Moosavi and Ronaghi, 2010)
28	dry bean	Fe/Mn mg/kg	shoot (g/pot)	0/0	3.3	2/0	3.1	0/1	3.4	2/1	3.1	n.e.		G	Moosavi and Ronaghi, 2010)
29	wheat	N/Zn mg/kg	grain (g/pot)	0/0	9.8	150/0	16	0/20	14	150/20	26	add	1.1	G	(Verma and Bhagat, 1990)
29	pearl millet	N/Zn mg/kg	shoot (g/pot)	0/0	5.2	200/0	28	0/20	4	200/20	21	add	1.0	G	(Kumar et al., 1985)
29	cauliflower	N/Zn kg/ha	product (t/ha)	0/0	8.8	120/0	17	0/4.2	14	120/4.2	23	add	0.9	F	(Balyan and Dhankar, 1978)
29	wheat	N/Zn kg/ha	grain (t/ha)	118/0	6.8	214/0	9.1	118/0.24	8.4	214/0.24	10.4	add	0.9	F	(Seadh et al., 2009)
31	potato	P/Zn umol/l	shoot (g/pot)	32/0.1	6.8	128/0.1	8.0	32/54	10	128/54	14	S	1.2	H	(Barben et al., 2011)
31	stevia	P/Zn kg/ha	shoot (g/pot)	0/0	22	30/0	20	0/10	23	30/10	23	n.e.	1.07	G	(Das et al., 2005)

Column (see explanation above the table)															
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
	crop	nutrients a/b	yield	T_0	y_0	T_a	y_a	T_b	y_b	T_{ab}	y_{ab}				
31	maize	P/Zn mg/kg	shoot (g/pot)	0/0	2	300/0	6	0/10	2	300/10	12	L-S	2.0	G	(Friesen et al., 1980)
31	wheat	P/Zn mg/kg	shoot (g/pot)	0/0	1.7	250/0	1.7	0/5	1.6	250/5	2.3	S	1.4	G	(Imtiaz et al., 2006)
31	bean	P/Zn mg/kg	seed (g/pot)	0/0	3.1	40/0	5.6	0/5	3.1	40/5	6.4	L-S	1.1	G	(Singh et al., 1988)
31	maize	P/Zn uM	biomass (g/pot)									n.e.		H	(Nichols et al., 2012)
31	soybean	P/Zn kg/ha	seed (kg/ha)	0/0	1.56	53/0	1.58	0/10	1.86	53/10	1.87	add	1.0	F	(Payne et al., 1986)
31	dwarf bean	P/Zn kg/ha	seed (g/plant)	0/0	13	200/0	11	0/40	13	200/40	17	L-S	1.5	G	(Gianquinto et al., 2000)
31	maize	P/Zn mg/kg	shoot (g/plant)	0/0	1.5	75/0	2.4	0/10	1.2	75/10	4.5	L-S		G	(Safaya, 1976)
31	maize	P/Zn mg/l	shoot (mg/plant)	0/0	49	80/0	35	0/20	49	80/20	48	neg		H	(Soltangheisi et al., 2014)
31	wheat	P/Zn kg/ha	grain (t/ha)									n.e.		F	(Zhang et al., 2012)
33	ryegrass	Ca*/Zn g/kg	grass (g/pot)	0/0	8.97	1.2/0	9.93	0/0.013	9.00	1.2/0.013	11	add	1.1	G	(Bailey, 1991)
34	Wheat	Mg/Zn mg/kg	Shoot (g/pot)	0/0	11.9	60/0	18.5	0/20	20.6	60/20	22.1	A	0.7	G	(Kumar et al., 1981)
35	rice	Fe/Zn kg/ha	grain (t/ha)	0/0	2.7	56/0	3.4	0/4	3.0	56/4	4.3	add	1.1	F	(Westfall et al., 1971)
35	rice	Fe/Zn kg/ha	grain (t/ha)	0/0	2.1	15/0	3.2	0/16	3.0	15/16	3.6	A	0.8	0/0	(Tandon, 1996)
35	soybean	Fe/Zn mg/kg	grain (t/ha)	0/0	2.73	50/0	3.12	0/40	3.32	50/40	3.8	add	1.00	F	(Kobraee and Shamsi, 2011)
36	wheat	Mn/Zn ug/l	grain (g wt/pot)	5.5/6.5	1.29	550/6.5	2.40	5.5/65	0.63	550/65	3.7	L-S		H	(Khurana and Chatterjee, 2000)
36	soybean	Mn/Zn mg/kg	grain (t/ha)	0/0	2.09	40/0	3.19	0/40	3.00	40/40	3.8	A	0.82	F	(Kobraee and Shamsi, 2011)
37	wheat	N/Cu kg/ha	grain (t/ha)	118/0	6.8	214/0	9.1	118/0.24	6.9	214/0.24	9.3	add		F	(Seadh et al., 2009)
37	wheat	N/Cu kg/ha	grain (t/ha)	0/0	1.30	44/0	1.08	0/14	1.50	44/12	2	L-S	1.6	F	(Wapakala, 1973)
37	oats	N/Cu mg/kg	grain (mg/plant)	0/0	31	2400/0	20	0/21	61	2400/21	465	L-S	12	G	(Dekock et al., 1971)
37	raya	N/Cu mg/kg	dm (g/pot)	0/0	0.8	80/0	11	0/5	0.7	80/5	12	L-S		G	(Antil et al., 1988)
37	wheat	N/Cu mg/kg	Shoot g/pot)	0/0	1	120/0	2	0/5	1	120/5	2.52	L-S	1.3	G	(Kumar et al., 1990)
37	rice	N/Cu mmol/l	shoot (g/plant)	0.6/0	2.1	3/0	4	0.6/0.0002	2.5	3/0.0002	4	add	1	H	(Dias and Oliveira, 1996)
39	maize	P/Cu mg/kg	shoot (g/plant)	0/0	28	50/0	27	0/5	35	50/5	29	A	0.9	G	(Awan and Abbasi, 2000)
39	wheat	P/Cu mg/kg	grain (g/plant)	0/0	10.5	50/0	13.5	0/5	12.5	100/5	15.8	add	1.0	G	(Shukla and Singh, 1979)
39	oats	P/Cu mg/kg	grain (mg/plant)	0/0	31	1200/0	25	0/21	61	1200/21	71	L-S	1.4	G	(Dekock et al., 1971)
43	oats	Fe/Cu mg/kg	grain (mg/plant)	0/0	44	1200/0	45	0/21	49	1200/21	769	S	15	G	(Cheshire et al., 1967)
44	cauliflower	Mn/Cu umol/l	shoot (g/plant)	0.01/0.01	10.2	10/0	9.8	0/1	6.5	10/1	16	L-S	3	H	(Nautiyal and Chatterjee, 2002)
44	wheat	Mn/Cu ug/l	grain (g wt/pot)	5.5/6.5	1.09	550/5.5	1.32	5.5/550	0.63	550/550	3.7	L-S	4.8	H	(Khurana and Chatterjee, 2000)
45	wheat	Zn/Cu ug/l	grain (g wt/pot)	5.5/6.5	1.26	55/6.5	1.32	5.5/65	2.40	55/65	3.7	S	1.5	H	(Khurana and Chatterjee, 2000)
45	rice	Zn/Cu mg/kg	grain (g/pot)	16/8	7.18	64/8	3.58	16/16	6.83	64/16	7.6	A		G	(Chaudhry et al., 1973)
46	wheat	Zn/Cu mg/kg	grain (g/plant)	0/0	0.90	16/0	0.10	0/7	1.40	16/7	1.7	L-S	10.9	G	(Chaudhry and Loneragan, 1970)
58	mustard	P/B mmol/l	shoot (g/plant)	0.15/0.0003	0.51	3/0.0003	3.54	0.15/0.3	0.79	3/0.3	7.8	S	1.4	H	(Sinha et al., 2003)
59	mustard	S/B mmol/l	shoot (g/plant)	0.02/0.0003	2.85	2/0.0003	6.13	0.02/0.3	3.91	2/0.3	26	S	3.1	H	(Khurana and Chatterjee, 2002)
60	peanut	Ca/B mg/kg	seed (g/plant)	0/0	0.25	100/0	0.63	0/2	0.25	100/2	4.50	L-S	7.2	F	(Keeratikasikorn et al., 1991)
60	carrot	Ca/B mmol/l	product (fw g)	0/0	25.6	3/0	35.9	0/0.005	32.4	3/0.005	46	add	1.0	H	(Singh et al., 2010)
60	pea, bean	Ca/B mmol/l	shoot (g/plant)	0.68/0.0093	0.29	1.36/0.0093	0.80	0.68/0.0465	1.01	1.36/0.0465	1.1	A	0.4	H	(Redondo-Nieto et al., 2003)

Column (see explanation above the table)															
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
	crop	nutrients a/b	yield	T_0	y_0	T_a	y_a	T_b	y_b	T_{ab}	y_{ab}				
64	mustard	B/Zn mg/l	seed (g/plant)	3.3/0.65	0.09	330/0.65	0.40	3.3/65	0.03	330/65	3.9	S	35.1	H	(Sinha et al., 2000)
67	tobacco	N/Mo mg/kg	grain (t/ha)	0/0	2.80	224/0	3.3	0/0.22	3.0	224/0.22	3.5	add	1.0	F	(Sims et al., 1975)
69	lentil	P/Mo mg/kg	shoot (g/plant)	0/0	1.22	50/0	1.7	0/50	2.3	50/1	3.0	add	0.9	G	(Mandal et al., 1998)
69	White clover	P/Mo mg/kg	shoot (g/plant)	0/0	1.9	200/0	11	0/6	7.7	200/9	13.4	A	0.3	G	*(Vistoso* et al*., 2012)*
69	brassica napus	P/Mo mg/kg	grain (g/plant)	0/0	6.9	160/0	9.0	0/0.3	7.2	160/0.3	13	S	1.4	G	(Liu et al., 2010)
70	sorghum	S/Mo mg/kg	dm (g/pot)	0/0	6.3	30/0	10	0/0.062	6	30/0.062	10	add	1.0	G	(Olsen and Watanabe, 1979)
70	raya crop	S/Mo mg/kg	dm (g/pot)									n.e.		G	(Dhankar et al., 1996)
70	tobacco	S/Mo mg/kg	leaf (t/ha)	0/0	2.7	224/0	2.7	0/2.2	2.6	224/2.2	3.0	S	1.1	F	(Sims et al., 1979)
73	sorghum	Fe/Mo mg/kg	dm (g/pot)	0/0	6.3	5/0	11	0/0.062	6	5/0.062	12	add	1.0	G	(Olsen and Watanabe, 1979)
74	canola	Mo/Mn kg/ha	grain (t/ha)	0/0	1.84	0.04/0	2.06	0/1	2.15	0.04/1	2.3	add	0.9	F	(Brennan and Bolland, 2011)

Table b. Legend for numbers in first column of Table a which refer to specific combination of nutrients, for example 2 refers to N and P. Studies have been found for all combinations in Table a.

	K	P	S	Ca	Mg	Fe	Mn	Zn	Cu	Cl	B	Mo	B	
	1	2	4	7	11	16	22	29	37	46	56	67	79	N
		3	5	8	12	17	23	30	38	47	57	68	80	K
			6	9	13	18	24	31	39	48	58	69	81	P
				10	14	19	25	32	40	49	59	70	82	S
					15	20	26	33	41	50	60	71	83	Ca
						21	27	34	42	51	61	72	84	Mg
							28	35	43	52	62	73	85	Fe
								36	44	53	63	74	86	Mn
									45	54	64	75	87	Zn
										55	65	76	88	Cu
											66	77	89	Cl
												78	90	B
													91	Ni

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