Models for predicting nutrient availability in soils from sub-Saharan Africa

Mirjam S. Breure

Propositions

1. Addressing potential micronutrient deficiencies does not require the highest priority in African smallholder farming systems.
   (this thesis)

2. Fertilising maize with zinc helps, but is not essential for reducing human zinc deficiency in sub-Saharan Africa.
   (this thesis)

3. Means are not always meaningful.

4. Teaching skills to acquire knowledge is more important than teaching knowledge itself.

5. A kid, kitten or kite a day, keeps the doctor away.

6. The best remedy against Calvinism is to spend some time in Belgium.

Propositions belonging to the thesis, entitled

Models for predicting nutrient availability in soils from sub-Saharan Africa

Mirjam S. Breure
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Models for predicting nutrient availability in soils from sub-Saharan Africa

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Thesis

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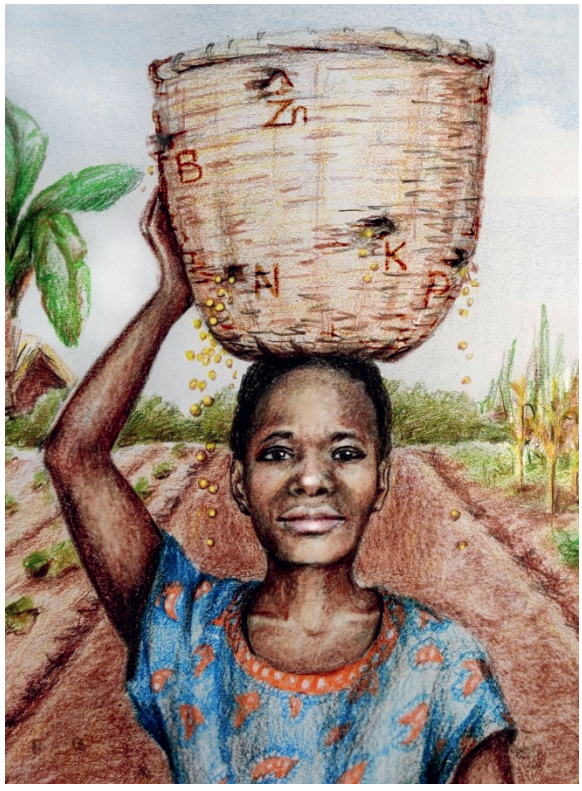
Chapter 1

General introduction

Mirjam S. Breure



1. Background

Food insecurity is threatening millions of lives today and many millions more in the decades to come. The highest rates of food insecurity are found in sub-Saharan Africa (SSA). In 2017, about 22% of the population in SSA was estimated to suffer from chronic hunger, although regional differences exist (FAO et al., 2018). One important contributor to food insecurity in this region is the low agricultural productivity. For example, average maize yields across the African continent were 2.1 Mg ha^{-1} in 2020, compared to a global average of 5.8 Mg ha^{-1} (FAOSTAT, 2022). The agricultural sector in SSA is dominated by smallholder farming systems, which are characterised by large yield gaps, i.e. large differences between potential and actual yields (Giller et al., 2021; Vanlauwe et al., 2014). These large yield gaps can be attributed to the inherent low soil fertility, which has been aggravated by continuous cropping without sufficient additions of (organic) fertilisers (Giller et al., 2011; Njoroge et al., 2017; ten Berge et al., 2019). With a projected 2.5-fold population increase by 2050, food production in SSA needs to increase significantly to reduce large-scale food insecurity (Van Ittersum et al., 2016). Although the demand for food can partly be met through imports, food security will only be achieved when the agricultural area is expanded and, more importantly, by closing existing yield gaps through intensification (Vanlauwe et al., 2014).

In combination with other agronomic practices, the use of mineral fertilisers is considered indispensable for closing yield gaps (Chivenge et al., 2022; Van Ittersum et al., 2016; Vanlauwe et al., 2015). The average fertiliser use in SSA is about 20 kg ha^{-1}, which is very low compared to the global average of 137 kg ha^{-1}, although large differences among and within countries in SSA can be found (Sheahan and Barrett, 2017; Vanlauwe and Dobermann, 2020; World Bank, 2022). The limited use of fertilisers has several causes, such as high costs and limited access (Chivenge et al., 2022). Furthermore, a strong driver for the use of fertilisers is their profitability, which depends on the crop response to fertilisation (Njoroge et al., 2017). The crop response to fertilisation can be highly variable and recent studies suggest that a poor response to fertiliser application is common in SSA (Kihara et al., 2016; Njoroge et al., 2017).

A poor response to fertilisers can have several causes. First, fertiliser recommendations in SSA are often national or regional blanket recommendations, which are based on a limited number of fertiliser response trials (Chivenge et al., 2022; Rurinda et al., 2020). Blanket recommendations do not always take into account differences in soil type, agro-ecological zone or even crop types (MacCarthy et al., 2018). Furthermore, farming systems are highly heterogenous: besides the agroecological environment, differences in resource endowment, farm size and management are found (Giller et al., 2011;

Zingore et al., 2007a). As a result, strong variation in soil fertility can be found among, but also within farms (Zingore et al., 2007b). Blanket fertiliser recommendations therefore are not suitable for sustainably increasing yields across the board (Giller et al., 2011; Tittonell et al., 2008; Zingore et al., 2007b). Secondly, blanket fertiliser recommendations often include only nitrogen (N), phosphorus (P) and potassium (K), and sometimes only N and P (Chivenge et al., 2022; Vanlauwe et al., 2015; Zingore et al., 2007b). In poorly responsive soils, likely multiple nutrients are yield-limiting (Njoroge et al., 2017; Vanlauwe et al., 2015). Some blanket fertiliser recommendations include the application of manure (Vanlauwe et al., 2015; Zingore et al., 2007b), which inevitably contains a range of nutrients. However, the majority of farmers do not own sufficient numbers of cattle to produce enough manure for fertilising all fields (Shepherd and Soule, 1998; Zingore et al., 2007a).

To close existing yield gaps in SSA, deficiency of potentially multiple nutrients needs to be addressed. The aim of this thesis is to develop and evaluate models for fertiliser recommendations which can help extension services, farmers and the fertiliser industry to make informed decisions about the kinds and quantities of nutrients farmers need to apply in order to close yield gaps.

2. Micronutrients

In addition to sufficient amounts of water and sunlight, plants require a range of nutrients to complete their life-cycle: macronutrients (nitrogen, phosphorus, potassium), secondary nutrients (calcium, magnesium, sulphur) and micronutrients (zinc, boron, iron, copper, manganese, molybdenum, nickel and chlorine). In contrast to macronutrients, good yields can be obtained without application of micronutrient fertilisers. Plants require only small amounts of micronutrients, which can be supplied by the soil in most cases. However, micronutrient deficiencies have frequently been reported for SSA.

Already several decades ago, it was reported that soil micronutrient levels in SSA are too low to sustain good crop production (Kang and Osiname, 1985; Sillanpää, 1982; Sillanpää and Vlek, 1985; White and Zasoski, 1999). More recent studies, based on the results of large-scale field trials, have also suggested that availability of secondary and micronutrients constrain crop production in large parts of SSA (Kihara et al., 2017, 2016; Wortmann et al., 2019). In addition, based on available soil maps, Vanlauwe et al. (2015) conclude that deficiencies of multiple secondary and micronutrients are common in SSA. Other evidence comes from a different field: human health. The micronutrient zinc (Zn) is not only essential for plants, but also for humans. An estimated 40% of the

African population is deficient in Zn, which is associated with the occurrence of several diseases, growth and developmental issues and cognitive problems (Das and Green, 2016; Joy et al., 2014). The low Zn intake in the SSA population can partly be attributed to the fact that the crops that are consumed grow on soils which have low levels of available Zn (Alloway, 2008; de Valença et al., 2017).

Despite abovementioned studies, it remains unclear which micronutrients are yield-limiting at which locations in SSA and in particular which soil parameters are associated with these deficiencies. As a consequence, micronutrients are not included in blanket fertiliser recommendations. Of the several micronutrients essential for plant growth, soil availability of zinc and boron (B) is considered the most problematic throughout SSA (Kang and Osiname, 1985). To close existing yield gaps, fertiliser recommendations therefore have to be developed for Zn and B. Chemical soil testing can play an important role in deriving fertiliser recommendations for these micronutrients.

3. Soil analysis

3.1. Soil nutrient pools

Soil nutrients are present in different pools or fractions: in the soil solution, reversely bound to the soil solid particles and fixed (Harmsen et al. 2005; Figure 1). The nutrients present in the soil solution, also called the actually available pool, are directly available for plant uptake. The labile or reactive pool comprise nutrients reversely bound to the soil solid particles. The labile pool is in equilibrium with the actual available pool, through adsorption/desorption and precipitation/dissolution processes, which are strongly governed by soil pH (Groenenberg et al., 2017). The combined labile and solution nutrient pool can be regarded as the nutrients that become available for plant uptake during a growing season, i.e., the potential availability. The fixed pool consists of nutrients present in primary minerals as well as occluded in secondary minerals (Groenenberg et al., 2017). Plants cannot take up nutrients from this pool, as this pool only becomes available through weathering, which is a slow process.

The world of soil testing is complex and not harmonised. Globally, various extraction methods are used to analyse the different soil nutrient pools. The actual availability of nutrients is often approximated using mild extractions with water or diluted salts, such as 0.01 M $CaCl_2$ (Degryse et al., 2009; Houba et al., 2000). A wide range of soil extraction methods are used as a proxy for the potentially available pool, depending on the nutrient and soil. For example, the potentially available P pool is assessed through extraction with

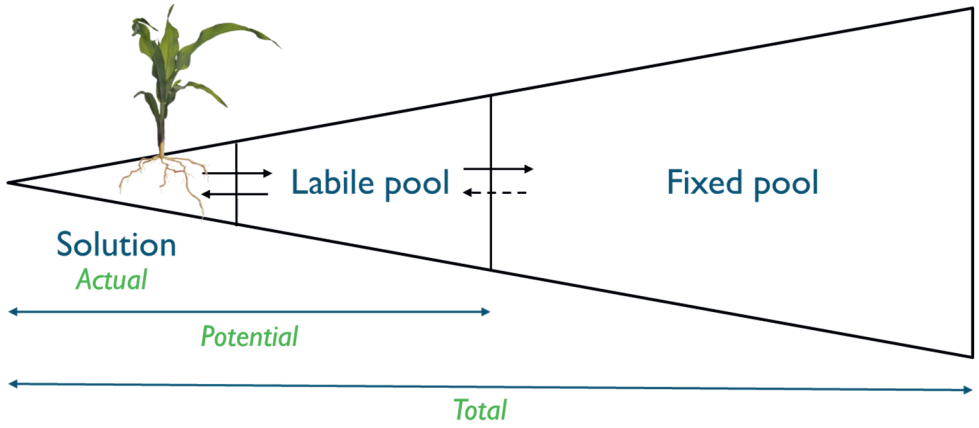


Figure 1: Schematic overview of the soil nutrient pools. After Mengel et al. (2001).

0.5 M $NaHCO_3$ (P-Olsen), ammonium oxalate or mixtures of chemicals such as the Mehlich 3 (M3) or Bray methods (Wuenscher et al., 2015). The potential available pool of K and other cations is determined using 1 M NH_4-acetate, M3, KCl or $BaCl_2$ (Alva, 1993; Amacher et al., 1990). Similar to macronutrients, a variety of soil tests exist for estimating the potentially available pool of micronutrients. For example, zinc and copper are commonly extracted with either DTPA, EDTA, M3, 0.1 M HCl or 0.43 M HNO_3 (Groenenberg et al., 2017; Pradhan et al., 2015; Tandy et al., 2011). The potential availability of boron is assessed with hot water, hot 0.01 M $CaCl_2$ and mannitol extractions, among others (Degryse, 2017). The total soil nutrient pool is quantified using the aqua regia method or X-Ray Fluorescence (XRF) technologies. This total pool is of limited relevance for plant growth as these nutrients are fixed (Marschner and Rengel, 2011) and is thus not often determined in routine analysis.

3.2. **Bioavailability**

A soil test value should give an indication of nutrient bioavailability. However, bioavailability and its quantification are not clearly defined (Harmsen et al., 2005; Kim et al., 2015). From a chemical perspective, bioavailability is operationally defined as the actual availability (i.e. nutrients in the soil solution) or the potential availability (a combination of the solution and labile pool; Figure 2), depending on the field of study (Harmsen et al., 2005). These bioavailability pools are quantified through several soil tests, which give an indication of the specific nutrient pools at a given time. From a biological perspective, bioavailability usually is defined in terms of uptake by organisms (Harmsen et al., 2005). As uptake reflects nutrient accumulation in a given time period, this can be considered to be a good measure of bioavailability on timescales relevant for ecological processes, such as crop growth.

Ideally, plant nutrient uptake relates well to chemical soil indicators. Relations between soil test values and plant uptake may be poor when yield is limited by factors other than the availability of the particular nutrient. For example, if biomass production of a crop is severely limited because of N deficiency, this will depress uptake of other nutrients such as P and hence no good relations between P uptake and P soil tests will be found. Throughout this thesis, bioavailability is therefore defined and quantified as the amount of a nutrient taken up in an entire growing season, when this nutrient is yield-limiting (Janssen et al., 1990). When a nutrient is yield-limiting, the maximum amount of this nutrient that a soil can supply, will be taken up by a crop.

Textbox 1: Definition of nutrient bioavailability

"Bioavailability equals the amount of a nutrient taken up in an entire growing season, when this nutrient is yield-limiting"

Bioavailability, according to the definition of Textbox 1, can be evaluated through nutrient omission trials (Dobermann et al., 2003). In these trials, a crop is subjected to several fertiliser treatments. In the control treatment, the crop is supplied with all nutrients that are potentially yield-limiting. Omission treatments are similar to the control, but the nutrient of interest is not fertilised. If all other growing conditions are optimal (i.e. water availability, limited pressure by weeds, pests and diseases, etc.), the nutrient omitted from the control treatment is expected to be the yield-limiting factor, which should translate into a lower yield compared to the fertilised control.

3.3. Crop response curves

Fertiliser recommendations are typically based on crop response curves. To derive these curves, data from nutrient omission field trials can be used. The relative yield of the nutrient omission treatment compared to the fertilised control is plotted against soil test values that are considered to be a proxy for bioavailability of the nutrient of interest (Figure 2). Using this method, several classes can be identified. When the soil test value is low, fertilising with the specific nutrient will lead to a large increase in yield. Medium soil test values indicate that the crop yield likely still responds to fertilisation, but to a lesser extent compared to fertilising at low soil test values. When the soil test value is high, i.e. above the critical concentration, fertilisation will not increase yields further. Extremely high soil test values (not presented in Figure 2), can be associated with a decrease in the relative yield, due to toxicity.

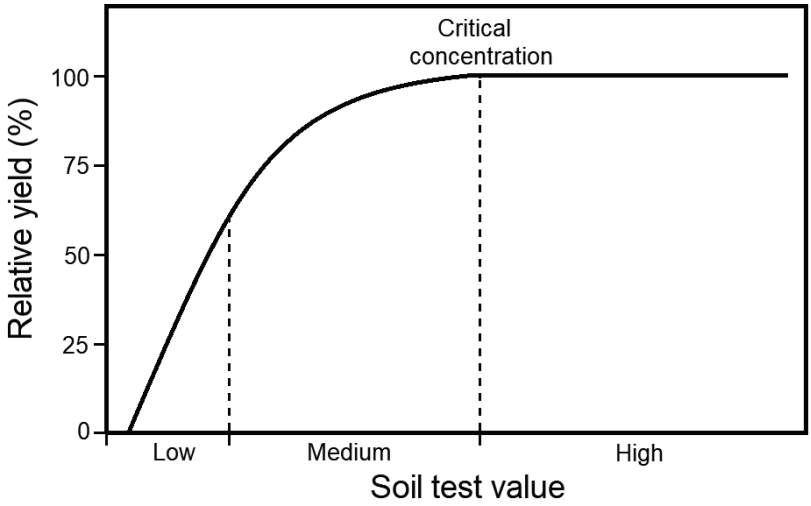


Figure 2: Schematic example of the yield response to fertiliser application as dependent on the soil test value.

Besides differences among nutrients and crops species, crop response curves and corresponding critical soil test concentrations differ among soil types (cf. Lindsay and Norvell 1978; Gupta et al. 1985; Farina et al. 1992; Bell 1997; Bai et al. 2013). For a given soil test, critical soil concentrations below which fertilisation is recommended, depend on e.g. soil texture or pH (Correndo et al., 2021; Jordan-Meille et al., 2012; Steinfurth et al., 2022). Consequently, to provide reliable fertiliser recommendations, these curves should be derived for a large range of crops grown on a wide range of soil types and under various climatic conditions. The interpretation of soil test results furthermore is complicated by the various extraction methods employed to estimate soil nutrient pools. Although results of different soil test can correlate well, relations may differ depending on other soil properties (Buondonno et al., 1992; Hanlon and Johnson, 1984; Seth et al., 2017; Sharpley, 1989). This implies that critical concentrations in one soil extraction method cannot simply be converted to critical concentrations in another and that the curves describing the crop response to fertilisation need to be derived separately for each soil testing method (Harmsen et al., 2005).

Soil testing for deriving fertiliser recommendation has several limitations. First, a single soil test may not be a good proxy for nutrient bioavailability, which is affected by multiple soil properties. Indeed, large variation is observed in the degree to which soil test values describe nutrient uptake, depending on extraction methods and soils (Aitken et al., 1987; Doll and Lucas, 1973; Joshi et al., 2014; Seth et al., 2017; Wuenscher, 2013). In addition, several authors have shown that inclusion of other soil properties, such as pH, improve relations between soil test values and plant nutrient uptake or

concentrations (Duffner et al., 2013; Seth et al., 2017; Sillanpää, 1982; Janssen et al., 1990). Secondly, measuring soil micronutrient availability in tropical soils is quite challenging because of the relatively low concentrations and related risks of contamination during lab analysis (Lindsay and Cox, 1985; Wendt, 1995). As a consequence, micronutrient concentrations can be below detection limits of the particular extraction method and generally available analytical equipment in soil testing laboratories. Analysis of micronutrient availability in tropical soil therefore requires the use of advanced analytical equipment and specialised laboratories. Furthermore, there is no consensus about which soil test is the most suitable for analysing availability of micronutrients (Duffner et al., 2013; Giller and Zingore, 2021).

Soil test values can be used to derive fertiliser recommendations of one nutrient at a time. However, when a soil test value indicates that availability of a given nutrient is suboptimal, fertilisation may not increase yields when another nutrient is even more yield-limiting. Fertiliser recommendations should thus be based on more than bioavailability of a single nutrient. In addition to soil tests and crop response curves, models can play an important role in predicting the interacting effects of bioavailability of multiple nutrients on yields. One of the models that is able to generate fertiliser recommendations, taking availability of several nutrients into account, is the QUantitative Evaluation of the Fertility of Tropical Soils (QUEFTS) tool.

4. QUEFTS

4.1. Rationale

QUEFTS is a widely-used model that can be used to predict yields and the yield response to fertilisation (Janssen et al., 1990; Sattari et al., 2014). Although originally developed for maize grown in western Kenya, the model has been calibrated and validated for various crops and regions (Das et al., 2009; Ezui et al., 2017; Shehu et al., 2019; Tabi et al., 2008; Xu et al., 2013). QUEFTS has two important assets. Firstly, bioavailability of N, P and K is described as a function of multiple soil properties, rather than based on a single soil test value. As a result, these functions can theoretically be applied to a wide range of soils. Secondly, QUEFTS is unique in taking interactions among nutrients into account. Several studies have shown that QUEFTS can be used adequately to derive balanced fertiliser recommendation of N, P and K (Maiti et al., 2006; Mesfin et al., 2021; Xu et al., 2013). Furthermore, fertiliser recommendations generated with tools based on the QUEFTS methodology, have been shown to increase yields, fertiliser use efficiency and profits for farmers in SSA (Chivenge et al., 2022).

4.2. **Model description**

QUEFTS requires four input parameters: soil pH (H_2O), soil organic carbon content (SOC), P content measured in an Olsen extract (P-Olsen) and content of exchangeable K measured in a neutral 1 M ammonium acetate extract (Exch-K). QUEFTS output is calculated in four steps (Figure 3).

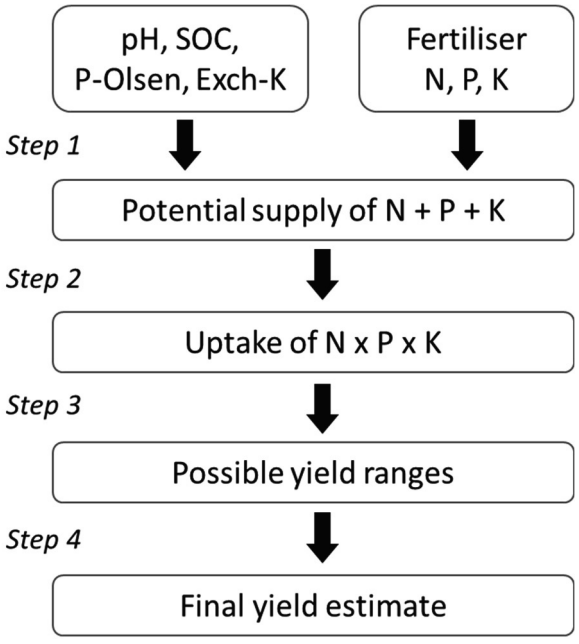


Figure 3: Schematic overview of QUEFTS, after Sattari et al. (2014)

In Step 1, the potential supply (i.e. bioavailability) of N, P and K are calculated based on the four soil chemical parameters (soil supply), as well as N, P and K applied through fertilisation (fertiliser supply). The supply functions describe availability of N as a function of SOC and pH, availability of P as a function of SOC, pH and P-Olsen and availability of K as a function of SOC, pH and Exch-K (Textbox 2). Availability of P and K increase with P-Olsen and Exch-K, respectively. The SOC and pH parameters have different effects on the availability of the three nutrients.

Textbox 2: QUEFTS soil supply functions (Janssen et al., 1990)

Supply N = *f*N*6.8*SOC	**with *f*N = 0.25*(pH – 3)**
Supply P = *f*P*0.35*SOC + 0.5*P-Olsen	**with *f*P = 1 - 0.5*(pH-6)^2**
Supply K = $\frac{fK*400*\text{Exch-K}}{2+0.9*SOC}$	**with *f*K = 0.625 (3.4 - 0.4*pH)**

In Step 2, interactions among N, P and K are taken into account, by estimating the uptake of a given nutrient based on its supply, as well as on the supply of the other two nutrients. This is based on the observation that uptake of a nutrient may not further increase despite high soil availability in case another nutrient is limiting crop growth. In Step 3, with a given uptake, the minimum and maximum yields are calculated, using crop physiological limits. Then in Step 4, based on these yield ranges, six yield estimates are derived based on uptake of two nutrients (i.e. N and P, N and K, P and N, P and K, K and N, K and P). The average value of these six yield estimates is then taken as the final yield estimate.

4.3. Extending application of QUEFTS

The QUEFTS yield estimate is valid under the assumption that yield is a function of availability of N, P and K and thus not limited by other factors such as soil depth, water availability, presence of pests and diseases, as well as availability of other nutrients (Janssen et al., 1990). Given the potential of using QUEFTS for deriving balanced fertiliser recommendations, it is relevant to know when and where micronutrient availability is limiting yields, as QUEFTS predictions will correspond poorly to reality in these locations. Models describing bioavailability of micronutrients can be a useful tool for this.

Using the QUEFTS approach, supply functions similar to the ones for N, P and K (Textbox 2) could be derived for micronutrients Zn and B. These functions likely include soil parameters that are known to affect micronutrient availability in addition to a soil test describing relevant nutrient pools. To date, hardly any attempts have been made to derive such supply functions. Often, models are derived that predict plant concentrations rather than uptake (e.g. Gunkel et al., 2004; Jin et al., 1988; Sillanpää, 1982), which is mostly relevant from the perspective of toxicity. Although a number of studies have focussed on plant uptake (e.g. Aitken et al., 1987; Das et al., 2009; Duffner et al., 2013; Maiti et al., 2006; Seth et al., 2017), most of these studies used pot experiments, with the exception of Das et al. (2009) and Maiti et al. (2006). Generally, results from pot experiments cannot be extrapolated to the field (de Vries, 1980).

Supply functions for Zn and B could provide valuable insights into soil parameters and combinations of soil parameters associated with Zn and B deficiency in crops. These models can help to assess the need for micronutrient fertilisers as well as yield benefits to expect from fertilisation. The information derived from these models can be used to complement QUEFTS NPK recommendations.

In addition to models describing bioavailability/supply of Zn and B, high resolution soil maps present a source of potentially relevant information for developing fertiliser recommendations (Chivenge et al., 2022; Vanlauwe et al., 2015). Digital soil mapping has taken a flight since the beginning of the 21st century (Arrouays et al., 2020). These maps are a relatively low-cost source of soil information that provide estimates of uncertainty and can be easily updated (Arrouays et al., 2020). Several digital soil maps of macro-, secondary and micronutrients, as well as general soil properties have been developed for SSA at 250m spatial resolution (Hengl et al., 2017, 2015). These maps could be used as input for the micronutrient bioavailability functions, for broad assessment of regions where fertilisation with micronutrients could be beneficial for closing yield gaps. Furthermore, soil maps can be used as input for QUEFTS to generate regional fertiliser NPK recommendations, which can be used as a more specific alternative for the general national blanket fertiliser recommendations.

5. Thesis objectives and outline

Tailoring fertiliser recommendations is indispensable for sustainably increasing yields in SSA. In order to develop balanced fertiliser recommendations, cost-effective tools are needed for predicting nutrient availability and the yield response to fertilisation, taking interactions among nutrients into account. The general objective of this thesis therefore is to develop and evaluate models for predicting soil nutrient availability and to increase the understanding of the interactive effect of nutrient availability on crop yields and nutritional quality in sub-Saharan Africa.

Textbox 3: General objective

"Developing and evaluating models for predicting soil nutrient availability and increasing understanding of the interactive effect of nutrient availability on crop yields and nutritional quality in sub-Saharan Africa"

The focus of this thesis will be on availability of macronutrients N, P and K as well as micronutrients Zn and B. To address the general objective, several methods are used, including soil statistical modelling, soil mapping and micronutrient fertiliser omission field trials. The QUEFTS model and its underlying principles are an important component of this thesis. A framework for this thesis is given in Figure 4.

The **first objective** of this thesis is to evaluate a spatial application of the QUEFTS model. As soil testing for obtaining field-specific fertiliser recommendations currently is not widely (financially) accessible for smallholder farmers, low-costs alternatives are needed, such as soil maps. Although QUEFTS can be used to predict nutrient availability and develop fertiliser recommendations with field-specific information, it is unknown how well the model performs when applied spatially and which method of spatial application leads to the most reliable results. To address this objective, available soil maps are used as input for the QUEFTS model as an alternative to direct soil measurements. The M3 extraction method is commonly used and as a consequence, available soil maps are typically based on this method. However, QUEFTS requires P-Olsen and Exch-K parameters as input for predicting available of P and K and not M3. Therefore, in **Chapter 2**, transfer functions are derived that relate P-Olsen and Exch-K to P and K extracted by the M3 method. This will be done by exploring extraction mechanisms of the different methods, identifying soil properties relevant for describing the relations and deriving the relations using linear regression on a dataset comprised of soil sample information from a wide range of tropical soils. Then in **Chapter 3**, using the transfer functions derived in Chapter 2 and digital soil maps of Rwanda, two methods are explored to predict QUEFTS maize yield and yield-limiting nutrient estimates on a spatial scale.

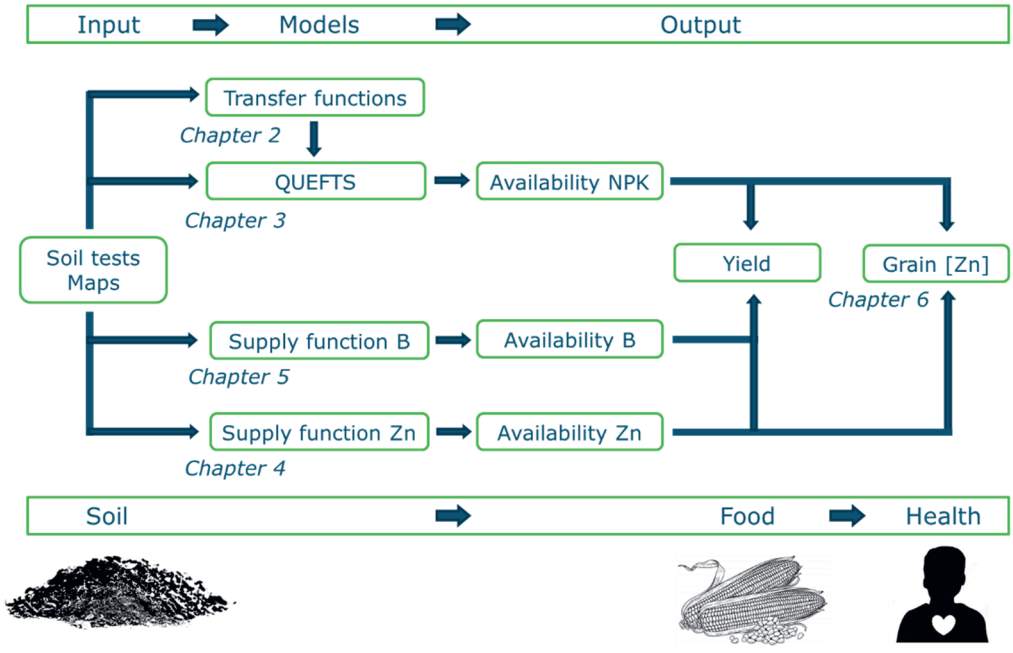


Figure 4: Framework for this thesis. (Image courtesy: www.freepik.com)

Correcting deficiencies of N, P and K through fertilisation is ineffective as long as other nutrients are yield-limiting. Although there are indications that micronutrients Zn and B are limiting yields in SSA, fertiliser recommendations are constrained by (1) analytical challenges measuring low micronutrient concentrations and (2) the lack of a proper soil test for evaluating bioavailability. The **second objective** of this thesis therefore is to derive generic models describing bioavailability of micronutrients zinc and boron based on soil parameters than can be measured in routine analysis. To derive these models, data from micronutrient fertiliser omission trials with zinc and boron, from three countries in SSA, will be used. Field trial locations were selected based on the suspicion of low micronutrient bioavailability. In the omission treatments, micronutrient availability is expected to be the yield-limiting factor. Following the definition of bioavailability as specified in Textbox 1, plant uptake in the omission treatments is expected to provide a good estimate of the amounts of micronutrients that soils can provide to the crop during an entire growing season. **Chapter 4** focusses on bioavailability of zinc and **Chapter 5** on boron. In both chapters, plant uptake will be related to different soil micronutrient pools assessed with several extraction methods and other general soil properties that can be measured easily and at low costs, similar to the QUEFTS supply functions for N, P and K (Textbox 2).

Zinc fertilisation can potentially increase Zn concentrations in the edible parts of plants, thereby benefitting human health. Therefore, the **third objective** of this thesis is to assess the effect of zinc availability, in combination with availability of other nutrients, on maize yield (quantity) and grain Zn concentrations (nutritional quality). In **Chapter 5**, zinc concentrations in maize grains as well as the response in these concentrations to zinc fertilisation will be modelled based on several soil properties, including zinc extracted with various methods. To this end, data from the micronutrient fertiliser omission trials are used. In **Chapter 6**, the relation between zinc availability and grain zinc concentrations is placed in a broader context, taking into account the availability of other nutrients, as well as other agronomic practices. This chapter is based on the micronutrient fertiliser omission trials, in combination with data from field trials in SSA with different designs.

In **Chapter 7**, the objectives of this study are addressed by placing the main findings of chapters 2 to 6 into a broader context. Practical implications of the findings, limitations of this study and recommendations for further research are also presented. In addition, I will elaborate on two topics related to the work in this thesis which deserve more attention in the scientific community, in my opinion. The first topic regards the harmonisation and standardisation of soil testing methods. For the second topic, I will

review literature evidence for large-scale problems with soil micronutrient availability in SSA and discuss to what extent micronutrient fertilisers can contribute to closing existing yield gaps.

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Chapter 2

Transfer functions for phosphorus and potassium soil tests and implications for the QUEFTS model

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Abstract

Multi-element soil extractions such as Mehlich 3 (M3) have gained popularity in recent years, but comparing outcomes to other soil testing methods is not always straightforward. In this study, extraction mechanisms of M3, Olsen and neutral 1 M ammonium acetate (AA) soil tests were explored and transfer functions were derived between P-Olsen and P-M3 as well as between K-AA and K-M3. Soils from tropical and temperate areas were used to derive these P and K transfer functions and were evaluated separately. The application of these transfer functions for tropical soils was evaluated by using them as input for the Quantitative Evaluation of the Fertility of Tropical Soils (QUEFTS). AA and M3 generally extracted similar amounts of K, but relations between K-AA and K-M3 were different for tropical and temperate soils. For tropical soils, the transfer function did not require additional parameters besides K-M3 to predict K-AA, but for temperate soils inclusion of clay content and pH was needed. This difference between tropical and temperate soils was explained by clay mineralogy. The relation between P-Olsen and P-M3 in tropical soils was found to be dependent on pH, Al-M3, Fe-M3 and Ca-M3. P-Olsen and K-AA values, calculated with their respective transfer functions, were used as input for QUEFTS. The yields predicted with measured P-Olsen and K-AA were used as benchmark. For 63 out of 81 soil samples, predicted maize yields with transfer functions deviated less than 10% from the benchmark. The largest deviations from the benchmark were found for low P-Olsen and K-AA values, which corresponds to QUEFTS maize yield predictions up to 3000 kg ha^{-1}. We conclude that M3 extraction results and soil pH can reliably be transferred to, and thus replace P-Olsen and K-AA determinations with the functions developed for tropical soils. The transfer functions can be used to generate input for the QUEFTS model with minor effects on yield predictions, thus expanding its applicability in cases where only M3 extraction results are available.

1. Introduction

Multi-element soil extractions have gained popularity in recent years. Their convenience and lower costs make them more attractive than the use of separate single element extractions (Iatrou et al., 2014). Mehlich 3 (M3) is a multi-element extraction employed in several parts of the world (Wuenscher et al., 2015). The M3 extraction contains a combination of chemicals (CH_3COOH, NH_4NO_3, NH_4F, HNO_3 and EDTA) designed to extract both macro- and micronutrients, among which phosphorus (P) and potassium (K). Single element extraction methods, such as Olsen, Bray, H_2O and $CaCl_2$, have been developed to quantify available soil P pools (Wuenscher et al., 2015), whereas plant available or exchangeable K and other cations have commonly been estimated using 1 M ammonium acetate (Barbagelata, 2006).

Soil extraction methods are based on different mechanisms and vary in their extraction efficiency (Wuenscher et al., 2015). Ultimately, soil nutrient test results should relate to bioavailability, i.e. the amount of a nutrient available for plant uptake over a growing season. They are also used as input for decision support tools such as the Quantitative Evaluation of the Fertility of Tropical Soils (QUEFTS) model, which requires P-Olsen and K determined by a 1 M ammonium acetate extraction to estimate the soil's capacity to supply a crop with P and K (Janssen et al., 1990). P-Olsen and Exch. K extraction methods are not always routinely measured however, as other extraction methods such as M3 are more commonly employed in many countries (Wuenscher et al., 2015). Comparing the results of different soil testing methods is often not straightforward and requires transfer functions that include specific soil properties to translate the outcome of one soil test into another. Exploring the mechanisms behind soil extraction methods is needed to understand, describe and effectively apply relations between the nutrient pools measured by the different soil extractions. The focus in this study will be on comparing P and K in M3 to P-Olsen and K in ammonium acetate extractions, respectively.

The mechanisms for extracting soil K are similar for the 1 M ammonium acetate (AA) and M3 extraction methods. Extraction solutions differ considerably in pH (2.5 for M3 *vs* 7.0 for AA) and shaking time (5 min for M3; variable shaking times for AA), but both methods use high concentrations of NH_4^+ (0.25 M for M3 *vs* 1 M for AA) and a similar solution-to-solid ratio (SSR) of 10 L kg^{-1} to displace exchangeable cations such as K from soil surfaces. For M3, H^+ ions present at the extraction solution pH of 2.5, can displace additional cations. Relations between K-AA and K-M3 have previously been derived in various studies. The transfer functions between K-AA and K-M3 that were reported in literature (Table S1) show that regression slopes vary between 0.54 and 1.54

across studies. In each study, K-M3 was the only variable used to explain K-AA and the regressions showed an average R^2 value of 0.95, indicating K-M3 explains a substantial part of the variation in K-AA. The large variation in regression slopes, however, imply limitations for generic application among different soil taxonomic classes.

For P extraction, Olsen and M3 are based on contrasting mechanisms. The high concentration of bicarbonate in the Olsen extraction, buffered at pH = 8.5, leads to extraction of phosphate through (1) precipitation of Ca as $CaCO_3$, thereby releasing Ca-bound phosphates, and (2) displacement of phosphate from the soil surfaces by increased competition with HCO_3^-, CO_3^{2-} and OH^- anions (Olsen et al. 1954).

M3 extracts P through two mechanisms, namely dissolution and complexation reactions. The high acidity of the extract (pH = 2.5) causes dissolution of Ca-P precipitates and of P bound to Al/Fe (hydr)oxides (Penn et al., 2018). At a solution pH of 2.5, the presence of NH_4F promotes the release of P from Al (hydr)oxides through Al-F complex formation. The pH of the M3 extraction solution increases throughout during the procedure, its increase depending on soil pH (Penn et al., 2018). When the solution pH of M3 increases above 2.9 during the extraction procedure, fluoride also complexes Ca, thereby facilitating the release of P from Ca-P precipitates (Penn et al., 2018). Phytates, the largest pool of organic P, are desorbed from Al and Fe oxide surfaces and solubilised through protonation (Penn et al., 2018; Wang et al., 2017). The amount of organic P extracted with M3 can vary strongly from soil to soil (Iatrou et al., 2014; Mallarino, 2003; Pittman et al., 2005). Weak but significant correlations were found between the amount of organic P in a M3 extraction and pH (R^2 = 0.32) and organic carbon (R^2 = 0.16) (Mallarino, 2003).

Besides a difference in composition and contrasting P extraction mechanisms, the Olsen and M3 methods also differ in shaking time (5 minutes for M3 *vs* 30 minutes for Olsen), although in both methods no chemical equilibrium is reached (Olsen et al., 1954; Penn et al., 2018). An additional difference is the P species that are measured in the extracts. In the M3 extraction, often multiple elements are determined, using inductively coupled plasma – optical emission spectroscopy (ICP-OES) (Penn et al., 2018). As a result, total dissolved P (including organic P) in the extractant is measured. The standard Olsen extraction procedure includes a molybdate blue colorimetric determination of ortho-phosphate (ISO 11263, 1994; Olsen et al., 1954). Although certain kinds of organic P molecules can also be determined by colorimetric methods (Baldwin, 1998; Van Moorleghem et al., 2011), it is assumed that P-Olsen represents the inorganic P pool.

The transfer functions that have been reported in literature to predict P-Olsen based on P-M3 alone, show a fivefold variation in regression slopes, which range between 0.14 and 0.70 across studies (Table S2). The average R^2 value across studies is 0.74, but shows more variation compared to the K transfer functions, as R^2 values between 0.45 and 0.94 are reported. These findings indicate that also for P extractions, transfer functions derived on one soil set may not be applicable to another. Several studies furthermore have shown that inclusion of additional soil properties such as pH, $CaCO_3$ content, organic matter, Fe and Al can improve relations between P-Olsen and P-M3 (Buondonno et al., 1992; Elrashidi et al., 2003; Iatrou et al., 2014; Schick et al., 2013; Sen Tran et al., 1990). In addition, categorization of soils based on pH and $CaCO_3$ content has resulted in different transfer functions for each category (Iatrou et al., 2014; Sen Tran et al., 1990) with a higher goodness-of-fit (R^2) compared to models fitted on the entire dataset (Buondonno et al., 1992; Zbiral and Nemec, 2002; Table S2).

The above review of transfer functions between P-Olsen and P-M3 and between K-AA and K-M3 shows that P and K transfer functions mostly have been derived for soils from temperate regions such as North America and Europe (Table S1 and Table S2). Due to prolonged weathering, soils from tropical climatic regions generally differ from temperate soils in properties such as clay mineralogy and types and amounts of Fe and Al hydroxides (De Campos et al., 2018), which are known to affect P and K availability and may exert significant influence on relations among soil P and K tests (Buondonno et al., 1992; Sharpley, 1989). As a consequence, transfer functions that have been developed based on temperate soils may not be applicable to soils from tropical areas. The first aim of this study, therefore, was to develop P and K transfer functions for soils from (sub)tropical regions. We compared these with transfer functions for temperate soils. The second aim of this work was to evaluate the application of the transfer functions for tropical soils. To this end, P-Olsen and K-AA values, estimated based on M3 data with the developed transfer functions, were used as input for QUEFTS and compared with yields predicted with measured P-Olsen and K-AA values as the benchmark.

We hypothesize that K-M3 will be the only parameter needed to explain K-AA, but that the relation between P-Olsen and P-M3 requires additional variables. As the partitioning of total soil P in the soil solution is highly pH dependent (Sims and Pierzynski, 2005) and soil pH affects P extraction efficiency of Mehlich 3 (Penn et al., 2018), we expect that soil pH will be an important factor in explaining the relation between P-Olsen and P-M3. Due to their contrasting mechanisms, M3 and Olsen are expected to extract different amounts of P bound as Ca-phosphates and adsorbed to Al and Fe

(hydr)oxides. We therefore hypothesize that Al, Fe and Ca in M3 can describe additional variation in the relation between P-Olsen and P-M3. We expect that organic carbon (C_{org}) can potentially also play a role in the P transfer function as organic P is determined in M3 extractions, but to a limited extent in Olsen. Finally, we expect that the uncertainty associated with predictions of P-Olsen and K-AA using the transfer functions will have an acceptable effect on yield predictions by the QUEFTS model, as C_{org} and pH are the most important determinants of the predicted yields (Janssen et al., 1990).

2. Materials and Methods

2.1. Data availability

Three sets of soil samples and soil data were used for deriving the transfer functions. The first set consisted of 90 top soils (0-20 and 0-30 cm) that were sampled in several countries in sub-Saharan Africa, including Burundi, Congo, Ethiopia, Gabon, Kenya and Zambia. Soil properties of these samples were analysed for the purpose of this study (see section 2.2). The second dataset was a subset of the World Soil Reference Collection (WSRC, 2020) of the International Soil Reference and Information Centre (ISRIC). From the WSRC, 51 soil samples from Ghana, Indonesia, Suriname and Russia were selected that included the required analytical data. The third dataset consisted of soil data from the Wageningen Evaluating Programmes for Analytical Laboratories (WEPAL, 2020). The WEPAL data were generated by several laboratories participating in this evaluation program. Laboratories remained anonymous as WEPAL only provided mean values and standard deviations for each soil parameter. The WEPAL dataset included analytical data from 81 soils, originating from several African, South East Asian and European soils.

Both the WSRC and WEPAL datasets contained information on P-Olsen, pH-H_2O, C_{org}, K-AA and P, K, Al, Ca and Fe in M3. Additional soil data, such as clay content, $CaCO_3$ and Fe and Al measured in acid ammonium oxalate (AO), were also part of these datasets.

2.2. Soil analysis

Soil samples

The soil samples from Burundi, Congo, Ethiopia, Gabon, Kenya and Zambia that were obtained, were air-dried and passed through a 2 mm sieve before chemical analysis. Soil

pH was measured in a suspension of the soil in water, prepared at a solution-to-solid ratio (SSR) of 2.5 L kg^{-1} and after shaking for 2 h on a linear shaker at 180 strokes min^{-1}. For C_{org} determination, soil samples were colloid grinded (50 μm) before analysis (NEN-16179, 2012). C_{org} was then determined spectrophotometrically at 585 nm after chromic acid wet oxidation (Heanes, 1984). To determine P-Olsen, 2.5 g of soil was extracted with 50 mL of a freshly prepared solution of 0.5 M $NaHCO_3$ (pH = 8.5), followed by shaking in a horizontal shaker at 180 strokes min^{-1} for 30 min. After filtration over a Whatman 110 mm filter paper, a subsample was diluted 5 times with 0.15 M HCl and placed in an ultrasonic bath to remove excess CO_2. Afterwards, the inorganic P concentrations were determined with the molybdenum-blue method (Kuo, 1996) and measured by a fully automated segmented flow analyser (SFA). Exchangeable K was extracted by adding 20 mL of a freshly prepared solution of 1 M NH_4 acetate (pH = 7.0) to 2 g of soil and shaking for 2 h in a horizontal shaker at 180 strokes min^{-1}. After extraction, suspensions were centrifuged for 15 min at 3000 rpm and filtered with a Whatman 110 mm filter paper. A subsample was taken and diluted 5 times with 0.14 M HNO_3 for measurement of K on ICP-OES. The shaking time of 2 h for the K-AA extraction was chosen in correspondence with the extraction time of the percolation method, that was originally used for calibration of QUEFTS (Houba et al., 1995; Van Reeuwijk, 2002). For 18 soil samples, we compared extractable K by using both the percolation method and the batch extraction procedure as described above and no significant differences in the amount of K were observed (data not presented). A M3 extraction solution was freshly prepared as a mixture of 0.2 M CH_3COOH, 0.25 M NH_4NO_3, 0.015 M NH_4F, 0.013 M HNO_3 and 0.001 M EDTA. The pH of the extraction solution was adjusted to 2.5 using concentrated HNO_3. The samples were extracted at a SSR of 10 L kg^{-1} and shaken for 5 minutes in a horizontal shaker at 180 strokes min^{-1} (Mehlich, 1984). Afterwards, suspensions were passed through a Whatman 110 mm filter paper, diluted 10 times with 0.14 M HNO_3 and analysed for P, K, Al, Ca and Fe on ICP-OES.

WSRC soils

The soil samples in the WSRC dataset were analysed between 2017 and 2019 by the Kellogg Soil Survey Laboratory in Lincoln, Nebraska, USA (USDA, 2014). Analyses were performed on air-dried samples that were passed through a 2 mm sieve. Soil pH was determined in water at a SSR of 1 L kg^{-1} after an extraction time of 1 h (USDA, 2014; p. 276). C_{org} was calculated as the difference between $CaCO_3$ and total C of a given soil. Total C was determined in the soil fraction < 180 μm with an elemental analyser (USDA, 2014; p. 464). $CaCO_3$ was only determined in samples with a pH-$CaCl_2$ > 6.95. After addition of 3 M HCl, samples were placed in a rotating shaker for 10 min

at a rate of 140 rpm. The samples were shaken again at the last 10 min of a 1h interval. Bottle stoppers were pierced with a hypodermic needle connected to a manometer to measure CO_2 development. The amount of carbonate was then calculated as percent $CaCO_3$ (USDA, 2014; p. 370). P-Olsen was determined in 1 g soil extracted with 20 mL of 0.5 M $NaHCO_3$ at pH 8.5. After shaking for 30 min at 200 oscillations min^{-1}, samples were centrifuged at 2000 rpm for 10 min. The P concentration was then determined spectrophotometrically after adding molybdenum-blue colour reagent to an aliquot of the centrifuged sample (USDA, 2014; p. 336). K-AA was determined by extracting 2.5g of soil with 50 mL of 1 M ammonium acetate at pH 7.0. Extraction was done with a mechanical vacuum extractor and total extraction time was around 13 hours. Samples were then shaken manually, and a subsample was submitted for analysis on the atomic absorption spectrophotometer (AAS) (USDA, 2014; p. 230). Nutrients in M3 were measured on the ICP-OES after extracting samples at a SSR of 10 L kg^{-1}, shaking for 5 minutes at 200 oscillations min^{-1}, centrifugation for 10 min at 2000 rpm and filtration with a Whatman no. 42 filter (USDA, 2014; p. 345). Fe and Al were determined in ammonium oxalate using a mechanical vacuum extractor and measured on ICP-OES. A quantity of 0.5 g soil was extracted with 50 mL of 0.2 M ammonium oxalate solution buffered at pH 3.0 for a total period of around 13 hours. Afterwards, samples were shaken manually, diluted 10 times with reverse osmosis water, vortexed and submitted for analysis on the ICP-OES (USDA, 2014; p. 432). Clay content was determined using the pipette method (USDA, 2014; p. 48).

WEPAL soils

The soil samples in the WEPAL dataset were analysed by several labs, with potentially different soil-to-solution ratios (SSR) and extraction times for a given soil parameter as method details were not specified.

2.3. Data selection

The soils in this study were categorised based on their geographical location as "temperate" or "tropical". These categories are inexhaustive and soil classification based on climatic zone has been criticised for being non-scientific (Hartemink, 2015). For the majority of soils however, soil taxonomic class and dominant clay mineralogy were not known; classification based on these soil properties therefore was not possible. The aim of this study furthermore was to derive functions that are generally applicable rather than being applicable to certain soil taxonomic classes only. In addition, weathering and climate are important controlling factors in the formation of clay minerals (Grim, 1968); commonalities within the categories of temperate and tropical soils are therefore

expected. Despite its limitations, classification based on climatic zones was therefore considered most suitable for the purposes of this study.

From the WSRC dataset, only soils that were sampled within a depth of 0-60 cm were included, as layers beyond this depth were not considered relevant for agricultural production. Exact sampling location and sampling depth of the WEPAL soils were unknown and no selection based on this criterion was made.

To derive the K transfer functions for tropical and temperate soils, QUEFTS criteria for soil chemical parameters were used to select the soils that were included in the analysis: C_{org} below 70 g kg^{-1} and exchangeable K below 30 mmol kg^{-1} or 1173 mg kg^{-1} (Janssen et al., 1990). The pH limits were set between 4.0 and 8.0, as most agricultural soils will have pH values within this range. After applying the selection criteria to the 114 samples available for tropical soils, a dataset with 101 samples remained (medians: C_{org} = 15.0 g kg^{-1}, pH = 5.61, K-AA = 2.6 mmol kg^{-1} or 103 mg kg^{-1}; Figure S1). K-M3 concentrations in the tropical dataset ranged between 20 and 710 mg kg^{-1}. This dataset included samples from Africa (not specified; n = 1), Burundi (n = 23), Congo (n = 1), Gabon (n = 6), Ghana (n = 7), Indonesia (n = 2), Ivory Coast (n = 3), Kenya (n = 26), Mali (n = 1), Philippines (n = 1), Suriname (n = 2), Thailand (n = 2) and Zambia (n = 26). For temperate soils, a total of 67 out of 86 samples remained after applying the selection criteria: South Africa (n = 1), The Netherlands (n = 41), Russia (n = 17), Spain (n = 1) and Switzerland (n = 7). K-M3 and K-AA concentrations in the temperate dataset ranged between 43-706 and 55-661 mg kg^{-1} respectively.

To derive the P transfer functions for tropical and temperate soils, QUEFTS criteria for soil chemical parameters were used to select the soils that were included in the analysis: C_{org} below 70 g kg^{-1} and P-Olsen below 30 mg kg^{-1} (Janssen et al., 1990). The pH limits were set between 4.0 and 8.0. After applying the selection criteria to the 119 samples available for tropical soils, a dataset with 92 soil samples remained (medians: C_{org} = 14.7 g kg^{-1}, pH = 5.61, P-Olsen = 6.1 mg kg^{-1}; Figure S1). M3 concentrations in the tropical dataset ranged between 0.6-93.5 (P), 215-2114 (Al), 3-3283 (Ca) and 25-1171 (Fe) mg kg^{-1}, respectively. This dataset included samples from Burundi (n = 23), Congo (n = 1), Gabon (n = 5), Ghana (n = 14), Indonesia (n = 2), Ivory Coast (n = 2), Kenya (n = 24) and Zambia (n = 21). For temperate soils, a total of 22 out of 72 samples remained after applying the selection criteria: The Netherlands (n = 5), Russia (n = 13) and Switzerland (n = 4). Mehlich 3 concentrations in the temperate dataset ranged between 3-204 (P), 133-1220 (Al), 101-12335 (Ca) and 67-1703 (Fe) mg kg^{-1} respectively.

2.4. **Statistical analysis**

The P and K transfer functions were developed using R software, version 3.4.4. Results were visualized using the ggplot2 package (version 2.2.1). Models were evaluated using R^2 and root mean squared errors (RMSE). Model residuals were checked for normality, homogeneity and independence.

For the P transfer function, all soil parameters including the dependent variable P-Olsen, except pH, were transformed using the natural logarithm to prevent negative predicted values and to normalise input data. No data transformations were applied for the K transfer function. Before running regressions, input parameters were checked for multicollinearity (vif >4), using the vif function (package usdm, version 1.1-18). After checking for multicollinearity, model selection was done with stepwise regression (forward and backward) using the stepAIC function from package MASS (version 7.3-50) using the Akaike Information Criterion as selection criterion that compromises between goodness of fit and parsimony (Webster and McBratney, 1989). The residuals of the selected model were inspected visually and checked for normality using the skewness function (package e1071, version 1.6-8) and using the Shapiro-Wilk test (function shapiro.test from package stats, version 3.4.4). Homogeneity and independence of residuals was visually evaluated by plotting residuals against fitted values and explanatory variables. The RMSE was retrieved using function rmse from package ModelMetrics (version 1.1.0). The contribution of each soil parameter to R^2 was evaluated using function calc.relimp from package relaimpo (version 2.2-3). Regression outliers were identified by checking Cook's distance (D), which is a measurement to identify data points with a high residual value as well as leverage. Data points were further inspected when D was greater than 0.5.

Ln(P-Olsen) predictions were back-transformed using Equation 1 (Lark and Lapworth, 2012):

Equation 1: prediction = exp(ln-prediction + 0.5*variance)

To test whether the K transfer function was different for temperate and tropical countries, a regression model was fitted to predict K-AA (mg kg^{-1}) values based on K-M3 (mg kg^{-1}), an origin factor (i.e. temperate or tropical) and interaction of both predictors. The function lstrends from the package lsmeans (version 2.30-0) was applied to this regression model in order to test whether origin had an effect on the relation between K-AA and K-M3. Output of the lstrends function consisted of trends (i.e. slopes) per origin as well as the confidence intervals of these trends.

Additional analysis included exploration of the relations between M3 and ammonium oxalate (AO) extraction methods for Fe and Al. The AO extraction is often used as a proxy to measure the micro-crystalline or short-range-order oxide minerals in soils which are considered the most reactive surfaces for adsorption of anions such as PO_4 (Hiemstra et al., 2010; Schwertmann, 1973). The relation between Fe and Al measured in M3 and AO indicates the efficiency of M3 to extract the reactive Fe and Al (hydr)oxides, which in turn could explain the extraction efficiency of P in M3. The soils that contained information on Fe-AO and Al-AO were used to explore relations between Fe-M3 and Fe-AO (n = 55) and between Al-M3 and Al-AO (n = 55).

2.5. Application

To evaluate application of the transfer functions, the QUEFTS model was used. The sensitivity of QUEFTS to deviations between measured and predicted P-Olsen and K-AA values was analysed for this purpose. QUEFTS can be used for the evaluation of soil fertility, potential crop yield and fertilizer recommendations. QUEFTS requires four soil chemical parameters as input, being exchangeable K (K-AA; in mmol kg^{-1}), P-Olsen, pH and C_{org} (Janssen et al., 1990; Sattari et al., 2014). These variables are used to calculate the soil supply of N, P and K (step 1), which is then used to calculate the potential uptake of nutrients by a crop (step 2). The interactions among nutrients define the actual uptake of nutrients (step 3), and the final yield estimate (step 4). Soils that were used to derive both the P and K transfer functions (n = 81) were used as input for QUEFTS. The most recent QUEFTS version for maize was used (Sattari et al., 2014), with potential yield set to 10 Mg ha^{-1}. QUEFTS was run with both measured and predicted P-Olsen and K-AA values. For pH and C_{org}, measured values were used.

3. Results

3.1. K transfer function

The relation between K-AA and K-M3 in tropical soils could be described with a single linear relationship. The best model that was fitted for tropical soils, violated assumptions however, as model residuals were not normally distributed ($p < 0.001$). Further inspection showed one data point with Cook's Distance >1 (encircled in Figure 1). The high residual value of this data point could not be explained by soil pH or C_{org}. This sample was consequently removed for further analysis. After rerunning the regression, K-M3 was the only significant variable for predicting K-AA (Figure 1; Equation 2) and residuals showed a normal distribution (p = 0.567). The model explained 99% of the variation and RMSE was 11.2 mg kg^{-1}.

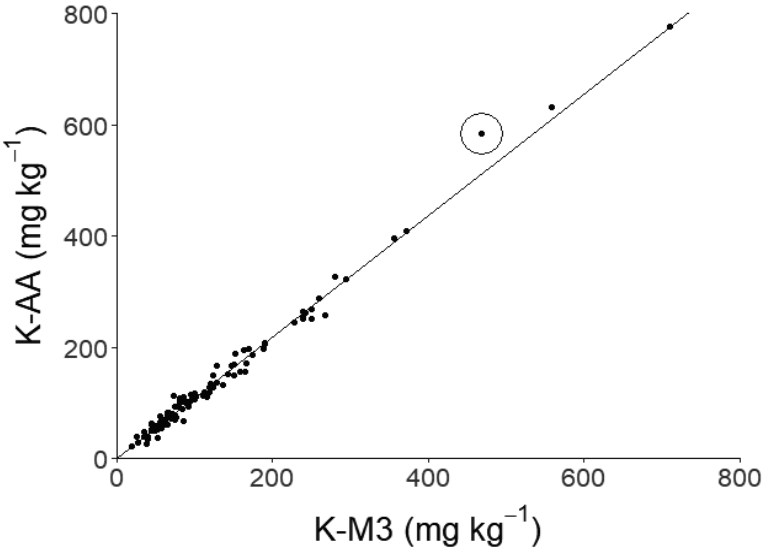

Figure 1: Relation between K extracted with Mehlich 3 (M3) and ammonium acetate (AA) in tropical soils. The line represents the K transfer function. The circled data point was considered an outlier based on Cook's D and was not included in the regression.

Equation 2 (tropical soils): K-AA (mg kg^{-1}) = 0.59 + 1.09*K-M3 (mg kg^{-1})

The K transfer function was found to be dependent on the origin of the soil (Figure 2). In tropical soils, AA extracted significantly more K ($p < 0.001$) than M3 compared to temperate soils. The best model that was fitted for temperate soils selected K-M3, C_{org} and clay content as predictors, but violated assumptions as model residuals were not normally distributed ($p < 0.001$). Further inspection showed two data points with high Cook's D values. The first data point had the highest K-M3, K-AA and C_{org} values, the second data point did not have soil parameters with extreme values. Soil pH could not explain the high residual value of these data points and they were consequently removed from the dataset. Regressions were re-run and the best model that was fitted on temperate soils required K-M3, clay content, C_{org} and pH to explain K-AA. Although residuals were normally distributed ($p = 0.062$), a regression was run without C_{org} as input parameter, as it contributed only 0.3% to R^2. The best model that was fitted without C_{org}, selected K-M3, clay content and pH as predictors (Equation 3). The R^2 of the regression model was 0.996. Residuals showed a normal distribution ($p = 0.498$) and RMSE was 7.70 mg kg^{-1}. K-M3 explained 79% of the R^2 value, clay content 16% and soil pH 6%.

Equation 3 (temperate soils): K-AA (mg kg^{-1}) = 12.97 + 0.99*K-M3 (mg kg^{-1}) + 0.05*Clay (g kg^{-1}) – 2.52*pH

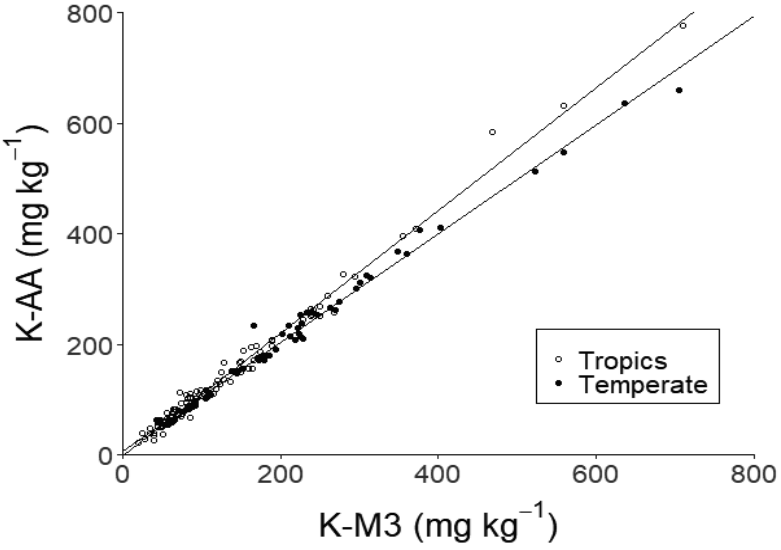

Figure 2: Relations between K extracted with Mehlich 3 (M3) and ammonium acetate (AA), grouping based on climatic zone: (sub)tropical or temperate. Lines represent linear model fits for both groups.

A simpler model without clay content as predictor was tested, as the laboratory procedure to determine soil texture is relatively time-consuming, compared to e.g. soil pH. The model that was fitted based on K-M3 and pH as predictors (Equation 4), explained 99.4% of the variation. Residuals showed a normal distribution (p = 0.731) and RMSE was 9.44 mg kg^{-1}. K-M3 explained 93% of the R^2 value and soil pH the remaining 7%.

Equation 4 (temperate soils): K-AA (mg kg^{-1}) = 15.21 + 1.01*K-M3 (mg kg^{-1}) – 2.12*pH

3.2. P transfer function

In tropical soils, P-Olsen and P-M3 were strongly correlated (r = 0.87, p < 0.001; Table S3). Both parameters were significantly positively correlated with Ca-M3, whereas P-M3 also showed a significant positive correlation with pH and a significant, negative correlation with C_{org}. For 14 out of 92 samples, Olsen extracted more P than M3. On average, these samples had lower pH values (5.22 *vs* 5.75, p = 0.013), higher Al-M3 (1565 *vs* 860 mg kg^{-1}, p < 0.001) and higher C_{org} values (36 *vs* 14 g kg^{-1}, p < 0.001) compared to the (larger) subset in which P-Olsen concentrations were lower than P-M3. No differences in Fe-M3 contents were found (p = 0.317).

The best model that was fitted to explain P-Olsen, violated assumptions: model residuals were not normally distributed (p = 0.006). Further inspection showed two outliers based on Cook's D, that were characterised by having the lowest Ca-M3 and pH values in the dataset. The sample with the highest residual value (a soil from Indonesia) was removed from the dataset and regressions were rerun. The new dataset contained 90 samples from SSA, as well as one Indonesian sample from the same soil profile as the sample that was removed. Although residuals of the model excluding the first Indonesian soil sample were normally distributed (p = 0.200, skewness = -0.35), regressions were also run without the second Indonesian sample, as this could be considered an outlier based on geographical location. The model without both Indonesian samples performed slightly better in terms of R^2 (0.81 *vs* 0.80), but not RMSE (0.45 *vs* 0.41). The model predicting P-Olsen in soils from SSA only, used pH, and P-M3, Al-M3, Fe-M3 and Ca-M3 as explanatory variables (Equation 5). Residuals were distributed normally (p = 0.309, skewness = -0.27), but were positively correlated with ln(P-Olsen) predictions (p < 0.001; Figure S2). Further inspection showed one outlier based on Cook's D, although its value was below 0.5, characterised by having the lowest Ca-M3 (2.8 mg kg^{-1}) and pH (4.10) values in the dataset. As Cook's D value of the outlier was below 0.5 and no clear patterns between residuals and explanatory variables were observed, no attempt was made to further improve the model.

Equation 5: ln(P-Olsen) = 0.77*ln(P-M3) + 0.62*ln(Al-M3) + 0.13*ln(Fe-M3) + 0.10*ln(Ca-M3) – 0.19*pH – 4.31

The P transfer function described 81% of the variation in P-Olsen and RMSE was 0.45 (ln mg kg^{-1}). Model predictions are presented in Figure 3. Relative contribution to R^2 was highest for P-M3 (87%), followed by Al-M3 (7%), Ca-M3 (2.6%) and pH (2.5%). Fe-M3 contributed less than 1% to the R^2.

The dataset with temperate soils was considered too small (n = 22) to derive a P transfer function for temperate regions. The low number of remaining samples was partly due to the high P-Olsen values in the available data: more than half of the samples had P-Olsen values above 30 mg kg^{-1}, i.e. the QUEFTS limit for this parameter that was used in our data selection (section 2.3). The remaining 22 soil samples in the temperate dataset were compared to the tropical dataset for discussion purposes (Table S4). Temperate soils had significantly higher P-M3 (p = 0.001), Ca-M3 (p < 0.001) and Fe-M3 (p < 0.001) concentrations compared to tropical soils. Al-M3 concentrations were lower in temperate soils, but the difference with tropical soils was not significant (p = 0.051).

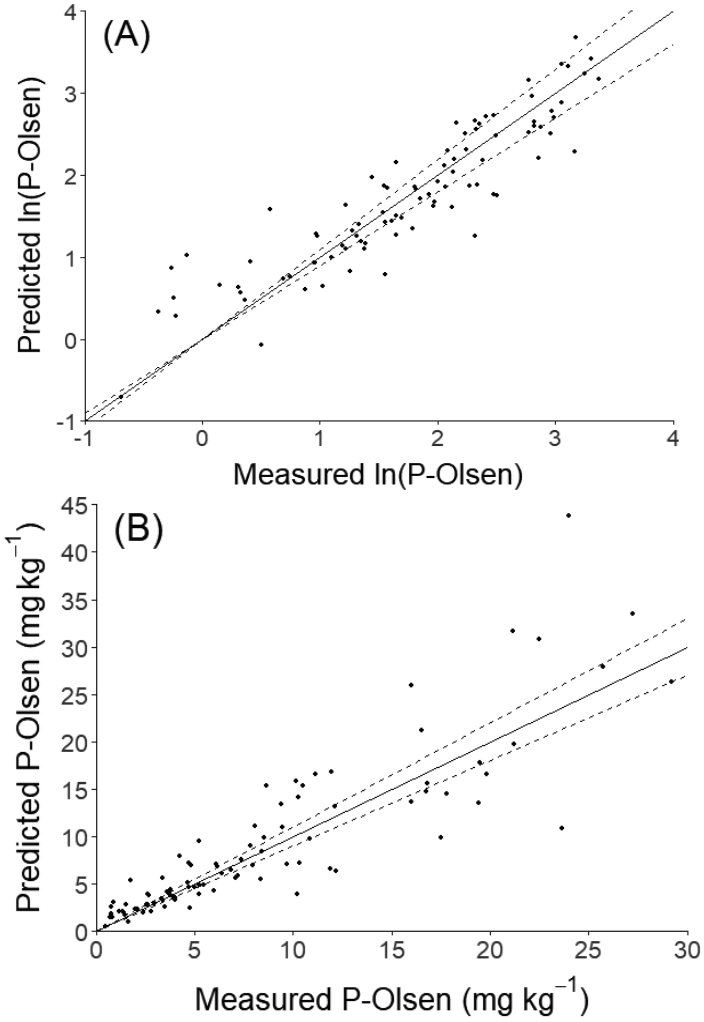

Figure 3: Measured versus predicted P-Olsen on (A) a natural log scale and (B) after back-transformation. Dashed lines represent 10% deviation from the solid 1:1 line.

3.3. **Application**

When P-Olsen and K-AA values were predicted using the P and K transfer functions and subsequently used as input for QUEFTS, yield predictions for 63 out of 81 soils deviated less than 10% from the benchmark scenario in which the measured P-Olsen and K-AA values were used as input for QUEFTS (Figure 4). Yield predictions of 10 observations deviated more than 15% from yield predictions that were based on measured P-Olsen and K-AA input. The corresponding soils were characterized by low P-Olsen and K-AA values: a maximum of 11.9 mg kg^{-1} for P-Olsen and 2.9 mmol kg^{-1}

for K-AA, compared to the respective maximum values of 30 mg kg^{-1} and 8.4 mmol kg^{-1} for the complete dataset. Overall, when yield predictions surpassed 3000 kg ha^{-1}, deviations were less than 10% (Figure 4). The corresponding soils were characterized by higher average P-Olsen (11.0 *vs* 7.7 mg kg^{-1}, $p = 0.037$) and K-AA (4.5 *vs* 2.1 mmol kg^{-1}, $p < 0.001$) values. Average C_{org} values for these samples also tended to be higher (21.2 *vs* 16.5 g kg^{-1}), but the difference was not significant ($p = 0.080$).

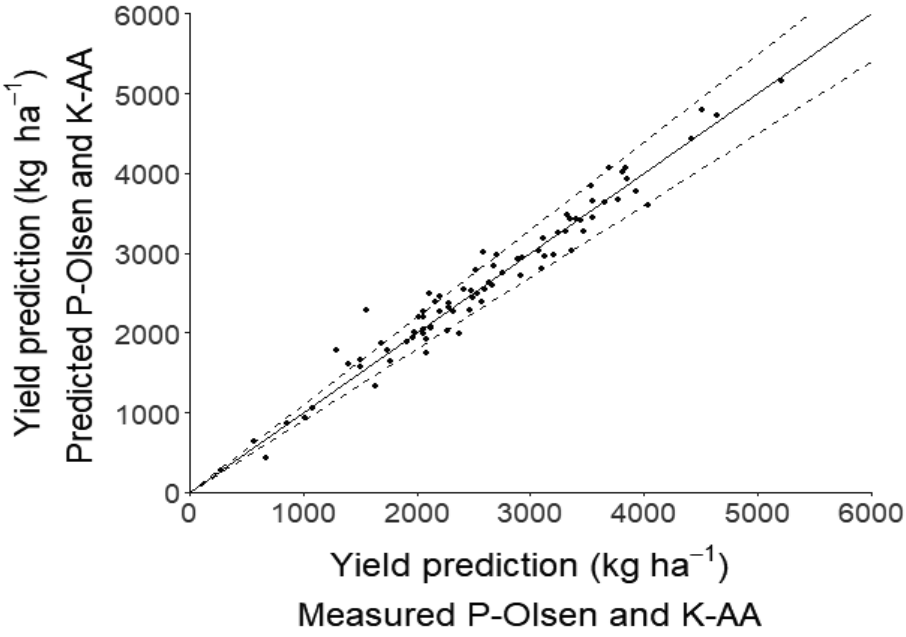

Figure 4: QUEFTS yield predictions based on measured P-Olsen and K-AA values versus QUEFTS yield predictions based on predicted P-Olsen and K-AA values. Dashed lines represent 10% deviation from the solid 1:1 line.

4. Discussion

4.1. Potassium

The AA and M3 methods extracted similar amounts of K (the regression slope was approximately 1.09 for tropical soils), which suggests a corresponding extraction mechanism, most likely $NH_4^+ \leftrightarrow K^+$ ion exchange. The differences between the K transfer functions for tropical and temperate soils may be partly methodological. The majority of data on temperate soils was obtained from WEPAL (50 out of 67 samples) for which exact protocols that were used for K-AA analysis are not known. The different extraction times employed in studies described in Table S1 (5, 10 or 30 min)

indicate that methods can differ among laboratories. However, when a comparison was made between temperate (n = 50) and tropical soils (n = 9) within the WEPAL dataset, the ratio of K-AA/K-M3 was significantly higher in tropical soils compared to temperate soils ($p < 0.001$; data not presented). As K-AA measurements for tropical and temperate samples within the WEPAL dataset will have the same variability in extraction methods, it is unlikely that possible differences in extraction time are the main cause of the different K transfer functions obtained for tropical and temperate soils. This difference is more likely related to clay mineralogy, which influences bioavailability and exchange rate of cations (Grim, 1968). Relations among several K extraction methods were indeed found to be different for kaolinite, smectite and mixed clay soils (Sharpley, 1985). Weathering and climate are important factors in the formation of clay minerals; (sub)tropical soils generally contain kaolinite as the dominant clay mineral, whereas in temperate soils, illite or smectite clay minerals are more abundant (Grim, 1968). In tropical soils, AA was relatively more efficient than M3 in extracting K compared to temperate soils. In temperate soils, K is largely selectively bound, particularly to illite clay minerals (Blume et al., 2016), while in tropical soils K is more likely bound to general and less selective cation-exchange sites, such as those of kaolinite and organic matter. The high NH_4^+ concentrations in both extracts can rapidly displace the relatively weakly-bound K from kaolinite and organic matter. NH_4^+ also displaces selectively-bound K from illite clay minerals, but K-release from those sites is characterized by relatively slow exchange kinetics (Sumner and Bolt, 1962). These differences may explain the lower K-extraction efficiency of AA in temperate soils compared to tropical soils.

In contrast to tropical soils, the best model predicting K-AA in temperate soils required clay content and pH in addition to K-M3. It is unclear why clay content was a significant variable in this model. Results of the model without clay content (Equation 4) indicate that exclusion of this parameter does not affect precision of the predictions, although accuracy was lower. Soil pH had a negative coefficient in both models (with and without clay content), implying that M3 is relatively more efficient in extracting K than AA when soil pH increases. The acid M3 extract (pH 2.5 *vs* 7.0 for AA) may release additional K by partial dissolution of illite, smectite or other K-containing minerals that occur in temperate soils. Penn et al. (2018) showed that pH of the M3 solution increased with soil pH during the extraction procedure from 2.5 to ~3.1 and dissolution rates of illite and smectite clay minerals decrease across this pH range (Amram and Ganor, 2005; Köhler et al., 2003). We would thus expect that K-M3 extraction efficiency decreases with increasing soil pH, which is in contrast to our findings.

The two soils that were excluded in the final models for temperate soils, were Solonetz and Solonchak soils from Russia, which both are characterised by having high Na^+ concentrations(FAO, 2001a), as was also confirmed by additional data present in the WSRC dataset. The first soil that was removed from the dataset (Solonchak), was most likely identified as an outlier as it had the highest K-AA, K-M3 and C_{org} values (high leverage). The second soil that was removed (Solonetz) did not have soil parameters with extreme values. The ratio of K-AA/K-M3 for this soil was extremely high compared to the other temperate soils (1.41 *vs* average ratio of 1.03). As M3 and AA most likely have a corresponding mechanism to extract K, i.e. $NH_4^+ \leftrightarrow K^+$ ion exchange, the high concentration of Na^+ may have interfered with the K extraction in M3, that has lower NH_4^+ concentrations compared to AA (0.25 M *vs* 1 M). Although this may indicate limitations for applying the K transfer function to temperate soils in saline soils, in practice these soils are unlikely to be used for intensive agriculture.

The protocol developed for this study is based on an extraction time of 2 h for determination of K-AA, which resembles the extraction time in the percolation method that was originally used to calibrate QUEFTS (Janssen et al., 1990; Van Reeuwijk, 2002). We therefore consider the K transfer function for tropical soils developed in this study more suitable for generating K-AA input for QUEFTS than previous relations described in literature.

4.2. Phosphorus

The properties in the P transfer function in this study were able to explain 81% of the variance in ln(P-Olsen) predictions, which is within the range reported in Table S2 (R^2 between 0.45 and 0.94, average 0.74). After back-transformation of ln(P-Olsen) values, uncertainty increased with P-Olsen levels (Figure 3B), which is a consequence of fitting regression models to log-transformed variables. However, in terms of soil P status and P fertiliser recommendations, predicting low P-Olsen concentrations accurately is most relevant. Though dependent on other soil properties, the critical P-Olsen concentration below which P is expected to be yield-limiting is around 10 mg kg^{-1} for maize (Bai et al., 2013; Ussiri et al., 1998). The increasing uncertainty with increasing predicted P-Olsen concentrations, especially for values above 10 mg kg^{-1}, is therefore not likely to have an effect on fertiliser recommendations.

Removal of one Indonesian sample from the dataset was needed to derive a model that did not violate the assumption of normality. This soil was classified as an Acrisol and was not used for agricultural purposes at the time of sampling. The results of the final P transfer function similarly showed a sample with a high Cook's D value (although

below 0.5) due to very low Ca-M3 concentrations and pH. This soil from Congo was classified as a Ferralsol and was sampled from a rubber plantation. Acrisols and Ferralsols are known for their high P fixation and low nutrient availability (FAO, 2001b). This may indicate that the P transfer function may not predict P-Olsen concentrations well in P fixing soils. A number of other soil samples were also classified or could potentially be classified (based on geographical position) as Acrisols or Ferralsols, however, but were not found to be outliers. A second reason for the Indonesian and Congolese samples being identified as outliers, could therefore be the very low Ca-M3 concentrations (19.6 and 2.8 mg kg^{-1} respectively) or pH (4.16 and 4.10 respectively). This observation may indicate that the P transfer function has a limited applicability to predict P-Olsen in soils with a pH below 4.4 or Ca-M3 concentrations below ~50 mg kg^{-1}.

This study has shown that Al-M3 is relevant for describing the relation between P-Olsen and P-M3 in tropical soils. This presumably is because Al-M3 is a good proxy for the amount of amorphous Al (hydr)oxides as confirmed by the strong similarity between Al measured in AO and M3 ($r = 0.79$, $p < 0.001$; Figure S3). The relation between Al-M3 and Al-AO was curvilinear and similar relations have been reported by Sen Tran et al. (1990) and Sims et al. (2002). The clear effect of Al-M3 was demonstrated by the fact that ratios of P-Olsen/P-M3 above 1 were associated with significantly higher Al-M3 concentrations compared to soils where the ratio was below 1, which was also reported by Buondonno et al. (1992). Thus the Olsen method was apparently more efficient than M3 in extracting P from soils with high amorphous Al content. We hypothesize that in these soils, saturation of the fluoride ion with Al^{3+} during the M3 extraction plays an important role in the reduced extraction efficiency of P associated with Al hydroxides. In the protocol that was used, 20 mL of M3 solution contains 0.3 mmol of F^-, which can complex maximally 0.1 mmol of Al^{3+} in 2 g soil. This corresponds to around 1350 mg Al kg^{-1} soil. In the 14 tropical soils in this study where P-Olsen concentrations were higher than P-M3, Al-M3 concentrations were 1565 mg kg^{-1} on average, which indicates that saturation of the fluoride ions may have limited P-M3 extraction in these soils. As the P extraction efficiency of Olsen is not affected by Al concentrations, this method can extract more P than M3 from soils with high Al-M3 values. These findings support inclusion of Al-M3 or Al-AO when developing P transfer functions for M3 extractions. In contrast to Al, M3 and AO were not equally efficient in extracting Fe: Fe-M3 was found to be around 10% of Fe-AO (Figure S3), which is in line with results reported by Sims et al. (2002). Fe-M3 therefore is not a good proxy for amorphous Fe-oxides, which may explain its limited contribution to the P transfer function.

As expected, soil pH was an important factor in the P transfer function for tropical soils. M3 was relatively more efficient in extracting P compared to Olsen when soil pH increased. Buondonno et al. (1992) argued that M3 is very efficient in dissolving Ca-bound phosphates that are relatively more abundant in alkaline soils (Sims and Pierzynski, 2005) and would consequently lead to higher P-M3 levels when soil pH increases. The positive correlation between P-M3 and Ca-M3 that was found in the tropical soils in this study confirms this hypothesis. We expect that complexation of Ca with fluoride plays an important role in extracting P when soil pH increases. For neutral and alkaline soils, the pH of the M3 solution is expected to increase above 2.9 during the extraction, which will consequently lead to Ca-F complexation and release of P from Ca-P minerals (Buondonno et al., 1992; Penn et al., 2018). Penn et al. (2018) however postulated that an increase in M3 solution pH would lead to a decrease in P-M3 concentrations, as a result of decreased desorption of P from Fe and Al (hydr)oxides. Penn et al. (2018), as well as Wuenscher et al. (2015) reported negative correlations between P-M3 and soil pH and between P-M3 and $CaCO_3$, which is in contrast to our findings (Table S3). These studies used temperate soils in their analysis, however. This difference in soil types could indicate that the effect of soil pH on P extraction efficiency of M3 is dependent on soil mineralogy, which supports inclusion of proxies for Al, Fe and Ca reactive surfaces. Given the differences in P, Al, Ca and Fe-M3 values between temperate and tropical soils (Table S4), the applicability of the P transfer function to temperate soils may be limited.

In the tropical soils in this study, C_{org} was not found to be a significant factor in explaining the relationship between P-Olsen and P-M3, despite being correlated to P-M3 ($r = -0.27$, $p = 0.009$; Table S3). Although organic P can be a considerable fraction of total P-M3 concentrations (e.g. Iatrou et al., 2014; Pittman et al., 2005), correlations with C_{org} were weak (Mallarino, 2003). Correlations between the amount of organic P extracted by M3 and soil pH were stronger however (Mallarino, 2003). The work of Iatrou et al. (2014) also showed that the amount of organic P extracted was pH dependent. We therefore hypothesize that C_{org} does not affect P-M3 concentrations directly and that the use of soil pH in the regression made inclusion of C_{org} redundant.

4.3. Application

The use of the P and K transfer functions for predicting QUEFTS input yielded satisfactory results for the majority of soils, as QUEFTS yield predictions deviated less than 10% from yield predictions based on measured P-Olsen and K-AA input. Extracted data from Figure 6b by Sattari et al. (2014), show that QUEFTS yield predictions deviated more than 10% from observed yields for the majority of their

fields. The uncertainty introduced by the application of the transfer functions is thus less than the general uncertainty associated with QUEFTS predictions. The effect of the additional uncertainty introduced by the transfer functions on QUEFTS final yield estimate in relation to actual yields, currently is unknown. To gain insights in how the transfer functions affect QUEFTS ability to estimate actual yields, QUEFTS yield predictions based on M3 will have to be validated with field observations in future studies.

Using the transfer functions rather than measured P-Olsen and K-AA inputs had a limited effect on QUEFTS yield predictions. This can partly be explained by the high accuracy of the K-AA predictions using the K transfer function, but is also due to the fact that QUEFTS predictions of N, P and K supply to a crop are also based on soil pH and C_{org} values, besides P-Olsen and K-AA. As a result, only part of the uncertainty associated with P-Olsen and K-AA predictions will result in uncertainty in the final yield predictions. Furthermore, the uncertainty associated with P-Olsen concentrations, especially at higher levels is not propagated within QUEFTS, as yield predictions for soils with higher P-Olsen levels are more likely limited by N or K supply, than by P supply. In contrast, soils low in P-Olsen (and K-AA) were associated with deviations of more than 15% in QUEFTS yield predictions. The prediction uncertainty at low P-Olsen and K-AA values is relatively more important in QUEFTS yield predictions, as the crop is more likely to be P or K limited. As a result, the largest model deviations occur when predicted yields were below 3000 kg ha^{-1}. Sattari et al. (2014) showed that QUEFTS yield predications below 3000 kg ha^{-1} generally have a higher degree of uncertainty than predictions above this level. This suggests that QUEFTS yield predictions below this level should be interpreted with caution, especially when P-Olsen and K-AA inputs are predicted with the transfer functions developed in this study.

To minimise the uncertainty associated with the use of M3 data as input for QUEFTS, recalibration of QUEFTS P and K supply functions based on M3 soil data is recommended (Sattari et al., 2014). This requires, however, substantial time and capital investments, as NPK fertiliser omission trials need to be executed on a wide range of soils. Until such recalibrated P and K supply functions become available, the P and K transfer functions developed in this study can serve to generate P-Olsen and K-AA inputs for QUEFTS, with introduced uncertainties similar to those of current QUEFTS yield predictions.

5. Conclusions

We conclude that a Mehlich 3 (M3) extraction can be used effectively to predict K extracted by 1 M ammonium acetate (K-AA) in tropical soils, using the K transfer function developed in this study. The P transfer function that was developed in this study to estimate Olsen-P from P extracted by Mehlich 3, is associated with more uncertainty than the K transfer function. However, given that M3 extractions are more commonly used than Olsen soil tests in several parts of the world, the P transfer function can prove useful to estimate P-Olsen values in tropical soils when only M3 data are available. Log-transformation of input variables furthermore ensures that uncertainty in the relevant range up to 10 mg kg^{-1} P-Olsen is minimised. QUEFTS is a decision support tool that can be used for the evaluation of soil fertility, potential crop yield and fertilizer recommendations. As QUEFTS requires P-Olsen and K-AA as input parameters, its application may be limited when these soil parameters cannot be analysed in local laboratories. We conclude that a M3 extraction and soil pH-H_2O can replace P-Olsen and K-AA determinations for predicting QUEFTS input for tropical soils, by using the P and K transfer functions developed in this study. These functions thus expand the applicability of the QUEFTS model to cases where only M3 extraction results are available.

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Supporting Information

Table S1: Transfer functions between K (mg kg^{-1}) in AA and M3 derived from literature. Some functions were calculated from study data when relations were not reported or when M3 was expressed as a function of K-AA.

Study	Soil origin	*n*	Transfer function	R^2
Tropical soils				
Bibiso et al. (2015)	Ethiopia	7	AA = 1.19*M3 – 14.4	0.97
Bortolon & Gianello (2010)	Brasil	35	AA = 1.00*M3	0.98
Chilimba et al. (1999)	Malawi	30	AA = 0.89*M3 + 0.1	0.81
Fukuda et al. (2017)	Mozambique	326	AA = 0.79*M3	0.96
Mamo et al. (1996)	Ethiopia	22	AA = 1.04*M3 + 56	0.99
Wendt (1995)	Malawi	112	AA = 0.95*M3 – 2.0	0.99
Temperate soils				
Alva (1993)	USA	118	AA = 0.87*M3 – 0.5	0.95
Barbagelata (2006)	USA	117	AA = 1.03*M3 + 2.6	0.97
Beegle & Oravec (1990)	USA	67	AA = 1.19*M3	0.92
Eckert & Watson (1996)	USA	NA	AA = 1.03*M3 – 6.2	0.86
Gartley et al. (2002)	USA	300	AA = 1.03*M3 + 4.0	0.99
Hanlon & Johnson (1984)	USA	65	AA = 1.09*M3 – 43	1.00
Mamo et al. (1996)	Germany	10	AA = 1.12*M3 – 4.4	0.99
Mehlich (1984)	USA	105	AA = 0.93*M3	0.97
Michaelson et al. (1987)	USA	360	AA = 0.96*M3 + 1.5	0.95
Nathan et al. (2005)	USA	162	AA = 1.11*M3 – 24	0.99
Schmisek et al. (1998)	USA	99	AA = 1.54*M3 – 144	0.94
Yang et al. (2011)	China	294	AA = 0.54*M3 – 11.2	0.90

Table S2: Transfer functions between P (mg kg^{-1}) in Olsen and M3 derived from literature. Some functions were calculated from study data when relations were not reported or when M3 was expressed as a function of Olsen. In case multiple functions could be derived from a study, the function with the highest R^2 values was reported.

Study	Origin	*n*	Soil type	Transfer function	R^2
Tropical soils					
Bibiso et al. (2015)	Ethiopia	7	Various	Olsen = 0.66*M3 + 3.9	0.79
Mamo et al. (1996)	Ethiopia	22	Various	Olsen = 0.19*M3 + 8.9	0.81

Table S2 (cont).

Study	Origin	*n*	Soil type	Transfer function	R^2
			Temperate soils		
Buondonno et al. (1992)	Italy	66	Noncalcareous	Olsen = 0.70*M3 - 0.4	0.71
		54	Calcareous	Olsen = 0.37*M3 + 0.2	0.73
		120	All	Olsen = 0.50*M3 - 0.1	0.64
Burt et al. (2002)	USA	268	Various	Olsen = 0.35*M3 + 2.2	0.87
Csathó et al. (2005)	Hungary	36	Various	Olsen = 0.43*M3 - 3.4	0.85
Elrashidi et al. (2003)	USA	20	Alkaline	Olsen = 0.51*M3 + 5.49*$CaCO_3$ - 25.2	0.94
Eriksson (2009)	Baltics	99	Various	Olsen = 0.27*M3 + 7.9	0.74
Iatrou et al. (2014)	Greece	200	Acidic	Olsen = 0.19*M3 + 3.4	0.77
			Neutral, $CaCO_3$ free	Olsen = 0.26*M3 + 1.9	0.85
			Alkaline, low $CaCO_3$	Olsen = 0.27*M3 + 0.9	0.84
			Alkaline, high $CaCO_3$	Olsen = 0.16*M3 - 0.74* pH + 15.5	0.61
Ige et al. (2006)	Canada	115	Various	Olsen = 0.54*M3 + 0.49	0.94
Mallarino (1995)	USA	NA	Acidic	Olsen = 0.47*M3 + 2.1	0.62
			Neutral	Olsen = 0.47*M3 + 0.7	0.45
			Alkaline	Olsen = 0.45*M3 + 1.8	0.66
			All	Olsen = 0.46*M3 + 1.5	0.58
Mamo et al. (1996)	Germany	10	Various	Olsen = 0.17*M3 + 11.2	0.53
Matejovic & Durackova (1994)	Slovakia	56	Various	Olsen = 0.14*M3 - 3.0	0.71
Schick et al. (2013)	Baltics	217	Various	Olsen = 0.13*M3 + 3.0*C + 0.01*Fe - 0.01*Al + 21.6	0.67
Schmisek et al. (1998)	USA	97	Alkaline	Olsen = 0.68*M3 - 7.9	0.90
Sen Tran et al. (1990)	Canada	67	Acidic	Olsen = 0.28*M3 - 1.7	0.75
		15	Calcareous	Olsen = 0.39*M3 + 1.9	0.88
Wolf & Baker (1985)	USA	91	Noncalcareous	Olsen = 0.33*M3 + 2.2	0.79
Wünscher (2013)	Austria/ Germany	50	Various	Olsen = 0.21*M3 + 19.9	0.70
Zbiral & Nemec (2002)	Czech Republic	655	Noncalcareous	Olsen = 0.25*M3 + 12.1	0.74
		434	Calcareous	Olsen = 0.30*M3 + 10.7	0.63
		1098	All	Olsen = 0.26*M3 + 11.8	0.69

Table S3: Pearson's correlation coefficients of the untransformed parameters in the dataset with tropical soils. Asterisks indicate significance at the 0.05 level.

	P-Olsen	P-M3	pH	C_{org}	Al-M3	Ca-M3
P-M3	0.87*	-				
pH	0.12	0.32*	-			
C_{org}	-0.10	-0.27*	-0.47*	-		
Al-M3	0.07	-0.13	-0.53*	0.75*	-	
Ca-M3	0.30*	0.32*	0.63*	-0.05	-0.23*	-
Fe-M3	-0.09	-0.11	-0.35*	0.15	0.05	-0.17

Table S4: Average values of nutrients in Mehlich 3 (in mg kg^{-1}) In the temperate (n = 22) and tropical (n = 92) datasets.

	P-M3	Al-M3	Ca-M3	Fe-M3
Temperate	37.5	775	3295	372
Tropics	17.5	967	689	152
***p* level**	0.001	0.051	<0.001	<0.001

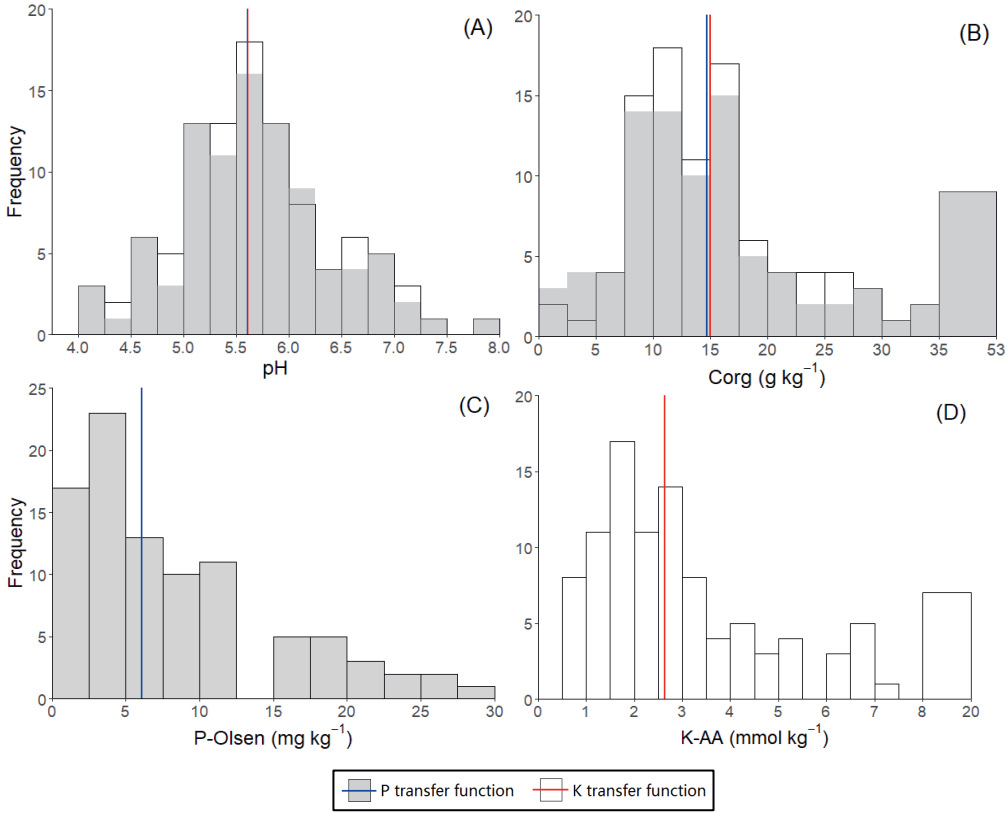

Figure S1: Histograms of pH (A), C_{org} (B), P-Olsen (C) and K-AA (D) input data for tropical soils. Figures 1A and 1B present input data of both P and K transfer functions, 1C and 1D for respectively P and K transfer functions only. Blue lines represent the median for the P transfer dataset, red lines the median for the K transfer dataset.

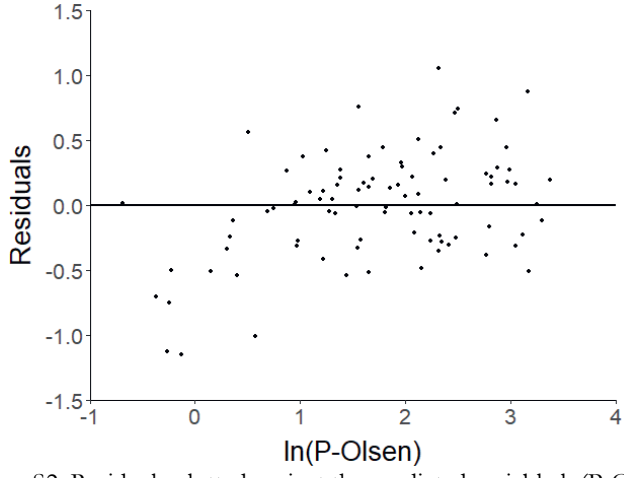

Figure S2: Residuals plotted against the predicted variable ln(P-Olsen)

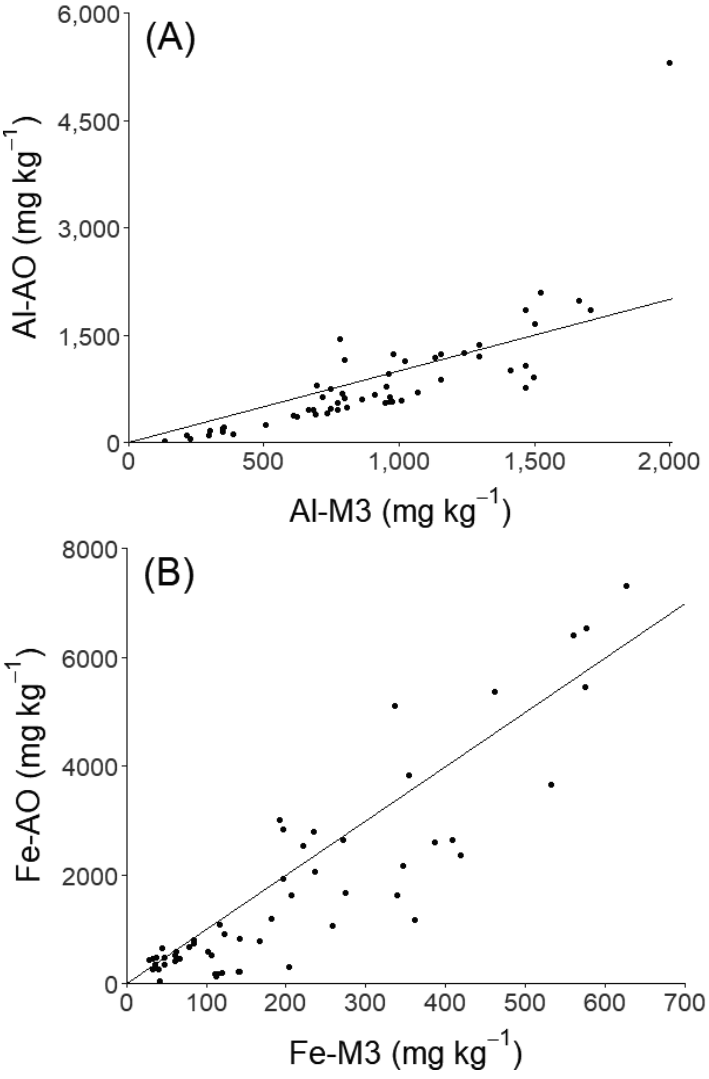

Figure S3: Comparisons between (A) Al-AO and Al-M3 and between (B) Fe-AO and Fe-M3. Lines represent the (A) 1:1 and (B) 1:10 lines.

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Chapter 3

Spatial predictions of maize yields using QUEFTS – a comparison of methods

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Abstract

Using fertilisers is indispensable for closing yield gaps in sub-Saharan Africa. Current fertiliser recommendations, however, are often blanket recommendations which do not take spatial variation in soil conditions within a region or country into account. Soil maps can potentially support fertiliser recommendations at a higher spatial resolution. The QUantitative Evaluation of the Fertility of Tropical Soils (QUEFTS) model is a decision support tool that predicts crop yields as an indicator of soil fertility and can be used to evaluate yield responses to fertilisers. It was designed for field level output and runs on field-specific soil information. The aim of this study was to compare two methods for developing maps of QUEFTS output, i.e. maize yield and the yield-limiting nutrient, with Rwanda as a case study. We used a database containing soil analysis results of 999 samples collected across Rwanda. Transfer functions were applied to predict the required P-Olsen and Exchangeable K input for QUEFTS based on the soil data. For the "Calculate-then-Interpolate" (CI) method, transfer functions and QUEFTS were applied to point data, and the final output was then interpolated using random forest modelling. For the "Interpolate-then-Calculate" (IC) method, maps of the soil parameters were developed first, before applying calculations. Implications of the chosen method (i.e. CI or IC) on QUEFTS predictions on a national scale were evaluated using set-aside locations. Results showed low precision and accuracy of QUEFTS maize yield predictions across Rwanda. The CI method performed better in predicting QUEFTS yield and yield-limiting nutrient than the IC method. Correlations between mapped yield predictions and predictions on set-aside evaluation locations were similar for the CI ($r = 0.444$) and IC ($r = 0.439$) methods. The poorer performance of the IC method was mostly due to overestimation of yields, which was most likely caused by the effect of smoothing on the soil maps used as input for QUEFTS. We conclude that the CI method is the preferred method for spatial application of QUEFTS.

1. Introduction

Agricultural productivity in sub-Saharan Africa should increase in order to sustain its growing population. In African soils, often multiple nutrients are depleted and the use of fertilisers is indispensable for closing yield gaps (Giller et al., 2011; Ichami et al., 2019; Shehu et al., 2019). Current fertiliser recommendations are often blanket recommendations that do not take into account spatial heterogeneity of soils and other site-specific factors, leading to either a waste of resources or low productivity of land (Giller et al., 2011; Vanlauwe et al., 2015). Site-specific fertiliser recommendations based on soil testing have been shown to lead to increased revenues over blanket recommendations (Njoroge et al., 2015). However, high costs, limited access to soil testing services and difficulty in interpreting results (Chianu et al., 2012), as well as uncertainties associated with sampling and analytical procedures (Schut and Giller, 2020) complicate the use of soil testing to increase productivity on a large scale.

Soil maps, in combination with information on crop response to nutrient availability, can potentially be used to refine blanket fertiliser recommendations. The QUantitative Evaluation of the Fertility of Tropical Soils (QUEFTS) model is a simple yet versatile tool that can be used to predict yield and yield response to fertilisers, taking interactions among nitrogen (N), phosphorus (P) and potassium (K) into account (Janssen et al., 1990; Sattari et al., 2014). QUEFTS requires few input parameters: soil pH, soil organic carbon (SOC), P measured in an Olsen extract (P-Olsen), exchangeable K measured in an ammonium acetate extract (Exch-K) and crop-specific physiological efficiency parameters. It has been developed and validated for a wide range of crops and regions (e.g. Das et al., 2009; Ezui et al., 2017; Shehu et al., 2019; Tabi et al., 2008) and has proven adequate for developing fertiliser recommendations (e.g. Maiti et al., 2006; Mesfin et al., 2021; Xu et al., 2013). QUEFTS was designed for field level output and runs on field-specific soil information, but can be applied to soil maps as well (Leenaars et al., 2018b). In this study, different methods will be explored to arrive at maps of maize yield and the yield-limiting nutrient at a country level using QUEFTS.

There are two pathways to develop maps of a target variable: model calculations can be applied to soil maps or to the point data underpinning these maps. When models are applied to data points, the model output is calculated for each data point, followed by spatial interpolation of these points to develop a map of the target variable. When models are applied to soil maps, the point data underpinning the maps are interpolated before applying model calculations. Both methods were previously described as the calculate-then-model and model-then-calculate methods (Kempen et al., 2019; Orton et al., 2014) or calculate-then-interpolate and interpolate-then-calculate methods

(Heuvelink and Pebesma, 1999). We will refer to both methods as the calculate-then-interpolate (CI) and interpolate-then-calculate (IC) methods. The IC method is computationally more intensive, but application of the CI method may be limited in case of missing point data for one or more input parameters, or when only maps are available as input data and not the underpinning data points (Orton et al., 2014).

The aim of this work is to evaluate the implications of the chosen method (i.e. CI or IC) on QUEFTS predictions on a national scale, using Rwanda as a case study. In our case, two consecutive steps of model calculations are needed: First, the transfer functions developed in Chapter 2 are used to calculate QUEFTS input parameters P-Olsen and Exch K from available data. Second, QUEFTS model calculations are made. Minor differences between outcomes of the CI and IC methods have been reported for simple linear models (Kempen et al., 2019; Orton et al., 2014; Styc and Lagacherie, 2019), but substantial differences for non-linear models (Addiscott and Tuck, 1996). Based on Heuvelink and Pebesma (1999), we hypothesise that the IC method will result in the most accurate spatial predictions. As QUEFTS is a non-linear model involving several interacting calculation steps, we expect that results of the CI and IC methods will differ more compared to the work of Kempen et al. (2019), Orton et al. (2014) and Styc and Lagacherie (2019). The outcomes of this work will help to evaluate whether QUEFTS can be used to develop fertiliser recommendations at scale.

2. Materials and Methods

2.1. Data availability

A geo-referenced dataset containing 999 topsoil (0-20 cm) samples with a good spatial coverage across Rwanda (Figure 1) was provided by the International Fertiliser Development Center (IFDC). Soils were sampled in 2014 as part of the CATALIST-2 programme and analysed by the Crop Nutrition Laboratory Services, Nairobi, Kenya. The dataset contained pH-H_2O measured in a 1:2 soil:water suspension, organic matter content (%) determined with the Walkley-Black method and several nutrients measured in a Mehlich 3 extraction (mg kg^{-1}). SOC values were calculated from organic matter, assuming 50% of organic matter is carbon (Pribyl, 2010). The dataset was randomly split into a calibration (n = 699) and evaluation (n = 300) dataset. Part of the data were excluded based on selection criteria (Figure 1; sections 2.3 and 2.4).

In addition, 134 covariate layers at 250 m spatial resolution were available for random forest modelling that we used for spatial interpolation (section 2.5). These layers were

previously prepared for and described in Kempen et al. (2015). Briefly, the covariate layers were acquired from six sources: the Africa Soil Information Service (AfSIS), ISRIC WorldGrids, USGS Africa Ecosystems Mapping database, Soil and Terrain database of Central Africa (SOTERCAF), soil and terrain database for north-eastern Africa (SOTERNEA) and the Multipurpose Africover Databases on Environmental Resources (MADE). Covariate layers contained information on soil type, terrain, climate, land cover, vegetation indices, primary production, spectral reflectance, albedo and soil moisture.

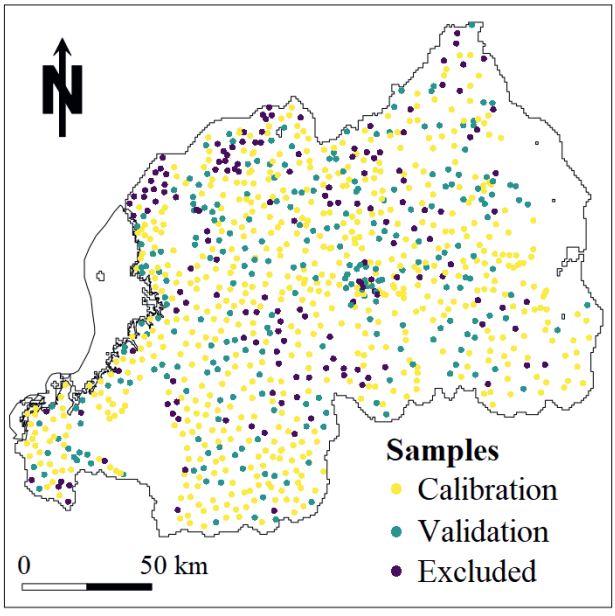

Figure 1: Distribution of calibration, evaluation and excluded data points across Rwanda. Note that the white areas are lake Kivu (west) and national parks (south-west and east).

2.2. Workflow

Two methods were used to develop maps with QUEFTS for Rwanda, in a two-step approach (Figure 2). In Step 1, QUEFTS input data were derived from available data. Besides pH-H_2O and SOC (in g kg^{-1}), QUEFTS requires P-Olsen (in mg kg^{-1}) and Exch-K (in mmol kg^{-1}) measured in ammonium acetate at pH 7.0, which were not available in the dataset and were therefore predicted using transfer functions (section 2.3). In Step 2, QUEFTS was applied to compute yield and the most yield-limiting nutrient (considering N, P and K), based on pH, SOC, P-Olsen and Exch-K data (section 2.4). QUEFTS was run for the situation that no fertilisers are applied. For the CI method, Steps 1 and 2 were applied to the calibration dataset. The yield and most yield-limiting nutrient predictions at these locations were spatially interpolated using

random forest modelling (section 2.5). For the IC method, input parameters of the transfer function and QUEFTS model were first interpolated (using the calibration dataset) to produce maps for each of these parameters. Steps 1 and 2 were subsequently applied to the soil maps to derive maps of maize yield and the yield-limiting nutrient.

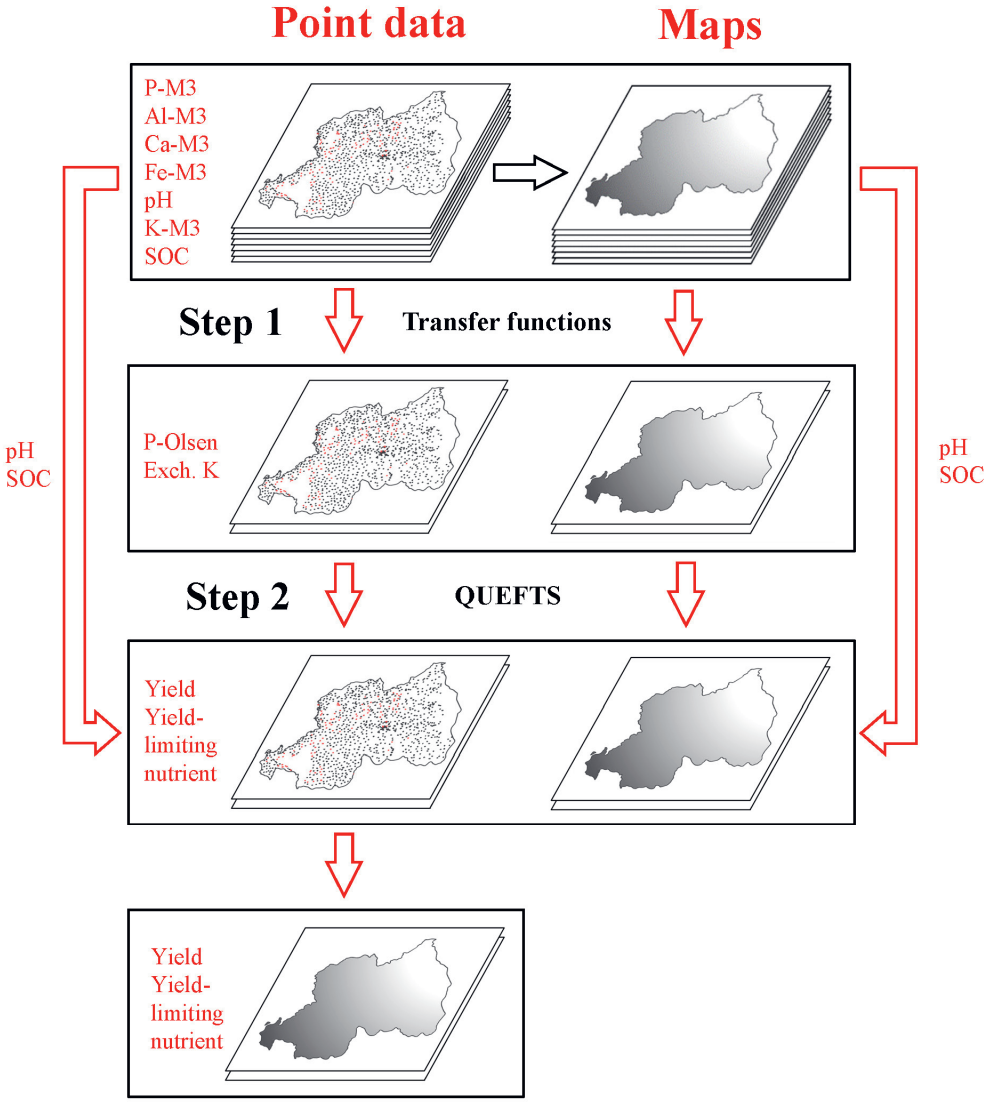

Figure 2: Two methods of applying P and K transfer functions and QUEFTS to data points: Calculate-then-Interpolate (vertical pathway on the left) or Interpolate-then-Calculate (right). Black horizontal arrow indicates the process of spatial interpolation of data points to maps. Red arrows represent input that is used for either the P and K transfer functions (Step 1) or for QUEFTS (Step 2).

2.3. Transfer functions for QUEFTS inputs

P-Olsen and Exch-K were estimated from available Mehlich 3 (M3) data using the transfer functions from chapter 2, as presented in Equations 1 and 2. Note that Equation 1 was adjusted to estimate Exch-K values in mmol kg^{-1} instead of mg kg^{-1}.

Equation 1: Exch-K (mmol kg^{-1}) = 0.028*K-M3 (mg kg^{-1}) + 0.015

Equation 2: ln(P-Olsen) = 0.769*ln(P-M3) + 0.620*ln(Al-M3) + 0.131*ln(Fe-M3) + 0.095*ln(Ca-M3) – 0.191*pH - 4.307

The nutrients in Mehlich 3 (P, Al, Ca and Fe; in mg kg^{-1}) were transformed to natural logarithms for application of the P transfer function (Equation 2). The predicted P-Olsen values were obtained by back-transformation of the ln(P-Olsen) predictions following Lark and Lapworth (2012):

Equation 3: P-Olsen = exp(ln(P-Olsen) + 0.5 * σ^2_{pred}),

where ln(P-Olsen) is the predicted value with the P transfer function and σ^2_{pred} denotes the prediction error variance. The prediction error variance for the CI method, where the transfer function was applied to the data points, was computed using Equation 4:

Equation 4: $\sigma^2_{pred} = \sigma^2(\hat{y}) + \sigma^2_\varepsilon$

where $\sigma^2(\hat{y})$ is the variance of the regression estimate $\hat{y}$ and σ^2_ε the residual variance (Hastie et al., 2009 Chapter 3, Eq. 3.22). The prediction error variance is specific for each calibration point, its magnitude depending on the values of the input parameters of the P transfer function. For the IC method the prediction error variance was approximated using a quantile regression forest (Equation 6; section 2.5).

The transfer functions of chapter 2 were derived from data within certain ranges. It is currently unknown whether application of the transfer functions to data outside these ranges leads to reliable Exch-K and P-Olsen predictions. Limits were therefore applied to the data used in this study to select only those data points that fell within the transfer function calibration range. All data points fell within the ranges for Al-M3 and Al-Fe, though some data points exceeded the maximum calibration values for P-M3 (950 *vs* 94 mg kg^{-1}) and Ca-M3 (9800 *vs* 3283 mg kg^{-1}). Therefore, cut off values of 150 mg kg^{-1} for P-M3 and 3500 mg kg^{-1} for Ca-M3 were applied, which were somewhat higher than the

maximum values in the P transfer dataset, but minimised data exclusion. Although K-M3 values in the dataset extended beyond the range of the K transfer function data (2960 *vs* 710 mg kg^{-1}), no limit was applied, as relations between K-M3 and Exch-K are expected to be linear also for higher concentrations (Mamo et al., 1996). Finally, pH limits of 4.0 – 8.0 were also applied to the data.

For the CI method, applying these limits led to exclusion of 70 calibration and 31 evaluation data points. This left 629 samples as input for step 2 in the workflow; a number of 269 samples remained for evaluation. For the IC method, limits were applied to the maps that were developed based on the calibration data. As a consequence of applying these limits, no P-Olsen predictions could be made for 2.2% of the total number of grid cells.

2.4. QUEFTS

The latest version of QUEFTS calibrated for maize was used here (Sattari et al., 2014). QUEFTS calculates nutrient-limited yield and does not account for other potentially yield-limiting factors, such as water availability or presence of pests and diseases. On a site level, these factors can be accounted for by reducing the maximum yield (Y_{max}) parameter. In this study however, Y_{max} was fixed at 10 Mg ha^{-1} across Rwanda. The yield-limiting nutrient was calculated using QUEFTS output and Equation 5 (Heinen, pers. comm. 2020):

Equation 5: $$DF_X = \frac{U_X - U_{Xd}}{U_{Xa} - U_{Xd}} = \frac{U_X - \frac{Y}{d_X} - r_X}{\frac{Y}{a_X} - \frac{Y}{d_X}}$$

DF_X is the dilution factor of nutrient X (i.e. N, P or K), ranging between 0 and 1. U_X refers to uptake of nutrient X (kg ha^{-1}). U_{Xd} refers to the uptake of X in the case this nutrient is maximally diluted in the crop, which is calculated as yield (Y) divided by the maximum physiological efficiency parameter *d* for X, corrected with *r*. Parameter *r* refers to the minimum uptake of a nutrient needed to produce any yield. U_{Xa} refers to the uptake of X in the case this nutrient is maximally accumulated in the crop, which is calculated as yield (Y) divided by the minimum physiological efficiency parameter *a* for X, corrected with *r*. The crop-specific *a*, *d* and *r* values specified by Sattari et al. (2014) for maize were used. The principle behind Equation 5 is to estimate how much the shoot concentrations differ from the physiological minimum. The nutrient with the lowest dilution factor is considered to be yield-limiting.

A second set of limits was applied to the data, according to the limits set for application of QUEFTS (Janssen et al., 1990): SOC < 70 g kg^{-1}, P-Olsen < 30 mg kg^{-1} and Exch-K < 30 mmol kg^{-1}. For the CI method, applying these limits left 591 calibration and 251 evaluation data points. For spatial interpolation of the QUEFTS output, predictions were made on locations with values outside set limits. Locations of these grid cells were identified using the IC maps and values were set to NULL. As a consequence, for the IC method, together with previously applied limits to the P-Olsen and Exch-K maps, QUEFTS predictions could not be made for 2.3% of the total number of grid cells.

2.5. Random Forest modelling

Gridded maps of the yield and the most yield-limiting nutrient for the CI method, and P-M3, Al-M3, Ca-M3, Fe-M3, K-M3, pH and SOC for the IC method were developed using random forest modelling (Breiman, 2001; Strobl et al., 2009). A model was fitted for each variable using the data points included in the calibration dataset and the 134 covariate layers that served as the explanatory variables.

It is considered good practice to remove redundant covariates (i.e. covariates with limited predictive power) prior to modelling, for instance using recursive feature elimination (RFE) (Hounkpatin et al., 2018; Poggio et al., 2021). In addition, correlated covariates should preferably be removed (Poggio et al., 2021). Redundant covariates were not removed in this study, as this would increase the computational load substantially without having direct benefits. First, removing redundant covariates can have computational advantages when data sets are large, which is not the case here. Second, when one aims to understand what drives the model it can be advantageous to remove redundant variables so that these do not confound predictive relationships. Eliciting and understanding predictive relationships, however, is outside the scope of this study. Last, Poggio et al. (2021) show that the effect of removing redundant covariates with RFE on model performance is only very marginal. We therefore do not expect relevant differences in this study in the performance of models fitted with the full covariate stack and models fitted with a reduced stack.

Subsequently, the fitted random forest models were applied to the stack of covariate layers to predict each target variable across Rwanda at 250 m spatial resolution. Each fitted random forest model was composed of 1000 trees. The number of randomly selected candidate covariates for splitting a node was set as the square root of the total number of covariates (default setting of the *mtry* argument of the ranger function in R). Model residuals were inspected for presence of spatial correlation (Oliver and Webster, 2015); variogram analysis, however, indicated residual kriging was not required.

Variables P-M3, Ca-M3 and K-M3 were transformed to natural logarithms before fitting random forest models, as these maps had better evaluation statistics than maps based on models fitted to variables on the original scale. Maps of the log-transformed variables were back-transformed using Equation 3. Unlike kriging methods, the random forest model does not provide an estimate of the prediction error variance required for back-transformation of log-scale predictions to the original scale (Lark and Lapworth, 2012). The variance was therefore approximated using the values of the 0.05 ($Q_{0.05}$) and 0.95 ($Q_{0.95}$) quantile outputs of a quantile regression forest (Meinshausen, 2006), assuming the prediction error is normally distributed:

Equation 6: $$\text{variance} = \left(\frac{Q0.95 - Q0.05}{1.645 * 2}\right)^2$$

For the IC method, the P and Ca maps on log-scale were used directly as input for the P transfer function, which requires log-transformed input for the nutrients in M3.

2.6. Evaluation

To evaluate the maps, grid predictions at the set-aside evaluation locations were compared to the observed (predicted for P-Olsen, Exch-K, yield and yield-limiting nutrient) values. No grid predictions could be derived at 29 out of 251 evaluation locations, which were located outside the prediction area. The remaining 222 evaluation locations were used to compute a set of evaluation statistics, including the mean error (ME) which is a measure of prediction bias, the root mean squared error (RMSE) as a measure for prediction accuracy, and the Modelling Efficiency Coefficient (MEC; Janssen and Heuberger, 1995; Equation 7). The MEC is a measure of how well the model performs compared to using the mean of the calibration dataset as a predictor:

Equation 7: $$\text{MEC} = 1 - \frac{\sum(P_i - O_i)^2}{\sum(O_i - \bar{O})^2}$$

In which *P* refers to grid predictions extracted on evaluation locations *i*, O*i* refers to values observed at evaluation locations *i*, and $\bar{O}$ to the mean value of the calibration data. The MEC is a unitless goodness-of-fit statistic that measures deviation of the predicted values from the 1:1 line and allows comparison with similar models from other studies.

2.7. Software

All analyses for this study were done with the statistical software R (version 3.6.3; R core team, 2020). Plots were made using the spplot (sp package, version 1.4-2; Bivand

et al., 2013; Pebesma and Bivand, 2005) and ggplot (ggplot2 package, version 3.3.2; Wickham, 2016) functions. For application of the P and K transfer functions and the random forest models, the generic predict function of the stats package (version 3.6.2), was used. Random forest models and quantile regression forests were fitted with the ranger package (version 0.12.1; Wright and Ziegler, 2017). Spatial data processing was done with the sp and raster (version 3.3-13; Hijmans, 2020) packages.

3. Results

3.1. Input point data

Data that were excluded based on P-M3, Ca-M3, pH or QUEFTS limits, were located across Rwanda, but tended to be clustered in the north-west and centre (Figure 1). Calibration and evaluation data represented the total dataset well in terms of spatial coverage. Data distributions of the soil parameters were similar between the calibration and evaluation datasets (Table 2); distributions were furthermore relatively similar to the total dataset (Table 1), except for Ca-M3 and P-M3, of which most descriptive values were lower than the original dataset because of the application of limits.

Table 1: Descriptive statistics of the soil parameters in the original IFDC dataset (n = 999)

	pH	SOC	Mehlich 3 (mg kg^{-1})				
	-	(g kg^{-1})	P	K	Al	Ca	Fe
Min.	3.2	2.2	0.2	14	342	51	61
1st Q	4.9	16.8	5.4	83	913	398	125
Median	5.6	20.6	9.3	153	1140	792	177
Mean	5.6	21.1	29.6	226	1182	1192	201
3rd Q	6.2	25.2	22.1	267	1400	1480	260
Max.	8.5	42.2	950	2960	2590	9800	764

Table 2: Descriptive statistics of Al, Ca, Fe, P and K in Mehlich 3, pH and SOC of the calibration (C; n = 591) and evaluation (E; n = 251) datasets.

	pH		SOC		Mehlich 3 (mg kg^{-1})									
	-		(g kg^{-1})		P		K		Al		Ca		Fe	
	C	E	C	E	C	E	C	E	C	E	C	E	C	E
Min.	4.0	4.0	2.2	9.4	0.2	1.2	14	31	342	379	57	107	61	66
1st Q	4.9	4.9	16.5	16.5	5.0	5.0	80	79	939	875	389	360	123	128
Median	5.4	5.4	19.9	20.2	8.2	8.2	142	145	1160	1160	705	691	171	178
Mean	5.5	5.5	20.7	20.4	13.7	12.7	194	185	1190	1184	913	898	195	195
3rd Q	6.0	5.9	25.0	23.8	15.9	16.2	246	215	1410	1465	1275	1220	255	248
Max.	7.9	7.9	42.2	34.4	105	66.2	1070	952	2590	2390	3330	3490	533	449

3.2. Soil maps

For the IC method, the degree to which the individual soil parameters could be predicted from available covariates, varied substantially (Table 3). Variation in Ca-M3 and Fe-M3 was described best, with MEC values above 0.50, followed by pH (MEC = 0.45), Al-M3 (MEC = 0.39) and SOC (MEC = 0.37). Variation in K-M3 and P-M3 was described less well, with MEC values of 0.23 and 0.07 respectively. For most properties, ME values were small compared to the mean values in the calibration and evaluation sets (Table 2) and relatively small compared to the RMSEs. For some soil properties, such as Ca and pH, the ME was relatively large compared to the RMSE. RMSE values furthermore are relatively high compared to mean values in the calibration and evaluation sets (Table 2), especially for P, K and Ca, indicating predictions are associated with large uncertainty.

Table 3: Evaluation statistics for the maps developed with the interpolate-then-calculate (IC) method. Statistics for K, P and Ca are given on log-transformed and original scale, after back-transformation. K, P, Al, Ca and Fe in Mehlich 3 (in mg kg^{-1}).

	ln(K)	ln(P)	ln(Ca)	K	P	Al	Ca	Fe	pH	SOC
ME	0.03	0.07	0.07	1.4	0.26	-7.1	123	2.3	0.10	0.03
RMSE	0.75	1.04	0.73	257	71.6	324	927	72	0.70	4.7
MEC	0.27	0.24	0.47	0.23	0.07	0.39	0.51	0.53	0.45	0.37

Table 4: Evaluation statistics for the P-Olsen (mg kg^{-1}) and Exch-K (mmol kg^{-1}) maps developed with the interpolate-then-calculate (IC) method. Statistics for P-Olsen are given on log-transformed and original scale, after back-transformation

	ln(P-Olsen)	P-Olsen	Exch.K
ME	0.15	-1.2	-0.07
RMSE	0.70	11.1	7.3
MEC	0.19	0.16	0.22

3.3. Application of transfer functions

For the CI method, the P and K transfer functions were applied to the calibration data. The median predictions were 7.8 mg kg^{-1} for P-Olsen and 4.0 mmol kg^{-1} for Exch-K (Table 5 and Figure 4). For the IC method, P-Olsen and Exch. K maps were developed by applying the transfer functions to maps of the input soil properties. Evaluation of the P-Olsen map showed that 16% of the variation in the (modelled) P-Olsen observations was explained (MEC = 0.16; Table 4), compared to a MEC of 0.07 for P-M3 (Table 3), the main parameter in the P transfer function. P-Olsen predictions had a ME of -1.2 mg kg^{-1}, indicating that they were somewhat underestimated. P-Olsen predictions were furthermore associated with a high degree of uncertainty, as the RMSE

of 11.1 mg kg^{-1} is higher than the mean value of P-Olsen predictions (9.8 mg kg^{-1}, Table 5). Exch-K predictions were a linear transformation of the K-M3 grid. Not surprisingly, the MEC value of Exch-K predictions (0.22; Table 4) was almost identical to that of K-M3 (0.23; Table 3). Exch-K predictions were slightly underpredicted with an ME of -0.07 mmol kg^{-1}. Similar to P-Olsen, the accuracy of Exch K predictions was low, with RMSE being higher than the mean of predicted values (7.3 *vs* 5.9 mmol kg^{-1}).

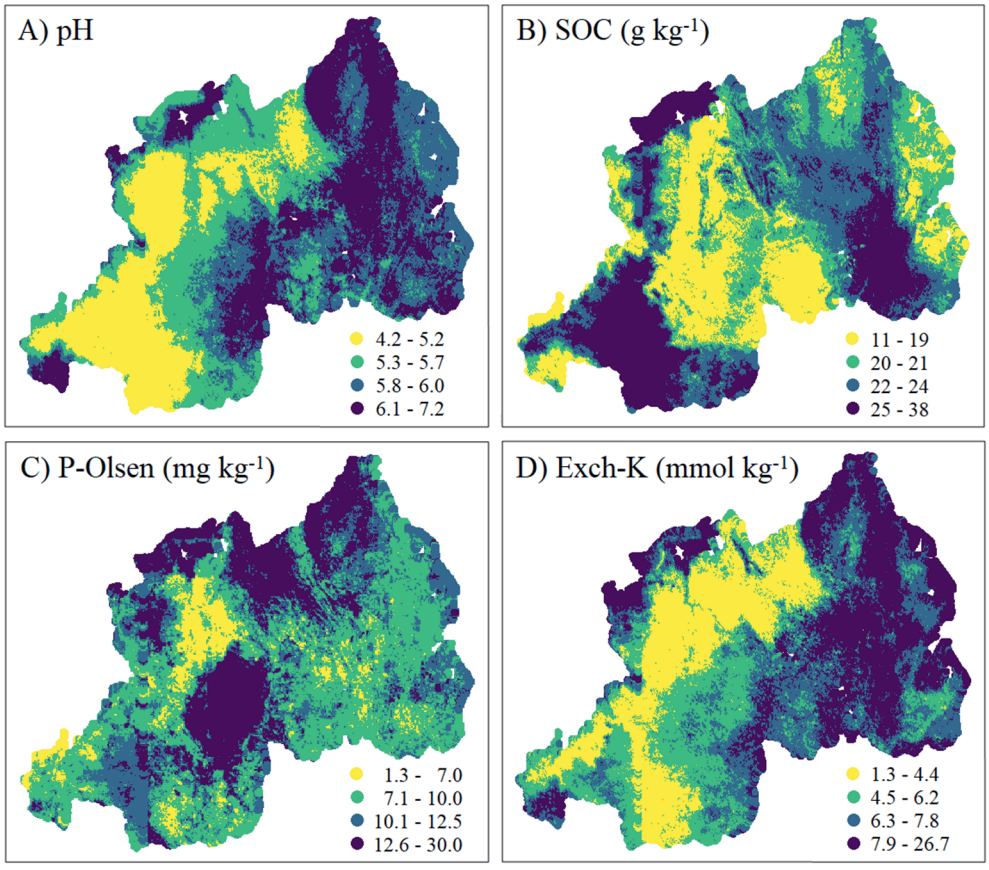

Figure 3: Spatial plots of pH (A), SOC (B), P-Olsen (C) and Exch-K (D) inputs required by QUEFTS, for the interpolate-then-calculate (IC) method. Class boundaries are based on the quantile distribution of the grid values, except for the P-Olsen map, where boundaries were adjusted to clearly represent values below the critical limit for maize (10 mg kg^{-1}).

3.4. Application of QUEFTS

Data distribution

Spatial predictions show that pH values are lowest (between 4.2 and 5.2) in the west and highest (between 6.1 and 7.2) in the east of Rwanda (Figure 3). Regions with the highest SOC values (between 25 and 38 mg kg^{-1}) are clustered in the south-west, north-west and south-east. For a large proportion of the surface area of Rwanda (51%), P-Olsen predictions are below the critical value of maize of 10 mg kg^{-1} (Bai et al., 2013; Ussiri et al., 1998), whereas for Exch-K, only a negligible part of the predictions are below the critical value of 2 mmol kg^{-1} (0.03%; Chilimba et al., 1999). Smoothing is visible for the gridded maps of each of the four QUEFTS input parameters: compared to the calibration data of the CI method, distributions have become narrower as the lowest and highest values are under-represented compared to mean values (Figure 4). As a consequence of smoothing, median values of SOC (20.6 *vs* 19.9), pH (5.53 *vs* 5.44), P-Olsen (8.8 *vs* 7.8) and Exch-K (5.0 *vs* 4.0) were higher for the gridded maps than for the calibration data (Table 5). Similar to the QUEFTS input parameters, gridded maps of the QUEFTS yield showed smoothing and a higher median value than direct QUEFTS predictions on the calibration points (4.0 *vs* 3.4 Mg ha^{-1}).

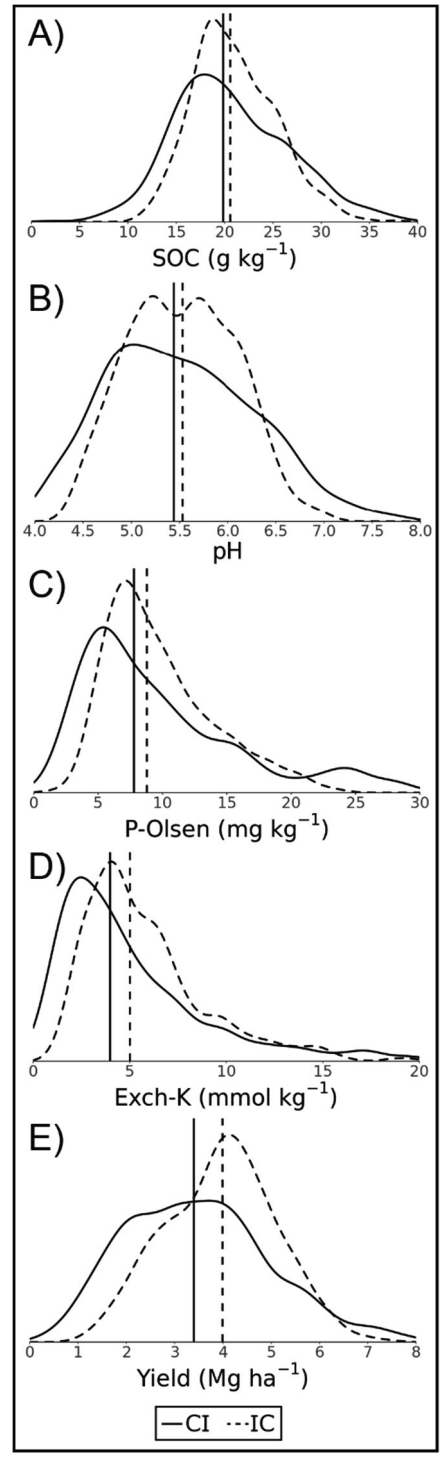

Figure 4: Density plots of SOC (A), pH (B), P-Olsen (C) and Exch-K (D) inputs and yield (E) on calibration locations of the calculate-then-interpolate (CI) method, and extracted from the interpolate-then-calculate (IC) maps at calibration locations. Vertical lines represent median values.

Table 5: Data distributions of QUEFTS input and yield predictions at calibration locations (C; n = 591) and extracted from the grids at the calibration locations

	SOC (g kg^{-1})		pH (-)		P-Olsen (mg kg^{-1})		Exch-K (mmol kg^{-1})		Yield (Mg ha^{-1})	
	C	Grid	C	Grid	C	Grid	C	Grid	C	Grid
Min.	2.2	11.5	4.02	4.40	0.4	1.3	0.4	1.3	0.4	1.2
1st Q	16.5	18.1	4.91	5.10	5.2	6.7	2.3	3.7	2.3	3.1
Median	19.9	20.6	5.44	5.53	7.8	8.8	4.0	5.0	3.4	4.0
Mean	20.7	21.1	5.51	5.53	9.8	9.8	5.5	5.9	3.5	4.0
3rd Q	25.0	23.9	6.05	5.96	12.5	12.0	6.9	7.1	4.4	4.7
Max.	42.2	37.7	7.86	7.01	29.8	23.8	29.9	20.8	7.8	7.4

Table 6: Data distributions of yield predictions on all, calibration (C) and evaluation (E) point locations, as well as the CI and IC predictions of the grids and on evaluation locations.

Yield	Point data			CI		IC	
(Mg ha^{-1})	All	C	E	Grid	E	Grid	E
Min.	0.4	0.4	0.8	1.3	1.8	1.2	2.1
1st Q	2.3	2.3	2.4	3.0	3.0	3.6	3.5
Median	3.4	3.4	3.3	3.6	3.5	4.5	4.3
Mean	3.5	3.5	3.5	3.5	3.5	4.3	4.2
3rd Q	4.4	4.4	4.3	4.0	4.0	5.0	4.9
Max.	8.2	7.8	8.2	6.0	4.8	7.5	5.9
n	842	591	251	355,178	251	355,178	251

Yield predictions

Yield maps produced with the CI and IC methods show similar patterns, with lower yields in the west of Rwanda and higher yields in the east (Figure 5). The low-yielding locations in the west are under-represented in both maps however, compared to the yield predictions at the calibration locations, while for the IC method, the high-yielding locations in the east are overrepresented. The median yield prediction of the maps developed with the IC method was substantially higher than for maps developed with the CI method (4.5 *vs* 3.6 Mg ha^{-1}, respectively; Table 6). In addition, despite smoothing of each of the four QUEFTS input variables for the IC method (Figure 4), the interquartile range in yield predictions was broader compared to the CI method (i.e. 3.0 - 4.0 *vs* 3.6 - 5.0 Mg ha^{-1}; Table 6).

The patterns of spatial yield predictions correspond strongly with the distribution of pH predictions across Rwanda, and to some extent with Exch-K predictions (Figure 5 *vs* Figure 3). The lowest yields (below 2.3 Mg ha^{-1}) are found in areas with low pH, and low P-Olsen and Exch-K values. The high yield predictions in the east of Rwanda furthermore correspond to high pH, SOC and Exch-K values.

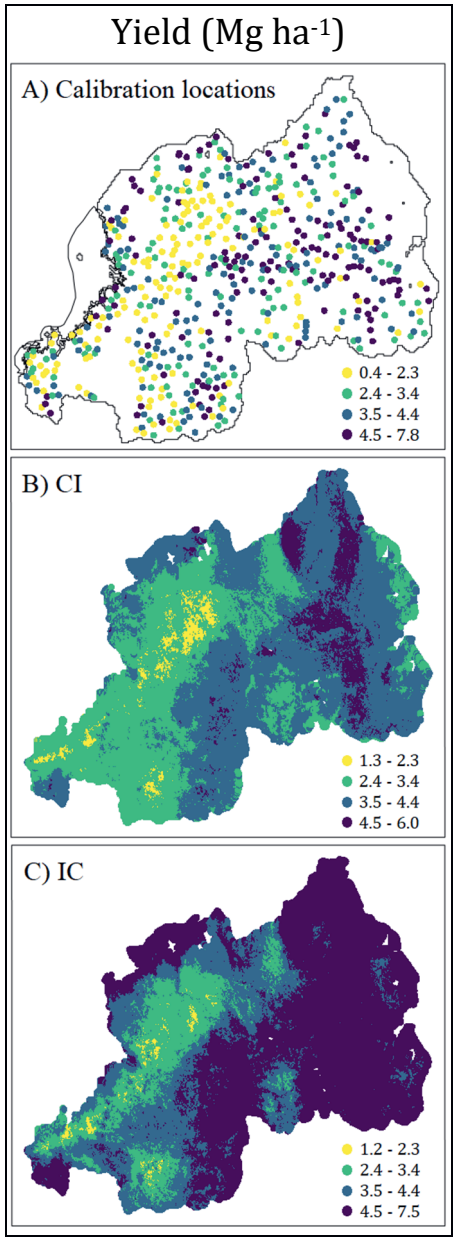

Figure 5: Yield predictions (A) at the calibration data (n = 591) and for maps developed with the (B) calculate-then-interpolate (CI) and (C) interpolate-then-calculate (IC) methods. Categories are based on the quantile distribution of the calibration points. Note that distributions have different minimum and maximum values.

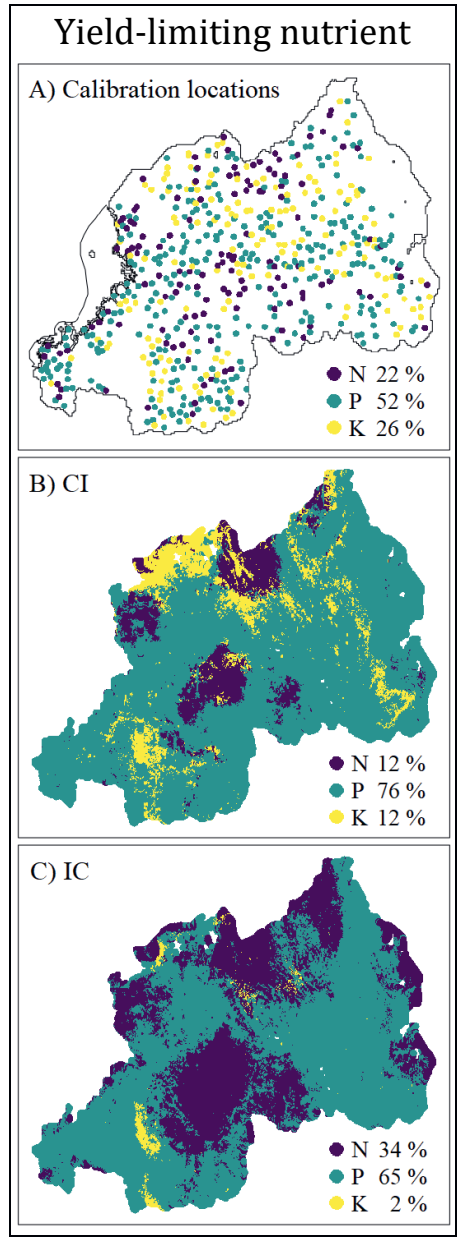

Figure 6: Predicted yield-limiting nutrient (A) at the calibration locations (n = 591) and for maps developed with the (B) calculate-then-interpolate (CI) and (C) interpolate-then-calculate (IC) methods. Percentages indicate the proportion of data being yield-limited by N, P or K.

The IC method overpredicted maize yields (Figure 7, resulting in a ME of 0.8 Mg ha^{-1}, compared to a relatively small overestimation of 0.04 Mg ha^{-1} for the CI method. Evaluation statistics furthermore indicate that IC yield predictions are less accurate compared to results of the CI method (MEC = -0.03 *vs* 0.28 and RMSE = 1.54 *vs* 1.27 Mg ha^{-1} respectively). Despite the poor MEC and RMSE results for IC, which are mostly caused by overprediction of yields, correlation coefficients of both evaluation plots are similar, with 0.444 and 0.439 for the CI and IC methods, respectively (Figure 7). This indicates that the IC and CI methods differentiate equally well between higher and lower yielding locations. In accordance with the data distribution of the grids, yield predictions by the IC method at the evaluation locations furthermore spanned a broader range than for those by the CI method (Table 6).

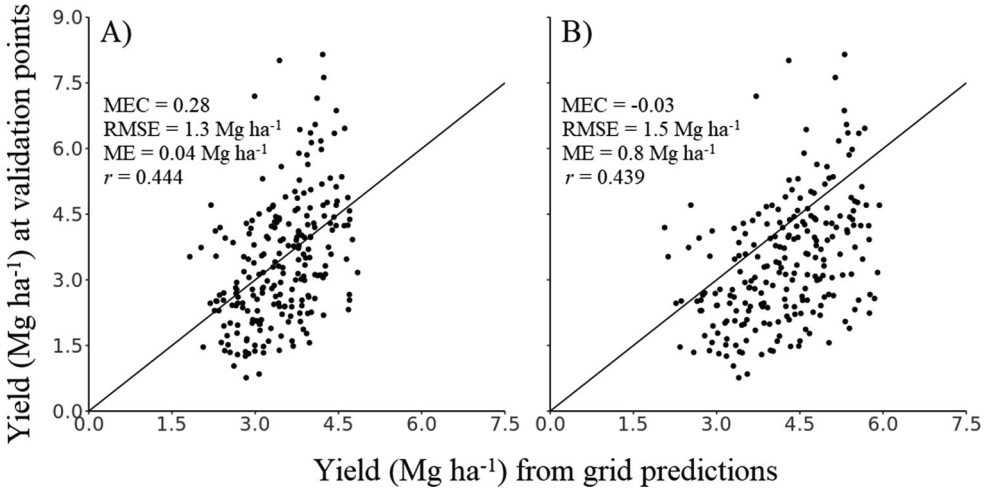

Figure 7: Evaluation plots of yield predictions by the (A) calculate-then-interpolate (CI) and (B) interpolate-then-calculate (IC) methods. The x-axis represents grid predictions extracted on evaluation locations. Lines represent the 1:1 lines.

Yield-limiting nutrient

For both the CI and IC methods, P was predicted most often as the yield-limiting nutrient, for 76% and 65% of the grid cells, respectively (Figure 6). These are higher percentages compared to the calibration data, for which P was predicted to be yield-limiting at 52% of the locations. N and K were yield-limiting at 22% and 26% of the calibration locations. The CI method underestimated both N and K as yield-limiting nutrient compared to the calibration data, as only 12% of the grid cells were predicted to be yield-limiting for each nutrient. The IC method overestimated N as yield-limiting (34%), but strongly underpredicted K as yield-limiting (2%).

Patterns of P-Olsen predictions strongly overlapped with predictions of the yield-limiting nutrient (Figure 6 *vs* Figure 3). Generally speaking, P was identified as yield-limiting in regions with P-Olsen values below 12.5 mg kg^{-1}, irrespective of soil pH and SOC. In areas with P-Olsen values above 12.5 mg kg^{-1}, N tended to be yield-limiting. Although K was strongly underpredicted to be yield-limiting, areas with K as yield-limiting nutrient tended to have SOC values above 22 g kg^{-1}.

Evaluation of QUEFTS yield-limiting nutrient predictions showed that the CI method predicted the yield-limiting nutrient correctly at 133 out of 222 (60%) evaluation locations, whereas IC predicted the yield-limiting nutrient correctly at 120 out of 222 (54%) evaluation locations (Table 7 and Table 8). The CI method predicted P as yield-limiting more accurately than the IC method (110 *vs* 87 out of 126 locations), whereas the opposite was true for N (17 *vs* 31 out of 56 locations). Both methods perform poorly when it comes to predicting K as the yield-limiting nutrient, with only 6 and 2 out of 40 cases predicted correctly for the CI and IC method, respectively.

Table 7: Confusion matrix of the observed *vs* predicted yield-limiting nutrient at the evaluation locations for the CI method.

CI		Predicted				
		N	P	K	Tot.	Tot.
Observed	N	**17**	32	7	56	25%
	P	6	**110**	10	126	57%
	K	3	32	**5**	40	18%
	Tot.	26	174	22	222	
	Tot.	12%	78%	10%		**59%**

Table 8: Confusion matrix of the observed versus predicted yield-limiting nutrient at the evaluation locations for the IC method.

IC		Predicted				
		N	P	K	Tot.	Tot.
Observed	N	**31**	25	0	56	25%
	P	38	**87**	1	126	57%
	K	11	27	**2**	40	18%
	Tot.	80	139	3	222	
	Tot.	36%	63%	1%		**54%**

4. Discussion

4.1. Comparing methods

This study showed three main findings: i) the choice of method has large effects on the outcomes: yield and yield-limiting nutrient predictions were more accurate for the CI method than the IC method, as the latter caused a large overprediction of yields across Rwanda, ii) the range in yield predictions was wider for the IC method than for the CI method, and iii) large errors were associated with spatial predictions of both methods.

Compared to Kempen et al. (2019) and Orton et al. (2014), differences between the CI and IC methods were more pronounced. This confirmed our hypothesis and is most likely related to the non-linear nature of QUEFTS (Heuvelink and Pebesma, 1999). In

contrast to our findings, Heuvelink and Pebesma (1999) argued that the IC method will generally lead to more accurate results than the CI method. They attribute this to the optimal use of available information, as each input parameter of the IC method has a specific correlation structure with the covariates. The CI method does not take these individual correlation structures into account, as only the model output is interpolated. Although in this study the IC method performed worse than the CI method, due to an overprediction of yields, we hypothesise that the broader range in yield predictions can be attributed to the more optimal use of covariate data.

We hypothesise that the CI method performed better than the IC method, because of the effects of smoothing and applications of limits (see below). However, although spatial yield predictions of the CI method were better compared to the IC method, RMSE still was 1.27 Mg ha^{-1}. This level of error corresponds to variability of maize yields within smallholder farms (Tittonell et al., 2007; Vanlauwe et al., 2006). This raises the question whether spatial application of QUEFTS, can be used to develop fertiliser recommendations on a national scale.

Smoothing

A striking difference between both methods was that IC yields were overestimated compared to CI yield predictions (Table 6). We believe this is caused by smoothing: data distributions of predictions (i.e. the soil maps) were more narrow than the datasets on which the predictions were based. For IC, smoothing as a result of spatial interpolation occurred early on in the workflow (Figure 2) and for each of the seven soil parameters used as input for the transfer functions and QUEFTS. For the CI method, on the other hand, smoothing occurred only once, at the end when the final yield and yield-limiting nutrient predictions at the calibration locations were interpolated.

Smoothing led to a smaller range in predictions for the QUEFTS input parameters, but also to higher median values for P-Olsen (7.8 *vs* 8.8 mg kg^{-1}) and Exch-K (4.0 *vs* 5.0 mmol kg^{-1}; Table 5). Although smoothing had a limited effect on median pH and SOC values, predictions were relatively more centred around the median after spatial interpolation. Low pH values (<4.7) are unfavourable for N availability, high pH values (>6.8) are unfavourable for K availability and P availability is suboptimal below pH 6 and above pH 6.7 (Sattari et al., 2014). After interpolation, data distributions were more centred around pH 5.0 - 6.5, which could be considered the optimal range for availability of each of the three nutrients. In combination with the overestimation of the lowest P-Olsen and Exch-K values, we hypothesise that smoothing of pH predictions is the main reason that yields were overpredicted for the IC method compared to the CI method.

The way and extent to which smoothing affects spatial predictions, depends on the predictive power of the covariates. In regression, variation in the data is the sum of the variation among the regression estimates and the residual variation (Snedecor and Cochran, 1989). In case covariate data explain the variation of a soil parameter completely, the residual variance equals zero and the variance of the predictions thus equals the variance of the data, hence no smoothing will occur. In other words, the lower the degree of variation in the target variable that can be explained by the covariates (i.e. MEC), the higher the degree of smoothing. The MEC value was 0.37 for SOC, 0.45 for pH, 0.16 for P-Olsen and 0.22 for Exch-K, while the MEC of the QUEFTS yield predictions with the CI method was 0.28. Variation in QUEFTS yield is thus explained less well by the covariates than variation in SOC and pH, but better than variation in P-Olsen and Exch-K. As SOC and pH play a prominent role in QUEFTS yield predictions, we hypothesise that the relatively good predictability of these soil characteristics is the reason for the wider range in yield predictions for the IC method.

From an agronomic perspective, predicting low P-Olsen and Exch-K values accurately is more relevant than predicting high values accurately. Although depending on other soil and agro-ecological properties that control crop yield, the critical P-Olsen concentration below which P is expected to be yield-limiting for maize, is 10 mg kg^{-1} (Bai et al., 2013; Ussiri et al., 1998). The Exch-K concentration below which K is expected to be yield-limiting is 2 mmol kg^{-1} (Chilimba et al., 1999). Smoothing thus led to an overprediction of values in the agronomically relevant range. As a consequence, QUEFTS P and K fertiliser recommendations in those regions would be inadequate for sustainably increasing yields.

Smoothing can be avoided by using stochastic simulation (Heuvelink and Pebesma, 1999). Such approach, however, requires a geostatistical modelling framework instead of machine learning and was beyond the scope of the current study.

Data limits

Application of data limits for use of the transfer functions and QUEFTS increased differences between outcomes of both methods. For the CI method, application of limits led to the exclusion of 108 out of 699 data points for the calibration set (591 points remaining). For the IC method, maps were developed based on all 699 calibration data points and limits were applied to the maps. Application of limits mostly led to exclusion of data points with high values. Basing maps based on the complete calibration set thus resulted in higher yield predictions for the IC method. Developing soil maps based on the subset of 591 calibration points, resulted in a lower

overprediction of yields for the IC method, although the average yield still exceeded that of the CI method (results not presented). The yield predictions by the IC method furthermore still spanned a broader range than the yields predicted by the CI method, indicating that it is smoothing rather than application of limits that caused the relatively narrow range in CI yields.

4.2. Limitations

Evaluation

To evaluate the extent to which QUEFTS spatial predictions correspond to reality, external evaluation of the yield maps developed in this study is indispensable. To this end, a dataset with unfertilised maize yields from a substantial number of replicated, geo-referenced field trials is needed. Trial locations should ideally be spread across Rwanda, covering a wide range in values for each of the relevant soil properties. Such dataset for Rwanda was not available to us and compiling an evaluation dataset from literature is complicated by e.g. different study designs or missing information. As more data are becoming (publicly) available, evaluation of QUEFTS spatial predictions may be possible in the future.

Sources of uncertainty

In the process of developing maps with QUEFTS, several sources of uncertainty can be identified. Although error propagation analysis was considered outside the scope of this study, the different sources of uncertainty will be discussed here.

Firstly, soil analysis data contain measurement errors, which can be attributed to varying measurement conditions, methods and measuring instruments (Van Leeuwen et al., 2021). As a consequence, results can differ among laboratories. Uncertainty associated with the Mehlich 3 extraction method is of considerable importance for this study, as five of the seven soil properties (P, Al, Ca, Fe and K) used as input for QUEFTS were determined with this analytical procedure. As part of a different study, a small subset (n = 19) of the IFDC samples was analysed at the CBLB laboratory of Wageningen University for M3 extractable nutrients using the same protocol as used in chapter 2. The M3 measurements by CropNuts were roughly 5% (P), 23% (Al), 10% (Ca) and 17% (Fe) higher compared to CBLB results. For K, no significant differences were found. Application of the P transfer function to the IFDC data led to an 19% overestimation of P-Olsen predictions compared to using CBLB measurements. This confirms that inter-laboratory variability for a given method, when used as input for models, can have a substantial effect on model output, as also shown by Schut and Giller (2020).

Secondly, the accuracy of random forest predictions were modest to poor for most soil properties, as RMSE values were relatively high compared to mean values (Table 2 and Table 3). Available covariate data generally explained variation in soil properties only to a limited extent. In line with Hengl et al. (2017a), variation in P-M3 was described poorly compared to other nutrients. Reasons may include historic management which can affect P availability (Njoroge et al., 2019), P fixation in tropical soils (de Campos et al., 2018) and other soil properties which affect P extractability, such as pH (e.g. Penn et al., 2018). As P-M3 is the most relevant parameter in the P transfer function, P-Olsen predictions were not modelled well (MEC = 0.16). Exch-K predictions were only slightly better (MEC = 0.22). Although variation in pH (MEC = 0.45) and SOC (MEC = 0.37) was explained better based on covariate data, the combination of uncertainty associated with each of the QUEFTS input parameters culminated in a large error in yield predictions (RMSE of 1.54 Mg ha^{-1}; Figure 5).

Thirdly, the use of transfer functions is necessary in case required input data are not available, but introduce additional uncertainty (Heuvelink and Pebesma, 1999). The uncertainty associated with the P and K transfer functions used in this study, can cause deviations in QUEFTS yield of more than 10%, compared to using measured P-Olsen and Exch-K values (chapter 2). Finally, QUEFTS yield predictions contain uncertainty; when observed maize yields were compared to QUEFTS predictions, MEC values of 0.84 and 0.67 were reported by Tabi et al. (2008) and by Shehu et al. (2019) after partial reparameterization of QUEFTS.

Spatial-temporal heterogeneity

Agronomic practices such as fertiliser application, liming and organic matter management impact soil nutrient availability, pH and SOC and can differ between farmers depending on socio-economic status and within-farm depending on distance from the homestead (Chikowo et al., 2014; Zingore et al., 2007). Njoroge et al. (2019) furthermore showed that historic management can impact yields even seven growing seasons after changing practices. Management practices typically vary at short spatial scales and are difficult to capture with (spatially exhaustive) environmental covariates. Hence, it is challenging to capture management effects on soil conditions in digital soil mapping models, which contributes to poor performance of the prediction models for soil nutrients. Soil maps developed at regional or national level may therefore lack the precision to describe short-distance spatial heterogeneity (Vanlauwe et al., 2015) and one should be careful to use these to derive information at field level. Maps furthermore are not able to capture temporal change and maps of soil parameters that are subject to short-term change should be used and interpreted with caution (Hengl et al., 2017b).

Data transformation

Adding half the prediction variance is required to ensure an unbiased estimation of the mean (Lark and Lapworth, 2012) when back-transforming a log-transformed variable. In some situations, existing soil maps are available, but not the underpinning data points. If these maps were created by back-transformation of log-scale predictions, variables would be log-transformed a second time in the process of applying the P transfer function. As a consequence, distributions of these log-scale predictions will have a higher mean than the initial log-scale predictions. In this study, log-scale predictions of P-M3 and Ca-M3 were used directly as input for the P transfer function. When using log-transformed P-M3 and Ca-M3 grid predictions on the original scale (after back-transformation) as input for the P transfer function, the median P-Olsen predictions increased from 9.9 to 16.8 mg kg^{-1}. The critical P-Olsen range, below 10 mg kg^{-1} for maize is thus strongly under-represented as a result of this 'transformation error' and may potentially have a large effect on fertiliser recommendations. The magnitude of this error depends on which and how many nutrients were log-transformed twice. As P-M3 is the most relevant parameter in the P transfer function (chapter 2), it had a substantial effect. When using maps developed with unknown methods as input for the P transfer function, or any model that requires log-transformed parameters as input, one should take into account that the model output may be substantially overestimated as a result of the transformation error.

4.3. Opportunities

Several developments may improve QUEFTS spatial predictions of yield and most yield-limiting nutrient. The large error associated with spatial yield predictions can mainly be attributed to the low predictive power of the covariates to explain variation in the soil and (for this study modelled) yield observations. As high (50-100 m) resolution covariate layers are becoming more and more available, spatial prediction models for soil and agronomic variables are likely to be improved (Hengl et al., 2017b; Poggio et al., 2021).

QUEFTS spatial predictions can also improve strongly in case P-Olsen measurement data become available. Variation in P-Olsen predictions was described least well of the four QUEFTS input parameters. This can partly be attributed to the use of a transfer function rather than measurements, and due to the uncertainty associated with each of the input maps for the P transfer function. Alternatively, Shehu et al. (2019) reparametrized QUEFTS using P-M3 instead of P-Olsen, which enables (spatial) application of QUEFTS without the use of the P transfer function.

QUEFTS spatial predictions can be adjusted to local conditions by using covariate layers directly as input. In this study, the QUEFTS maximum yield (Y_{max}) was assumed to be constant at 10 Mg ha^{-1}, but is likely to vary strongly in practice depending on local growing conditions. Covariate layers containing information on e.g. rooting depth, water availability or expected yield gap, currently not accounted for in this study, could be used to adjust the Y_{max} parameter to local conditions, thereby improving the accuracy of QUEFTS predictions (Leenaars et al., 2018a, 2018b; Steinbuch et al., 2016).

5. Conclusions

Spatial predictions of QUEFTS yield and yield-limiting nutrient were more accurate for the CI method than the IC method. The IC method overestimated yields, caused by the effect of smoothing on the distributions of the QUEFTS input (soil) parameters. Based on the results of this study, the CI method would thus be the preferred method for spatial application of QUEFTS. However, although the CI method performed better than the IC method, yield predictions were associated with large errors in our case study. This indicates that QUEFTS should be applied spatially with caution.

The large error of QUEFTS spatial predictions is caused by the low predictive power of the covariates to explain variation in the QUEFTS input parameters. When higher quality input soil maps become available, spatial application of QUEFTS could provide a low-cost, science-based alternative to national blanket recommendations. Evaluation with independent geo-referenced field data of measured yields remains necessary however, to gain insights in the current performance, as well as opportunities for improvement of QUEFTS spatial predictions.

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Chapter 4

Soil zinc fertilisation does not increase maize yields but improves nutritional quality

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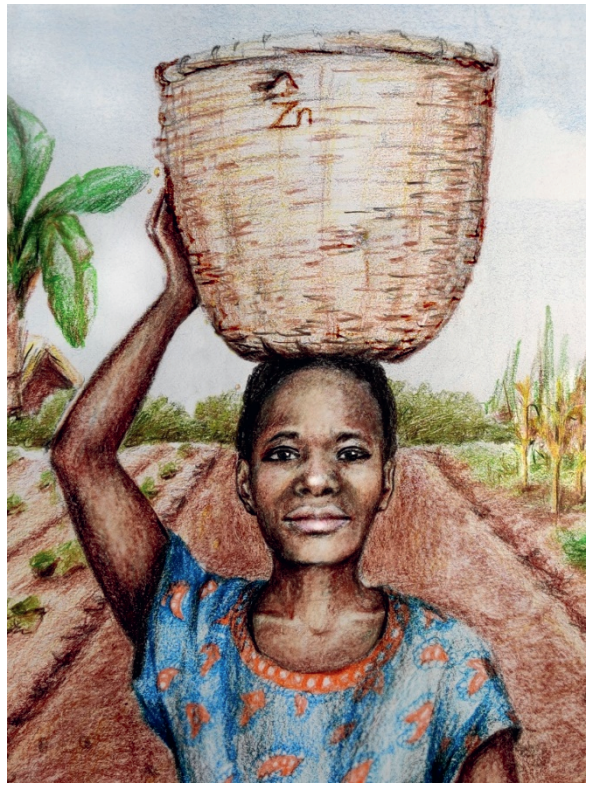

Abstract

Fertilisation of crops with zinc (Zn) is considered important to enhance agricultural productivity and combat human deficiencies in sub-Saharan Africa. However, it is unclear on which soils Zn fertilisation can lead to higher yields and increase grain Zn concentrations. This study aimed to find soil properties that predict where soil Zn is limiting maize yields and grain Zn concentrations, and where yields and grain Zn concentrations respond positively to Zn fertilisation. Zinc fertiliser omission trials were set up at multiple farm locations in Kenya (n = 5), Zambia (n = 4) and Zimbabwe (n = 10). Grain yields and tissue Zn concentrations were analysed from plots with a full fertiliser treatment as compared to plots where Zn was omitted. Zinc uptake (R^2 = 0.35) and grain Zn concentrations (R^2 = 0.26) in plots without Zn fertiliser could be related to a limited extent to soil Zn measured in extractions that measure labile Zn. A positive maize yield response to soil Zn fertilisation was found at only two out of nineteen locations, despite soil Zn levels below previously derived critical concentrations at most locations. Neither soil properties nor plant concentrations were able to explain maize yield response to Zn fertilisation. However, a positive response in Zn uptake and grain Zn concentrations to Zn fertilisation was found at the majority of sites. We conclude that soil Zn fertilisation can increase maize grain Zn concentrations, especially in soils with low pH and organic carbon content. Predicting a yield response to Zn fertilisation based on soil properties remains a challenge.

1. Introduction

Maize (*Zea Mays*) is an important staple crop in sub-Saharan Africa (SSA). It provides a significant proportion of the human daily intake of calories and mineral nutrition (Goredema-matongera et al., 2021). The production of maize in SSA is dominated by smallholder farming, generally characterized by little use of inputs on soils with low fertility (Santpoort, 2020; Ten Berge et al., 2019). As a result, maize yields are often limited by multiple nutrient deficiencies, which can be addressed by the use of mineral and organic fertilisers (Goredema-matongera et al., 2021; Ten Berge et al., 2019; Vanlauwe et al., 2015). It has been recognized decades ago that soils which have been cropped with little or no inputs for prolonged periods lack not only the macronutrients but also micronutrients to sustain crop growth (Kang and Osiname, 1985; Rodel and Hopley, 1972). Nevertheless, soil fertility and crop nutrition research in SSA has mainly focused on macronutrients, i.e. nitrogen (N), phosphorus (P) and potassium (K) (Kihara et al., 2017; Stoorvogel et al., 1993; Vanlauwe et al., 2015). Research on micronutrient deficiencies in crops has received less frequent attention (Mutsaers et al., 2017).

With regards to maize, studies on yield response to micronutrient fertilisation in SSA have often been conducted for only limited sets of locations with either a positive or absent yield response (Abbas et al., 2007; Abunyewa and Mercer-Quarshie, 2003; Chiezey, 2014; Chilimba et al., 1999; Eteng et al., 2014; Njoroge et al., 2018; Osiname et al., 1973; Shehu et al., 2018; Yerokun and Chirwa, 2014). Other studies have focused on the effect of micronutrient fertilisation on yields at the regional or global scale in order to understand where micronutrients may be yield-limiting. In 1990, Sillanpää (1990) published the results of 190 single-micronutrient omission field trials distributed over 15 countries. It was found that among all micronutrients, zinc (Zn) was most of the time yield-limiting, with a positive yield response to Zn fertilisation for 49% of all locations. More recently, maize nutrient omission trials including treatments with a mixture of secondary nutrients and micronutrients have been conducted across various countries in SSA. Kihara et al. (2017, 2016) concluded that application of secondary and micronutrients (calcium (Ca), magnesium (Mg), sulphur (S), boron (B) and zinc (Zn)) increased maize yields in several SSA countries by 0.8 Mg ha^{-1} on average, an increase of 25% compared to application of NPK alone. Similar results were found by Wortmann et al. (2019), who reported a mean increase in maize yields between 20 and 30% when S, Zn and B were fertilised. These studies suggest that secondary and micronutrient deficiencies limit maize yields across SSA. On the other hand, Rurinda et al. (2020) concluded that the overall maize yield response to secondary and micronutrients (S, Ca, Mg, Zn, and B) was small, i.e. between 0 and 0.3 Mg ha^{-1}, across all studied sites in Nigeria, Tanzania and Ethiopia.

The aforementioned studies by Kihara et al. (2017) and Wortmann et al. (2019) suggest that deficiencies of secondary and micronutrients limit maize yields across SSA. Since mixtures of secondary and micronutrients were used in these studies, it remains unclear which particular micronutrients are deficient at which locations. Furthermore, using mixtures of nutrients makes it challenging to identify soil properties that explain particular nutrient limitations for maize growth (Kihara et al., 2017). Such analyses are however indispensable for extending existing science-based fertiliser recommendation schemes that currently include only NPK, with secondary and micronutrients (Rurinda et al., 2020; Sattari et al., 2014).

Apart from yield quantity (Abbas et al., 2007; Abunyewa and Mercer-Quarshie, 2003; Kihara et al., 2017; Manzeke et al., 2014; Njoroge et al., 2017; Sillanpää, 1990), Zn is also relevant for human health and insufficient intake can result in severe health issues. More than 17.3% of the global population is prone to insufficient Zn intake (Kiran et al., 2022) and 50% of all children in SSA are estimated to be at risk of Zn deficiency (Black et al., 2008). The risk of human Zn deficiency is considered high especially in Eastern and Southern African countries (Joy et al., 2014). Micronutrient deficiencies in humans are widespread in regions where crops are grown in soils with low micronutrient levels, as soil availability determines plant uptake and therefore micronutrient concentrations in the edible parts of plants (Cakmak, 2004; Dimkpa and Bindraban, 2016; Gashu et al., 2021; Manzeke et al., 2012). Berkhout et al. (2019) indeed found significant relations between soil concentrations of micronutrients such as Zn and Cu in SSA, and prevalence of child mortality, stunting, wasting and underweight, which are typical health problems associated with micronutrient deficiencies. However, current assessments of possible micronutrient deficiencies among humans are based on standard food composition tables and consequently do not take into account variability in soil properties and associated soil Zn availability, which can significantly affect grain Zn concentrations, and subsequent Zn intake by humans (Gashu et al., 2021; Manzeke et al., 2012). It has been shown that increasing soil Zn availability through fertilisation is a feasible strategy to increase grain Zn concentrations, and thereby reduce the risk for human Zn deficiency (Cakmak, 2008; de Valença et al., 2017; Joy et al., 2015; Manzeke et al., 2012), also known as agronomic biofortification (Kiran et al., 2022). Next to soil Zn availability, the genetic variation among cultivated maize varieties has great implications on the Zn uptake from the soil, and the translocation of Zn to the edible parts (Brkic et al., 2004; Oikeh et al., 2007). Knowledge on the effect of soil properties and maize variety on total Zn uptake and associated grain Zn concentrations, and how these factors affect the effectiveness of agronomic biofortification, can enhance target-based intervention programs to combat human Zn deficiencies.

Soil Zn availability for plant uptake decreases with increasing pH, due to precipitation and increased adsorption to reactive surfaces such as soil organic matter and metal (hydr)oxides (Alloway, 2009; Van Eynde et al., 2022). With increased amounts of soil organic matter, the availability of Zn may decrease due to increased adsorption (Van Eynde et al., 2022), or increase due to soil organic matter mineralization (Tella et al., 2016) or formation of soluble organic Zn complexes (Hernandez-Soriano et al., 2013). Different chemical extractions have been formulated to evaluate soil Zn availability for plant uptake, the associated yield response to Zn fertilisation (Chilimba et al., 1999; Duffner et al., 2013; Lindsay and Norvell, 1978; Mertens and Smolders, 2013) and Zn concentrations in the edible plant parts (Kihara et al., 2020; Manzeke et al., 2012). For example, a soil test with diethylenetriaminepentaacetic acid (DTPA) as chelating agent is widely used for near-neutral and calcareous soils (Lindsay and Norvell, 1978), while others have used acidic soil extracts such as HCl or Mehlich 3 (M3) for more acidic soils (Alloway, 2009; Mehlich, 1984; Mertens and Smolders, 2013). The DTPA and M3 soil extracts are currently most often used for Zn fertiliser recommendations and critical extractable soil Zn levels have been derived below which a positive maize yield response to Zn-fertilisation can be expected. Based on field and greenhouse experiments, these critical soil Zn levels range from 1 - 2.5 mg kg^{-1} Zn-M3 (Chilimba et al., 1999; Cuesta et al., 2020; Wendt, 1995), or 0.5 - 1 mg kg^{-1} Zn-DTPA (Chilimba et al., 1999; Cuesta et al., 2020; Lindsay and Norvell, 1978). Alternatively, weak salt extractions such as 0.01 M $CaCl_2$ have been used for measuring soil available Zn (Houba et al., 2000), assuming that these extractions approximate more the directly available pool for plant uptake (Duffner et al., 2013; Menzies et al., 2007). Validation of soil extracts such as DTPA, M3 or 0.01 M $CaCl_2$ as diagnostic criteria for Zn availability to field-grown maize, however, is limited.

Therefore, this study aims to test whether soil properties can be used to predict where Zn availability is limiting maize yields (quantity) and grain Zn concentrations (quality), and whether the application of Zn fertilisers increases yield quantity and/or quality. Using Zn fertiliser omission trials in several African countries, we aimed to test the following hypothesis, namely that crop yield, Zn uptake and grain Zn, and their response to Zn fertilisation, can be predicted based on soil parameters that have been shown before to predict Zn in the soil solution: pH, soil organic matter, the Zn quantity, and perhaps metal (hydr)oxides (Van Eynde et al., 2022). Findings from this study will help to understand under which circumstances Zn fertilisation can increase maize yields, as well as grain Zn concentrations in SSA.

2. Materials and Methods

2.1. Field trials

Researcher-managed omission trials with maize were executed at 19 locations in three countries: Kenya (5 locations with 5 replications), Zambia (4 locations with 4 replications) and Zimbabwe (10 locations with 6 replications). Based on soil maps (Figure 1), soil Zn levels were expected to be generally low (i.e. below the potentially critical level of 2.5 mg kg^{-1} Zn-M3; Chilimba et al., 1999) at all locations.

The Zn fertiliser omission trials were executed as part of a larger experiment, in which zinc, copper and boron fertiliser omissions were studied. The plots with the different treatments were laid out as a randomized block design. As the focus of this work is on Zn, only details of the relevant treatments are presented. These include a full treatment including all nutrients (hereafter denoted as "full") and a Zn omission treatment including all nutrients except Zn (hereafter denoted as "-Zn").

The maize variety, planting densities, plot sizes, fertiliser application rates and number of replications, differed between countries based on the availability of resources and local practices. Details of each of these trials are specified below; rainfall data are presented in the supplementary information (Figure S1).

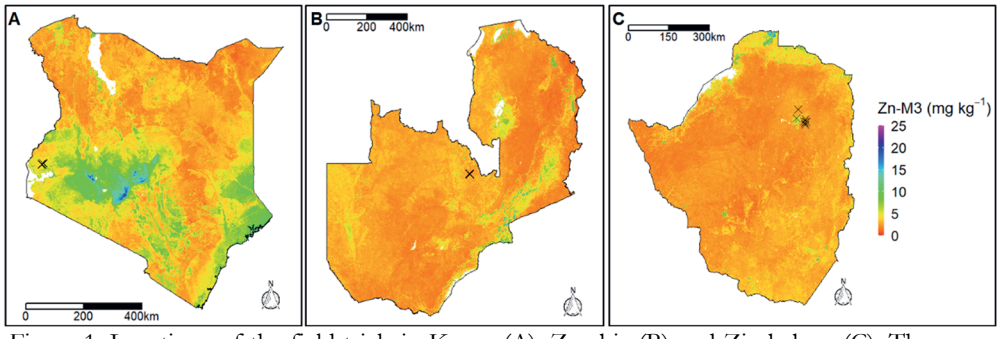

Figure 1: Locations of the field trials in Kenya (A), Zambia (B) and Zimbabwe (C). The maps represent soil Zn concentrations in a Mehlich-3 (Zn-M3) extraction (Hengl et al., 2021).

Kenya

Field trials in Kenya were set up in collaboration with the International Plant Nutrition Institute (IPNI), Nairobi, Kenya. They were conducted in the long rainy season in 2018 (March - August) at five on-farm locations in Siaya county, Western Kenya (Figure 1), in the humid cool tropics agroecological zone (Sebastian, 2009). Soils were classified as Haplic Acrisols (Hengl et al., 2017). During the ten preceding cropping seasons prior to

this experiment, these locations had been used for NPK fertiliser omission trials in which no inputs were applied besides chemical N, P and K fertilisers (Njoroge Kinyanjui, 2019). Short season maize variety DK8031 was used at all locations. Two seeds were planted per hole with a plant spacing of 25 cm × 75 cm and were thinned to one plant per hole after emergence, resulting in a final plant density of 53,333 plants ha^{-1}. Plot sizes were 4.5 m × 4.5 m, with five replicates per treatment at each location. Weeding and pest control was done when needed. The following fertiliser application rates (in kg ha^{-1}) were used: 350 N, 180 P, 120 K, 59 Ca, 20 Mg, 31 S, 5 Zn, 5 copper (Cu) and 5 B. Nitrogen was applied as urea in three equal splits, with a basal application at planting, and two topdressings at stages V6 and V10 of plant growth. Phosphorus and Ca were applied as TSP, K as muriate of potash (KCl), Mg and S as $MgSO_4$, Zn as $ZnSO_4$, Cu as $CuSO_4$ and B as Solubor. The P and K fertilisers plus those supplying secondary and micronutrients were applied together in the planting hole during planting. At physiological maturity, a net plot of three rows of 3 m length (6.75 m^2) was harvested from the inside of each plot, omitting border plants to avoid edge effects.

Zambia

Field trials in Zambia were set up in collaboration with students in agricultural sciences from the Foundations for Cross-cultural Education (FCE) training centre in Zambia. Micronutrient omission trials were conducted from November 2018 - April 2019 at the FCE training centre and at three on-farm locations in surrounding villages in the Masaiti district, Copperbelt, Central Zambia (Figure 1). These locations are situated in the semiarid cool tropics agroecological zone (Sebastian, 2009) and the soils were classified as Haplic Ferralsols (Hengl et al., 2017). At each location, legumes were cultivated in the preceding season. At the training centre, compost had been added annually to the field to conserve soil fertility. At the three on-farm locations, no organic or chemical inputs had recently been applied and crop residues had usually been burned in the fields. At each location, the open pollination maize variety Afric1 (Klein Karoo, South Africa) was used. Three seeds were planted per hole with a plant spacing of 60 cm × 75 cm. Two weeks after emergence the plants were thinned to two plants per hole, resulting in a final plant density of 44,444 plants ha^{-1}. Plot sizes were 4.5 m × 4.2 m. Weeding and pest control was done when needed. The following fertiliser application rates (kg ha^{-1}) were used: 180 N, 35 P, 100 K, 26 Ca, 2.3 Mg, 5.6 S, 3 Zn and 3 B. Nitrogen was applied as urea, as one basal application with the other elements during planting, and two topdressings. Boron was applied as borax, mixed with the urea and applied only during the two topdressings at stages V6 and V10 of plant growth. Phosphorus and Ca were applied as TSP, K as muriate of potash (KCl), Mg as $MgSO_4$ and Zn as $ZnSO_4$. Copper was not applied given the high soil concentrations found during preliminary lab analysis.

At physiological maturity, a net plot of 4 rows by 5 plants (9 m^2) was harvested from the inside of each plot, omitting border plants to avoid edge effects.

Zimbabwe

Field trials in Zimbabwe were set up in collaboration with the Department of Plant Production Sciences of the University of Zimbabwe (UZ), Harare, Zimbabwe. Micronutrient fertiliser omission trials were conducted from November 2019 – April 2020 at nine on-farm locations in several villages in the Goromonzi district as well as one location on UZ campus (Figure 1). All locations are situated in the semiarid cool tropics (Sebastian, 2009) and soils were classified as Haplic Lixisols or Haplic Acrisols (Hengl et al., 2017). Maize was cultivated in the preceding growing season at each location. The farming systems were characterised by low NPK inputs, and at best received cattle manure once every 4 years at a dose of 2 - 4 Mg ha^{-1}. At each location, the hybrid maize variety SC637 (SeedCo) was used. Two seeds were planted per hole with a plant spacing of 25 cm × 90 cm. Two weeks after emergence, plants were thinned to one plant per hole, resulting in a final plant density of 44,444 plants ha^{-1}. Plot sizes were 5.4 m × 4 m. Weeding and pest control was done when needed. The following fertiliser application rates (kg ha^{-1}) were used: 180 N, 80 P, 120 K, 61 Ca, 20 Mg, 26 S, 5 Zn, 5 Cu, 3 B and 0.3 Mn. Nitrogen was applied as ammonium nitrate, one basal application and two topdressings at 4 and 8 weeks after emergence. Phosphorus and Ca were applied as TSP, K as muriate of potash (KCl), Mg as $MgSO_4$, Zn as $ZnSO_4$, Cu as $CuSO_4$, Mn as $MnCl_2$ and B as Solubor. Fertilisers were applied together in the planting hole during planting. At physiological maturity, a net plot of 3 rows by 2 m (5.4 m^2) was harvested from the inside of each plot, omitting border plants to avoid edge effects.

Field data and sample collection

Field-dry stover and grain biomass were measured for each plot during harvest. A 200g subsample was taken from each plot for further analysis. Dry matter contents of these subsamples were used to convert field-dry biomass measurements to dry weights. Throughout the manuscript, the grain yield data are reported using a standardized moisture content of 13%. Composite topsoil samples (0-20 cm) from each block were collected during harvest. Soil samples were taken between the rows, as fertilisers were applied in the planting hole. Soil and field-dry plant samples were shipped to the soil chemical laboratory CBLB (Wageningen, the Netherlands) for further analysis.

2.2. Plant analysis

Stover and grain samples were dried at 70 ºC until dry weight was reached, and ground to < 1 mm size before analysis. Stover and grain samples were analysed for N, P, K, S,

Mg, Ca, iron (Fe), Zn, B, Cu and manganese (Mn) concentrations. Plant N concentrations were measured after a 0.8 M H_2SO_4/Se/H_2O_2 digestion (Novozamsky et al., 1983) using a Segmented Flow Analyser. All other elements were measured after microwave digestion with concentrated HNO_3 (Novozamsky et al., 1983) using Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES, Thermo Scientific iCAP6500) or High Resolution Inductively Coupled Plasma - Mass Spectrometry (HR-ICP-MS, Element 2, Thermo Scientific), depending on their concentrations.

2.3. Soil analyses

Soil samples were air-dried and sieved over 2 mm prior to further analysis. Relevant soil properties were chosen based on previously obtained knowledge about the processes controlling soil Zn availability (Van Eynde et al., 2022): reactive surfaces for adsorption (i.e. soil organic matter, dissolved organic matter and micro-crystalline metal (hydr)oxide nanoparticles) and soil pH.

Total soil organic carbon (SOC) content was analysed using a wet oxidation method according to the Kurmies procedure and measured with a spectrophotometer (Walinga et al., 2008). An ammonium oxalate (AO) extraction with a solution-to-solid ratio of 20 L kg^{-1} and an equilibration time of 4 hours (ISO, 2012) was used to measure micro-crystalline Fe and Al. The concentrations of Fe and Al were analysed using ICP-OES. For further data analysis, the sum of Al and Fe hydroxides in ammonium oxalate (AlFe-AO; in mmol kg^{-1}) was used. Soil pH was measured with a glass electrode in a 0.01 M $CaCl_2$ soil extract, with a solution-to-solid ratio of 10 L kg^{-1} and an equilibration time of 2 h (Houba et al., 2000). The dissolved total carbon and dissolved inorganic carbon concentrations were measured in the same $CaCl_2$ extract after centrifugation and filtration with a 0.45 µm membrane filter, with a Segmented Flow Analyzer (SFA-TOC, San^{++}, Skalar) equipped with an IR detector that measures the amount of CO_2 (g) after an internal acidification and destruction step. The dissolved organic carbon (DOC) concentrations were calculated as the difference between total and inorganic carbon.

Soil Zn was measured in a 0.43 M HNO_3 extraction, a Mehlich 3 (M3) extraction, a diethylenetriamine pentaacetate (DTPA) extract and a 0.01 M $CaCl_2$ extraction. The first three tests are expected to approximate the Zn quantity or labile content, while the latter was considered to be an estimation of the intensity or the actual availability. The HNO_3 soil extraction was done using a solution-to-solid ratio of 10 L kg^{-1} and an equilibration time of 4 h (ISO, 2016). After centrifugation and filtration over a 0.45 µm membrane filter, Zn-HNO_3 was measured in the supernatant with ICP-OES. The Zn-M3 was

measured with ICP-OES in a centrifuged and filtered (0.45 μm) M3 extract. The M3 extract consisted of 0.1 M CH_3COOH, 0.25 M NH_4NO_3, 0.015 M NH_4F, 0.013 M HNO_3 and 0.001 M EDTA (Mehlich, 1984). Samples were extracted for 5 min with a solution-to-solid ratio of 10 L kg^{-1}. For the Zn-DTPA analysis, soils were extracted with a solution-to-solid ratio of 2 L kg^{-1} and an equilibration time of 2 h, using a solution consisting of 0.005 M DTPA, 0.1 M triethanolamine and 0.01 M $CaCl_2$ that was buffered at a pH of 7.3 (Lindsay and Norvell, 1978). Suspensions were centrifuged, filtered over a 0.45 μm membrane filter and analysed for Zn using ICP-OES. In the same 0.01 M $CaCl_2$ soil extraction as described before for DOC analysis, Zn-$CaCl_2$ was measured in an acidified (0.14 M HNO_3) subsample of the supernatant with HR-ICP-MS.

2.4. Data analysis

Data analysis was done using the R software, version 4.0.2 (R Core Team and R Development Core Team, 2020). Results were visualized with the ggplot2 package (Wickham, 2016).

Treatment effects

The effect of fertiliser treatment (i.e. full and -Zn) on maize yields, Zn uptake and grain Zn concentrations was assessed with linear mixed effect models (LME) using the lme function from the nlme package (Pinheiro et al., 2013) with the REML method, and tested by analysis of variance (function Anova). Homogeneity of variances was tested with the Levene's test, using the leveneTest function from the car package (Fox and Weisberg, 2019). Normality of model residuals were checked with the Shapiro-Wilk test using the shapiro.test function from the stats package (R Core Team and R Development Core Team, 2020). This analysis was done for each location, taking all replications into account with treatment as fixed factor, and block as random factor (i.e. random = ~1|block). At country level, the differences between locations were also assessed using the same LME model but now with location as additional fixed factor.

Treatment effects on plot-level were assessed by calculating the empirical cumulative distribution (ecdf function) of the response in yield, Zn uptake and grain Zn concentrations to Zn fertilisation. To do so, the fertiliser response was calculated based on the data for each block as follows:

Equation 1: $\text{Response} = (Y_{Full}) / (Y_{-Zn})$

in which Y represents grain yield, Zn uptake or grain Zn concentrations in the full and the -Zn treatments.

Determination of yield-limiting nutrient

Zinc uptake depends on the soil Zn availability and on the availability of other nutrients. In situations where Zn is the most yield-limiting factor, Zn uptake by a crop equals the amount of Zn that a soil can supply during a growing season (Janssen et al., 1990) and good relations are expected between soil properties and Zn uptake.

Whether Zn is the most yield-limiting nutrient can be assessed based on the yield response to Zn fertilisation, or by the degree of Zn dilution in the maize crop (Janssen et al., 1990; Sattari et al., 2014; Witt et al., 1999). The latter refers to the internal efficiency (IE) of Zn in maize, which is the grain yield produced per amount of nutrient taken up in the above-ground plant biomass in kg dry weight kg^{-1} Zn (Witt et al., 1999). The IE ranges between a crop- and nutrient-specific physiological minimum and maximum. When the IE for Zn is close to its maximum, Zn is maximally diluted in the crop, and is most likely yield-limiting. The maximum and minimum IE can be derived from the relation between grain yield (kg ha^{-1}) and nutrient uptake (kg nutrient ha^{-1}), using data from large numbers of field trials (Witt et al., 1999). For the macronutrients N, P and K, these parameters have been derived for maize (Janssen et al., 1990; Sattari et al., 2014). In order to derive the physiological minimum and maximum Zn concentrations for maize, data from field trials in Nigeria (Rurinda et al., 2020) and Zimbabwe (Kurwakumire et al., 2015) were combined with data collected for this study. From these combined data, the upper and lower 2.5% of the datapoints were excluded and then the minimum Zn uptake (r) needed to produce any grain, and the maximum (d) and minimum (a) slopes or IE values were derived (Witt et al., 1999).

Using the IE parameters for N, P, K and Zn in combination with yield and nutrient uptake measurements, the relative dilution of each nutrient can be calculated as follows (Heinen, pers. comm. 2020):

$$\text{Equation 2: Relative dilution} = \frac{U_i - U_{i,D}}{U_{i,A} - U_{i,D}} = \frac{U_i - \frac{Y}{d} - r}{\frac{Y}{a} - \frac{Y}{d}}$$

with U_i the uptake of nutrient i, $U_{i,D}$ and $U_{i,A}$ the uptake of nutrient i at maximum dilution and accumulation respectively, Y the actual yield, d the maximum IE and a the minimum IE and r the minimum nutrient uptake require to produce any yield. The principle behind Equation 2 is to estimate how the actual nutrient uptake differs from the uptake that belongs to the maximum physiological efficiency for the measured yield, relative to the maximum range in uptake. The nutrient with the lowest value obtained

based on Equation 2, is expected to be the most yield-limiting nutrient. Based on this analysis, a subset was created with only the -Zn plots for which Zn was found to be the most yield-limiting nutrient. This subset was subsequently used to derive soil-plant relations between yield, Zn uptake and grain Zn concentrations and soil properties.

Soil-plant relations

Relations between soil properties and yield, Zn uptake and grain Zn concentrations in the -Zn treatments as well as their response to Zn fertilisation were assessed using LME models based on maximization of the log-likelihood (method ML). Soil properties pH, Zn-HNO_3 Zn-DTPA, Zn-M3, Zn-$CaCl_2$, AlFe-AO and SOC were used as fixed effects, whereas the effect of agroecological zone and maize variety were included as random effects, represented by a single variable namely country (i.e. random = ~1|Country). The soil properties were included in the models. Since DOC data were not available for the soils in Zimbabwe, this soil property was not included in the analysis. The effect of potentially competing cations such as Cu-M3 and Ca-M3 on Zn uptake and Zn grain concentrations was also tested. The selection of variables was done based on the LME model with the lowest Akaike's Information Criterion (AIC) value (Webster and McBratney, 1989) using the dredge function from the MuMIn package (Barton, 2020). Normality and homogeneity of variances of the residuals from the final LME model were checked with the Shapiro-Wilk test using the shapiro.test function from the stats package (R Core Team and R Development Core Team, 2020). The dependent and independent variables were log10 transformed when a normal distribution of the residuals was not found with the Shapiro-Wilk test. Since the Zn measurements in the DTPA, M3 and HNO_3 extracts were strongly correlated (see results), the model selection analysis was done with each of these Zn pools separately as input in addition to the other soil properties (i.e. pH, SOC, Fe and Al, Zn-$CaCl_2$), and final models were compared using the anova function. The final LME models were checked for multicollinearity between the independent variables, using the vif function from the car package in R (Fox and Weisberg, 2019). The variance explained by the regression models was calculated using the r2 function from the performance package in R (Ludecke et al., 2021), which reports the variance of the fixed effects (R^2_{fixed}) and the variance explained by both the fixed and random effects (R^2_{total}). The relative contribution of different variables in the LME models to the total variation of the dependent variable, was tested using the r2beta function from the r2glmm package (Jaeger, 2017) or the calc.relimp function from the relaimpo package (Gromping, 2006) in case no contribution of country as random factor was found in the model.

3. Results

3.1. Soil properties

The soil properties are given in Table 1. The soils in this study are characterized by low SOC contents which do not exceed 20 g kg^{-1}. In addition, the field trials covered a limited range in soil pH between 4 and 6.1. Within countries, the range in pH values was even more limited, with the Kenyan locations covering pH 4.4 - 5.4 and the Zambian locations covering pH 4.5 - 5.7. The pH values of the locations in Zimbabwe ranged between 4.0 and 6.1, covering the entire range in pH values reported in this study. The soils in this study were characterized by low Zn levels. Lowest soil Zn levels were found in Zambia and Zimbabwe, and the highest in Kenya. For the majority of soils, Zn levels were below the critical values reported in literature (Figure 2), pointing towards potential Zn deficiency for maize grown in these soils.

Table 1: Soil properties per country, means and the minimum-maximum range are presented.

Soil property	Kenya		Zambia		Zimbabwe	
	Mean	Min-Max	Mean	Min-Max	Mean	Min-Max
pH-$CaCl_2$	4.9	4.4 - 5.4	5.0	4.5 - 5.7	4.6	4.0 - 6.1
SOC (g kg^{-1})	14	9 - 20	8	6 - 11	7	4 - 15
DOC (mg L^{-1})	18	6 - 72	2	0.3 - 5	-	-
Fe-AO (mmol kg^{-1})	34	23 - 53	7	4 - 13	9	2 - 30
Al-AO (mmol kg^{-1})	47	27 - 83	30	19 - 44	18	6 - 45
Zn-HNO_3 (mg kg^{-1})	5.8	2.3 - 13.0	1	0.3 - 2.1	2.3	0.4 - 9.7
Zn-DTPA (mg kg^{-1})	2.0	0.8 - 4.6	0.3	0.1 - 0.7	0.9	0.2 - 3.6
Zn-M3 (mg kg^{-1})	3.0	1.3 - 6.4	0.7	0.3 - 1.4	1.6	0.2 - 6.0
Zn-$CaCl_2$ (µg kg^{-1})	674	245 - 1193	69	8 - 280	467	9 - 2989
P-Olsen	10.4	2.1 - 38.2	2.1	1.0 – 3.9	9.9	3.1 - 25.5

3.2. Crop responses to Zn fertilisation

Yield

Maize yields ranged between 1.9 and 9.8 Mg ha^{-1}, and were highest in Kenya, followed by Zimbabwe and Zambia (Figure 3). Variation in maize yields was relatively large within locations and treatments, ranging up to 2.7 Mg ha^{-1} in Kenya. Across countries, Zn fertilisation led to an average yield increase of 0.03 Mg ha^{-1} or 4 % compared to the -Zn treatment, however, this effect was not significant ($p = 0.97$). Fertilisation with Zn significantly increased maize yields at two out of 19 locations: one location in Zambia and one in Zimbabwe (Figure 3). Zinc fertilisation however also reduced maize yields,

at one location in Kenya and one in Zambia. Within each of the countries, significant differences in maize yields among locations were found (Figure 3).

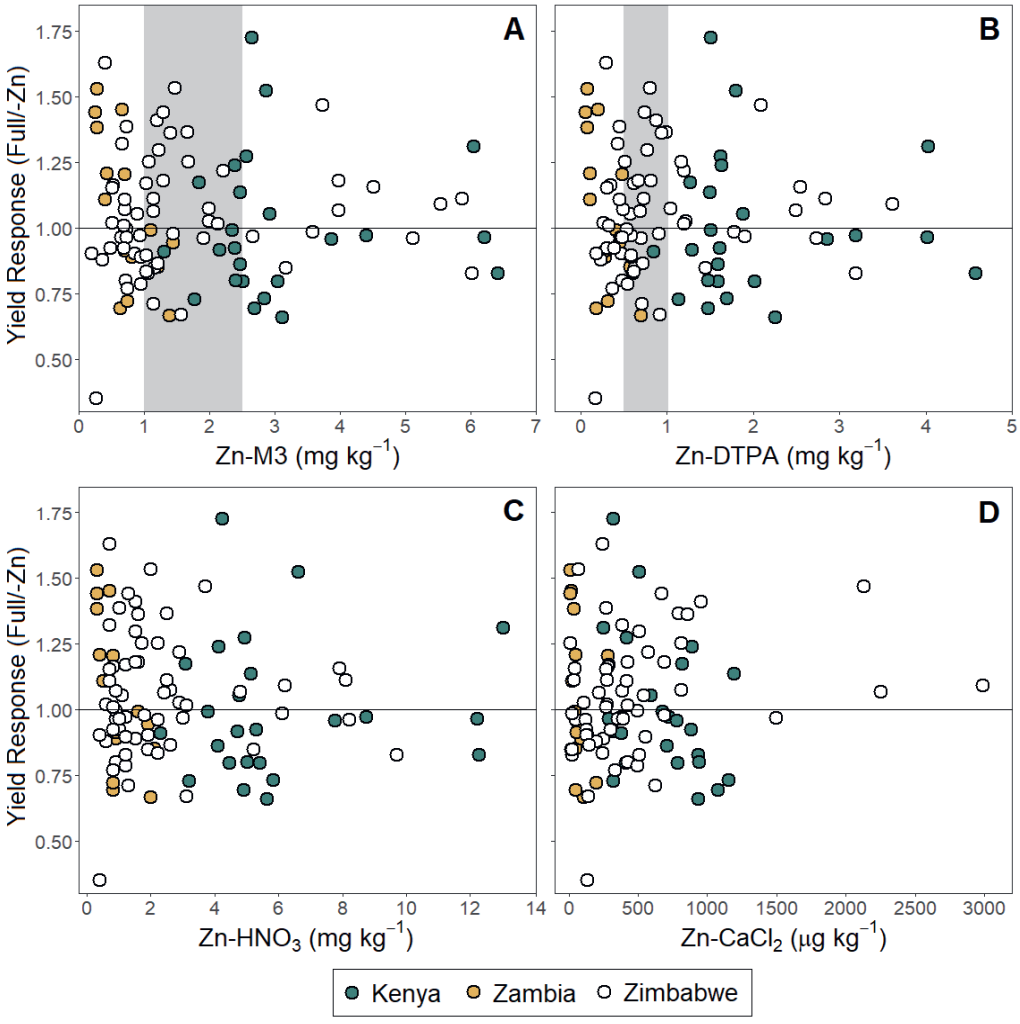

Figure 2: Relations between the yield response and Zn in M3 (A), DTPA (B), HNO_3 (C) or 0.01 M $CaCl_2$ (D) extracts. Above dotted horizontal lines, Zn fertilisation increased yields; below these, it decreased yields. Grey areas in A and B represent the range of critical values of Zn-M3 and Zn-DTPA below which it is expected that Zn fertilisation leads to an increase in maize yields (Chilimba et al., 1999; Cuesta et al., 2020; Lindsay and Norvell, 1978; Wendt, 1995).

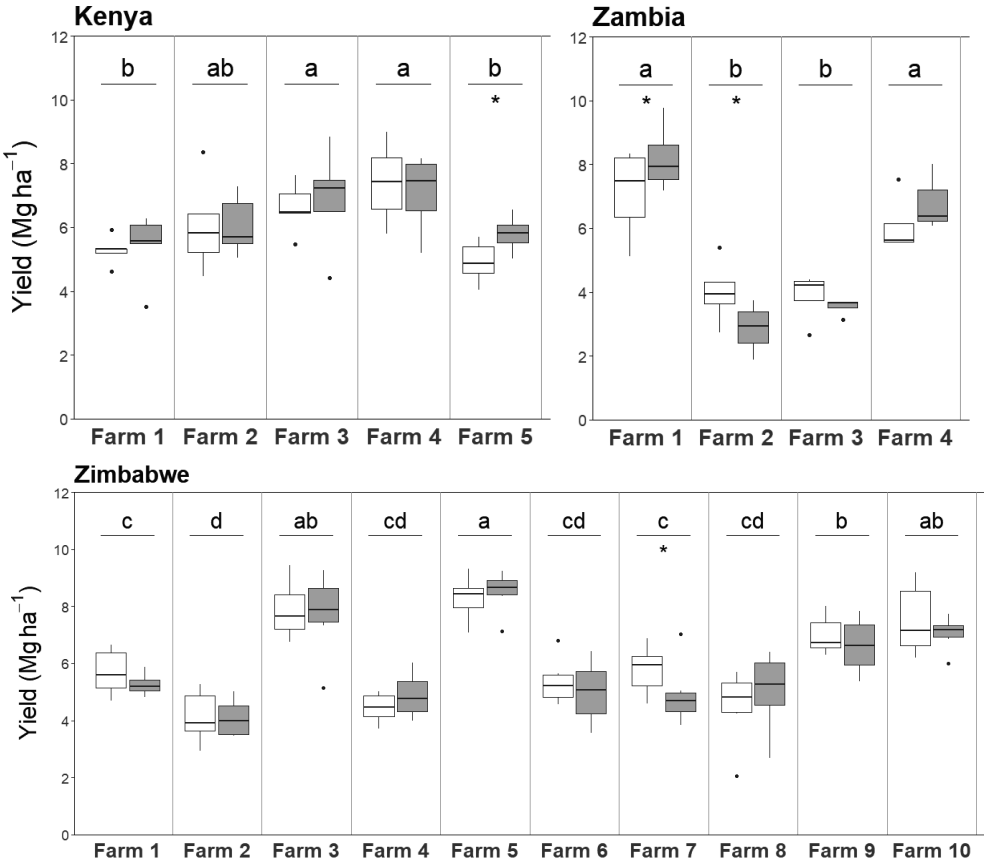

Figure 3: Yields in the full (white) and the -Zn (grey) treatments, presented per country. The boxplots show the median (line), first and third quartiles (hinges), the minimum and maximum based on the interquartile range (whiskers) and outliers (markers). Asterisks indicate a significant treatment effect. Letters indicate significant differences among farms within a country.

The effect of Zn fertilisation was also assessed by calculating the yield response for each block (Equation 1). The cumulative distribution of this yield response shows that yield responded positively to Zn fertilisation in 47 blocks (48%), while for 52 blocks (52%) a negative response was found (Figure 4A). The majority of blocks (61%) had a yield response ratio between 0.8 and 1.2, which could be considered natural variation, given the relatively large variation in yields within locations (Figure 3). Similar results were found for the response in total aboveground biomass (Figure S2).

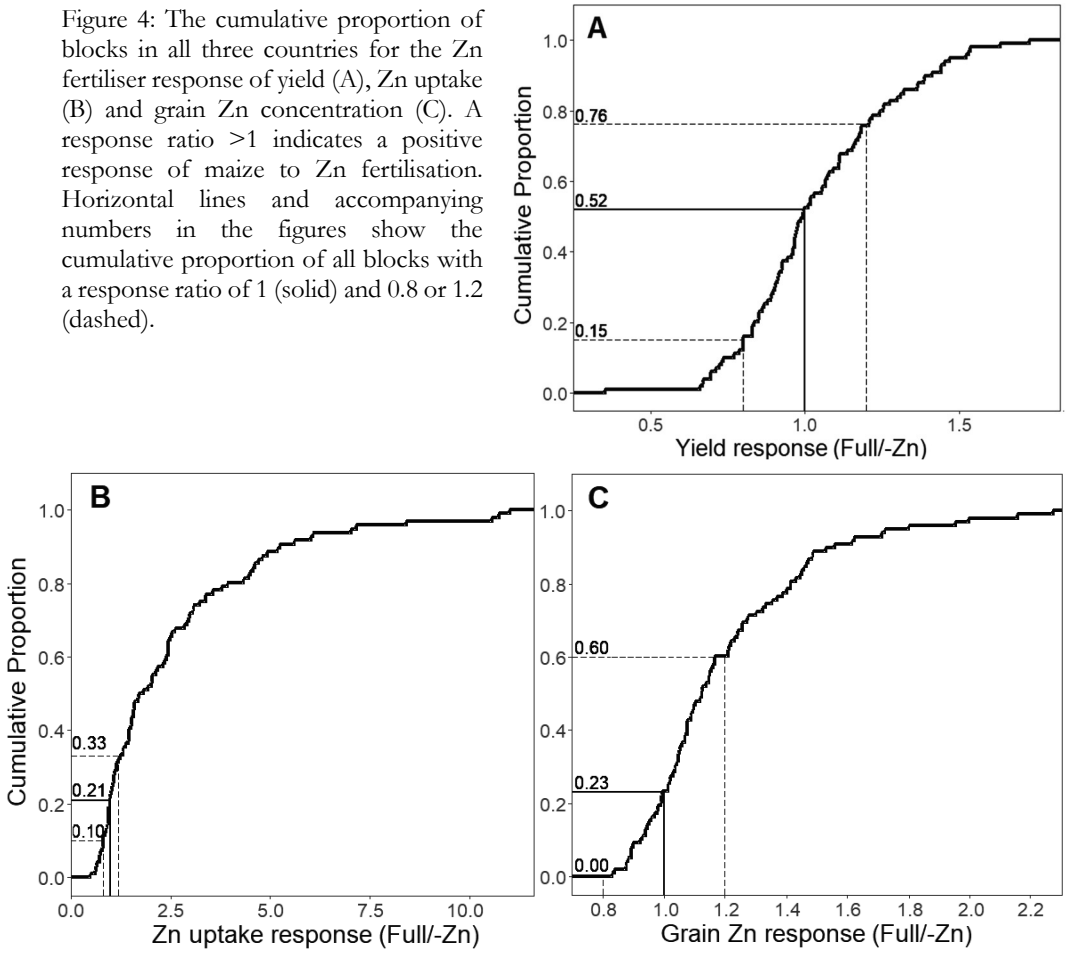

Figure 4: The cumulative proportion of blocks in all three countries for the Zn fertiliser response of yield (A), Zn uptake (B) and grain Zn concentration (C). A response ratio >1 indicates a positive response of maize to Zn fertilisation. Horizontal lines and accompanying numbers in the figures show the cumulative proportion of all blocks with a response ratio of 1 (solid) and 0.8 or 1.2 (dashed).

Zn uptake

Zinc fertilisation led to an average increase in Zn uptake of 177 g ha^{-1} or 175% compared to the -Zn treatment ($p < 0.05$). It significantly increased maize Zn uptake at ten out of the 19 locations: one location in Zambia and nine in Zimbabwe (Figure 5). In Kenya, Zn uptake was rather constant among the five locations, and ranged between 200 and 300 g ha^{-1} (Figure 5). In Zambia and Zimbabwe, a wider range in Zn uptake was found and significant differences among locations and treatments were found (Figure 5). The effect of Zn fertilisation was also assessed by calculating the response ratio of Zn uptake for each block (Equation 1). The cumulative distribution of this response ratio shows that a positive response in Zn uptake was found for 79% of all blocks (Figure 4B).

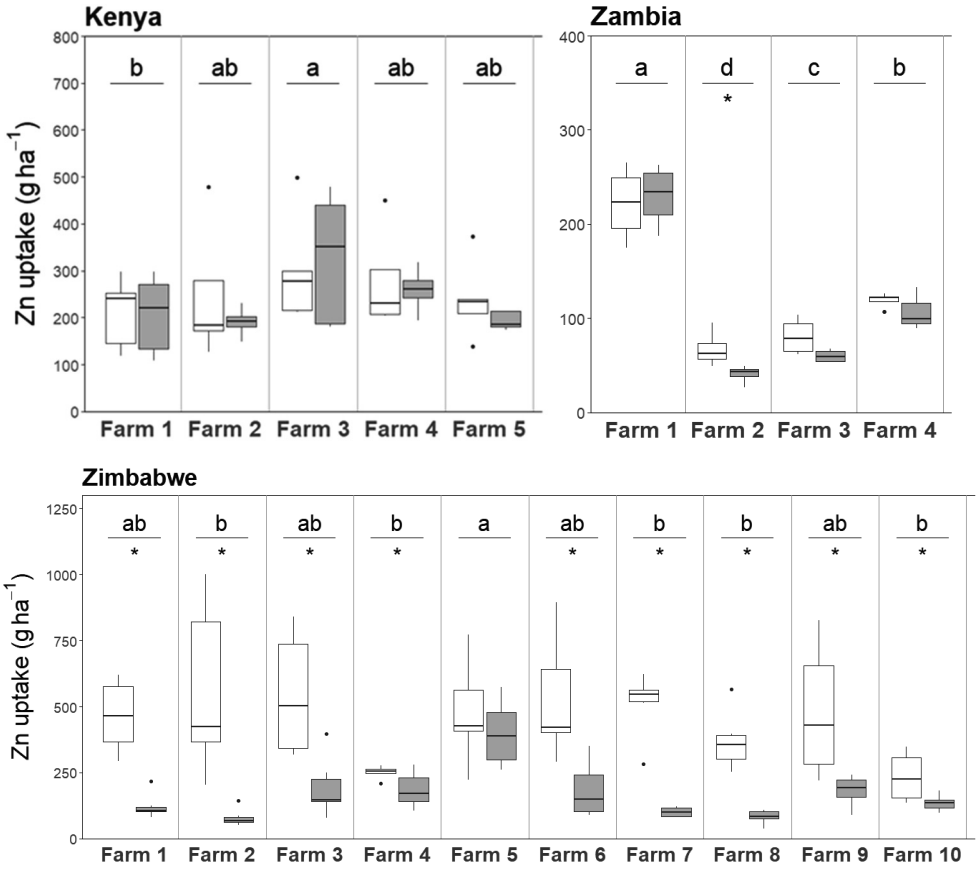

Figure 5: Zn uptake in the full (white) and the -Zn (grey) treatments, presented per country. Boxplots are similar as shown in Figure 3.

Grain Zn

Zinc grain concentrations ranged from 9 to 27 mg kg^{-1} across countries and treatments (Figure 6). Similar to Zn uptake, grain Zn concentrations varied less in Kenya compared to Zambia and Zimbabwe. Across countries, grain Zn concentrations increased 2.4 mg kg^{-1} or 20% as an effect of Zn fertilisation ($p < 0.05$). Zinc fertilisation significantly increased maize grain Zn concentrations at nine out of the 19 locations: one in Zambia and eight in Zimbabwe (Figure 6). Except for one location in Zimbabwe, these were the same locations at which Zn fertilisation increased Zn uptake (Figure 5). The effect of Zn fertilisation was also assessed by calculating the response ratio of grain Zn concentration for each block (Equation 1). The cumulative distribution of this response ratio shows that a positive response in grain Zn concentrations was found for 77% of all blocks (Figure 4C). For the 23% of bocks with a negative response, the ratio varied between 0.8 and 1, which can be considered natural variation.

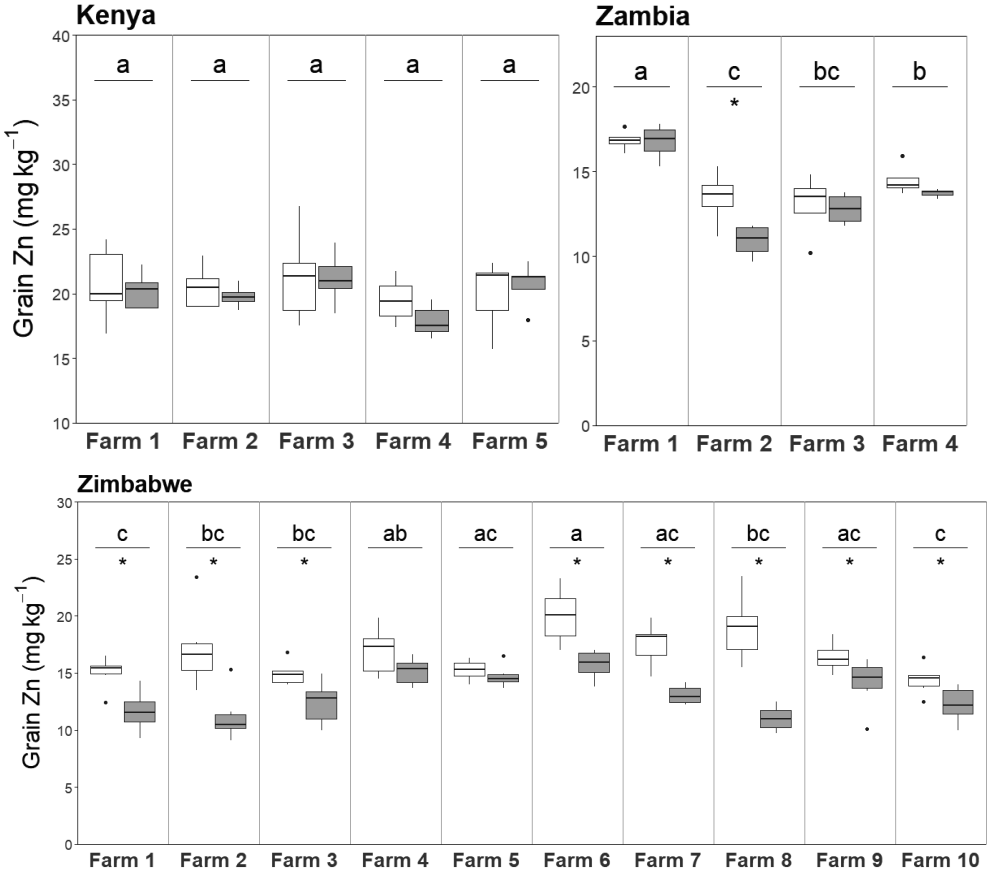

Figure 6: Zn uptake in the full (white) and the -Zn (grey) treatments, presented per country. Boxplots are similar as shown in Figure 3.

3.3. Determination of yield limiting nutrient

Before studying the soil-plant relations in the next section, we analysed in which plots Zn was the most yield-limiting nutrient since good relations between soil properties and Zn uptake are expected especially in these situations. Based on literature data and results of this study, the maximum and minimum IE of Zn for maize were 71 and 8 kg grain g^{-1} Zn uptake (Figure S3). Using these parameters, as well as those for N, P and K that have been previously derived (Janssen et al., 1990), the most yield-limiting nutrient was determined (Equation 2; Figure 7A). Including both full and -Zn treatments, Zn was identified as the most yield-limiting nutrient in 85 blocks (42%), followed by P (67 blocks or 33%), N (33 blocks or 16%) and K (13 blocks or 6%). Of the 101 plots that did not receive any Zn fertiliser, Zn was the most yield-limiting nutrient in 61 blocks (60%) (Figure 7A). These plots were mainly located in Zimbabwe (38) followed by

Kenya (13) and Zambia (10). For the other -Zn plots, N, P or K was found to be more yield-limiting than Zn, despite the applied NPK fertilisers. Of the 47 blocks where a positive yield response to Zn fertilisation was observed, zinc was identified as the most yield-limiting nutrient in 34 blocks. In the other 27 blocks for which Zn was identified as the most yield-limiting nutrient, a negative yield response was observed. So the degree of Zn dilution in the maize crop was not consistently associated with a positive yield response to Zn fertilisation.

The maximum dilution of Zn in maize was found to be large, as shown by the steep line in Figure 7A: at a relatively low Zn uptake, yields up to 8 Mg ha^{-1} were found. Low Zn concentrations in maize were found, *i.e.* below 10 mg kg^{-1} (Figure 7B), without finding a clear yield response to Zn fertilisation (Figure 7B).

3.4. Soil-plant relations and fertiliser response

For the analyses below, two different subsets are used: the -Zn plots for which Zn was identified as the most yield-limiting nutrient based on the analysis in the previous section (n = 61) and all the -Zn plots (n = 101).

Yield

The best model predicting grain yields for the 61 -Zn plots in which Zn was found to be the most yield-limiting nutrient, included solely pH as fixed variable. Grain yields increased with pH, but the model explained limited variation, as illustrated by low R^2 of 0.06 and this model was not significantly different from the model with only the intercept (p = 0.06).

The locations at which Zn fertilisation decreased or increased grain yields could not be separated from the other locations based on soil properties and nutrient concentrations in the maize crop. No relations between maize yield response to Zn fertilisation and soil Zn test concentrations in the M3, DTPA, HNO_3 or $CaCl_2$ soil extracts were found (Figure 2). In the critical range of Zn-M3 and Zn-DTPA concentrations, an equal number of plots showed a positive or a negative response to Zn fertilisation (Figure 2). Linear mixed effects modelling was used to assess which soil properties explain the maize yield response to Zn fertilisation at the block level. Based on model selection with pH, SOC, FeAl-AO, and Zn pools as input parameters, a model with these soil properties was not significantly different from a model with only an intercept (p = 0.06). The residuals of this model were significantly correlated with the grain yield in the -Zn treatments (Pearson correlation coefficient of -0.47, $p < 0.05$) The plots with low yields in the -Zn treatments, showed a higher response to Zn fertilisation (Figure 8).

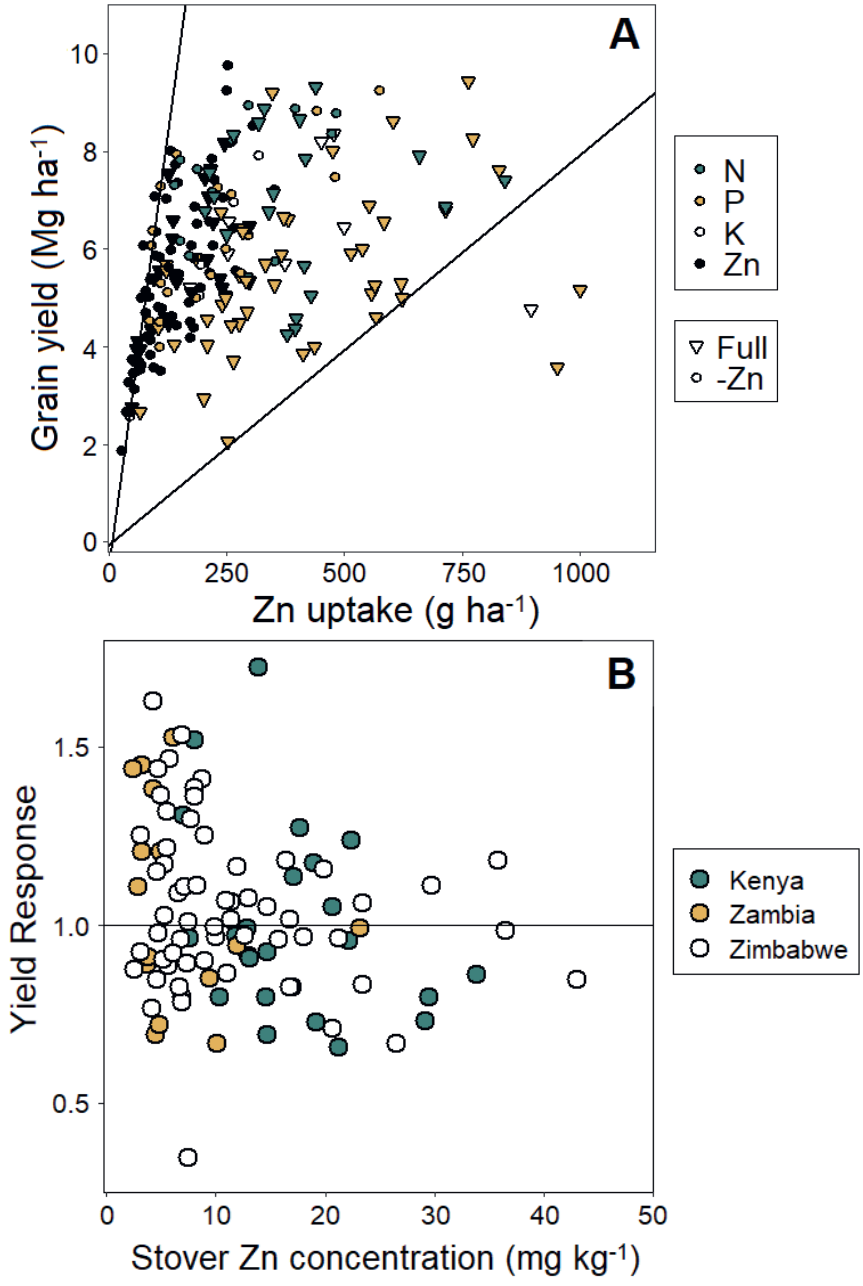

Figure 7: (A) Relation between grain yield and aboveground Zn uptake. The lines represent the maximum dilution and accumulation of Zn in the maize crop. The colours refer to the most yield-liming nutrient, shapes indicate whether datapoints belong to the full or -Zn treatment. (B) The yield response in relation to stover Zn concentrations for the 101 blocks. Above the dotted horizontal lines, Zn fertilisation increased yields; below these lines, it decreased yields.

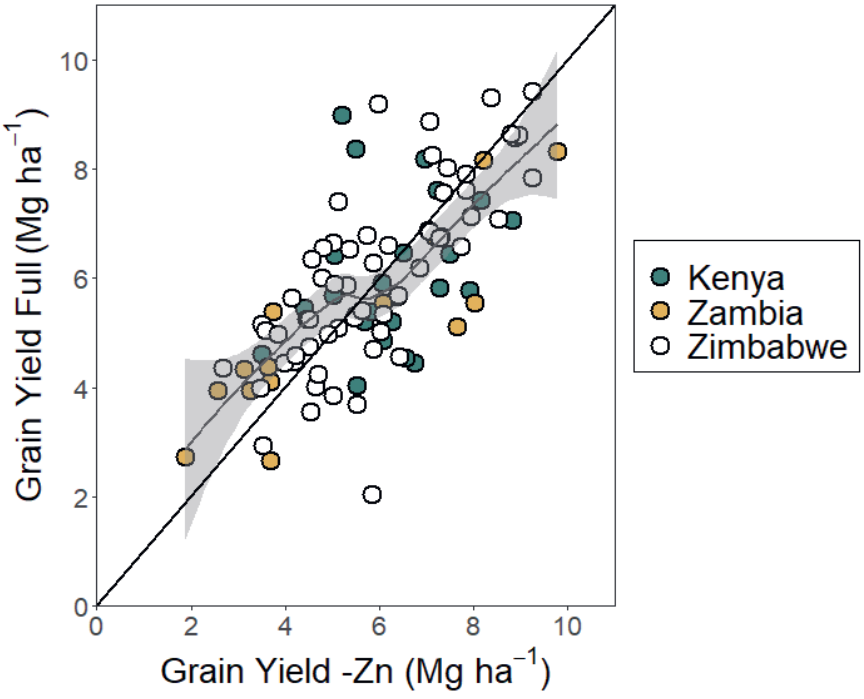

Figure 8: Yields obtained in the full treatment in relation to the yields in the -Zn treatment. The solid black line represents the 1:1 line, the grey line shows the local polynomial regression line using the loess method in R (Vanlauwe et al., 2016).

Zn uptake

The best model predicting Zn uptake in the 61 -Zn plots where Zn was identified as the most yield-limiting nutrient, included solely Zn-HNO_3 as a significant variable; none of the other soil parameters explained additional variation. Zinc uptake increased with soil Zn-HNO_3 concentrations (Figure 9 and Table 2). The Zn-HNO_3 explained 35% of the variation in Zn uptake (Table 2). Model residuals were normally distributed (p = 0.90). The effect of country, representing agroecological zone and/or variety, did not explain any variation in Zn uptake, as illustrated by the identical total and fixed R^2 (Table 2). Inclusion of possibly competitive nutrients, such as Cu, K or Ca, did not have a significant effect on Zn uptake. When the model was applied to all 101 -Zn plots, model coefficients for the intercept and the slope for Zn-HNO_3 were similar to those of the model based on the subset of plots for which Zn was found to be the most yield-limiting nutrient (Figure 9). The relation between Zn uptake and soil Zn-M3 or Zn-DTPA was also significant, in contrast to Zn-$CaCl_2$ (Figure 9). Based on AIC criteria, the model with Zn-HNO_3 as input variable explained more variation than Zn-M3 or Zn-DTPA.

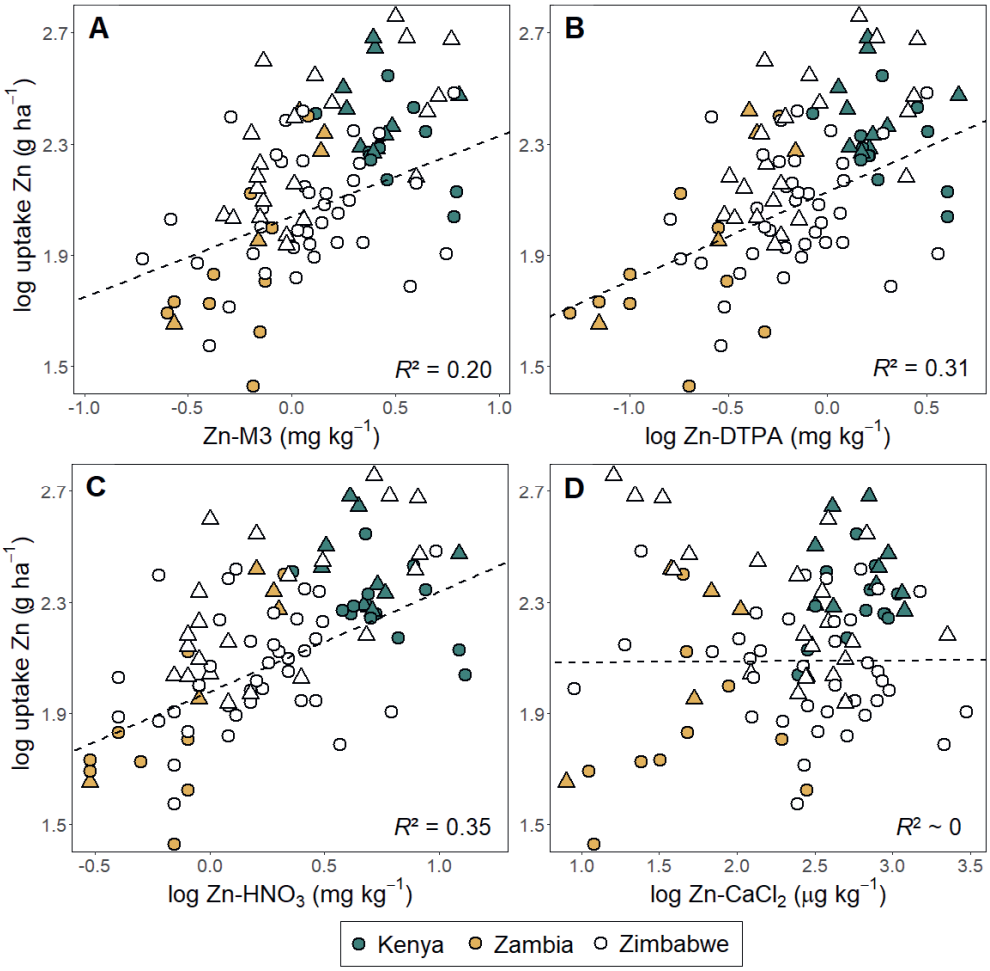

Figure 9: Relations between Zn uptake and Zn measured in the Mehlich 3 (A), DTPA (B), HNO_3 (C) and $CaCl_2$ (D) extraction for the -Zn plots. Shapes indicate whether Zn (circles) or N, P or K (triangles) was identified as the most yield-limiting nutrient. Dotted lines show output of a LME model with country as random factor and the respective soil Zn measurement as fixed variable (n = 61). R^2 values represent the explained variation by the soil Zn measurement.

With linear mixed effects models, we assessed the relation between the Zn uptake response to fertilisation and soil properties, using country as random variable. The analysis was done for all 101 -Zn plots. The final model explained the Zn uptake response ratio based on pH and SOC (Figure 10), with pH having a larger contribution in explaining the variation. Model residuals were normally distributed (p = 0.23). The response in Zn uptake to Zn fertilisation was largest in soils with low pH and SOC contents. Country as a random factor contributed to the model, illustrated by a higher total than fixed R^2 value (Table 2). With similar pH and SOC levels, the response in Zn

uptake to Zn fertiliser is the highest in Zimbabwe, followed by Kenya and Zambia (Figure 10). This means that underlying variables such as maize variety and/or agro-ecological zone have an effect on the Zn uptake response to Zn fertilisation. Using only the 61 plots for which Zn was identified as the most yield-limiting nutrient instead of all 101 plots, gave a model with similar coefficients for pH and SOC.

Table 2: Relations between soil properties, uptake, grain Zn concentrations and their response to Zn fertilisation. R^2_{total}, refers to the models including country as a random variable; R^2_{fixed} to the model with fixed variables only. The *p*-values for all models are < 0.001. The models for the yield and the yield response are only discussed in the text, as they were not significant.

Dependent variable	Model	R^2_{total} / R^2_{fixed}	RMSE
Zn uptake (g ha^{-1}) (*n* = 61[1])	$\log_{10}(Y) = 3.70 + 0.36 \log_{10}(Zn\text{-}HNO_3)$	0.35 / 0.35	0.20
Zn uptake response (*n* = 97)	$\log_{10}(Y) = 1.73 - 0.23pH - 0.46\log_{10}(SOC)$	0.44 / 0.33	0.23
Grain [Zn] (mg kg^{-1}) (*n* = 61[1])	$\log_{10}(Y) = 1.71 + 0.12 \log_{10}(Zn\text{-}HNO_3)$	0.56 / 0.26	0.06
Grain [Zn] response (*n* = 98)	$\log_{10}(Y) = 0.42 - 0.04pH - 0.16 \log10(SOC)$	0.30 / 0.27	0.07

[1]Data from the -Zn plots in which Zn was the most yield-limiting nutrient.

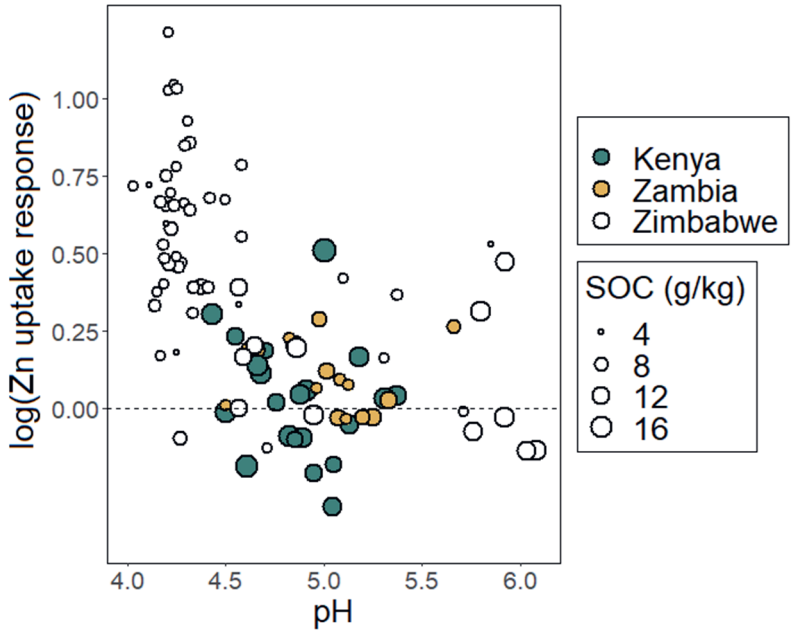

Figure 10: The Zn uptake response to fertilisation plotted against pH, with size of the data points indicating SOC content. An uptake response above 0 (dotted line) indicates a positive response in Zn uptake by maize when Zn fertiliser is applied, i.e. a higher uptake in the full treatment.

Grain Zn

Grain Zn concentrations in the -Zn plots on which Zn was the most yield-limiting nutrient (Section 3.2) were positively related to Zn-HNO_3 (Table 2; Figure 11). Including country as a random variable, the model explained 56% of the variation in grain Zn concentrations. Model residuals were normally distributed ($p = 0.50$). A model with Zn-M3 or Zn-DTPA instead of Zn-HNO_3 as independent variable performed similarly, albeit with a higher AIC value (difference of ~2-3). In contrast to the model for Zn uptake, country as random variable increased the explained variation in grain Zn concentrations (Table 2), indicating that agro-ecological zone, maize variety, or country-dependent management factors affected within-plant Zn allocation to the grain. For similar soil Zn-HNO_3 levels, highest grain Zn concentrations were found in Kenya, followed by Zambia and Zimbabwe. When using all -Zn plots to calibrate the model for grain Zn concentrations, similar coefficients for the intercept and slope were found. When relating the grain Zn concentration response to fertilisation to soil properties ($n = 101$), a similar model was found as for the response in Zn uptake, namely a negative contribution of SOC and soil pH to the response in grain Zn concentrations (Table 2). Model residuals were normally distributed ($p = 0.40$). There was a contribution of country as random variable, with the highest increase in Zn grain concentrations for Zimbabwe, followed by Kenya and Zambia, i.e., the same order as found for Zn uptake.

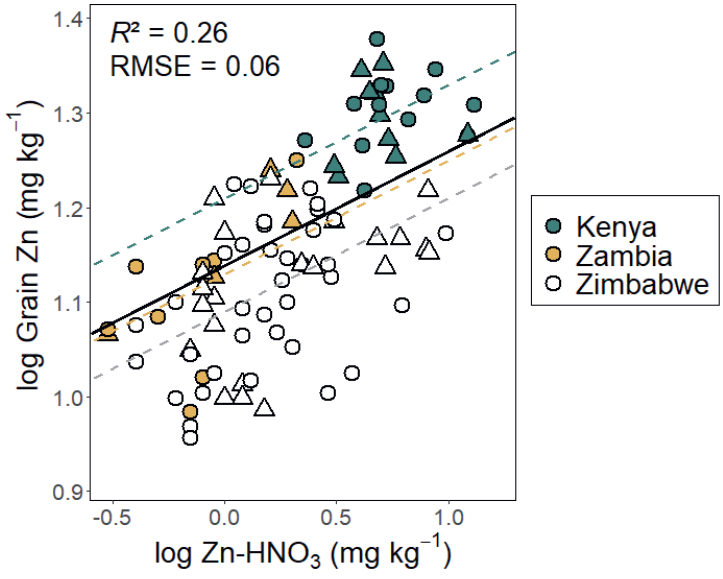

Figure 11: Grain Zn concentrations plotted against Zn-HNO_3 in the -Zn plots. Shape indicates whether Zn (circles) or N, P or K (triangles) was identified as the most yield-limiting nutrient. The black solid line shows the overall relation between grain Zn concentrations and Zn-HNO_3, whereas dashed lines represent this relation with different intercepts for each of the countries.

4. Discussion

4.1. Zn fertilisation does not result in higher maize yields

Field trials on 19 locations in three different countries showed that Zn fertilisation led to significant increases in maize yields at only two locations. These two locations did not differ from the other locations in terms of soil properties, nutrient uptake or tissue nutrient concentrations. A clear positive yield response above 20% to Zn fertilisation was only observed for a minority of all replicates.

The lack of yield responses to fertilisation was not expected, given that the majority of these locations had soil Zn levels below the critical values reported in literature. Critical soil Zn levels, below which a positive maize yield response to Zn fertilisation is expected, have been derived previously from field and greenhouse experiments (Chilimba et al., 1999; Cuesta et al., 2020; Lindsay and Norvell, 1978; Wendt, 1995). Both positive and negative yield responses were found for soils that had soil Zn concentrations below these critical levels (Figure 2). In addition, no extraction method was capable of predicting the yield response to Zn fertilisation. This result points towards the challenges associated with the use of soil extractions as diagnostic criteria for nutrient deficiencies and corresponding fertiliser recommendations (Schut and Giller, 2020).

The relative dilution of Zn dilution in maize was also found to be a poor indicator of yield response to Zn fertilisation. For the majority of the -Zn plots, Zn was found to be highly diluted in the maize crop, approaching its maximal IE, indicating Zn may have been yield-limiting. This was however not the case, since no positive response to Zn fertilisation was observed. One explanation may be that other factors and/or nutrients may be still more yield-limiting than Zn, despite low soil Zn levels and despite the applied fertilisation with a range of macro-and micronutrients. Another explanation can be that this IE approach may not be suitable for Zn. Generally, it has been shown that Zn deficiency in maize rapidly decreases with increasing Zn availability, after which the yields remain constant with increasing Zn supply (Singh and Banerjee, 1987). This may suggest that a critical threshold may exist, above which Zn uptake does not determine maize grain yields but that Zn uptake is merely driven by grain (and stover) yields, despite strong Zn dilution in the crop. Our results have shown that Zn can indeed be highly diluted in the crop, resulting in tissue Zn concentrations below 10 mg kg^{-1} which is lower than previously reported critical tissue concentrations (Reuter and Robinson, 1997; Singh and Banerjee, 1987). It must be noted that these critical tissue concentrations are often derived based on measurements of plant parts during the

growing season and not after harvest. Tissue concentrations measured in this study were, however, found to be a poor indicator of a positive yield response to Zn fertilisation (Figure 7).

The most important diagnostic criteria of Zn deficiency for maize growth that can be derived from this study, is the yield in the control treatment that received optimal fertilisation with macro-and micronutrients except Zn. This effect of yield in the control treatment on the yield response has been previously observed when soil fertility treatments were tested in the field (Ichami et al., 2019; Vanlauwe et al., 2016). Generally, the plots with yields below ~6 Mg ha^{-1}, had the highest probability for a positive yield response to Zn fertilisation (Figure 8). Kihara et al. (2017) reported a similar trend for the results from field trials in various SSA countries, where the yield response to secondary and micronutrients decreased with increasing maize yields in the plots that received only NPK fertilisers. Combining literature data from field trials in SSA countries (Kihara et al., 2017, 2016; Rurinda et al., 2020) shows that the yield level below which there is a high probability that maize shows a positive response to secondary and micronutrients also points at a diagnostic threshold value of around 6 Mg ha^{-1} (Figure S5), similar to what has been found in this study (Figure 8). In addition, previous studies with Zn omission trials in SSA that reported a positive yield response of maize to Zn fertilisation, are also characterized by relatively low yields compared to the yields in this study (i.e. below 6 Mg ha^{-1}) in the plots receiving no Zn fertiliser (Abbas et al., 2007; Eteng et al., 2014; Manzeke et al., 2014; Nziguheba et al., 2009).

The quantities of NPK fertilisers given to all treatments in this study, ranging between 180-350 kg N ha^{-1}, 35-180 kg P ha^{-1} and 100-120 kg K ha^{-1}, were relatively high in comparison with Kihara et al. (2016). These high NPK doses, in combination with a range of secondary and other micronutrients, were applied in order to assure that other nutrients than Zn were not yield-limiting and that possible Zn deficiencies would become visible. However, these high quantities of NPK fertilisers could also have masked the incidence of micronutrient deficiencies, such as Zn. For example, the work of Manzeke et al. (2014) in Zimbabwe showed that maize yields responded less to Zn fertilisation when larger quantities of N and P were applied. The application of relatively high amounts of macro- and secondary nutrient fertilisers in our study may have led to healthier crops, whose root systems were able to explore a larger soil volume. This may have led to sufficient Zn uptake even when Zn was not fertilised and despite low soil Zn availability as previously suggested by Pasley et al. (2019) based on field trials in Kenya and Zimbabwe. Others have also demonstrated the significant response in root

traits and associated increased Zn uptake, due to macronutrient fertilisation (Ma et al., 2014), but the underlying processes are still unclear.

It has been stated that the supply of secondary and micronutrients is vital for enhancing agricultural productivity in SSA (Kihara et al., 2017; Wortmann et al., 2019). However, these conclusions are based on an average positive maize yield response to secondary and micronutrient fertilisation. One may argue whether it is justified to use an average yield response as a basis for such recommendations (Vanlauwe et al., 2016), given the large variation in yield responses found in these studies (Figure S6) as well as for the 19 locations in this study and the relatively low chance of a positive yield response to Zn fertilisation (Figure 4). In addition, caution should be made when such averages are used to calculate the economic return of micronutrient fertiliser application (Kihara et al., 2020), given the high probability for absent or even negative yield responses as illustrated by our results (Figure 4).

4.2. Soil Zn availability

Soil Zn availability was measured using four different extraction methods: DTPA, 0.43 M HNO_3, M3 and 0.01 M $CaCl_2$. The first three extraction methods are considered to approximate the available Quantity (Q), which represents the directly available Zn in the soil solution as well as the Zn adsorbed to the soil solid particles, which can become available throughout a growing season (Groenenberg et al., 2017; Lindsay and Norvell, 1978; Mehlich, 1984; Robson, 1993). The $CaCl_2$ solution is more related to the Intensity (I) or the Zn in the solution phase, which represents the Zn directly available for plant uptake (Houba et al., 2000). The Zn concentrations measured in DPTA, HNO_3 and M3 soil extracts were strongly correlated (Figure S2). The Zn measured in $CaCl_2$ can be derived from the Zn measured in HNO_3 and soil pH (Van Eynde et al., 2022).

The results from our study have shown that Q-tests, and more specifically the HNO_3 extraction, performs best in quantifying the soil available Zn for the unfertilised plots, based on the significant relation with Zn uptake (Figure 9). In terms of practical applications, this is a promising result, since soil Zn data available for SSA mostly comprises Q-tests (Hengl et al., 2021) rather than I-tests (Keskinen et al., 2019).

In literature, contrasting results have been found on whether I-or Q-tests are the best approximation of the soil available Zn content. Based on a review, Kim et al. (2015) recommended the use of I-tests to quantify bioavailability of relatively mobile metals such as Zn in contaminated soils, in line with other studies (Impellitteri et al., 2003; Nolan et al., 2005). For low Zn soils, both Q-tests (Tian et al., 2008) and I-tests (Duffner

et al., 2013; Menzies et al., 2007) have been found to be related to plant Zn concentrations and uptake. Due to the low pH and SOC contents of the soils in this study, the adsorption affinity for Zn in the solid phase is relatively low as illustrated by the fact that a large proportion of the Zn measured in the HNO_3 is also extracted by the $CaCl_2$ solution (Table 1). This low adsorption affinity for Zn also explains the significant response in Zn uptake and grain Zn concentrations since fertilised Zn is readily available as it stays in solution (see next section). In terms of Zn adsorption affinity, the soils from this study differ from the typical calcareous soils that are often associated with Zn deficiency, as investigated for example by Duffner et al. (2014, 2013). Their soils are characterized by a pH above 6, and by higher Zn-HNO_3 concentrations (up until 20.8 mg kg^{-1}) and lower Zn-$CaCl_2$ concentrations (mostly below 0.1 mg kg^{-1}) than found for the soils from this study (Table 1). In soils with high Zn adsorption affinity, Duffner et al. (2013) found that Zn-$CaCl_2$, in combination with pH-$CaCl_2$, related better with Zn shoot concentrations in wheat than Zn-DTPA. We hypothesize that the relatively low adsorption affinity for Zn in the soils in this study explains why Q-tests relate better with Zn uptake than I-tests, similar to what has been found and discussed previously for phosphorus by Nawara et al. (2017). The low adsorption affinity may imply that not the concentration in the soil solution (~Zn-$CaCl_2$) is limiting Zn uptake by maize, but the buffering capacity of the soil to provide Zn to maize during the whole growing season, as reflected by Zn-HNO_3 (or DTPA or M3).

Soil Zn-HNO_3 explained only 35% of the variation in the total Zn uptake for the plots receiving no Zn fertiliser (Figure 9). The relatively low explanatory power for Zn uptake may be attributed to the fact that Zn was not the most yield-limiting factor in many cases, as illustrated by the absence in yield response to Zn fertilisation and the IE analysis. In addition, soil Zn concentrations from samples taken at lower depth could have given more information about Zn availability, in line with the previously suggested hypothesis about the maize root system. No clear effect of country or maize variety was found on Zn uptake. However, differences in Zn uptake among maize varieties have been reported earlier (Bender et al., 2013).

4.3. Response in Zn uptake

Our data show that the Zn uptake response to fertilisation decreases with pH and SOC content. Previous studies have shown the importance of pH and SOC for the solid-solution partitioning of Zn in similar soils from SSA countries, with SOC being the most important adsorption surface and a strong increase in Zn adsorption with increasing pH (Groenenberg et al., 2017; Van Eynde et al., 2022). Our results indicate that the highest increase in Zn uptake can be expected in soils with a low adsorption

capacity (i.e. where fertiliser-Zn remains mainly in solution). However, for the response in Zn uptake, a contribution of country as a random factor was found, with the highest response in Zimbabwe (Figure 10 and Table 2). There may be several explanations for this observation, as country represents differences in both maize variety as well as in agro-ecological zone. At low Zn availability (i.e. in the unfertilised plots), the three different varieties may explore the same volume of soil for Zn, and effectively translocate this Zn supply from the root to the shoots. In a situation of excess Zn (i.e. in the fertilised plots), varieties can differ in the reduction of active Zn transport from roots to shoots, and may be less effective in coping with relatively higher Zn tissue concentrations (White and Broadley, 2011). Next to variety, the agro-ecological zone may play a role in the Zn uptake response ratio. Not only soil properties, but weather events associated with the different agroecological zones may also affect the fertiliser use efficiency. Analysis of the rainfall data (Figure S1) shows that the cumulative rainfall surplus is the highest in Kenya (348 mm), and the lowest in Zimbabwe (144 mm). The latter may result in a higher nutrient use efficiency of fertiliser Zn due to reduced leaching in these soils with relatively low Zn adsorption capacity, explaining the higher Zn uptake response ratio in Zimbabwe.

4.4. Grain Zn concentrations

Soil Zn availability (Zn-HNO_3) only explained 26% of the variation in grain Zn concentrations in the -Zn plots, compared to 35% of the variation in Zn uptake. In contrast to Zn uptake, maize variety and/or agro-ecological zone, represented by the random country variable, significantly contributed to the model. Although the effect of variety and agro-ecological zone cannot be separated, both effects are feasible. Strong variation in maize grain Zn concentrations, between 4 and 96 mg kg^{-1}, have been found among genotypes (Prasanna et al., 2020). In addition, environmental factors can also affect grain Zn concentrations. For example, it has been shown that the maximum grain Zn concentration can be increased by increasing N availability (Manzeke et al., 2020).

Gashu et al. (2021) collected around 2000 maize samples in Malawi and Ethiopia and found that grain Zn concentrations increased with increasing soil pH and SOC content. With regard to SOC, our results are in agreement with those from Gashu et al. (2021). In our study, Zn-HNO_3 was the most important variable explaining grain Zn concentrations and Zn-HNO_3 was strongly correlated with SOC (r = 0.75; not presented). However, the relationships between grain Zn and soil properties found by Gashu and other authors (Bevis and Hestrin, 2021; Gashu et al., 2021) were not always clear and straightforward, as opposite trends were found. Based on our findings in this study, we question the general feasibility of using soil properties as proxy for grain Zn

concentrations and the associated likelihood of human Zn deficiencies, since soil properties only explained 26% of the variation in grain Zn concentrations. Giller and Zingore (2021) posed the same question after reading the study by Gashu et al. (2021), particularly with regard to challenges associated with estimating soil bioavailable Zn and the effect of management practices that may weaken the relation between soil and grain Zn concentrations. Our analyses raise additional challenges with regard to this question. First of all, soil-plant relations in terms of Zn uptake may only be significant when Zn is the most yield-limiting nutrient (Janssen et al., 1990). Secondly, we have shown that there is a strong effect of variety and/or agro-ecological zone on grain Zn concentrations. Thirdly, tissue concentrations such as grain Zn, may also depend on the relative dilution of Zn in the maize, and thus on the availability of other nutrients that affect biomass production. These factors may all lead to a weak relationship between soil properties and grain Zn concentrations, thus challenging the assignment of areas with high risk of Zn deficiency in humans due to low grain Zn concentrations based only on soil properties.

4.5. Agronomic biofortification

Goredema-matongera et al. (2021) argued that the application of soil Zn fertilisers may benefit the crop by increasing its yield, but without increasing grain Zn concentrations, because of the low soil Zn content for most countries in SSA. Based on our results, we argue that the opposite is true, and that the application of Zn fertilisers may be beneficial for grain Zn content while it does not increase yields despite low soil Zn levels. Our results have demonstrated that the application of 5 kg ha^{-1} Zn fertiliser can lead to an average increase of 20% in grain Zn concentrations. This finding is in line with a review of Joy et al. (2015), who found an average increase in maize grain Zn concentration of 28% with fertilisation of ~16 kg ha^{-1} Zn. However, despite Zn fertilisation, grain Zn concentrations were still below the target level of 38 mg kg^{-1} of the HarvestPlus program (Bouis and Welch, 2010). We have shown that soil properties affect the effectiveness of agronomic biofortification through soil fertilisation. The increase in grain Zn concentrations by fertilisation was the largest for soils with low pH and SOC content, similarly as found for Zn uptake. Next to soil properties that are related to the adsorption of fertiliser-Zn, country as random variable was also found to affect agronomic biofortification, with the largest increase in grain Zn concentrations found in Zimbabwe (Table 2). Similarly as discussed for uptake, this result can be explained by variety and/or agro-ecological zone effects. Finally, the effectiveness of agronomic biofortification may also depend on the availability of other nutrients, such as nitrogen (Manzeke et al., 2020; Pasley et al., 2019) and phosphorus (Amanullah et al., 2020).

5. Conclusions

Zinc fertilisation did not lead to higher yields. It requires further research to find out why a fertiliser-induced increase in Zn uptake does not generally lead to higher maize yields, despite Zn being strongly diluted in the crop. Conclusions regarding the use of micronutrient fertilisers should not be based on average yield responses, given the large variability that was observed in this study and previous work.

The application of Zn fertilisers can be a feasible strategy to combat human Zn deficiencies in communities that are heavily reliant on maize as a staple crop since we found that Zn fertilisation improved Zn uptake and grain Zn concentrations. However, grain Zn concentrations were still below target values, pointing towards the use of more efficient fertiliser strategies such as foliar application when improvement of the nutritional quality is the main objective.

Existing critical levels based on commonly used soil tests, such as DTPA and Mehlich 3, failed to predict Zn deficiencies and a positive yield response of maize to Zn fertilisation. Other soil extractions such as a 0.43 M HNO_3 or 0.01 M $CaCl_2$ were also not able to predict maize yield responses to Zn fertilisation. Soil tests could reasonably predict Zn uptake, albeit that only 35% of the variation was explained. Soil tests that measured the Zn quantity performed better in predicting Zn uptake than soils tests that measure the Zn intensity. We explained this observation by the relatively low adsorption affinity for Zn of the soils used in this study. The response in both grain Zn concentrations and Zn uptake to Zn fertilisation was explained by the soil properties associated with the Zn adsorption affinity of these soils, namely soil organic carbon and pH. Grain Zn concentrations were found to be less related to soil properties than aboveground Zn uptake, with only 26% explained by the soil Zn levels estimated by a 0.43 M HNO_3 extraction. An effect of variety and/or agroecological zone was found to contribute to the variation in grain Zn levels, but not Zn uptake. Our results show that the identification of areas in which crop and human Zn deficiencies may be problematic, based on soil properties, remains challenging.

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Supporting information

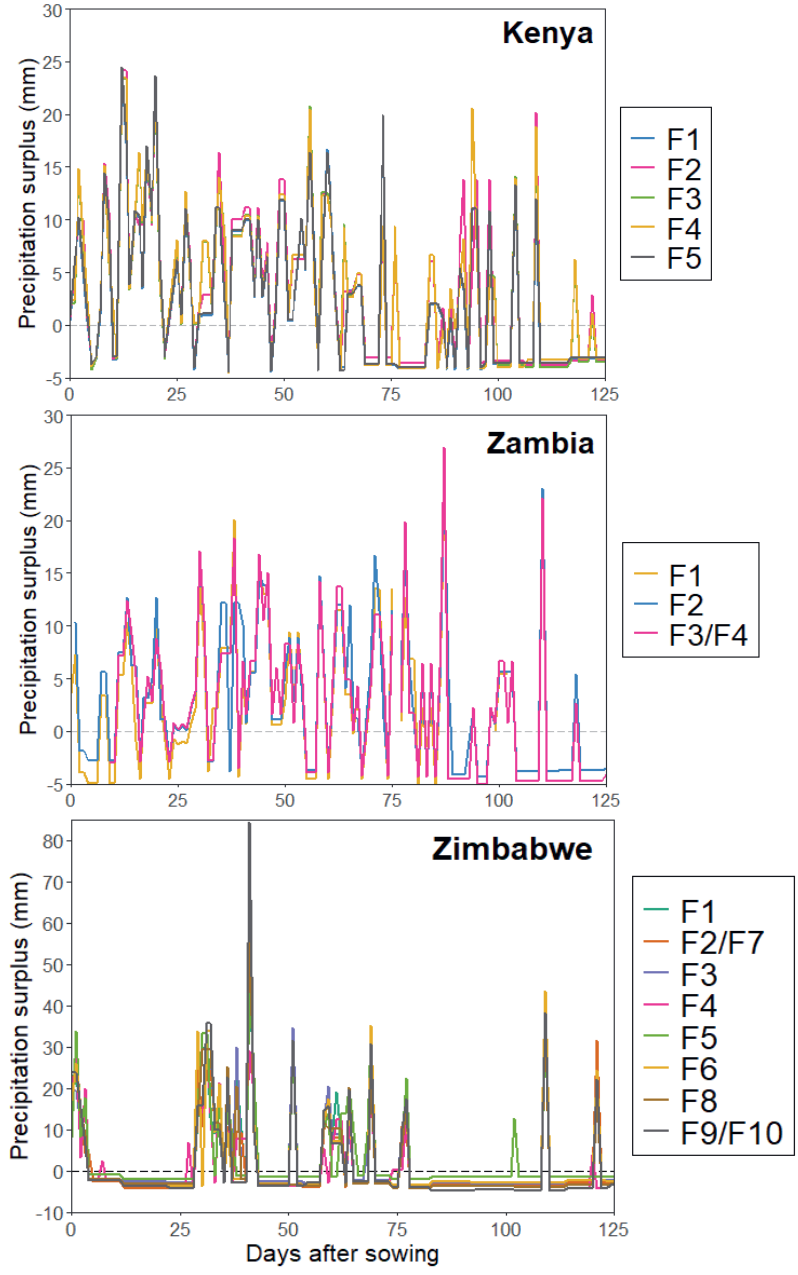

Figure S1: Precipitation surplus for individual farms in Kenya, Zambia and Zimbabwe, for the 125 days after sowing. The precipitation surplus was calculated as the difference between the daily precipitation and the average dekadal actual evapotranspiration. Data were extracted from the WaPOR portal of the Food and Agriculture Organisation (WaPOR, 2022).

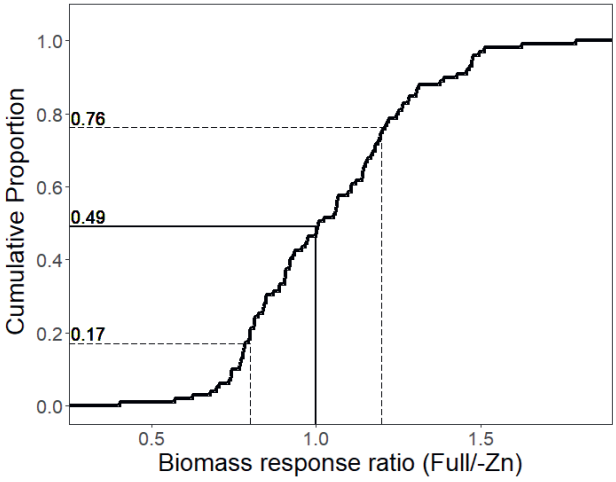

Figure S2: The cumulative proportion of blocks for the aboveground biomass response to fertilisation with Zn. A response > 1 indicates a higher biomass for the full treatment. Horizontal lines and accompanying numbers show the cumulative proportion of all blocks with a response ratio of 1 (solid) and 0.8 or 1.2 (dashed).

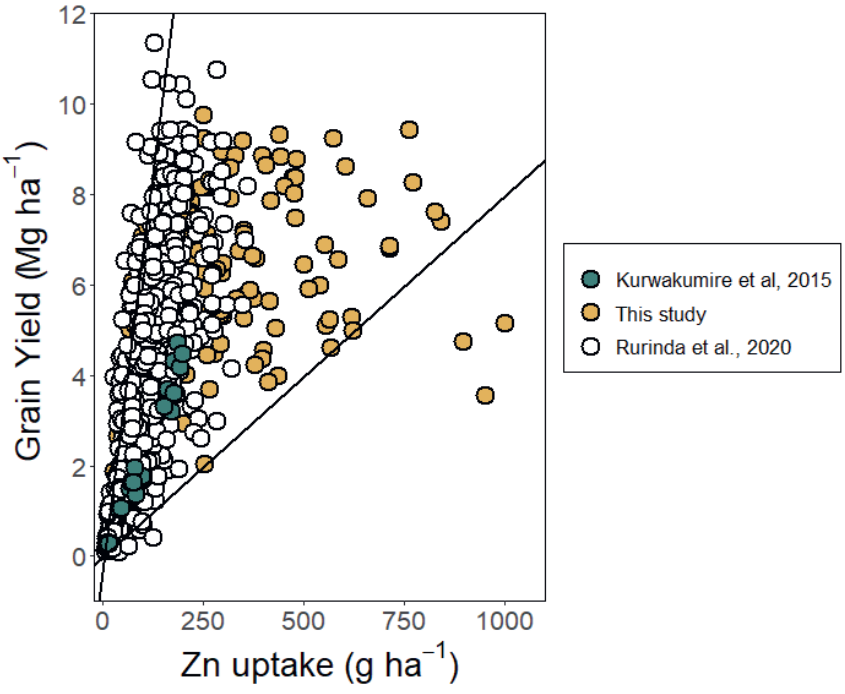

Figure S3: Maize yields plotted against Zn uptake. Data from this study was combined with available literature data on maize trials in SSA. Kurwakumire et al. (2015) executed trials in three locations in Zimbabwe, with an NPKS fertiliser treatment alone or in combination with lime, manure and micronutrients. Data from Rurinda et al. (2020) belong to the TAMASA trials in Nigeria. For each dataset, all fertiliser treatments were included. Lines represent the maximum and minimum internal efficiency (IE) of 71 and 8 Mg grains produced per g Zn uptake, respectively. The intercept represents the minimal Zn uptake needed to produce any yield (6.1 g ha^{-1}). Minimum and maximum IE parameters were derived based on the data in this figure, excluding the upper and lower 2.5 % of the datapoints based on their internal efficiency.

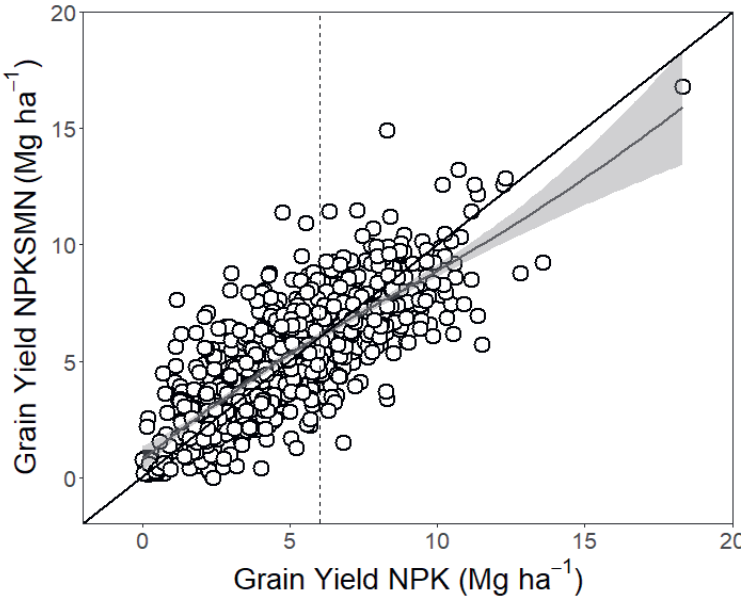

Figure S4: Maize yields in NPK + secondary + micronutrient fertiliser (NPKSMN) treatments plotted against maize yields obtained with only N, P and K fertilisers at the same locations. Data from TAMASA trials in Nigeria, Ethiopia and Tanzania (Rurinda et al., 2020) and AfSIS trials in Mali, Kenya, Malawi, Tanzania and Nigeria (Kihara et al., 2016; 2017).

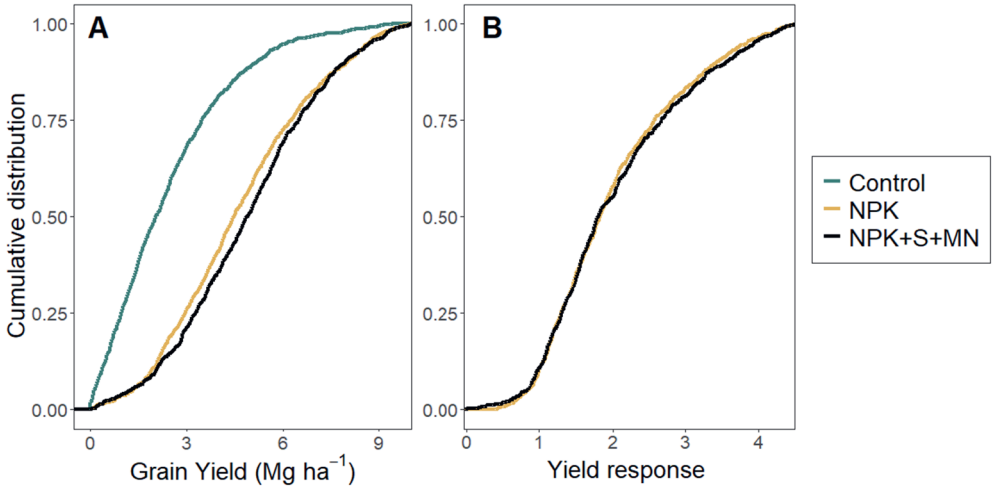

Figure S5: (A) Cumulative distributions of maize yields observed in the control (no fertiliser), NPK and NPK in combination with secondary (S) and micronutrients (MN) treatments for the Tamasa trials (Nigeria, Tanzania, Ethiopia; Rurinda et al., 2020) and the AfSIS trials (Kenya, Malawi, Nigeria and Tanzania; Kihara et al., 2017). (B) The grain yield response, calculated as yield in the NPK or the NPK+S+MN treatment divided by yield in the control treatment.

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Chapter 5

Boron availability and fertiliser response of maize in soils from sub-Saharan Africa

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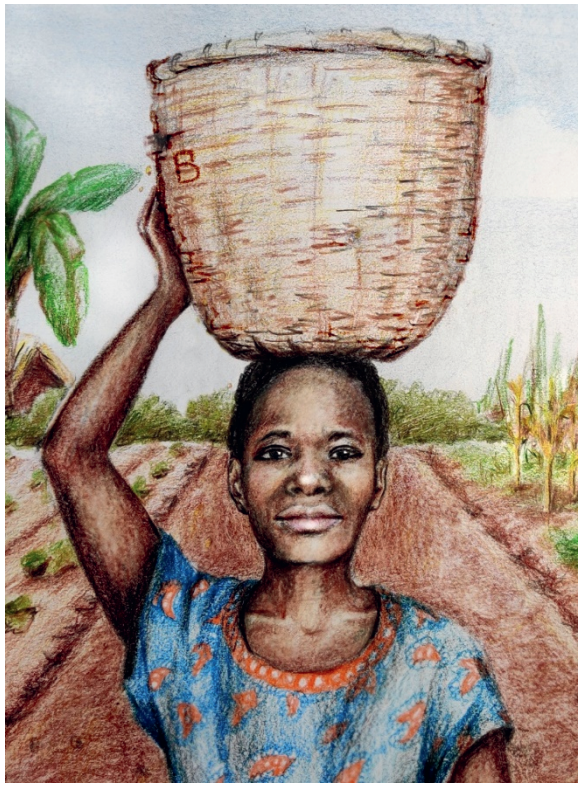


Abstract

Boron (B) deficiency is a global problem. Low soil B availability has been associated with strongly weathered and coarse-textured soils, as well as soils low in organic matter. Despite widespread occurrence of these soils in sub-Saharan Africa (SSA), a limited number of studies have addressed potential yield-limitations by B availability. As a result, it is currently unknown on which soils B fertilisation can improve yields. This study aims to increase the understanding on the soil properties that control bioavailability of B to field-grown maize in SSA. The experimental setup consisted of B fertiliser omission trials at fifteen on-farm sites within three African countries. Locations were selected based on suspicion of low B availability. Maize was fertilised with several nutrients (NPK, S, Mg, Ca, Cu, Zn) at adequate rates to ensure B was the yield-limiting nutrient. A similar treatment including B fertilisers was added as a control. Boron was applied during planting at rates of 5 kg ha^{-1} in Kenya and 3 kg ha^{-1} in Zimbabwe. In Zambia, B was fertilised through split application of 3 kg ha^{-1}. Data collection and analysis included biomass production of stover and grains and nutrient concentrations in both plant fractions. In soils, several extractable B pools (hot water, 0.01 M $CaCl_2$, 0.43 M HNO_3) were measured, as well as other parameters considered potentially relevant for B availability. Results indicated low soil and plant B concentrations compared to values reported in literature. Soil B concentrations in the different extraction methods were strongly correlated, with hot water extracting ~2 times as much B as 0.43 M HNO_3 and ~7 times as much B as 0.01 M $CaCl_2$. Yields varied strongly within and among sites, as well as within fertiliser treatments. Yields were significantly reduced through B fertilisation at six sites, likely because the high application rates of B induced toxicity. The yield response could not be predicted based on available soil parameters. Similarly, B uptake in the B omission plots, considered to be a proxy for B availability, was poorly described based on soil parameters. Given the large variability in yields and absence of a positive yield response, no critical plant and soil B concentrations could be derived. The validity of critical plant and soil B concentrations reported in literature is discussed. Furthermore, a number of recommendations are given for future research to overcome the identified challenges associated with studying B availability in tropical soils.

1. Introduction

Boron is an essential micronutrient for plants. It is required for various processes in the plant metabolism, such as root elongation, flower and seed formation and membrane functioning (Gupta, 2007). The occurrence of boron (B) deficiency is believed to be widespread globally since positive yield responses to B fertilisation have been reported for a wide variety of crops in at least 80 countries (Shorrocks, 1997). Low soil B availability has been associated with strongly weathered and coarse-textured soils, as well as soils low in organic matter content (Shorrocks, 1997). In sub-Saharan Africa (SSA), these particular soils associated with low B availability are widespread (Hengl et al., 2015). However, the number of studies addressing B deficiency in maize grown in SSA is limited (Sillanpää 1990; Shorrocks 1997; Wendt and Rijpma 1997; Vanlauwe et al. 2015; Tamene et al. 2016), despite maize being an important staple crop (Goredema-matongera et al., 2021). A large number of fertiliser response trials across several countries in SSA indicate that fertilisation with secondary and micronutrients, including B, can lead to higher maize yields in some cases (Kihara et al., 2017; Rurinda et al., 2020; Wortmann et al., 2019). However, the incidence of B deficiency could not be separated from the other secondary and micronutrients, as they were applied as a mixture. It is therefore currently unknown where B fertilisation can improve maize yields in SSA.

Understanding the soil, environmental and biotic factors that determine bioavailability of B, as well as the yield responses to B fertilisation in field trials, is key to deciding when to apply B fertilisers. Boron bioavailability in soils is, however, still poorly understood. Generally, B adsorption on the soil reactive surfaces such as organic matter, iron and aluminium oxides and clay minerals increases with pH and these processes are well described by Goldberg (1997). However, the work of Van Eynde et al. (2020) shows that adsorption plays only a minor role in controlling B availability in soils, as most of the reactive B was found in solution. Besides adsorption/desorption processes, atmospheric deposition, weathering of soil minerals and mineralisation of organic matter are believed to be the primary sources of B found in the soil solution (Kot et al., 2016; Park and Schlesinger, 2002), but the relevance of each of these processes may be different depending on the soil system (Van Eynde et al., 2020).

This study aims to increase the understanding on the soil properties that control the bioavailability of B to field-grown maize in SSA. Using B fertiliser omission trials at several sites within three African countries, we address the following research questions: (i) Which soil parameters determine bioavailability of B? (ii) Which soil parameters determine the yield response to B fertilisation? and (iii) Which critical soil and plant B concentrations indicate B deficiency in maize?

2. Material and methods

Boron fertiliser omission trials were executed as part of a larger experiment. Below we present the relevant methodology for this chapter. For a full overview of the materials and methods of the larger experiment, we refer to chapter 4.

2.1. Field trials

Boron fertiliser omission trials were conducted at 15 on-farm locations in three countries: Kenya (5 farms with 5 replications each), Zambia (4 farms with 4 replications each) and Zimbabwe (6 farms with 6 replications each). In Zimbabwe, the B fertiliser omission treatment was included in six out of ten farms of the larger experiment; farm names correspond to names used in chapter 4. Most farms are characterised by a history of low input use, except for Kenya, where chemical N, P and K had been applied in previous seasons. Within the individual countries, most farms were located in relatively close proximity of each other (< 5 km). Farms were selected based on low B availability as indicated by soil analysis. Layout of the experimental plots was based on a randomised block design. In each country, the treatment structure included a full fertiliser treatment with NPK, S, Mg, Ca, Zn, Cu and B and a B omission treatment, which was similar to the full treatment, except that B was omitted. Maize variety, planting densities, plot sizes, fertilizer application rates and number of replications, differed between countries based on the availability of resources and local practices.

In Kenya, B was applied as Solubor at a rate of 5 kg B ha^{-1} in the planting hole together with the other fertilisers, right before sowing. Boron application rates of 5 kg ha^{-1} are not uncommon for maize (e.g. Rurinda et al. 2020; Gotz et al. 2021). However, negative yield effects to application of 5 kg B ha^{-1} were observed in Kenya. Boron was therefore applied at a lower rate of 3 kg ha^{-1} in Zambia and Zimbabwe, to reduce the risk of B toxicity. In Zambia, two applications of 1.5 kg B ha^{-1} in the form of Borax were co-applied with urea during two topdressings at stages V6 and V10 of plant growth. In Zimbabwe, B was applied as Solubor in the planting hole together with the other fertilisers, right before sowing.

2.2. Data collection

Field-dry stover and grain biomass in each plot was weighed during harvest. Dry matter content of subsamples was determined to convert biomass weights to dry weights. Grain yield was expressed at a standardised moisture content of 13%. A range of plant essential elements was analysed in both stover and grain biomass samples using a 0.8 M H_2SO_4/Se/H_2O_2 digestion for N and a microwave digestion with concentrated HNO_3

for the other elements (Novozamsky et al., 1983). Boron uptake was derived from dry matter production of stover and grains, multiplied by their respective B concentrations.

Pooled topsoil (0-20 cm) samples were collected per block during harvest. Soil samples were taken between the rows, as fertilisers were applied in the planting hole.

As rainfall is known to potentially affect B leaching and associated availability (Degryse, 2017), daily precipitation was derived from satellite data (WAPOR, 2020). To estimate whether rainfall may have affected plant B uptake, the sum of precipitation in the 100 days after the first B fertiliser application was used.

2.3. Soil analysis

All soils were air-dried and passed through a 2 mm sieve prior to analysis. Soil B availability was assessed using hot water (B-HW), 0.01 M $CaCl_2$ (B-$CaCl_2$), 0.43 M HNO_3 (nitric acid; B-HNO_3) and Mehlich-3 (B-M3) soil extractions. Solutions were freshly prepared for each extraction. For the HW method, soils were extracted with 0.01 M $CaCl_2$ with a solution-to-solid ratio of 2 L kg^{-1} and a boiling time of 10 min (Aitken et al., 1987). Suspensions were heated in Teflon destruction tubes in a Mars 6 Microwave Digestion System (CEM corporation). The ramping time was set to 5 min before holding the suspensions at a temperature of 105±5 °C for 10 min. Tubes were removed immediately from the microwave when the program was finished and suspensions were decanted in 50 mL Greiner tubes for centrifugation. For the $CaCl_2$ method, soils were extracted with 0.01 M $CaCl_2$ at a solution-to-solid ratio of 10 L kg^{-1} and an equilibration time of 2 h (Houba et al., 2000). After centrifugation and filtration, extracts were acidified with concentrated HNO_3 before analysis. A HNO_3 soil extraction was done using a solution-to-solid ratio of 10 L kg^{-1} and an equilibration time of 4 h, according to the ISO standard (ISO, 2016). Lastly, soils were extracted with a M3 solution, consisting of 0.1 M CH_3COOH, 0.25 M NH_4NO_3, 0.015 M NH_4F, 0.013 M HNO_3 and 0.001 M EDTA, with a solution-to-solid ratio of 10 L kg^{-1} and an equilibration time of 5 min (Mehlich, 1984). Boron concentrations were measured using high resolution Inductively Coupled Plasma - Mass Spectrometry (ICP-MS, Element 2, Thermo Scientific) in all four soil extracts, after centrifugation and filtration of the suspensions over a 0.45 μm membrane filter.

Several other soil properties affecting B adsorption were determined. Soil pH was measured with a glass electrode in a distilled water extract, with a solution-to-solid ratio of 2.5 L kg^{-1}, after shaking for 2 h on a linear shaker at 180 strokes min^{-1}. Soil organic carbon (SOC) content was spectrophotometrically determined after the Kurmies wet

oxidation method (Walinga et al., 2008). Soil contents of Al and Fe hydroxides were determined with an ammonium oxalate soil extraction (ISO, 2012). For further data analysis, the sum of Al and Fe hydroxides in ammonium oxalate (AlFe-AO; in mmol kg^{-1}) was used. Clay content was determined with various methods (see chapter 4). Soil calcium, in the form of carbonates, calcium clays and free ions are also known to affect B adsorption (Goldberg, 1997). Calcium concentrations in M3 (Ca-M3) were analysed as a proxy for soil calcium levels. Concentrations were measured using Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES).

2.4. Analytical limits

The determination limits for the different methods were calculated as the average value of the blanks + three times its standard deviation, across different analytical series (Keskinen et al., 2019). Determination limits for B were found to be 0.78 μg kg^{-1} for hot water (n = 10 blanks), 4 μg kg^{-1} for 0.01 M $CaCl_2$ (n = 28), 0.03 mg kg^{-1} for 0.43 M HNO_3 (n = 14) and 0.78 mg kg^{-1} for Mehlich 3 water (n = 4). The determination limit for the B-M3 procedure is higher compared to B-HW, B-$CaCl_2$ and B-HNO_3 procedures, as the M3 extract needs to be diluted more for ICP-MS measurements because of its high salt content.

None of the samples had B concentrations below the determination limits for HW, $CaCl_2$ or HNO_3, but all of the samples were below the determination limit for M3. Even if the determination limit was calculated as the average value of the blanks + two instead of three times its standard deviation (0.52 mg kg^{-1}), all measured B-M3 concentrations were below this detection limit. No reliable B-M3 results were therefore obtained for the soils used in this study, and B-M3 was consequently not used in further data analysis.

2.5. Data analysis

Data was analysed using R software, version 4.0.2 (R Core Team and R Development Core Team, 2020). Results were visualized with the ggplot2 package (Wickham, 2016).

Treatment effects

The effect of fertiliser treatment (i.e. full and B omission) on maize grain yields (Mg ha^{-1}) and B uptake (g ha^{-1}) was assessed with linear mixed effect models (LME) using the lme function from the nlme package (Pinheiro et al., 2013). These analyses were done for each farm, with treatment as fixed factor, and block as random factor (random= ~1|Block). At country level, differences between farms were also assessed using an LME model with farm as additional fixed factor. Significance of factors, as well as their interaction, were tested with the Anova function from the car package (Fox and

Weisberg, 2019). Individual differences were analysed with Tukey's post hoc test, using the glht function from the multcomp package, version 1.4-17 (Hothorn et al., 2008). Normality of model residuals were checked with the Shapiro-Wilk test using the shapiro.test function from the stats package, version 4.1.0 (R Core Team and R Development Core Team, 2020). Homogeneity of variances was tested with Levene's test, using the leveneTest function from the car package. In case assumptions of normality of residuals or homogeneity were violated, data transformation was applied.

The effect of fertiliser treatment was also assessed on block-level by calculating the yield response as:

Equation 1: Yield response = (Yield Full) / (Yield B omission)

with Yield Full representing the yield (Mg ha^{-1}) in the full treatment, and Yield B omission the yield (Mg ha^{-1}) in the treatment where B was not fertilised.

Soil-plant relations

Boron uptake in the B omission plots was used as a proxy for B bioavailability, as the uptake of a nutrient equals soil supply when it is yield-limiting (Janssen et al., 1990). The relation between soil properties and B uptake in the B omission treatment, as well as the yield response, was assessed using LME modelling with method specified as maximum likelihood (ML). In these models, soil properties were used as fixed effects and the effect of agroecological zone and maize variety was represented by including country as a random factor (random= ~1|Country). Although this model treats all blocks within a country as pseudo-replicates, it was considered suitable given the large variability in soil and plant parameters within farms.

Based on Van Eynde et al. (2020) and Goldberg (1997), the soil properties considered relevant for B bioavailability were included in the modelling: pH, B-$CaCl_2$, B-HNO_3, B-HW, SOC, Ca-M3 and AlFe-AO. Although multicollinearity was observed among the explanatory soil parameters, no variable selection was made, since all of the variables are potentially relevant for controlling B availability. Model selection was done based on the Akaike's Information Criterion (AIC) value (Webster and McBratney, 1989) using the dredge function from the MuMIn package (Barton, 2020). The yield response was modelled on a log10-scale (Marcillo and Miguez, 2017), where each of the independent parameters was also log-transformed, except pH. Boron uptake was modelled on a normal scale.

Normality and homogeneity were checked with the Shapiro-Wilk and Levene's test. The r2 function from the performance package in R (Ludecke et al., 2021) was used to calculate the variance explained by the fixed factors only (marginal R^2) and the variance explained by both the fixed and random effects (conditional R^2). Throughout this manuscript, these will be referred to as fixed and total R^2 respectively. The relative contribution of each variable in the final LME model, was tested using the r2beta function from the r2glmm package (Jaeger, 2017).

3. Results

3.1. Soil parameters

The soils of the field trial locations generally had low SOC contents with no values exceeding 20 g kg^{-1} (Table 1). The Zambian and most of the Zimbabwean farms had the lowest SOC contents, which ranged from 4 - 11 g kg^{-1}, whereas the Kenyan farms had higher SOC contents, between 9 and 20 g kg^{-1}. The field trials covered a limited range in soil pH, with most of the values between 5.0 and 6.5, with the exception of two blocks in Zimbabwe (both on Farm 10). Within countries, the range in pH values was even more limited, with the Kenyan farms covering pH 5.1 - 6.3 and the Zambian farms covering pH 5.7 - 6.4. The pH values of the farms in Zimbabwe ranged between 5.0 and 7.0, covering the entire range in pH values reported in this study.

Table 1: Soil characteristics of the farms. Values represent averages per farm, except for clay content, which was analysed on farm level.

	Farm	pH -	SOC (g kg^{-1})	B-HNO_3 (mg kg^{-1})	B-$CaCl_2$ (µg kg^{-1})	B-HW (mg kg^{-1})	Ca-M3 (mg kg^{-1})	AlFe-AO (mmol kg^{-1})	Clay (%)
Kenya	1	5.9	15.6	0.34	74	0.67	1266	91	29
	2	5.7	15.8	0.18	34	0.34	1139	103	30
	3	5.6	11.3	0.21	50	0.29	537	51	29
	4	5.6	9.9	0.14	40	0.21	369	60	35
	5	5.3	16.2	0.26	75	0.65	622	97	40
Zambia	1	6.2	10.3	0.11	16	0.21	591	52	-
	2	6.1	8.3	0.08	17	0.05	307	34	-
	3	5.9	6.3	0.07	14	0.10	188	37	-
	4	6.3	6.5	0.09	16	0.11	243	25	-
Zimbabwe	4	5.6	13.0	0.32	132	0.91	1112	69	35
	6	5.6	5.2	0.10	48	0.07	123	11	7
	7	5.5	5.8	0.10	50	0.17	94	17	6
	8	5.3	4.8	0.11	50	0.12	83	22	2
	9	5.4	6.2	0.09	41	0.09	155	14	8
	10	6.2	4.7	0.36	93	0.50	444	21	2

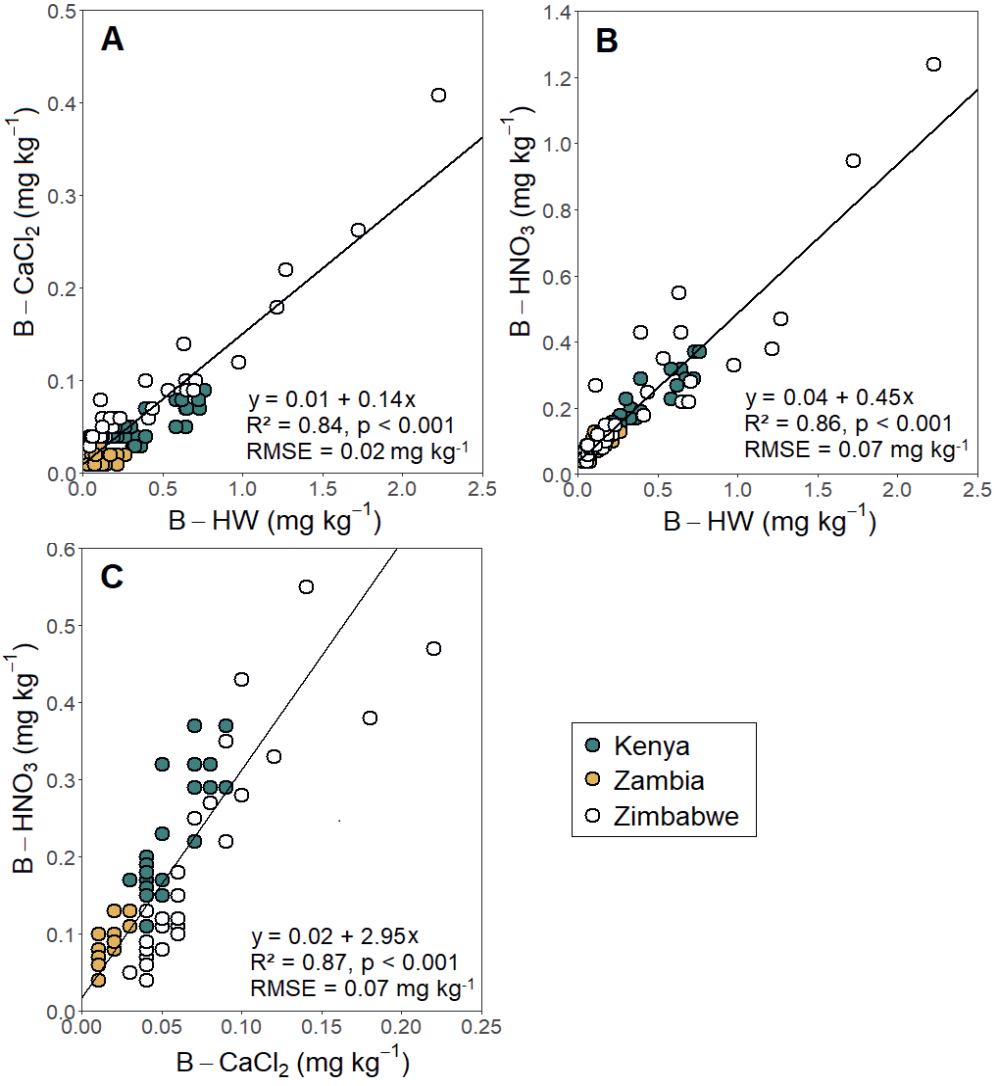


Figure 1: Relations between B concentrations in HW and $CaCl_2$ (A), HW and HNO_3 (B) and $CaCl_2$ and HNO_3 (C) soil extracts. Points represent individual blocks, colours indicate country. The two highest points in Figure 1A and B belong to Farm 5 in Zimbabwe (chapter 4), where only Zn and no B omission treatment was included. Data were included for discussion purposes.

The soils had B concentrations ranging between 0.03 - 1.27 mg kg^{-1} for B-HW, 0.05 - 0.22 mg kg^{-1} for B-$CaCl_2$ and 0.04 - 0.55 mg kg^{-1} for B-HNO_3 (Figure 1). Boron availability was lowest for the Zambian and some of the Zimbabwean soils; the Zimbabwean soils generally covered the widest range. Boron concentrations in HW were highest, followed by HNO_3 (~45% of HW) and $CaCl_2$ (~14% of HW). Boron concentrations in the different extracts were strongly correlated, but correlations were

relatively poor at lower concentrations (i.e. below ~0.1 mg kg^{-1} B-$CaCl_2$; Figure 1). Despite these strong correlations, the fractions of soil B exhibited different relations with different other soil properties. Of the three extraction methods, B-HW correlated best with SOC (r = 0.63, p < 0.001), AlFe-AO (r = 0.61, p < 0.001) and Ca-M3 (r = 0.76, p < 0.001). In contrast to B-HW, B-HNO_3 was also correlated with pH (r = 0.29, p = 0.010), in addition to SOC (r = 0.44, p < 0.001), AlFe-AO (r = 0.43, p < 0.001) and Ca-M3 (r = 0.66, p < 0.001). The B-$CaCl_2$ was only significantly correlated with SOC (r = 0.26, p = 0.022) and Ca-M3 (r = 0.44 , p < 0.001). Clay data were only available for the Kenyan and Zimbabwean farms, on farm level, and could thus not be used to derive correlations with other soil parameters. The ratio between B-HW/B-HNO_3 increased with SOC (r = 0.63, p < 0.001), AlFe-AO (r = 0.66, p < 0.001) and Ca-M3 (r = 0.60, p < 0.001) concentrations. Similarly, the ratio between B-HW/B-$CaCl_2$ increased with SOC (r = 0.56, p < 0.001), AlFe-AO (r = 0.62, p < 0.001) and Ca-M3 (r = 0.54, p < 0.001) concentrations, as well as pH (r = 0.29, p = 0.011).

3.2. Yield response

Maize yields in the majority of farms ranged between 4 and 8 Mg ha^{-1}. Within each of the countries, significant differences in maize yields among sites were found (Figure 2). Unexpectedly, fertilisation with B led to significantly lower yields on six out of fifteen sites (Farms 1 and 3 in Kenya, Farms 3 and 4 in Zambia and Farms 6 and 8 in Zimbabwe), indicating potential B toxicity. Visual symptoms of toxicity (or deficiency) were not observed in the field. A negative yield response (i.e. below 1) to B fertilisation was found for 48 out of 72 blocks (67%) across all sites, although the majority of blocks (n = 52, 72%) had a yield response between 0.8 and 1.2 (Figure 3). We consider this natural variation as a variation of 20% from the mean yield response roughly corresponds to the variation in yield response within a site and treatment (Figure 2).

Using LME modelling, variation in the yield response to B fertilisation could not be explained based on any soil parameter and rainfall data. Further inspection of the data showed three outliers in the yield response (< 0.6). In each of these farms (Farms 2 and 3 in Zambia and Farm 8 in Zimbabwe), the low yield response to B in one of the blocks coincided with a relatively low yield for the full treatment. At Farm 3 in Zambia and Farm 8 in Zimbabwe, the negative effect of B fertilisation on yield was significant (Figure 2), although not at Farm 2 in Zambia. Regressions were rerun after removing the three outliers in yield response to B, but again no soil parameter or rainfall was retained in the final model to explain the variation in the yield response to B. In addition, model residuals were not normally distributed (p = 0.015). Further inspection showed that the residuals were strongly correlated with yields in both treatments.

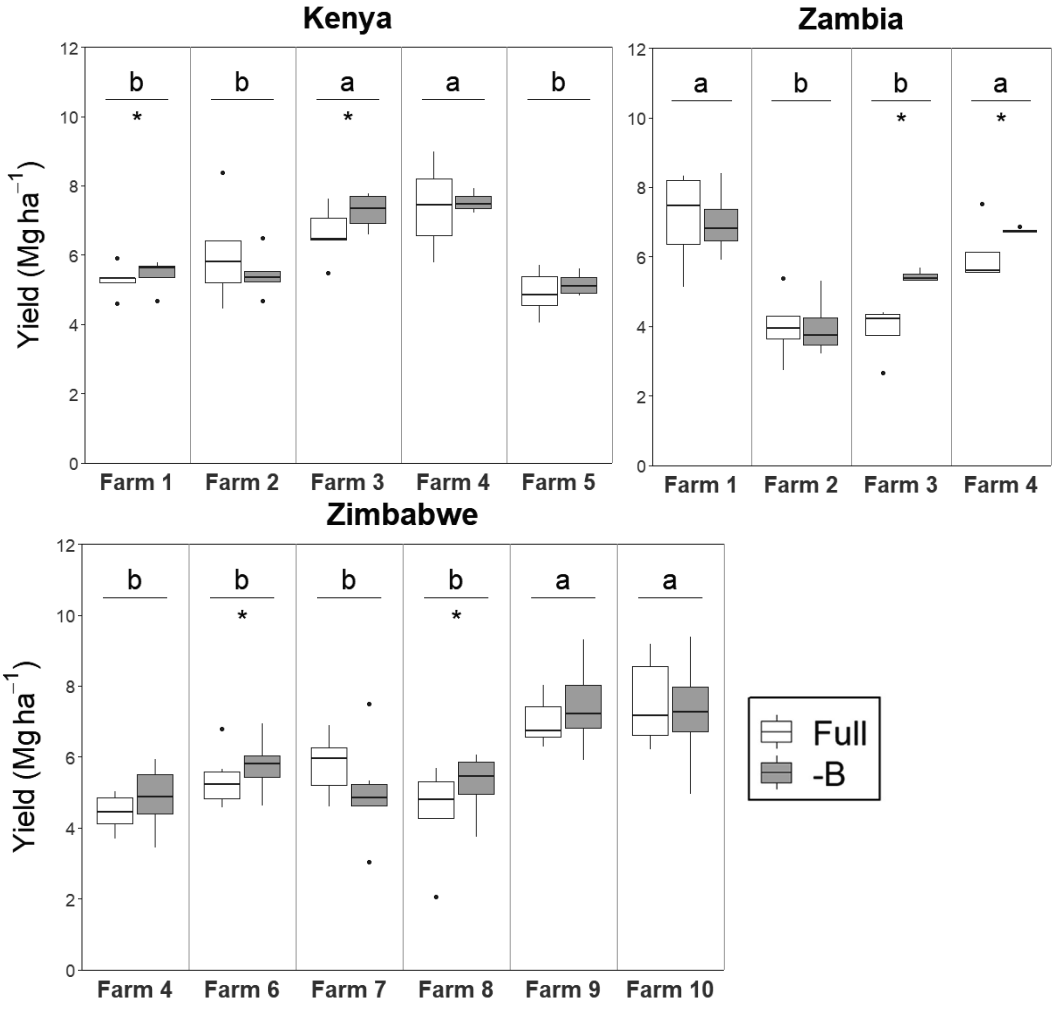


Figure 2: Boxplots of maize yield for individual farms, grouped per country. The boxplots show the median (line), first and third quartiles (hinges), the minimum and maximum based on the interquartile range (whiskers) and the outliers (points). Letters indicate significant differences among sites within a country, asterisks indicate a significant difference between treatments.

Although auto-correlated with the yield response, to normalise model residuals and gain insights in additional explanatory variables, it was decided to rerun the regression using yield of the B omission treatment as an explanatory variable for the yield response. This resulted in a model with normally distributed residuals ($p = 0.091$). This model described the yield response based on yields in the B omission treatment, B-$CaCl_2$, AlFe-AO, B-HNO_3, pH and Ca-M3. Fixed and total R^2 were both 0.32, indicating that limited variation in the yield response was described. In this model, yield in the B omission

treatment explained 68% of R^2. When rainfall was added as an explanatory variable, it was found to be the most important parameter in explaining the yield response, followed by yield in the B omission treatment, B-HW and B-$CaCl_2$. Residuals were normally distributed (p = 0.716). Fixed and total R^2 were 0.538 and 0.944, indicating that country as a random effect was significant when rainfall was included in the LME model. Despite more variation in the yield response explained by the model including rainfall, it was not significantly different from the model without (p = 0.064). Running a regression with data from farms where B application did not lead to a significant yield reduction (n = 43), resulted in a model with yield in the B omission treatment as most important variable, followed by B-$CaCl_2$, Ca-M3 and B-HNO_3. The model was not an improvement in terms of R^2 and RMSE compared to the model based on all data (not presented); inclusion of rainfall also did not further improve this model. Each of the three models included B-$CaCl_2$ with a negative coefficient, as well as either B-HW or B-HNO_3 with a positive coefficient. However, the contribution of the soil parameters generally was limited, given the large explanatory value of yield in the B omission treatment (Figure 4).

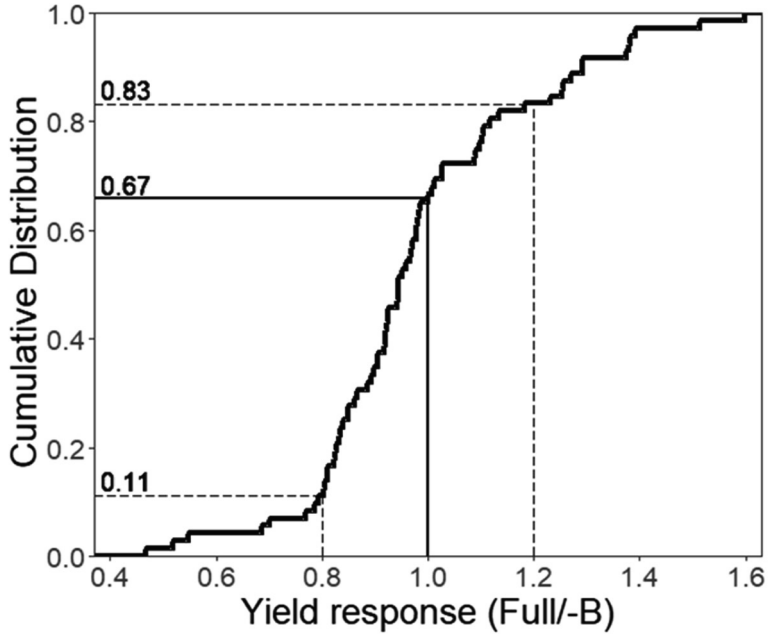


Figure 3: Cumulative distribution of the yield response per block (n = 72). A value of 1 indicates no yield difference between both treatments, a value below 1 a negative yield response (higher yield for the B omission treatment) and a value above 1 a positive yield response (higher yield for the full treatment). Dashed lines indicate yield responses of 0.8 and 1.2.

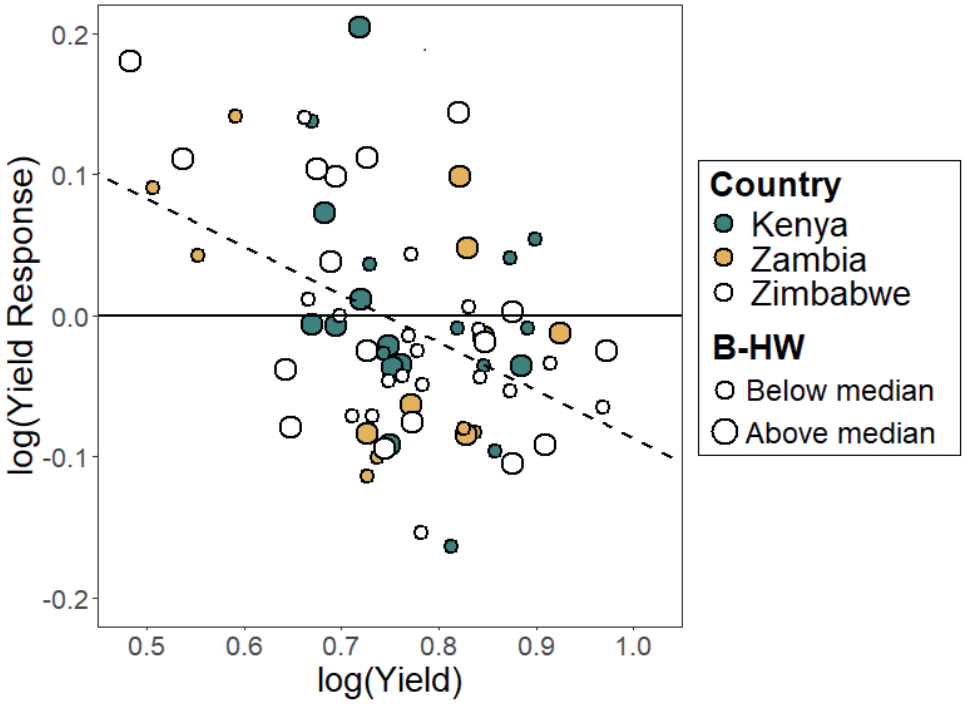
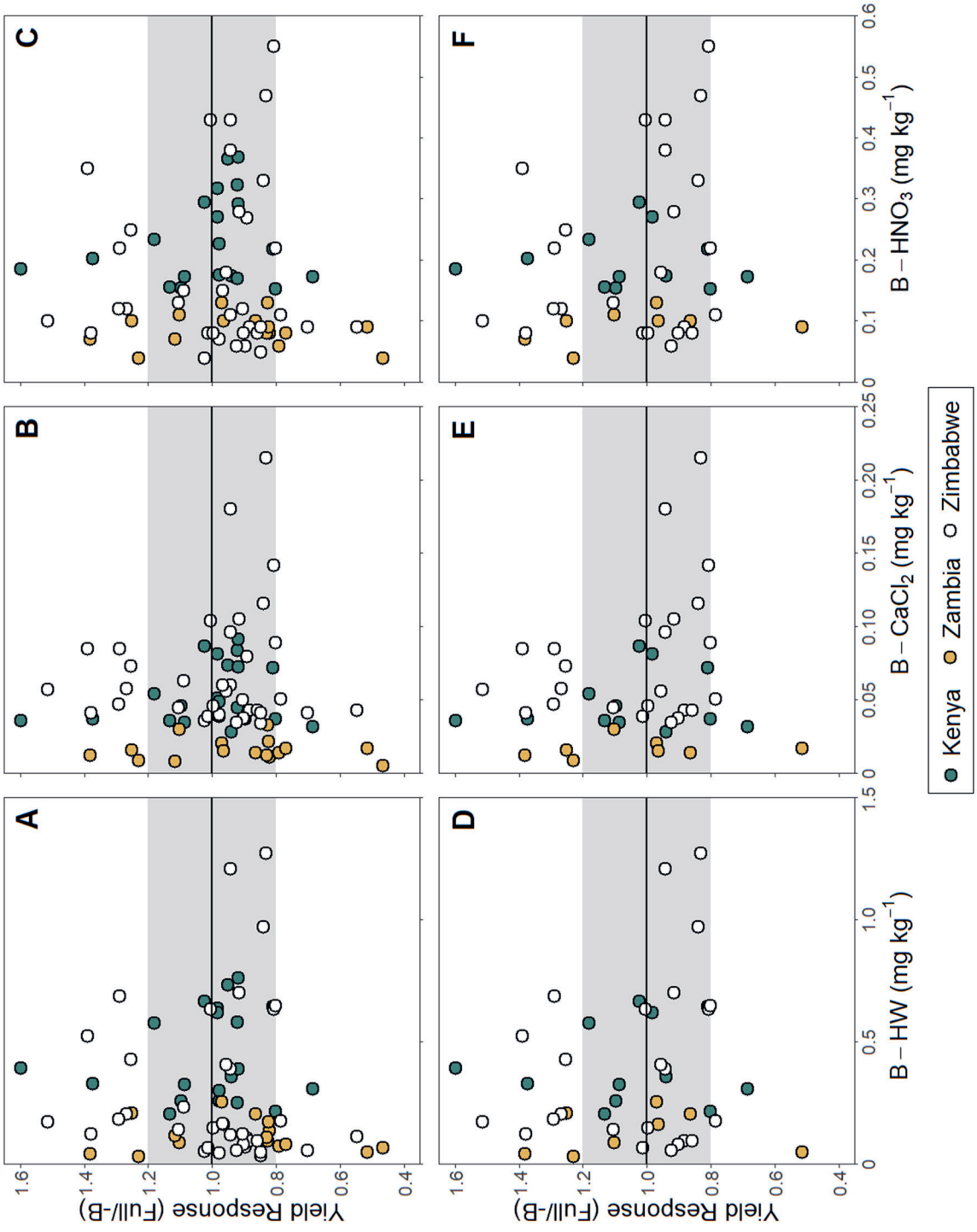


Figure 4: Yield response (full/B omission) per block plotted against yield in the B omission treatment. Size of the data points indicates whether B-HW concentrations were below or above the median value within each respective country. The dashed line represents the correlation between the yield response and yield in the B omission treatment (n = 72, r = -0.44, p < 0.001).

No clear trends between the yield response and soil B concentrations were found (Figure 5A, B and C). The variation in yield responses was large at low B concentrations, so it was not possible to derive critical soil B concentrations based on B-HW, B-$CaCl_2$ and/or B-HNO_3 soil extracts. Exclusion of the six farms where B application led to a significant yield reduction, strongly reduced the variation in yield response for soils with low soil B concentrations (Figure 5D, E and F). No positive yield responses (> 1.2) to B fertilisation were found when B-HW was above 0.69 mg kg^{-1}, B-$CaCl_2$ was above 0.085 mg kg^{-1} and B-HNO_3 was above 0.35 mg kg^{-1} (Figure 5). However, below these concentrations, negative yield responses (< 0.8) were still found.

Figure 5 (next page): The yield response per block (n = 72) plotted against B concentrations in (A) hot water, (B) $CaCl_2$ and (C) HNO_3. Similar plots are presented in D, E and F without data from the farms where boron led to a negative yield response (n = 43). Grey marked areas represent natural variation in the yield response.


A
B
C
D
E
F
Yield Response (Full/-B)
B – HW (mg kg^{-1})
B – CaCl$_2$ (mg kg^{-1})
B – HNO$_3$ (mg kg^{-1})
Kenya
Zambia
Zimbabwe

3.3. **Plant B concentrations**

Both stover and grain B concentrations significantly increased as a result of B fertilisation (Table 2). Across countries, median grain B concentrations increased from 1.25 to 1.92 mg kg^{-1}, while median stover B concentrations increased from 3.71 to 6.60 mg kg^{-1}. Grain B concentrations were less affected by B fertilisation compared to stover B concentrations (1.54-fold increase for grain vs 1.75-fold increase for stover). Differences among countries were observed, however: in Kenya and Zimbabwe stover B concentrations increased relatively more than grain B concentrations, while the opposite was observed for Zambia.

Table 2: B concentrations and concentration response to fertilisation (Full/B omission). Values represent medians, range between brackets. Within countries, average concentrations were all significantly different between the full and B omission treatments, with *p*-values below 0.001.

	Grain [B] (mg kg^{-1})		**Stover [B] (mg kg^{-1})**		**Response**	
Country	Full	B omission	Full	B omission	Grain	Stover
Kenya	1.77 (1.5 - 2.2)	1.27 (1.0 - 1.6)	6.40 (3.5 - 10.5)	3.68 (2.4 - 4.6)	1.40 (1.0 - 2.0)	1.74 (1.1 - 2.6)
Zambia	2.08 (1.7 - 2.4)	1.06 (0.7 - 1.7)	6.65 (4.7 - 10.6)	4.50 (3.7 - 6.5)	1.86 (1.2 - 3.1)	1.45 (0.9 - 1.9)
Zimbabwe	2.07 (1.4 - 4.9)	1.29 (0.9 - 1.9)	7.00 (3.4 - 20)	3.59 (2.7 - 5.0)	1.55 (0.9 - 4.1)	1.85 (0.9 - 5.7)
All	1.92 (1.4 - 4.9)	1.25 (0.7 - 1.9)	6.60 (3.4 - 20)	3.71 (2.4 - 6.5)	1.54 (0.9 - 4.1)	1.75 (0.9 - 5.7)

Across countries, grain B concentrations ranged between 0.69 - 1.88 (B omission) and 1.37 - 4.89 mg kg^{-1} (full treatment; Figure 6A; Table 2). Boron concentrations in stover were generally 2-6 times larger than in grains and ranged between 2.44 - 6.50 (B omission) and 3.36 - 20.00 mg kg^{-1} (full treatment; Figure 6B; Table 2). The highest stover B concentrations were associated with relatively low stover biomass production, indicating that the high concentrations may be a result of B accumulation in the crop (Figure 6B). For grain B concentrations, a similar trend was visible, but less clear than for stover B concentrations (Figure 6A). The seven highest stover B concentrations (>11 mg kg^{-1}) were found in the full treatment for farms Farm 6 and 8 in Zimbabwe. The ten highest grain B concentrations (>2.49 mg kg^{-1}) were found in these same farms. These were farms with a significant negative yield response to B fertilisation (Figure 2). In Kenya and Zambia however, no clear differences in plant B accumulation were found between farms where B fertilisation led to a significant yield reduction and farms where it did not.

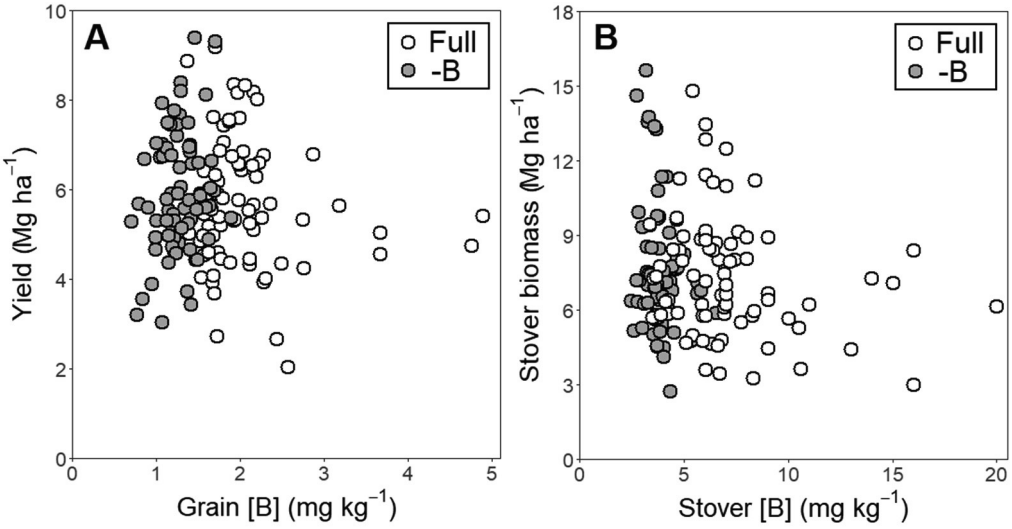


Figure 6: Boron concentrations in (A) grain and (B) stover, plotted against the biomass production of each fraction. Points represent individual blocks.

No clear patterns between grain and stover B concentrations of the B omission plots and the yield response were found (results not presented). It was therefore not possible to derive critical plant concentrations that are indicative of potential B deficiency.

3.4. **B uptake**

Across countries, B fertilisation led to a significant increase in B uptake for most farms (Figure 7). No increase in B uptake was observed in Farm 1 in Kenya, Farm 3 and 4 in Zambia and Farm 4 in Zimbabwe (Figure 7). Except for Farm 4 in Zimbabwe, the absence of an uptake response for those farms can be explained by the lower yields (and stover biomass production) in the full treatment (Figure 2), which translates into lower B uptake. Boron fertilisation led to an average increase in B uptake of 21 g ha^{-1} for Kenya, 9 g ha^{-1} for Zambia and 35 g ha^{-1} for Zimbabwe. Given the fertilisation rates of 5 kg ha^{-1} for Kenya and 3 kg ha^{-1} for Zambia and Zimbabwe, the fertiliser use efficiency is low (0.3-1.2%).

Equation 2: B uptake = 38.1 + 78.5*B-HNO_3 – 0.9*SOC – 150.6*B-$CaCl_2$

Boron uptake (g ha^{-1}) in the B omission plots was used as a proxy for B availability. The final model based on model selection included a positive effect of B-HNO_3, and a negative effect of B-$CaCl_2$ and SOC to describe the variation in B uptake (Equation 2). Fixed and total R^2 of this model were both 0.21, RMSE was 9.8 g ha^{-1} and residuals

were normally distributed ($p = 0.563$). The B-HNO_3 was the most important parameter in describing variation in B uptake (56% of R^2), followed by SOC (25%). Uptake of B generally increased with B-HNO_3 concentrations and decreased with SOC (Figure 8). However, much of the variation in B uptake remained unexplained. Adding rainfall as an explanatory variable did not improve the description of B uptake in the B omission treatment (results not presented).

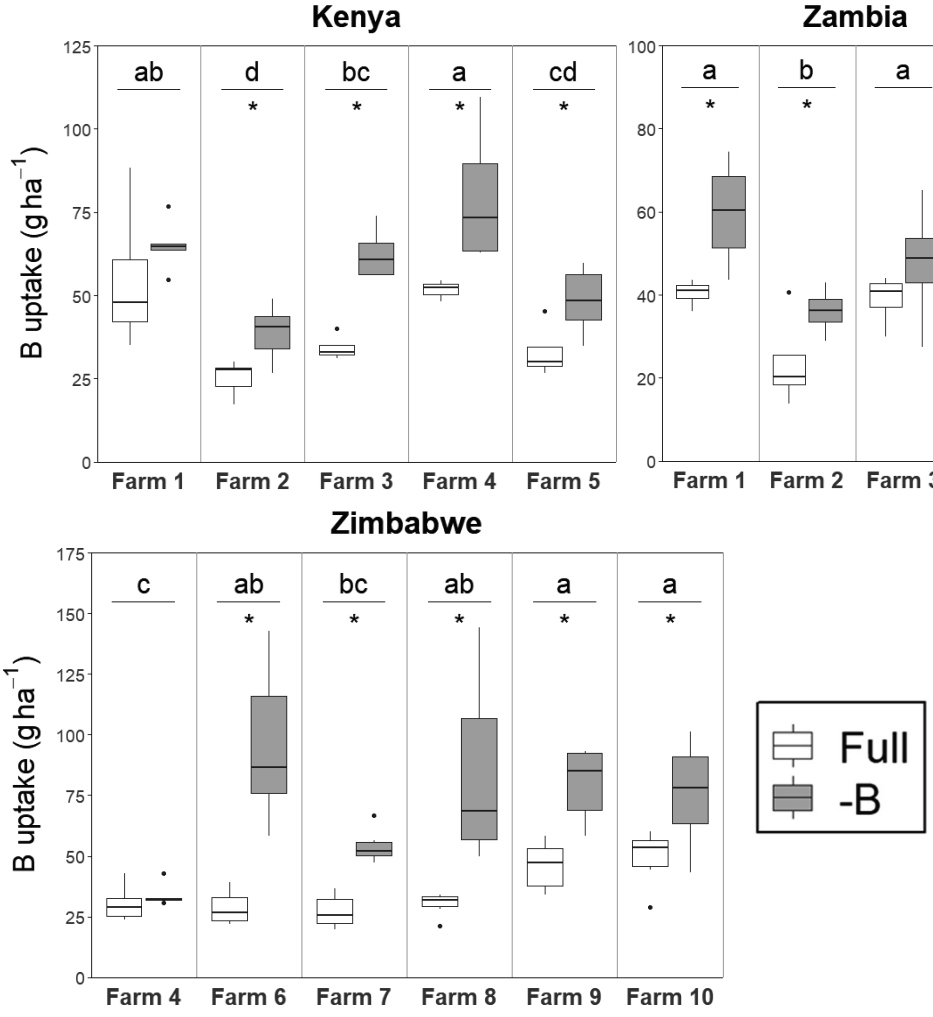


Figure 7: Boxplots of B uptake for individual farms, grouped per country. Boxplots show medians (line), first and third quartiles (hinges), minimum and maximum values based on the interquartile range (whiskers) and outliers (points). Letters indicate significant differences among sites within a country, asterisks indicate significant differences between treatments within a farm.

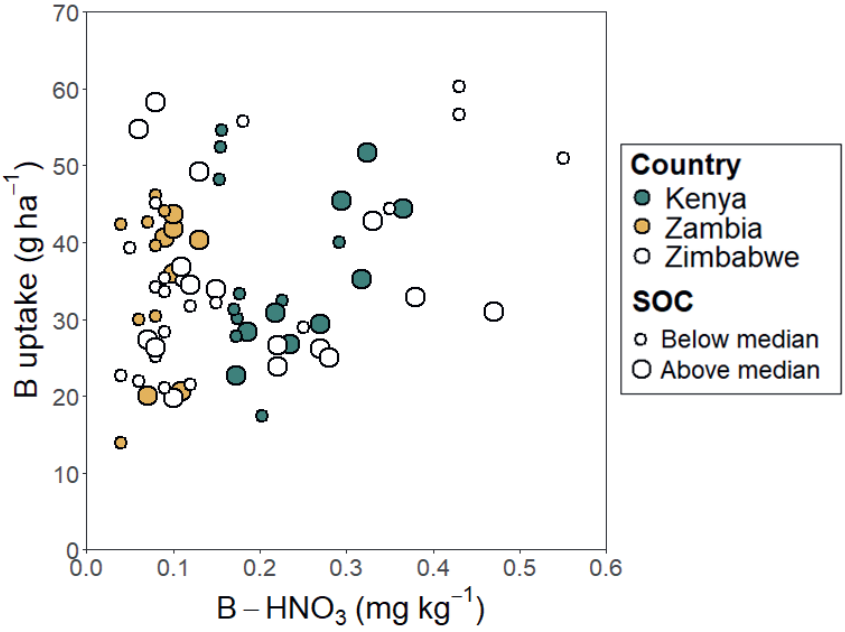


Figure 8: B uptake of the B omission plots plotted against B-HNO_3, with size of the data points indicating whether SOC concentrations were below or above the median, within each respective country. Data points represent individual blocks.

4. Discussion

4.1. Yield response

Despite low soil and plant B concentrations, B fertilisation did not increase maize yields. In line with our results, several studies report that B fertilisation mainly increases maize B concentrations, but not biomass production (Andrić et al., 2016; Jin et al., 1988; Lordkaew et al., 2011; Mozafar, 1987). Although B is beneficial for human health (Nielsen, 2014), it is unclear where and to what extent B intake is insufficient in SSA and whether fertilising maize with B could alleviate this. More importantly, farmers will be reluctant to use fertilisers when this does not lead to increased yields.

In the majority of plots, a negative yield response to B fertilisation was observed, with a significant yield reduction at 6 out of 15 farms. Both deficiency and toxicity can occur in the same growing season (Goldberg, 1997). In unfertilised situations, B toxicity is rare (Gupta et al., 1985). When fertilising, added B to soils will largely remain in solution as adsorption is limited, especially in acidic soils (Degryse, 2017; Van Eynde et al., 2020). As the range between deficient and toxic levels of soil available B is very narrow, this can easily lead to toxicity, especially when large quantities of B are applied (Gupta et al.,

1985). In this study, B was fertilised as 5 kg ha^{-1} basal application in Kenya, 3 kg ha^{-1} split application in Zambia and 3 kg ha^{-1} basal application in Zimbabwe, all applied in or close to the planting hole. Previously, application of 5 kg B ha^{-1} did not result in notable maize yield reductions in SSA (Rurinda et al., 2020) and ~5 kg ha^{-1} was found to be the optimal B application rate for field-grown maize in Brasil (Gotz et al., 2021). On the other hand, B application rates used in this study were considerably higher than the 0.5 to 1 kg ha^{-1} applied in several other field trials with maize in SSA (Kihara et al., 2017; Lisuma et al., 2006; Vanlauwe et al., 2015; Wendt and Rijpma, 1997; Wortmann et al., 2019). Wendt and Rijpma (1997) furthermore also noted potential B toxicity in maize grown in Malawi at a B application rate of 3 kg ha^{-1}, despite soil testing values indicating B deficiency. The B fertiliser application rates used in our field trials likely were too high and resulted in significant reductions in yields. Based on our findings and those of Wendt and Rijpma (1997) we conclude that application rates of 3 kg ha^{-1} are too high for maize in acidic soils. Given the low B requirements of maize, we recommend a maximum B application rate of 1 kg ha^{-1} for soluble B fertiliser sources. Based on Degryse (2017) and Abat et al. (2014), we furthermore recommend to apply B either through broadcasting of B-enriched macronutrient fertilisers, which enables a good distribution of the low quantity of B across a field, or in the planting hole as a slow-release fertiliser, which prevents B toxicity as well as losses through leaching.

The efficiency of B fertilisers in terms of expected yield gains depends on several factors, such as the method, chemical form, amounts and timing of application (Abat et al., 2014; Degryse, 2017). Data showing a timing effect of B fertilisation on maize yields are limited and ambiguous. As B application is known to have a stronger effect on reproductive than vegetative growth-factors (Lordkaew et al., 2011), application of B at a later growth-stage could be more effective in increasing yields, as shown for wheat (Sarkar et al., 2007). However, Gotz et al. (2021) showed that B application at V6 growth-stage led to lower maize yields compared to application at sowing in one soil, but not in another. For future research, we recommend to study the effect of B fertilisation at different times in the maize growing season, as well as the differences in the effects between single and split application of B gifts.

It is unclear why B application was toxic at some sites, but not at others, within the same country. The yield response to B fertilisation, whether positive or negative, could not be described based on available soil parameters alone. Although the strong negative yield responses likely were affected by the high B application rates, after removing data from farms with a negative response to B fertilisation, soil parameters still could not describe the yield response well. We have several hypotheses for this. First, the limited

explanatory power of soil variables may be due to the natural variation in the data. The majority of data points (72%) had a yield response that could be considered natural variation (i.e., deviating less than 20% from no effect). For these plots, no consistent relation between soil parameters and the yield response is expected. Second, factors other than soil properties may play an important role for the assessment of the yield response to B fertilisation. High rainfall is associated with leaching of B, especially in sandy soils (Degryse, 2017). High amounts of rainfall after B fertilisation could therefore potentially ameliorate the effect of B toxicity, while B may become toxic in locations with little rainfall. Our data neither disprove nor confirm the effect of rainfall on the incidence of B toxicity in maize. Generally, we were not able to derive models describing the yield response without adding the auto-correlated yields in the B omission plots. In addition, as rainfall data were collected per farm, only 5 (Kenya), 4 (Zambia) and 6 (Zimbabwe) observations per country were available. Rainfall also did not differ strongly within a country, as most farms were located in relatively close proximity of each other. For future research, we recommend to study the effect of water availability in combination with B fertilisation to gain insight in the best timing for B application in regard to expected rainfall.

4.2. **B uptake**

Soil B availability, quantified as B uptake in the B omission plots, was not described well, as only 20% of the variation in B uptake was explained by B-HNO_3, B-$CaCl_2$ and SOC. The sources of soil available B for crop uptake are believed to be desorption from the reactive surfaces, mineralisation of soil organic matter, weathering of soil minerals and atmospheric deposition with precipitation, in particular close to coastal areas (Park and Schlesinger, 2002; Shorrocks, 1997). As each of the B omission trials were located far away from any coast and since weathering is regarded as a slow process in comparison with mineralisation of soil organic matter (Kot et al., 2016), the latter is expected to be the primary source of available B in the soils from this study. At the same time, SOC may adsorb B. Our regression model showed that higher levels of SOC were associated with lower levels of B uptake, which is in contrast to what was expected and points to adsorption rather than mineralization processes that control B availability (Van Eynde et al., 2020). However, SOC contributed relatively little to variation in B uptake in comparison with B-HNO_3. The two were positively correlated (r = 0.44), whereas higher levels of B-HNO_3 were associated with higher levels of B uptake. These findings confirm that bioavailability/uptake of B is still poorly understood, and no straightforward identification of processes that control soil available B could be obtained from our results.

We hypothesise that B availability was poorly described based on soil parameters because of three constraining factors. First, B does not appear to have been yield-limiting in these field trials, as positive yield responses to B fertilisation were absent on a site level. In this situation, B uptake does not equal B availability, as other nutrients or biophysical factors constrain biomass production and therefore B uptake (Janssen et al., 1990). Secondly, although B deficiency is associated with soils low in organic matter content (Shorrocks, 1997), as the ones in our study, the sites described in this study only covered a limited range in SOC (between 4 and 20 g kg^{-1}). Inclusion of soils with a wider range in SOC might have revealed stronger (and possibly positive) trends between SOC and B uptake. For the same reason, soil pH was likely not identified as a significant factor in describing B availability. Most soils in this study had pH values between 5.0 and 6.5, which is a narrow range in which pH-dependent adsorption of B furthermore plays a limited role (Goldberg, 1997). Thirdly, B available for crop uptake may also depend on water availability (Degryse, 2017). Boron is relatively immobile within plants and a constant supply of soil B is therefore required (Kaur and Nelson, 2015; Mozafar, 1987). Drought can cause B deficiency as uptake of water and thus uptake of B by the roots is limited (Bell, 1997; Gupta et al., 1985); rainfall is thus expected to be positively correlated with B uptake. Based on the results described in this study, we cannot disprove or confirm this hypothesis. Rainfall was not a significant factor in the model describing B uptake, but this may have been due to data limitations as discussed above.

4.3. Critical concentrations

In this study, no critical soil B concentration could be derived that indicates potential B deficiency in maize. Based on field trials in India, critical B-HW concentrations were estimated to be 0.50 mg kg^{-1} (Kumar et al., 2018). In the USA, B application to maize is recommended only when B-HW levels are below 0.25 mg kg^{-1} (WARD Laboratories, 2020). In this study, positive yield responses to B fertilisation were associated with B-HW concentrations below 0.69 mg kg^{-1}. This observed threshold value is thus higher than the critical concentration reported in literature, which may be due to differences in soil type, maize variety and/or HW protocol used. However, B fertilisation did not lead to significant yield increases, despite many of the soils having B concentrations below this threshold. In line with our results, Wendt and Rijpma (1997) reported that B fertilisation significantly increased maize yields at only two out of eight locations in Malawi, while each of the locations had low (<0.32 mg kg^{-1}) B-HW concentrations. So this critical concentration is not a reliable indicator for B deficiency that can be generally applied. These findings could indicate that a single soil extraction method is not sufficient to identify whether B fertilisation is required. Furthermore, since B is prone to leaching, B concentrations in the subsoil often exceed those in the topsoil (Gupta et

al., 1985). Maize roots can reach a depth of 50 cm approximately 5 weeks after sowing (Hund et al., 2009). In practice and as well as in this study, often only the topsoil is sampled for analysis. For future studies, we recommend to also analyse subsoil samples (25-50 cm), as B concentrations in this soil layer may be more relevant for diagnosis of B deficiency.

The Mehlich 3 (M3) extraction method is sometimes used to evaluate B availability. In this study, B concentrations did not exceed the determination limit of the M3 procedure (0.52 mg kg^{-1}). To our knowledge, no critical B-M3 values for maize have been derived in field trials.

Critical plant B concentration indicating potential B deficiency in maize could not be derived in this study either. Critical maize B concentrations ranging between 7 and 12 mg kg^{-1} have been reported (de Souza Lima et al., 2007; Gupta, 2007; Joshi et al., 2014; Kumar et al., 2018; Sakal and Singh, 1995; Singh and Sinha, 1987). In this study, all plant concentrations in the B omission treatment were below 7 mg kg^{-1}. In the full treatment however, part of the samples also had concentrations below this level, which may indicate that the low B concentrations in this study are a physiological characteristic of the varieties used rather than symptoms of B deficiency. Gramineous species such as maize are known for their generally low B concentrations (Lordkaew et al., 2011). Establishing a universal critical plant B concentration may be difficult, given the variation among maize varieties and plant parts (Andrić et al., 2016; Mozafar, 1987). Although Lordkaew et al. (2011) and Gotz et al. (2021) showed that silk B concentrations were a reliable indicator for B deficiency, both studies arrived at different critical concentrations, indicating that these concentrations are not universal. Furthermore, although deficiency of several plant-essential nutrients can be derived from maize earleaf concentrations to some extent, this does not apply to B (Kovács and Vyn, 2017).

Establishment of critical plant concentrations is complicated by the fact that B is highly immobile within plants and that soil supply of B is not constant (Bell, 1997); plant concentrations therefore do not give a clear representation of the (actual) nutritional status of the crop. Timing of fertilisation may also affect plant B concentrations. As an effect of fertilisation, stover B concentrations increased relatively more than grain B concentrations in Kenya and Zimbabwe, but not in Zambia. We consider this difference is due to the timing of B application, as B was fertilised right before sowing in Kenya and Zimbabwe, but later in the growing season in Zambia. Gotz et al. (2021) showed that post-harvest soil B concentrations were significantly higher when 4 (and 12) kg ha^{-1}

B was applied at growth stage V6 compared to application at sowing. Similarly, they also found higher B concentrations in maize leaves when B was applied at stage V6. We therefore hypothesise that, as B leaches easily and is not mobile within plants, B concentrations of plant tissues that are formed within a few weeks after fertilisation are most strongly affected by B application.

4.4. Soil B pools

Hot water extractable B is seen as a good measure for B availability, and good relations with yield and plant B concentrations have been reported for maize and other crops (Aitken et al., 1987; Chaudhary and Shukla, 2004; de Souza Lima et al., 2007; Jin et al., 1988). To date, it is unclear which soil B pool is represented by the HW extraction method. The B-$CaCl_2$ can be viewed as a measure of B present in the soil solution, while B-HNO_3 may represent both the concentration in solution as well as B not directly available for plant uptake but reversibly bound to the soil solid phase (Groenenberg et al., 2017; Van Eynde et al., 2020). The latter may be interpreted as the B pool that becomes available for plant uptake during a growing season. Interestingly, B-HW concentrations were roughly twice as high as B-HNO_3 and seven times as high as B-$CaCl_2$, which may indicate that the HW method extracts B that is not (directly) available for plant uptake. The HW method was relatively more efficient in extracting B compared to HNO_3 with increasing SOC levels. We hypothesise that as suspensions are heated to boiling in the HW method, B from organic matter is disclosed, which is not extracted by the acidic (pH ≈ 0.5 - 1.0) HNO_3 extract. Although the difference between the HW- and HNO_3-extractable B seems to point at B not bound to external functional groups in soil organic matter, and possibly to B in undecomposed biomass, the exact nature of this source of B, and whether it is mineralised during the growing season, remains unclear. As organic matter is an important source of plant available B (Kot et al., 2016), B-HW could be a better proxy for the B pool that becomes available for plant uptake during a growing season compared to B-HNO_3 and B-$CaCl_2$. For future studies, we recommend to explore which soil B pools are extracted with the HW method and whether these pools have relevance for plant B uptake.

Boron concentrations in HW, $CaCl_2$ and HNO_3 methods were strongly correlated (Figure 1). Novozamsky et al. (1990), also found a good correlation between B-HW and B-$CaCl_2$ in 100 Dutch soils (R^2 = 0.74). They however found that $CaCl_2$ extracted around 27% of B compared to HW, in comparison to the 14% found in this study. These differences may be due to differences in hot water protocol (not clearly specified in Novozamsky et al. 1990) or soil properties such as organic matter content, pH or phosphate loading (Van Eynde et al., 2020).

Both B-HNO_3 and B-$CaCl_2$ were significant parameters in describing the yield response as well as B uptake, but with opposite coefficients, despite being positively correlated. This may imply that the interplay of these two B soil pools is relevant to understand B uptake and the yield response to B fertilisation. The B-HNO_3 contributed positively and B-$CaCl_2$ negatively to the yield response and B uptake. This suggests that soils with higher B-$CaCl_2$/B-HNO_3 ratios, and thus a larger proportion of fertiliser B remaining in solution, may have a higher chance of inducing B toxicity in fertilised plots (i.e. lower yield response). As B in solution is prone to leaching, high ratios of B-$CaCl_2$/B-HNO_3 may also imply that a large proportion of the soil B is easily leached and thus not available for plant uptake. However, we note that the models describing B uptake and the yield response explained limited variation. Furthermore, no models could be derived for the yield response without including the auto-correlated yield in the B omission treatment. These interpretations should thus be handled with care.

As discussed above, B-HW could be a good proxy for the B that becomes available for plant uptake during a growing season, as it potentially extracts mineralizable B. This method therefore deserves further attention for understanding B availability. However, we do not consider the hot water extraction method suitable for routine analysis of soil B availability. The HW method is not standardised (Degryse, 2017) and protocol details are often not explicitly specified in studies, which complicates interpretation of results. For example, soils are extracted with distilled water, $CaCl_2$ (Bingham, 1982) or $BaCl_2$ (Wear, 1965) and sometimes with the addition of activated charcoal to obtain a clear extract for colorimetric determination. Although correlations between extraction methods are high, a hot $CaCl_2$ solution extracts more B than pure hot water (Chaudhary and Shukla, 2004; Jeffrey and McCallum, 1988; Joshi et al., 2014). Activated charcoal also affects measurements as B concentrations decrease strongly with higher charcoal additions (McGeehan et al., 1989; Sahrawat et al., 2012). Many studies do not report cooling time, although B re-adsorbs to the soil during cooling over time (Jeffrey and McCallum, 1988; McGeehan et al., 1989). Both colorimetric and ICP determinations are used for analysis in the B-HW method, with colorimetric determinations generally resulting in higher B concentrations than ICP analysis (Gestring and Soltanpour, 1981; Jeffrey and McCallum, 1988; Sahrawat et al., 2012). As ICP measures total B in solution, B determined colorimetrically is likely to be overestimated due to interferences (Gestring and Soltanpour, 1981; Jeffrey and McCallum, 1988). Sahrawat et al. (2012) indeed found that ICP results were more reproducible than those of colorimetric determination. Furthermore, as ICP devices do not require colourless extracts for accurate measurements, charcoal additions are not needed (McGeehan et al., 1989). We therefore recommend ICP-AES or ICP-MS for the analysis of B-HW.

Standardisation and adjustments of the HW method are needed to reduce the uncertainty of the results. Alternatively, we would like to propose the standardised 0.01 M $CaCl_2$ or 0.43 M HNO_3 methods as an alternative for routine analysis of soil B concentrations. A clear advantage of these methods is the temperature of the extraction. As suspensions do not have to be heated, disposable plastics can be used in the procedure, preventing potential B contamination from glassware. In addition, the set-up needed for hot water B analysis restricts the number of samples that can be analysed simultaneously (Mahler et al., 1984), which is not the case for the $CaCl_2$ or HNO_3 procedures. A second advantage is shaking time of 2 h for $CaCl_2$ or 4 h for HNO_3. During 5 or 10 min shaking with hot water, no equilibrium is reached (Mahler et al., 1984; McGeehan et al., 1989). Consequently, any time spent on additional steps, such as bringing suspensions to boil, cooling down, filtration, adds variability in the results. We furthermore recommend to determine B concentrations in the $CaCl_2$ and HNO_3 extracts with ICP-OES of ICP-MS, rather than with colorimetric methods, given the uncertainty associated with the latter.

5. Conclusions

The results of this study indicate that it is difficult to describe B availability/uptake and yield response to fertilisation based on soil parameters. As a result, it remains unclear to what extent maize yields in SSA can be improved through the use of B fertilisers. Our results highlight the need for better understanding of the relevant B pools for plant uptake and extraction methods representing these. In regards to critical plant concentrations, we question the feasibility of using these as an indicator for B deficiency in maize. Critical soil B concentrations have been derived in other studies and may provide a more reliable indicator for B deficiency. Our results however indicate that more validation of these critical soil concentrations is needed. We present a number of recommendations for future studies that aim to derive critical soil B concentrations indicating B deficiency. First, B fertiliser should be applied at rates of 1 kg ha^{-1} to prevent toxicity, especially when applied banded. Second, we recommend to study the effect of timing and method of B application on maize yield response and the incidence of B toxicity. Third, we recommend to collect detailed data on precipitation and evapotranspiration during the growing season and use these to elucidate the effect of soil water availability on B uptake and the yield response to B fertilisation. Sampling and analysis of B concentrations in subsoil was also recommended. Lastly, to ensure transferability of results, we emphasise either to use standardised protocols like 0.01 M $CaCl_2$ or 0.43 M HNO_3 for measuring soil B concentrations or to provide extensive details of other (hot water) protocols used.

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Chapter 6

Options for increasing maize yields and grain Zn concentrations in sub-Saharan Africa

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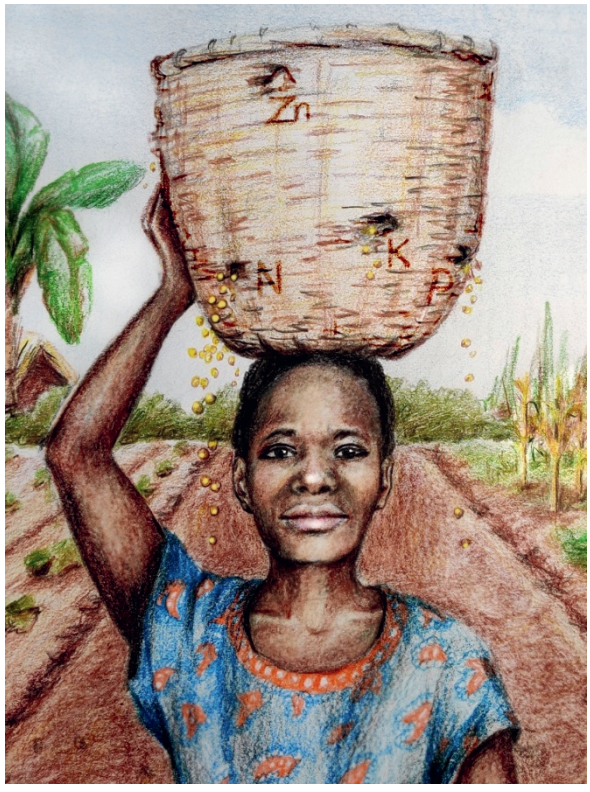

Abstract

Human zinc deficiency is considered widespread in sub-Saharan Africa. Increasing zinc (Zn) concentrations in the edible parts of plants is considered a feasible strategy to alleviate this problem. The HarvestPlus program has set a target concentration of 38 mg kg^{-1} for maize grains, which is considered adequate for reducing human Zn deficiency. While the low dietary Zn intake is a concern, increasing yields is prioritised over increasing Zn concentrations in crops. However, trade-offs between maize yields and grain Zn concentrations have been observed. The aims of this study are (i) to confirm whether this trade-off is found in current farming systems in sub-Saharan Africa (SSA) and (ii) to explore whether genotypic and management options, relevant for the African context, can increase both yields and grain Zn concentrations across several environments. Data from several field experiments that focussed on the effects of variety, N fertilisation, Zn fertilisation and NPK fertilisation on maize yields across different sites in Kenya, Zambia and Zimbabwe were analysed. We demonstrated a general trade-off between maize yields and grain Zn concentrations across all sites. Due to the nature of the dataset, it was impossible to separate the roles of genotype, environment and management in this trade-off. However, the data provided insights into current options for increasing yields and grain Zn concentrations. The commercially available varieties used in this study, seem to provide no option for increasing both yields and grain Zn concentrations by selecting a particular variety. This highlights the need for improved maize varieties. The results furthermore suggest that environmental factors, in particular soil organic carbon and availability of P and K, are positively related with grain Zn concentrations. Application of N increased yields, but had contrasting effects on grain Zn concentrations depending on the maize variety and site, indicating interactions between management, genotype and environment. Our results furthermore suggest that maize grown on soils with low Zn availability, may require Zn fertilisation to prevent dilution of grain Zn concentrations at high N application rates. We conclude that attaining grain Zn concentrations above the HarvestPlus target of 38 mg kg^{-1}, with the current commercially available maize varieties and presented management options, is not possible without compromising yield levels. Our results however imply that increasing soil organic matter content and balanced application of N, P and K fertilisers could increase grain Zn concentrations. As these practices likely also increase yields, they could be a viable option to bypass the trade-off between maize yields and grain Zn concentrations.

1. Introduction

Human zinc intake needs to increase in sub-Saharan Africa (SSA) in order to alleviate widespread and severe health problems related to zinc deficiency. An estimated 40% of the African population does not have sufficient intake of zinc (Zn). Zinc deficiency can lead to several diseases, growth and developmental issues and cognitive problems (Joy et al. 2014; Das and Green 2016). The prevalence of Zn deficiency can be attributed to unbalanced diets, rich in staple cereal crops and low in animal products, as well as low Zn availability in soils leading to low Zn concentrations in the crops that grow on them (Joy et al. 2014; de Valença et al. 2017; Cakmak and Kutman 2018). Increasing Zn concentrations in edible parts of staple crops such as maize can contribute to reaching a sufficient dietary intake of Zn in African countries (Joy et al. 2015). However, Zn concentrations in cereals are inherently low and have declined even further as a result of long-term breeding efforts to increase yields (Cakmak and Kutman 2018). In the past two decades, Zn concentrations of staple crops have increasingly received agronomists' attention. Agronomically, Zn concentrations above 20 mg kg^{-1} are considered adequate for optimal cereal production (Alloway 2008; Cakmak and Kutman 2018). The HarvestPlus biofortification program, however, has set a target of 38 mg Zn kg^{-1} maize grains in order to alleviate Zn malnutrition (Bouis and Welch 2010).

While low grain Zn concentrations are a concern, closing the large yield gaps faced by African smallholder farmers, a key contributor to food insufficiency (Van Ittersum et al. 2016), is prioritised. Although micronutrient bioavailability-induced yield limitations occur (Kihara et al. 2017; Wortmann et al. 2019), main solutions for closing yield gaps are considered to be fertilisation with macro- (and secondary) nutrients, improved varieties, as well as good agronomic practices (Tittonell and Giller 2013; Ichami et al. 2019). Farmers are unlikely to engage in management practises which can increase grain Zn concentrations if yields no not also increase. Approaches that improve grain yields and increase grain Zn concentrations simultaneously may therefore be best suited in helping African farmers address these two key concerns.

Efforts for increasing grain Zn concentrations have mainly focussed on biofortification through breeding for higher grain Zn concentrations, fertilisation with Zn or a combination of both strategies (de Valença et al. 2017). Breeding for cultivars with higher Zn concentrations is thought to be more cost-effective than a fertiliser based approach (Joy et al. 2015). Sufficient genetic variation has been demonstrated to increase maize grain Zn concentrations through breeding, but genetic trade-offs between yield and grain Zn concentrations have been demonstrated (Bänziger and Long 2000; Garcia-Oliveira et al. 2018).

Maize is considered very sensitive to low soil Zn bioavailability (Alloway 2008). Several studies have shown that the use of Zn fertilisers can increase yields (Wendt and Rijpma 1997; Chilimba et al. 1999; Eteng et al. 2014; Vanlauwe et al. 2015; Kihara et al. 2017), grain Zn concentrations (Joy et al. 2015; Kihara et al. 2020, chapter 4) or both (Manzeke et al. 2014, 2020; Liu et al. 2017). However, fertilisation with Zn does not always result in increased yields (Uyovbisere and Lombin 1990; Wendt and Rijpma 1997; Chilimba et al. 1999; Lisuma et al. 2006; Kihara et al. 2016; Rurinda et al. 2020; chapter 4), likely depending on the soil Zn availability status. Based on soil testing, it is currently difficult to assess whether Zn availability is yield-limiting (chapter 4). Economically, Zn fertilisation is an unattractive option for farmers if yields do not increase.

Nitrogen (N) fertilisation, either with or without Zn, has been found to increase yields and grain Zn concentrations in cereals (Kutman et al. 2011; Losak et al. 2011; Xue et al. 2014, 2019). In cereals, Zn in the grain is associated with proteins (Cakmak and Kutman 2018). In maize, N fertilisation leads to a small increase in grain protein content and large increase in biomass i.e. carbohydrates, which could potentially lead to dilution of grain Zn concentrations (Bänziger and Long 2000). A recent global meta-analysis by Zhao et al. (2022) however showed that maize grain Zn concentrations are maintained when yields increase as an effect of N fertilisation, as the dilution effect is counteracted by increased remobilisation of Zn from the stover during grain filling. This meta-analysis also revealed that limited data from SSA are available on grain Zn concentrations in relation to N fertilisation. Given the low soil Zn availability in large parts of SSA (Alloway 2008), application of N without addition of Zn could potentially also lead to excessive growth and dilution of grain Zn concentrations (de Valença et al. 2017; Cakmak and Kutman 2018; Zhang et al. 2021).

A trade-off between maize yields and grain Zn concentrations has been reported. The first aim of this study is to confirm whether this trade-off is found in current farming systems in SSA. The second aim of this work is to explore whether genotypic and management options, relevant for the African context, can increase both yields and grain Zn concentrations across several environments. Data from several field experiments focussing on the effects of variety, N fertilisation, Zn fertilisation and NPK fertilisation on maize yield across different sites in Kenya, Zambia and Zimbabwe were analysed. The outcomes of this study will help to develop an integrated approach for increasing yield levels while at the same time increasing grain Zn concentrations in maize.

2. Materials and Methods

2.1. Field trials

Embu, Kiboko, Harare

The first set of researcher-managed field trials was executed in Embu and Kiboko in Kenya, and in Harare, Zimbabwe. These trials focused on the effect of N fertilisation and maize variety on plant uptake and soil depletion of N and other nutrients. Complete details of these trials are described in Pasley et al. (2019). Briefly, experiments consisted of a split-plot design, replicated four times, with N rate as the main plot and variety as the sub-plot. In each site, six varieties were used, with one duplicated variety in Embu and Kiboko as well as in Embu and Harare. Of the six varieties, three were improved in regards to high tolerance to stress (drought, heat and/or nutrient), whereas the other three were not. All varieties were commercially available and commonly used by farmers in Kenya and Zimbabwe. Fertiliser application rates were 0, 30, 60, and 90 kg N ha^{-1} in Embu and 0, 40, 80, and 160 kg N ha^{-1} in Kiboko and Harare. A basal application of P at a rate of 20 kg ha^{-1} was also applied. Plant and soil samples were taken in the 2013 short rainy season in Kiboko, the 2014/2015 season in Harare and the 2015 short rainy season in Embu. Soil samples were collected per sub-plot in most cases.

Sidindi

The second set of researcher-managed on-farm field trials was executed in Sidindi, western Kenya. These trials (executed from 2013-2018) focused on the spatial and temporal patterns of maize yield responses to N, P and K omission. Complete details of the trials in are described in Njoroge et al. (2019). Data on yields and grain Zn concentrations were available for 10 farms collected in the 2016 and 2018 long rainy seasons. In 2016, nutrient omission experiments included five treatments namely: a control (no fertiliser), PK, NK, NP and NPK, with nutrients applied at the rates of 150 kg N ha^{-1}, 40 kg P ha^{-1} and 60 kg K ha^{-1}. Treatments were not replicated on-farm. In 2018, all five plots at each farm received NPK applied at the rates of 150 kg N ha^{-1}, 40 kg P ha^{-1} and 60 kg K ha^{-1}. Short season maize variety DK8031 was planted at all farms and in both years.

Kenya, Zambia, Zimbabwe

The third set of researcher-managed on-farm field trials was executed on 19 locations in Kenya (5 farms, 5 replications each), Zambia (4 farms, 4 replications each) and Zimbabwe (10 farms, 6 replications each). Complete details of these trials, which

focussed on availability of several micronutrients, are described in chapter 4. The trials were laid out as a randomized block design. For this study, only the Zn omission treatment was included. Briefly, nutrients N, P, K, S, Ca, Mg, Cu and B were applied at relatively high rates to prevent yield-limitations. Fertiliser application rates differed among countries. The maize varieties also differed among countries: DK8031 was planted in Kenya, Afric1 in Zambia and SC637 in Zimbabwe.

2.2. Plant and soil analysis

Plant samples were analysed for the following nutrient contents: N, P, K, S, Zn, Cu and Mn. Soil samples were analysed for the following parameters: pH-H_2O, soil organic carbon (SOC), nutrient availability as determined by a Mehlich 3 (M3) extraction and clay content. For details on analytical methods, see Pasley et al. (2019), Njoroge et al. (2019) and chapter 4. Median values for each of the soil properties of the N application trials are presented per site in Table 1.

Table 1: Soil characteristics for Embu, Kiboko and Harare (0-30 cm), values represent medians.

	-	g kg^{-1}	%	Mehlich 3 (mg kg^{-1})				
Site	**pH**	**SOC**	**Clay**	**P**	**K**	**Zn**	**Cu**	**Mn**
Embu	5.1	28	39	16	343	14.8	1.1	270
Kiboko	7.8	12	24	77	387	2.1	3.9	70
Harare	5.7	13	42	15	101	11.9	10.0	135

2.3. Data analysis

Data cleaning

Data with Harvest Indices (HI) below 0.25 were removed from the dataset, as these crops were considered to have failed and therefore unsuitable for addressing the objectives of this study. Yield was expressed at a standardised moisture content of 13%. Grain concentrations, as well as nutrient uptake are expressed based on dry weight. Nutrient uptake was calculated as the sum of stover and grain biomass, multiplied with their respective nutrient concentrations.

Analyses

To test for differences in yield and grain Zn concentration among varieties within each site, linear mixed effect models (LME) were fitted, with N application rate, maize variety and their interaction as fixed factors and N application rate nested in block as a random factor (random = ~1|Block/N rate) to account for the split-plot design. In case the interaction among the main factors was not significant, the model was rerun without

the interaction factor. This analysis was done separately for Embu, Kiboko and Harare. In addition, correlations among soil parameters, yield and grain Zn concentrations were explored. The soil factors earlier associated with Zn availability, i.e. Zn-M3, pH and SOC (Chilimba et al. 1999; Alloway 2008; chapter 4), were used for this analysis.

Software

Statistical software R, version 3.6.3 (R core team 2020) was used for all analyses. Plots were made with the ggplot function from the ggplot2 package, version 3.3.2 (Wickham 2016). LMEs were fitted using the lme function from the nlme package (Pinheiro et al. 2013). Significance of factors was tested with the Anova function from the car package (Fox and Weisberg 2019). Individual differences were analysed with Tukey's post hoc test, using the glht function from the multcomp package, version 1.4-17 (Hothorn et al. 2008). Normality of model residuals were checked with the Shapiro-Wilk test using the shapiro.test function from the stats package, version 4.1.0 (R Core Team and R Development Core Team 2020). Homogeneity of variances was tested with Levene's test, using the leveneTest function from the car package. In case assumptions of normality of residuals or homogeneity were violated, the data were transformed using log10-transformation. Correlations were explored using the rcorr function from the Hmisc package, version 4.5-0 (Harrell Jr and Others 2021).

3. Results

3.1. Overview

Maize yields ranged between 0.5 and 10.4 Mg ha^{-1} across field trials, while grain Zn concentrations ranged between 1.7 and 55 mg kg^{-1} (Figure 1). Across all data, yields and grain Zn concentrations were negatively correlated (r = -0.16, p = 0.001), suggesting an overall trade-off. However, the trade-off was not present within individual sites, as negative correlations were not significant (all p-values above 0.17). Some clustering per site was visible. Generally, data from Embu covered the entire range in grain Zn concentrations, whereas grain Zn concentrations in the other sites showed less variation. Yield levels in most sites covered the entire range, except for Embu, where most yields did not surpass 7 Mg ha^{-1}. Only 15 out of 301 datapoints for which Zn was not applied, met the HarvestPlus grain Zn target concentration of 38 mg kg^{-1} (Figure 1). These 15 datapoints all corresponded to maize crops grown in Embu, and consisted of four different varieties and three N application rates (30, 60 and 90 kg ha^{-1}). In all 15 cases, yields did not surpass 6.3 Mg ha^{-1} and were relatively low compared to the maximally obtained yield in these trials.

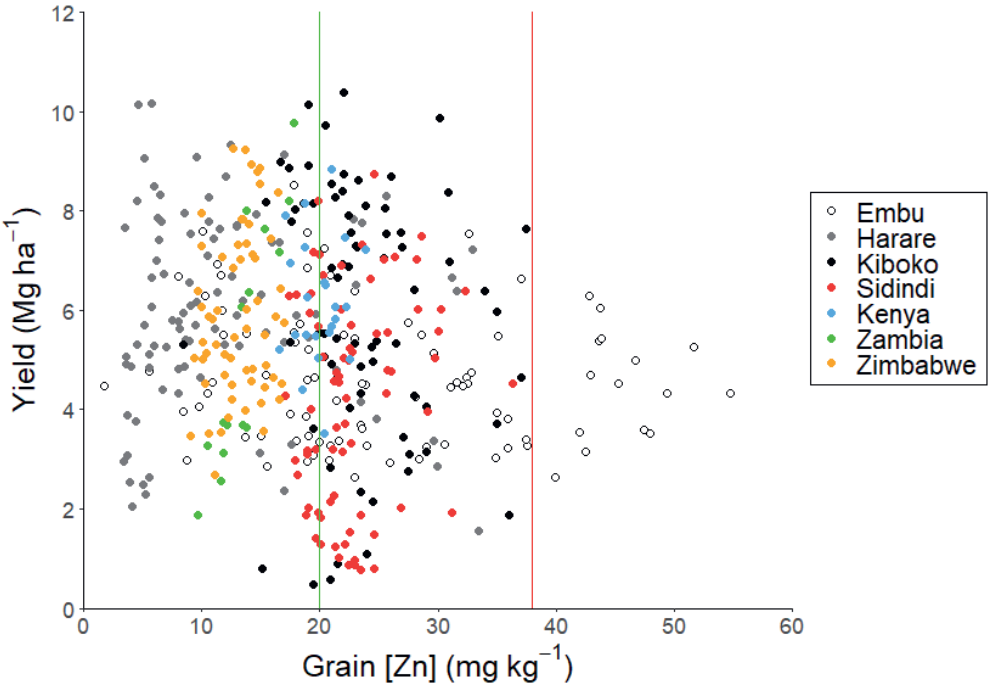

Figure 1: Maize yields plotted against grain Zn concentrations per site or country. The green line represents the adequate Zn concentration for optimal growth of maize, the red line the HarvestPlus grain Zn target concentration for maize.

3.2. Genetic factors

To compare the trade-off between yields and grain Zn concentrations among different maize varieties, data from the N application trials in Embu, Kiboko and Harare were used. Analysis was done per site, as there was limited overlap in varieties. Differences in grain Zn concentrations and yields were found among varieties in Embu, but not in Harare and Kiboko (Table 2; Figure 2). Although the ANOVA output (Table 2) suggested that maize variety was a significant factor affecting yields in Kiboko, post hoc analysis did not identify significant differences among maize varieties.

In Embu, four varieties had significantly higher grain Zn concentrations compared to the other two (Figure 2). Two of those four varieties were improved, the two others were not. However, these four varieties had significantly lower yield levels compared to the variety with the lowest grain Zn concentrations (DUMA43). Furthermore, the variety with the highest grain Zn concentrations (WH403) had the lowest yields. These results point towards a trade-off between yields and grain Zn concentrations.

Table 2: Results of the ANOVA analysis, with *p*-values for main and interaction effects. When interactions were not significant, only significance of main factors was tested.

Site	Factor	Yield	Grain [Zn]
Embu	N rate	0.08	< 0.001
	Variety	< 0.001	< 0.001
	N rate * variety	n.s.	n.s.
Harare	N rate	<0.001	0.86
	Variety	0.90	0.48
	N rate * variety	n.s.	n.s.[a]
Kiboko	N rate	< 0.001	0.01
	Variety	0.01	0.98
	N rate * variety	n.s.[b]	n.s.[b]

[a]One variety was left out of this analysis, because grain Zn concentrations deviated strongly in one N treatment. When this variety was included, only the interaction factor was significant, not the main factors. [b]Due to HI restrictions, limited data were available for the 0N treatment (n=3, only one variety). To test the interaction between N rate and variety, data from the 0N treatment were removed.

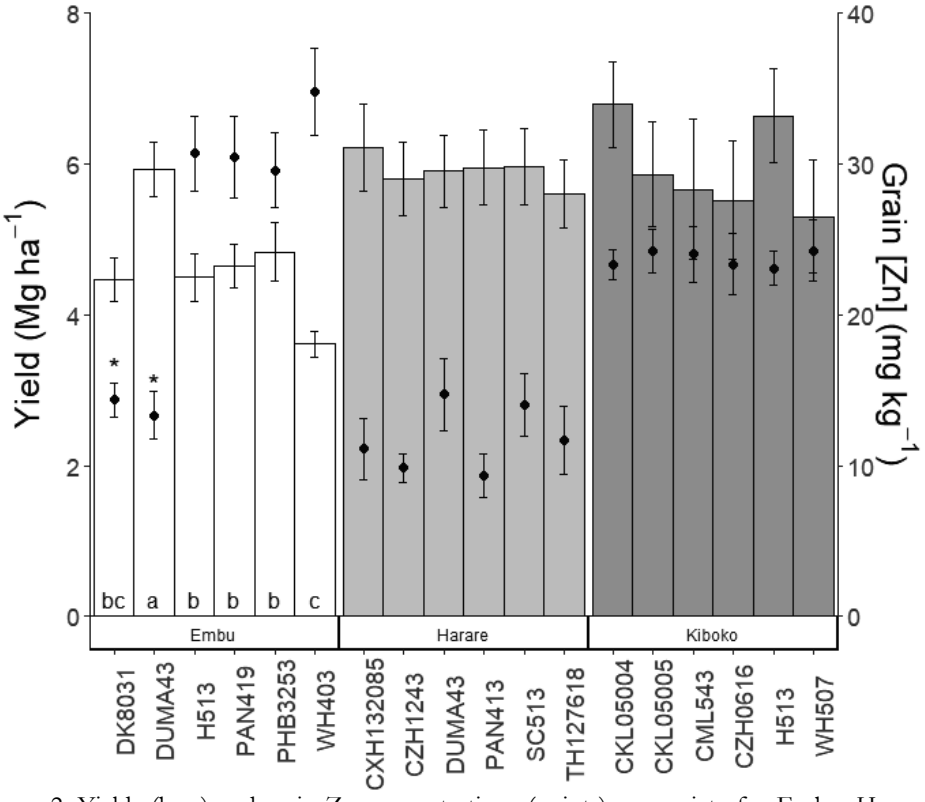

Figure 2: Yields (bars) and grain Zn concentrations (points) per variety for Embu, Harare and Kiboko (all N rates). Letters indicate significant yield differences within sites, asterisks indicate significant differences in grain Zn concentrations within sites. Error bars represent standard error.

3.3. Environmental factors

To explore whether soil characteristics explain grain Zn concentrations and yields, correlations among these factors were explored using data from the Embu, Kiboko and Harare trials. For the Sidindi trials, no corresponding soil data were available. Data from the Kenya, Zambia and Zimbabwe trials were presented in chapter 4.

Yields were positively correlated with pH and negatively correlated with Zn-M3 and SOC (Figure 3A-C). These correlations most likely do not indicate causality, as yields were strongly determined by N application rate (section 3.4). In addition, the soil parameters, mainly pH and SOC, showed strong clustering per site. Correlations could consequently be affected by other site-related factors, such as variety or climate. Grain Zn concentrations were only (positively) correlated with SOC (Figure 3D-F). When correcting for yield levels, which may affect grain Zn concentrations through dilution, SOC levels were also positively related with grain Zn concentrations.

To exclude the effect of maize variety on relations between soil parameters, yields and grain Zn concentrations, data from two duplicated varieties (H513 and DUMA43) were investigated, using the same N application treatment (0 kg ha^{-1}). For variety H513, grown in Embu and Kiboko, data from the 0N treatment in Kiboko had been removed based on HI restrictions, so no comparison was possible. For variety DUMA43, grown in Embu and Harare, no differences in yield ($p = 0.798$) and grain Zn concentrations ($p = 0.832$) were found. Differences in Zn-M3 and pH between sites were limited (Table 1). Although SOC levels differed between sites, data were insufficient to draw conclusions on the effect of soil parameters on grain Zn concentrations.

Identical N treatments were used in Kiboko and Harare and differences among varieties were absent (Figure 2). This allows for a comparison between these sites, with regards to a potential effect of soil characteristics on yield and grain Zn concentrations. The soil in Kiboko was alkaline (pH 7.8) and Zn-M3 levels were low (Table 1; Figure 3). The soil in Harare was acidic (pH 5.7) and was characterised by relatively high Zn-M3 levels; SOC contents were similar in both sites. This suggests that soil Zn availability was higher in Harare and higher grain Zn concentrations would therefore be expected compared to Kiboko. However, average grain Zn concentrations in Kiboko (24 mg kg^{-1}) were higher than Harare (12 mg kg^{-1}), whereas yield levels were similar (Figure 2). In addition, Zn uptake was higher ($p < 0.001$) for the maize crops grown in Kiboko (between 171 and 247 g ha^{-1}, depending on the N application rate) compared to Harare (between 91 and 215 g ha^{-1}). These findings do not point towards the relevance of the tested soil characteristics, but rather to other factors affecting grain Zn concentrations.

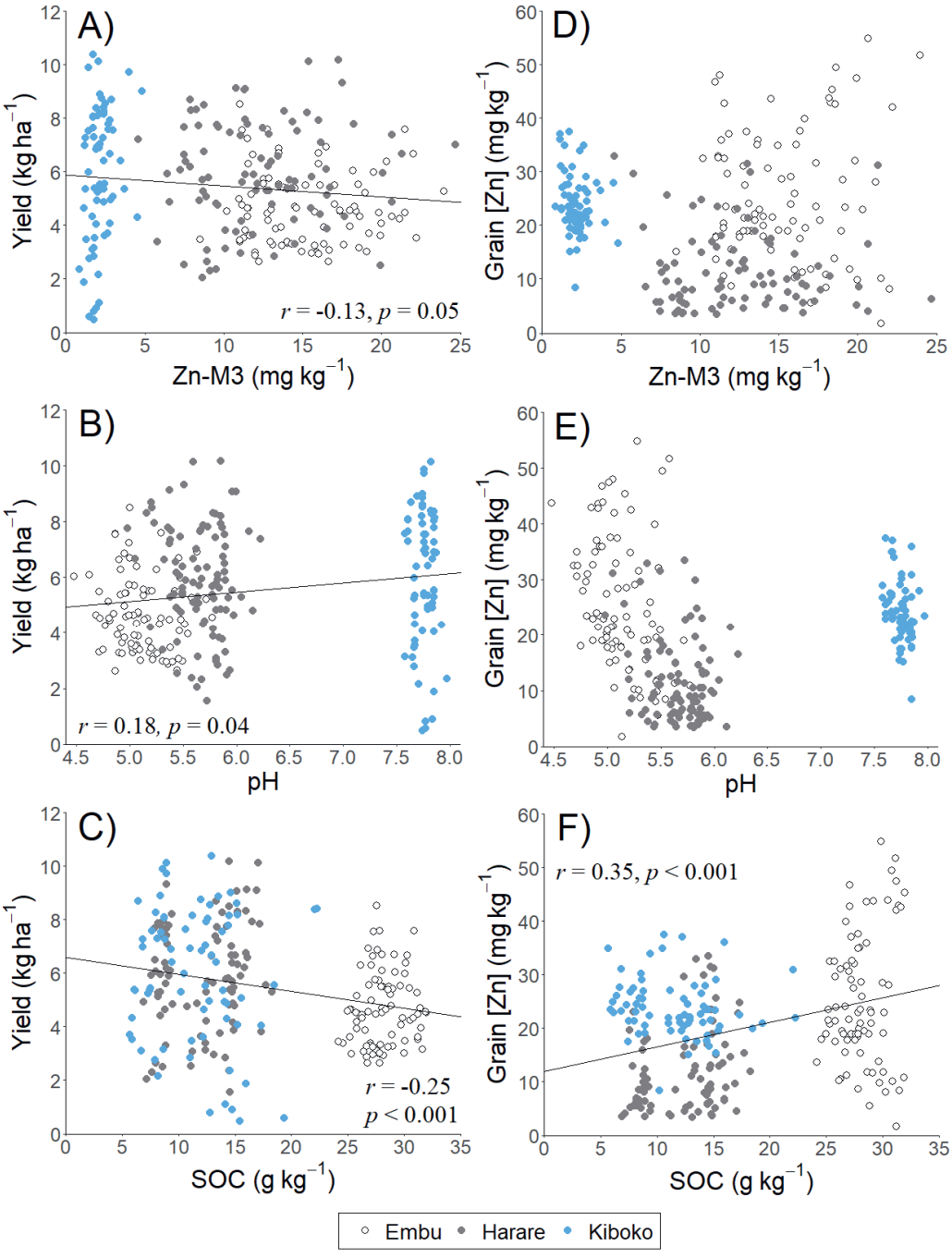

Figure 3: Correlations between Zn-M3, pH and SOC and yield (A, B and C), as well as grain Zn concentrations (D, E and F).

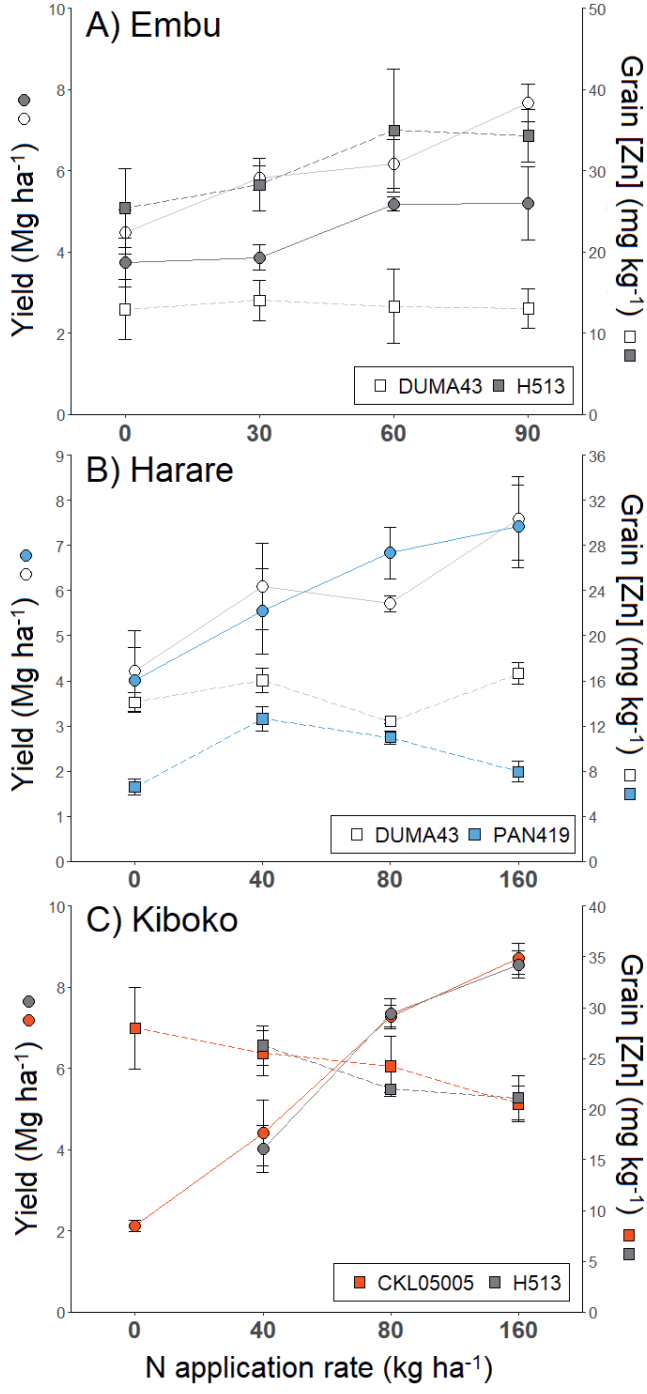

Figure 4: Yields (circles) and grain Zn concentrations (squares) plotted against N application rate. For each site, two representative varieties are presented. Error bars represent standard errors.

3.4. Management factors

To analyse the effect of N fertilisation on yields and grain Zn concentrations, data were analysed per site, as different N application levels were applied and most varieties were not duplicated. Main effects of N application rate on yields were positive in Kiboko ($p < 0.001$), Harare ($p < 0.001$) and Embu ($p = 0.08$; Table 1, Figure 4).

The effect of N application rate on grain Zn concentration was less straightforward. Main effects of N application treatment on grain Zn concentrations were significant for Embu and Kiboko, but not Harare (Table 1). Contrasting effects of N treatment on grain Zn concentrations were found in Embu. For four varieties, an increasing trend of grain Zn concentrations with N application rate was found, whereas for the other two varieties, grain Zn concentrations remained constant (a representative variety of both groups presented in Figure 4). In Kiboko, generally a negative trend of grain Zn concentrations with N application rate was found.

The response to N application of varieties DUMA43 and H513 was tested in two locations. For variety H513, contrasting trends were observed: an increase in both yields and grain Zn concentrations with N application rate was visible in Embu (Figure 4A), whereas a trade-off between both parameters was visible in Kiboko (Figure 4C). The response to N application of variety DUMA43 seems consistent, as yields increase and grain Zn concentrations are maintained at a similar level in both Embu (Figure 4A) and Harare (Figure 4B).

4. Discussion

This study confirmed the existence of a general trade-off between maize yields and grain Zn concentrations (Bänziger and Long 2000; White and Broadley 2011) in commercially available varieties grown under different environmental and management conditions in SSA. Combinations of high yields (> 6.3 Mg ha^{-1}) and grain Zn concentrations above HarvestPlus target grain Zn concentrations (38 mg kg^{-1}) were not observed. This is in line with findings of Manzeke et al. (2014, 2020), who reported grain Zn concentrations up to 35-40 mg kg^{-1}, corresponding with relatively low maize yields (below 4 Mg ha^{-1}).

As our dataset comprised several varieties, grown on several soils and under different fertiliser treatments, there can be multiple causes for this observed trade-off: genotype, environment and/or management. Due to the nature of the dataset, it is impossible to separate the roles of these three mechanisms. However, these data provide a good overview of current options for increasing yields and grain Zn concentrations.

4.1. Genetic factors

The set of commercially available varieties used in this study, seem to provide no option for increasing both yields and grain Zn concentrations by selecting a particular variety. The similarity in yields and grain Zn concentrations among varieties in Harare and Kiboko indicate that the genetic factors play a relatively minor role. Findings from the Embu trials show that selection of variety can matter when it comes to increasing grain Zn concentrations: four varieties had higher grain Zn concentrations (above 30 mg kg^{-1}) compared to the other two varieties (~13-14 mg kg^{-1}). However, the varieties with high grain Zn concentrations had relatively low yields. The relatively low yields in Embu likely are caused by the N application rates, which did not exceed 90 kg ha^{-1}. However, increasing N application rates could lead to a reduction in grain Zn concentrations due to dilution, as shown for variety H513 grown in Kiboko.

4.2. Environmental factors

The trade-off between yields and grain Zn concentrations was absent within individual sites. The clustering of data per site in Figure 1 indicates that environmental factors, such as soil and/or climate, affect the trade-off between yield and grain Zn concentrations, as also shown by Bänziger and Long (2000). None of the soil factors earlier associated with Zn availability (i.e. Zn-M3, pH and SOC), were related with both high yields as well as high grain Zn concentrations (Figure 3). However, the clustering in soil parameters hampers drawing meaningful conclusions from statistical relations. For instance, the negative correlation between yield and SOC can most likely be explained by the low N application rates in Embu, where the highest SOC levels were found (Figure 3C, Table 1). However, our results suggest that grain Zn concentrations increased with SOC levels, in agreement with Gashu et al. (2021) and chapter 4. In contrast to the findings of chapter 4, Manzeke et al. (2012) and Kihara et al. (2020), grain Zn concentrations were not related with extractable soil Zn. This may have been because soil Zn availability was not a limiting factor, as most soil Zn-M3 concentrations were above critical levels (Chilimba et al. 1999; Cuesta et al. 2021), except for Kiboko.

Results of Kiboko and Harare may indicate that other soil factors are relevant in the trade-off between yield and grain Zn concentrations. In Kiboko, consistently higher grain Zn concentrations and plant uptake were observed compared to Harare, despite similar yield levels (Figure 2). We cannot exclude the role of genetic factors in these findings, as no identical variety was grown in both locations, but the role of environmental factors in these results seem likely. The higher grain Zn concentrations and plant uptake in Kiboko cannot be explained by soil Zn availability, which was much lower in Kiboko than Harare (Table 1).

We hypothesise that the higher Zn uptake and grain concentrations in Kiboko can be explained by two mechanisms: facilitation by P and/or K and competition with Cu and/or Mn. We hypothesise that maize Zn uptake was higher in Kiboko than Harare due to higher levels of P-M3 and K-M3 (Table 1). The higher availability of soil K and P in Kiboko may have enabled a larger root system (de Valença et al. 2017), which can explore a larger volume of soil and therefore access more Zn, as well as other nutrients. This hypothesis is supported by a study with rice, where soil K concentrations were positively correlated with root length and diameter (de Almeida Carmeis Filho et al. 2017). Alternatively, the higher levels of Cu-M3 and Mn-M3 in Harare compared to Kiboko (Table 1) may have reduced Zn uptake through competition (Singh and Steenberg 1974; Adiloglu 2007; Alloway 2008).

4.3. **Management factors**

N application

Application of N increased yields, but had contrasting effects on grain Zn concentrations (Figure 4). Grain Zn concentrations can increase (Embu), remain constant (Embu and Harare) or decrease (Kiboko) with increasing N application rates. Our results are not in line with a recent meta-analysis, showing that maize grain Zn concentrations generally are not affected by N fertilisation (Zhao et al. 2022). Several studies reported that N fertilisation increased maize grain Zn concentrations (Losak et al. 2011; Xue et al. 2014, 2019; Manzeke et al. 2020), whereas others report the opposite (Feil et al. 2005; Miner et al. 2018). Our results provide several insights in the mechanisms that could explain the contrasting effects of N fertilisation on grain Zn concentrations.

First of all, N application can reduce grain Zn concentrations through increased biomass production, i.e. a dilution effect. This dilution effect has been shown for many nutrients, including Zn (e.g. Raymond et al. 2009; Hertzberger et al. 2021; Zhang et al. 2021). The results of Kiboko (Figure 4C) provide support for a dilution effect of grain Zn concentrations. However, the dilution effect was not observed in Embu and Harare (Figure 4A and B). For Embu, these results may be explained by the low N application rates, which did not exceed 90 kg ha^{-1}. However, the absence of a dilution effect in Harare, which had similar N application rates as Kiboko, points towards the relevance of additional factors.

Second, genetic factors may influence the effect of N application on grain Zn concentrations. This was shown for Embu. For four varieties, an increasing trend

between N application and grain Zn concentrations was found, whereas two other varieties maintained grain Zn concentrations. For variety DUMA43, the same trends in yields and grain Zn concentrations across N application rates were observed when grown in Harare, indicating this may be a variety characteristic (Figure 4).

Third, environmental factors, in particular soil Zn availability, could explain relations between N application rates and grain Zn concentrations. Dilution of grain Zn concentrations can be observed when biomass production increases strongly, which is not compensated for by a higher Zn uptake (Zhao et al. 2022). In Kiboko, the trade-off between yield and grain Zn concentrations as an effect of N application was clearly present, in contrast to Embu and Harare (Figure 4). Soil Zn availability in Kiboko was lower compared to Embu and Harare (Table 1) and Zn-M3 levels were close to critical values reported in literature. Soil Zn availability may thus have constrained Zn uptake in Kiboko, leading to a dilution effect of grain Zn concentrations at higher N levels. These findings could imply that N fertilisation should be complemented with Zn fertilisers in soils with low Zn availability, to avoid this trade-off.

Zn fertilisation

Although not covered in this study, application of Zn fertilisers is another management option that has the potential to increase both maize yields and grain Zn concentrations. Zinc fertilisation has been shown to increase maize grain concentrations to a maximum of 23-27 mg kg^{-1} (Joy et al. 2015; Liu et al. 2017; Kihara et al. 2020; Manzeke et al. 2020, chapter 4). This is well below the HarvestPlus target concentration of 38 mg kg^{-1}. Zinc fertilisation can thus help to increase both yields and grain Zn concentrations, in particular when soil Zn availability is limiting, but its contribution is minor.

5. Conclusions

In this study, we demonstrated that attaining grain Zn concentrations above the HarvestPlus target of 38 mg kg^{-1}, with the current commercially available maize varieties and presented management options, is not possible without compromising yield levels. However, increasing grain Zn concentrations, even if below the HarvestPlus target, can contribute to reducing human Zn deficiency in SSA (Manzeke-Kangara et al. 2021). Our results suggest that grain Zn concentrations increase with soil organic matter contents and are potentially affected by soil P and K availability. Our results furthermore indicate that maize grown on soils with low Zn availability, may require Zn fertilisation to prevent dilution of grain Zn concentrations at high N application rates.

Our results imply that improved maize could play a key role in increasing grain Zn concentrations without compromising yields. Recently, improved maize varieties with grain Zn concentrations close to the target value have been released in Latin America (Virk et al. 2021). However, we question whether the use of improved maize varieties with high grain Zn concentrations is a viable option for reducing Zn deficiency in the general SSA population on the *short term*. First, it is unknown whether these varieties bypass the trade-off between yield and grain Zn concentrations. Second, genotype and environmental interactions on grain Zn concentrations in maize have been demonstrated (Oikeh et al. 2003; Akhtar et al. 2018) and these improved varieties may perform differently under variable circumstances present in smallholder farming systems. Furthermore, farmers may not be willing to adopt improved varieties as local varieties can have more desirable traits (Tittonell and Giller 2013). Lastly, dissemination and adoption of new farming techniques historically has been slow in SSA (Frankema 2014). It therefore could take many years before the introduction of improved varieties will have an effect of human Zn deficiency.

As farmers are incentivised by economic returns, options for increasing grain Zn concentrations are more likely to be implemented when they also lead to higher yields. Our results imply that management could play a role in increasing both maize yields and grain Zn concentrations. Options include increasing soil organic matter contents and/or optimising N, P and K fertilisation. In contrast to using Zn fertilisers, these management practices likely will also improve yields, especially in nutrient-depleted soil with low SOC contents (Manzeke et al. 2012; Tittonell and Giller 2013; Njoroge et al. 2017). Future studies should confirm if these management options indeed have the potential to increase both maize yields and grain Zn concentrations, in several maize varieties and under various field conditions relevant for the SSA context.

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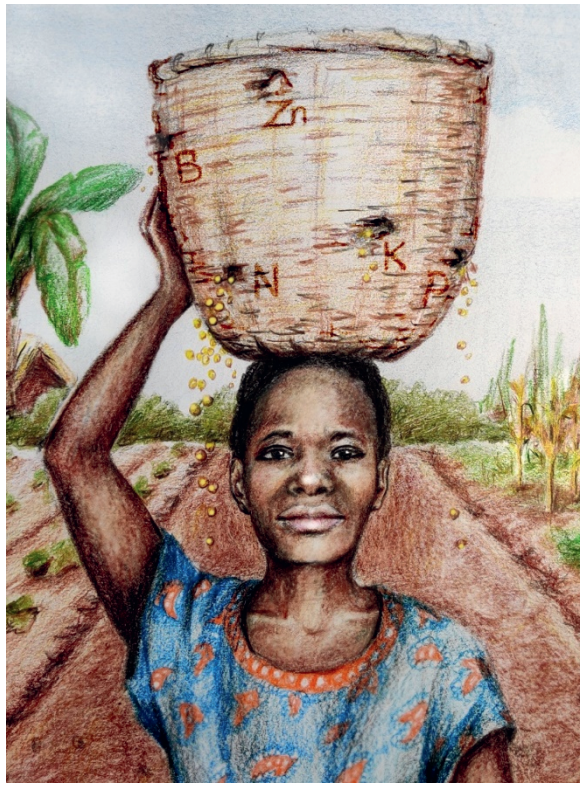
Chapter 7

General Discussion

Mirjam S. Breure



1. Overview

The use of fertilisers is indispensable for closing yield gaps in sub-Saharan Africa (SSA). To increase yields and prevent soil nutrient mining or nutrient losses to the environment, fertilisers need to be applied in balanced ratios. This refers to supplying amounts of nutrients sufficient for crop needs, while optimising the use efficiency of several plant-essential nutrients (Ezui et al., 2016). Balanced fertiliser recommendations need to take into account crop nutrient requirements as well as that soils supply part of these nutrients. Blanket fertiliser recommendations, which are common in SSA, are uniform recommendations for a country or region, that often include only macronutrients N, P and K. However, large heterogeneity in soil properties and therefore soil nutrient supply, is found within countries and regions. Furthermore, nutrients other than NPK have also been reported to limit yields in SSA, in particular zinc (Zn) and boron (B) (Kang and Osiname, 1985; Sillanpää and Vlek, 1985; Wortmann et al., 2019). Zinc is also essential for human health and widespread Zn deficiency in the SSA population has been reported (Joy et al., 2014). Increasing grain Zn concentrations through fertilising crops with Zn is seen as a viable option to reduce human Zn deficiency (de Valença et al., 2017).

Current blanket fertiliser recommendations are unsuitable for sustainably increasing yields across a country (Tittonell et al., 2008; Vanlauwe et al., 2015) and do not address nutritional quality (i.e. Zn contents) of yields. Site-specific, balanced fertiliser recommendations are seen as the way forward to close yield gaps (Chivenge et al., 2022; Ezui et al., 2016). However, obtaining site-specific fertiliser recommendations based on soil testing currently is not (economically) feasible for most small-holder farmers (Malima et al., 2020). Therefore cost-effective tools are needed for predicting nutrient availability and the yield response to fertilisation, taking into account interactions of several plant essential nutrients that may limit yields. The **main objective** of this thesis was to develop and evaluate models for predicting soil nutrient availability and to increase the understanding of the interactive effect of nutrient availability on yields and nutritional quality in SSA. The focus was on availability of macronutrients N, P and K (chapter 2, 3 and 6) as well as micronutrients Zn and B (chapter 4, 5 and 6). The QUEFTS model (Janssen et al., 1990) and its underlying principles were an important component of this thesis.

2. Main findings

2.1. Spatial application of QUEFTS

In order to tailor blanket fertiliser recommendations to specific regions, agro-ecological zones or soil types, the QUEFTS model could potentially be used in combination with high resolution digital soil maps, which have been developed for SSA (Hengl et al., 2017a, 2015). The **first objective** of this thesis therefore was to evaluate a spatial application of QUEFTS (chapter 2 and 3).

Transfer functions

To use soil maps as input for QUEFTS instead of observational (point) data, some modifications were needed. Besides soil organic carbon (SOC) and pH, QUEFTS requires P-Olsen and exchangeable K (Exch-K) measured in a neutral 1 M ammonium acetate extraction as input. The Mehlich 3 (M3) method is commonly used in SSA laboratories for evaluating nutrient availability, which consequently has led to the development of digital soil maps based on M3 data (Hengl et al., 2017a). Using a range of soil samples from various countries in SSA, transfer functions describing relations between P-Olsen and P-M3 as well as between Exch-K and K-M3 were derived (chapter 2). This provided insights into the mechanisms for extracting P and K and the suitability of the M3 method for estimating the availability of these nutrients.

We demonstrated that K-M3 relates well with Exch-K evaluated with the ammonium acetate extraction method, which we attributed to similar extraction mechanisms, being $NH_4^+ \leftrightarrow K^+$ ion exchange. Likely due to the contrasting extraction mechanisms of the Olsen and M3 methods, the results for P were less straightforward. Not only were multiple parameters needed to translate P-M3 to P-Olsen test results, the P transfer function was less accurate than the K transfer function. Our results furthermore showed that the P extraction efficiency of M3 is strongly reduced at high amorphous Al-(hydr)oxide contents. We presented support for our hypothesis that saturation of the fluoride ion in M3 with Al was the cause of this reduction. Our results show that (i) K-M3 can be used reliably to estimate Exch-K and (ii) P-M3 cannot be used to estimate P-Olsen without the use of additional soil parameters.

Our results highlighted the need for specific transfer functions for tropical soils. We showed that K transfer functions were significantly different between temperate and tropical soils, which we attributed to clay mineralogy. Although not tested for P, differences in the transfer functions between temperate and tropical soils are also

expected, given the effect of climate and weathering on soil properties such as Al-oxides (Mendez et al., 2022).

We demonstrated that the use of site-specific M3 soil data as input for the QUEFTS model, by applying the P and K transfer functions, added limited uncertainty to the final QUEFTS yield estimate when compared to using measured P-Olsen and Exch-K values as input. This was caused by the relatively large contribution of pH and SOC to the QUEFTS model output and log-transformation of the P transfer input variables, which ensured that uncertainty in the agronomically relevant range up to 10 mg kg^{-1} P-Olsen was minimised.

Spatial application of QUEFTS

In chapter 3, the transfer functions and QUEFTS were applied to soil maps for Rwanda, using two methods. For the first method, the transfer functions and QUEFTS were applied to data points and model outputs (yield and the yield-limiting nutrient) were spatially interpolated to develop a map of the target variable (Calculate-then-Interpolate; CI). For the second method, all individual model input parameters were first interpolated, after which model calculations of the target variables were applied to these maps (Interpolate-then-Calculate; IC).

The first main finding includes stark differences in outcomes between both methods. We attributed this to the non-linear nature of QUEFTS, as less pronounced differences between both methods were reported for linear models in literature. Generally, QUEFTS predictions using the CI method were more accurate as the IC predictions were overestimated due to smoothing of the model input parameters. Smoothing caused an overestimation of the lowest P-Olsen and Exch-K values, and moved spatial pH predictions towards an optimum. The CI method was less sensitive to smoothing, as only the final model output was spatially interpolated. Although IC method overestimated yields, the CI and IC methods were equally able to distinguish between lower and higher yielding regions.

Secondly, we demonstrated that application of QUEFTS to currently available soil maps of Rwanda, leads to spatial yield predictions associated with large uncertainty. For the CI method, which had the best results, 28% of the variation observed in QUEFTS yields modelled at the soil observation locations was explained by the yield maps. More importantly, the RMSE of yield predictions (1.3 Mg ha^{-1}) was larger than yields observed in small-holder farming systems when no fertilises are used (Manzeke et al., 2014; Tittonell et al., 2008). The uncertainty associated with QUEFTS spatial predictions

using the IC method, was mainly caused by the low accuracy of spatial P-M3 and K-M3 predictions. Despite the uncertainty associated with the spatial yield estimates, the yield-limiting nutrient was estimated correctly in 54% (IC) and 60% (CI) of the evaluation locations. Furthermore, we demonstrated that spatial patterns in QUEFTS yield and yield-limiting nutrient predictions clearly corresponded to predictions at the underlying point data.

2.2. Micronutrient bioavailability functions

Of the several micronutrients required for plant-growth, yield-limitations of Zn and B are considered most problematic in SSA (Kang and Osiname, 1985). The **second objective** of this thesis therefore was to derive generic models describing bioavailability of micronutrients Zn and B based on soil parameters that can be measured in routine analysis. Based on the underlying principles of QUEFTS, bioavailability was defined as *the uptake of a nutrient during an entire growing season, when this nutrient is yield-limiting*. To derive micronutrient bioavailability models, data from Zn and B fertiliser omission trials were used. Plant uptake in the omission treatments was related to chemical soil parameters which were expected to be relevant for controlling bioavailability of Zn and B, including several micronutrient pools. We assessed the actually available micronutrient pool, using the 0.01 M $CaCl_2$ extraction method and the potentially available pool, using the 0.43 M HNO_3, M3 and DTPA extraction methods. We also evaluated the hot water method for B; it is unknown which pool is represented by this method.

We showed that the potentially available soil Zn and B pools, in particular the pool extracted with 0.43 M HNO_3, were significantly related to uptake of these nutrients by a maize crop (chapter 4 and 5). The variation in uptake that could be described based on soil parameters, was however limited to 35% for Zn and 21% for B. This may have been caused by the fact that Zn and B were not yield-limiting in the micronutrient fertiliser omission trials, as demonstrated by a lack of yield response to fertilisation with these nutrients. The absent yield responses, in combination with low levels of soil Zn and B, also demonstrated that current critical Zn and B soil test concentrations reported in literature for maize grown in tropical soils, are no reliable indicator for deficiency.

Our results provide valuable insights into Zn availability and fertiliser response in soils with a low adsorption affinity for Zn. Many studies have focussed on Zn availability in alkaline soils, which are notorious for their strong Zn binding capacity and consequently low Zn availability (Cakmak and Kutman, 2018; Catlett et al., 2002). In contrast, few studies have investigated Zn availability in relation to plant uptake in acidic soils with low organic carbon contents, which are widespread in SSA. We found that the

potentially available pool (Zn in 0.43 M HNO_3, M3 or DTPA) was a better proxy for plant uptake than the actually available pool (Zn in 0.01 M $CaCl_2$) in soils with a low adsorption affinity for Zn (chapter 4). This implies that Zn uptake is limited by the buffering capacity of these soils rather than by the concentration of Zn in the soil solution. We furthermore demonstrated that the response in Zn uptake to Zn fertilisation decreased with increasing pH and SOC levels, showing that the fertiliser use efficiency of Zn is higher in low adsorption affinity soils.

We found a weak relation between plant B uptake and chemical soil parameters (chapter 5). This points towards the relevance of other factors, such as soil water content, transpiration, chemical weathering or mineralisation of organic matter as sources of plant available B. We also provided some insights into the pool of B that is extracted with the hot water method, commonly used for assessment of B availability. The hot water method extracted roughly twice the amount of B compared to 0.43 M HNO_3, indicating that the hot water method could overestimate the potentially available B pool. Our results suggest that the hot water extracts B from undecomposed biomass, which likely is not extracted by 0.43 M HNO_3 and 0.01 M $CaCl_2$.

2.3. Biofortification

In addition to the use of improved Zn-accumulating varieties (genetic biofortification), Zn concentrations in the edible parts of plants can be increased through adding Zn fertilisers (agronomic biofortification). The effects of Zn availability and fertilisation on maize grain Zn concentrations however, are not consistent and depending on soil characteristics and quantities of other nutrients applied (Manzeke et al., 2014; Obaid et al., 2022). The **third objective** of this thesis was to assess the effect of Zn availability, in combination with availability of NPK, on maize yield (quantity) and grain Zn concentrations (nutritional quality).

We demonstrated that soil Zn availability, in particular Zn extracted with 0.43 M HNO_3, is related with grain Zn concentrations (chapter 4). However, limited variation in grain Zn concentrations was described based on Zn-HNO_3 alone (26%). When allowing for differences in maize variety/agro-ecological zone, up to 56% of the variation in grain Zn concentrations was described based on Zn-HNO_3. This shows that (i) relations between maize grain and soil Zn concentrations are possibly variety-dependent, and/or (ii) that agro-ecological factors, such as management, climate or soil type can affect grain Zn concentrations. Our results also indicate that higher grain Zn concentrations can be expected in soils with higher SOC content, as we found a strong positive correlation between Zn-HNO_3 and SOC (chapter 4) and a positive correlation between SOC and

grain Zn concentrations (chapter 6). Additionally, our data suggest that at low soil Zn availability, grain Zn concentrations can be diluted when yields increase (as an effect of N fertilisation).

Fertilisation with 5 kg Zn ha^{-1} increased grain Zn concentrations in the majority (77%) of blocks, with an average increase of 20% (2.4 mg kg^{-1}) across countries (chapter 4). This increase was negatively related with pH and SOC, showing that the effectiveness of agronomic biofortification is high in soils with a low adsorption affinity for Zn. Adding Zn fertiliser increased grain Zn concentrations up to 27 mg kg^{-1} and the largest increases were observed in locations with the lowest grain Zn concentrations in the Zn omission plots. This could indicate that, once a physiological maximum grain Zn concentration is reached, Zn fertilisation will not further increase grain Zn concentrations. Findings from chapter 6 support this hypothesis: grain Zn concentrations at locations with high soil Zn-M3 concentrations (>11 mg kg^{-1}) were not higher compared to locations with lower Zn-M3 levels (~2 mg kg^{-1}).

The HarvestPlus target of 38 mg Zn kg^{-1} in maize grains is considered adequate for combatting human Zn deficiency (Bouis and Welch, 2010). We demonstrated that attaining this target, by applying Zn (chapter 4) or N fertilisers (chapter 6) to current commercially available maize varieties, is not possible without compromising yields.

Several of our findings indicate that a good nutritional status of the crop can benefit grain Zn concentrations when soil Zn availability is low. In chapter 4, we showed that Zn fertilisation did not increase maize yields, despite soil and plant concentrations pointing towards Zn deficiency. This could be an effect of the high gifts of NPK, secondary and micronutrients that were applied. In line with these results, we found higher maize grain Zn concentrations on soils with higher P and K levels (chapter 6).

2.4. Soil testing for fertiliser recommendations

Our results also provided insights in the reliability of chemical soil tests for assessing soil nutrient availability, in particular the M3 and hot water methods. In order for a given chemical soil extraction method to be suitable for deriving fertiliser recommendations, the results of this method results should be a good proxy for plant uptake and/or yield response to fertilisation and results should be reproducible across laboratories and over time (Olsen et al., 1954). The M3 and hot water extraction methods do not comply to both criteria. Although beyond the original aims of this study, I would like to elaborate on some our findings, as they have implications for the transferability of found results.

In chapter 3, we presented results on inter-laboratory variation in P, Al, Ca and Fe concentrations extracted with M3. Our findings confirm the work of Shahandeh et al. (2017) and Liu (2019) who showed that Mehlich 3 extractable P, Al, Fe and Ca are very sensitive to small errors/variations in the protocol used. We showed that inter-laboratory variation in M3 results caused a 19% difference in P-Olsen predictions when applying the P transfer function. We also showed that many variations of the hot water protocol are in use and that these variations have an impact on the results (chapter 5).

3. Limitations of this study and future research

3.1. Spatial application of QUEFTS

There are several important limitations regarding our study into the spatial application of QUEFTS. First, we were not able to evaluate the maps with yield data from field trials. Evaluation of QUEFTS spatial predictions was done with modelled yields and yield-limiting nutrients based on soil data from set-aside locations. Although this provides a clear overview of the spatial performance of QUEFTS, the use of external data can provide valuable insights into areas and associated covariates or soil properties affecting accuracy of spatial predictions. For future studies, I strongly recommend to evaluate the outcomes of QUEFTS spatial predictions with field data.

Second, the use of P-Olsen predictions based on M3 data, rather than using measured values, likely affected results of the IC method more than results of the CI method. The use of M3 data increases the number of input parameters for QUEFTS to eight, compared to four when using P-Olsen measurements. Our analysis indicated that smoothing of soil input parameters was an important driver for the overestimation of yield predictions using the IC method. Hence, increasing the number of input parameters makes outcomes of the IC method more sensitive to smoothing effects. The use of the P transfer function also has larger implications on the outcomes of the IC method, as uncertainty of the transfer function is multiplied with the uncertainty caused by smoothing of the input maps. This is not the case for the CI method, as only the final input is interpolated. Some P-Olsen data are available for SSA (Batjes, 2010). I recommend to develop P-Olsen maps based on direct measurements and evaluate whether they are associated with significantly less uncertainty than P-Olsen predictions based on M3 data and whether this results in more accurate spatial predictions using the IC method. Alternatively, P-Olsen maps can be developed based on M3 data using the CI method. This is expected to result in more accurate spatial P-Olsen predictions compared to using the IC method, since smoothing-effects are reduced to a minimum.

Third, we were not able to draw reliable conclusions on the suitability of QUEFTS for developing fertiliser recommendations at scale as we only evaluated QUEFTS spatial yield and yield-limiting nutrient predictions. The yield-limiting nutrient was estimated correctly relatively often, indicating that QUEFTS potentially can be used to develop regional fertiliser recommendations. However, we did not actually develop fertiliser recommendations, which I would recommend for future studies. This would provide valuable insights into whether QUEFTS spatial fertiliser recommendations are a step forward compared to using blanket fertiliser recommendations currently in place.

QUEFTS spatial predictions can greatly benefit from improving the quality of the P-M3 and K-M3 maps, which were associated with high uncertainty. I expect that P-M3 and K-M3 are difficult to map partly because of the strong impact of soil management on nutrient availability and consequent small-scale spatial heterogeneity (Chikowo et al., 2014; Njoroge et al., 2019; Zingore et al., 2007a). This heterogeneity is not fully captured by the 250m resolution covariates used in this study. As more high resolution (30-100m) covariate layers are becoming available, soil maps will likely improve in terms of precision and accuracy (Hengl et al., 2017b; Poggio et al., 2021). For future research, I recommend to evaluate whether spatial P-M3 and K-M3 predictions will improve when using covariate data at a resolution of 30-100m compared to 250m. I also suggest to explore options for including mapped variables as covariates, such as pH or soil type, which are known to affect nutrient availability. Although these maps will contain uncertainty themselves, they could improve spatial P-M3 and K-M3 predictions.

I furthermore recommend to map the maximum yield parameter for future spatial applications of QUEFTS. Several studies have already demonstrated the use of maps of maximum yields, yield gaps, or factors relevant for good productivity such as rootable depth and water availability (Leenaars et al., 2018; Steinbuch et al., 2016; Van Wart et al., 2013). Such a maximum yield map enables finetuning of QUEFTS spatial yield predictions to local conditions.

3.2. Micronutrient bioavailability functions

Based on available data, no satisfactory models could be derived that described micronutrient uptake or the yield response to fertilisation based on soil parameters. A lack of good relations, even if a nutrient is yield-limiting, can be caused by several factors. In addition to short-scale (within-farm) spatial heterogeneity in soil properties and errors in soil sampling and analyses, our results may have been affected by several important limitations of the data, as well as the underlying hypothesis that plant uptake is a good proxy for bioavailability of micronutrients.

We solely relied on chemical soil parameters for estimating micronutrient uptake and response to fertilisation. Nutrient supply is affected by several other (soil) properties which were not included in our analyses. Texture, soil type, bulk density and rooting depth significantly affect nutrient and water availability, which can all impact plant nutrient uptake, yields and fertiliser response (Correndo et al., 2021; Kihara et al., 2017; Leenaars et al., 2018). Rainfall/water availability furthermore is known to affect B leaching (Degryse, 2017). Although some of these data were available, they were not taken into account during the analyses. This was due to incomplete data, because data were only available on farm-level or showed limited variation within each country. For future studies I recommend to collect data on soil texture, rootable depth and precipitation, in addition to soil chemical parameters, as they may explain additional variation in micronutrient fertiliser responses and plant micronutrient uptake.

The micronutrient fertiliser omission trials covered a limited range in soil pH, SOC and texture. The trials furthermore covered only three soil types, which did not differ within a country, except for Zimbabwe where trials were executed on two different soil types. I therefore recommend to ensure a larger variability in soil properties of field trial locations when aiming for derivation of micronutrient bioavailability functions. Another important constraint was the use of different maize varieties for each of the countries. Although this choice was made because of locally available resources, this may have affected our results, as we were not able to distinguish between the effects of maize variety and differences in climatic or soil factors which were not measured. For future studies, I therefore highly recommend to use more than one maize variety, replicated in each of the locations.

The high rates of NPK, secondary and micronutrients provided to the maize crops in this study, may have masked deficiency of micronutrients. Optimal or balanced fertilisation could lead to healthier crops, with larger root systems that are able to explore a larger soil volume (de Valença et al., 2017; Pasley et al., 2019). This could explain why a positive yield response to Zn and B fertilisation was absent, despite soil test values for Zn (in M3 and DTPA) and B (in hot water) being below critical concentrations for maize reported by Chilimba et al. (1999), Cuesta et al. (2021) and Kumar et al. (2018). Compared to these literature studies, generally higher fertiliser rates and/or more nutrients were fertilised in this study. Our findings stress the need for more extensive evaluation of critical soil test values for deriving micronutrient fertiliser recommendations for maize. The hypothesis that optimal or balanced fertilisation could induce changes in the rooting system, thereby reducing the need for micronutrient fertilisation, also deserves further attention. I recommend to study the effect of fertiliser

regime on root architecture and plant nutrient uptake, in several maize varieties. This may provide valuable insights regarding fertilisation as well as breeding strategies for rooting systems that facilitate optimal nutrient use efficiency.

I would like to put forward two more hypotheses for the poor relations found between soil parameters and maize Zn and B uptake. First, I question whether plant uptake is a good measure for bioavailability of *micronutrients*. In order to be a good proxy for bioavailability, plant uptake of micronutrients should relate to yield to some extent, especially when these nutrients are yield-limiting. Our data showed that a fertilisation induced increase in plant uptake of Zn and B did not result in higher maize yields, despite soil and plant concentrations pointing towards deficiency of these nutrients. We also demonstrated in this study that the internal efficiency of maize ranged between 8 and 71 kg grain g^{-1} Zn uptake (chapter 4), a factor 9 difference between the extremes. In contrast, the difference between minimum and maximum internal efficiency for macronutrients is a factor 2.5 for N, 3 for P and 4 for K (Janssen et al., 1990). In other words, there is a much larger plasticity in plant micronutrient than macronutrient concentrations. Deficiency of N, P and K has clear impacts on maize yields (e.g. Njoroge et al., 2017; Pasley et al., 2019; Shehu et al., 2018) but less drastic yield effects are observed when Zn and B are not sufficiently available to plants (Awio et al., 2021; Mozafar, 1987; Vanlauwe et al., 2015). Obviously, Zn and B can be strongly diluted in the crop without affecting maize yields, as shown in chapters 4 and 5. This could imply that uptake of Zn and B, above a critical threshold, do not define crop yields. This hypothesis is supported by the work of Kovács and Vyn (2017), who demonstrated that relations between Zn and B earleaf concentrations and maize yields were very poor compared to N, P and S. If plant uptake or plant concentrations indeed are not a reliable indicator for micronutrient bioavailability, this would imply that deriving models of the yield response to micronutrient fertilisation is a more viable option for deriving bioavailability models.

The second hypothesis refers to the use of maize as a test crop. It has been suggested that maize is not susceptible to B deficiency (Lordkaew et al., 2011) and maize may thus not have been an ideal test crop to assess B availability. In contrast to B, maize is considered highly sensitive to Zn deficiency (Alloway, 2008). Although good relations have been found between soil test values and Zn uptake, those studies involved rice and wheat as test crops (Das et al., 2009; Duffner et al., 2013; Maiti et al., 2006; Seth et al., 2017). However, several studies showed that (grain) Zn uptake in maize is less responsive to Zn and N fertilisers compared to rice and wheat (Cakmak and Kutman, 2018; Zhao et al., 2022). Furthermore, Zn concentrations in these crops seem to be less

plastic compared to maize, as the minimum and maximum internal efficiency differ by a factor 7 for wheat and 5 for rice (Das et al., 2009; Maiti et al., 2006), compared to 9 for maize. These physiological properties of maize may complicate finding a clear yield response to Zn fertilisation in field trials and consequently could constrain derivation of models describing soil Zn availability.

3.3. Biofortification

With regards to biofortification, the study design imposed difficulties in drawing strong conclusions about the effect of Zn availability in combination with availability of NPK on maize yields and grain Zn concentrations. As the main purpose of the micronutrient fertiliser omission trials was to derive Zn (and B) bioavailability functions, only Zn and B fertiliser omission treatments were included. In order to gain insights into the interactive effect of Zn and N, P and K availability on maize yields and grain Zn concentrations, a full factorial design, including omission and different fertiliser applications rates of Zn, N, P and K is required. The current study design also complicated identification of relevant soil factors affecting grain Zn concentrations. The random factor 'country' explained large variation in the relation between soil and grain Zn concentrations (chapter 4). However, in each of the countries, a different maize variety was grown. We therefore do not know whether the country factor represents differences among maize variety, or soil (or environmental) factors which we did not measure. In chapter 6, relations between soil and plant were difficult to derive due to a potential confounding effect of maize variety and clustering in soil data. In addition to using multiple maize varieties (section 3.2), I recommend to explore interactions among Zn, N, P and K, using a full factorial fertiliser omission design in future studies. In case interactions are found, this could have an impact on fertiliser recommendations. Such a design would also allow to disentangle the individual and interacting roles of different nutrients in root architecture.

4. Practical implications

4.1. Soil testing for fertiliser recommendations

The M3 method is popular because it can be used to extract multiple nutrients simultaneously by combining several extraction mechanisms and can be applied to a wide range of soils (Wuenscher et al., 2015). These attributes make it a convenient and cost-effective method (Chilimba et al., 1999). The hot water method has been used for decades, as it was found to be a good proxy for B availability (Wear, 1965). Soil M3 data are widely available for SSA and are thus presumably used for assessment of soil nutrient

availability (e.g. Njoroge et al., 2017) and likely fertiliser recommendations. In my opinion, several changes are needed to use the M3 and hot water chemical soil tests for reliably assessing nutrient availability or deriving models describing availability, as well developing fertiliser recommendations.

First, the suitability of the hot water and M3 methods for evaluating yield responses to fertilisation requires more evaluation in field trials. The use of these methods for estimating P, K, Zn and B availability to maize grown in tropical soils, has been demonstrated in a limited number of studies (i.e. Chilimba et al., 1999; Cuesta et al., 2021; Kumar et al., 2018). Our work however showed that the critical concentrations derived in these studies, were no reliable estimators for Zn and B deficiency (chapter 4 and 5). We also showed that high soil amorphous Al contents reduce the P extraction efficiency of M3 (chapter 2), which could imply that P-M3 is not a reliable (universal) estimator of plant available P.

Second, standardisation of the M3 and hot water methods is needed. Variation in soil test results complicates their use for the development of accurate fertiliser recommendations (Schut and Giller, 2020; Van Leeuwen et al., 2021). We demonstrated that the M3 and hot water extraction methods are prone to errors, partly due to variations in the protocols used (chapter 3 and 5), highlighting the need for detailed reporting of used methods, standardisation of protocols, as well as quality control of lab results. This is internationally recognised and several initiatives are currently addressing this issue (Harmsen 2007; GLOSOLAN 2022; WEPAL 2022; ISO standards). Additionally, insights are needed into the nutrient pools that are extracted with M3 and hot water, as understanding the extraction mechanisms is essential for standardisation of methods (Harmsen, 2007).

I hypothesise that part of the uncertainty associated with the M3 and hot water methods is caused by the fact that no stable chemical equilibrium is reached within the 5 to 10 min extraction time (Mahler et al., 1984; McGeehan et al., 1989; Penn et al., 2018). Until the M3 and hot water methods are properly evaluated in field trials and protocols are standardised, I propose to use alternatives for these methods to assess availability of cations, P, Zn and B.

For determining exchangeable cations, I consider the ammonium acetate method (extraction time of ~2 h) more suitable than M3. Although M3 is a reliable alternative for Exch-K (chapter 2), poor results have been reported for cations that are usually also extracted with ammonium acetate, such as calcium (Michaelson et al., 1987) and sodium

(Fukuda et al., 2017), though not in all studies (Mamo et al., 1996; Wendt, 1995). The Olsen method seems a good alternative for P-M3. No stable chemical equilibrium is reached in the extraction time of 30 min (Olsen et al., 1954), but the P extraction mechanism is clear and the extraction efficiency likely does not depend on other soil properties. However, Schut and Giller (2020) report a relatively large interlaboratory variation in P-Olsen concentrations, especially in the agronomically relevant range, compared to methods for pH, SOC or even P-M3. This could be due to differences in extraction time or analytical methods, i.e. colorimetric or ICP analysis (Olsen et al., 1954; chapter 4), again highlighting the need for standardisation of protocols.

With regard to Zn availability in tropical soils, the standardised 0.43 M HNO_3 extraction seems to be a promising method. The method has an extraction time of 4 h and has been shown to be a good proxy for the Zn reactive pool (Groenenberg et al., 2017; Van Eynde et al., 2022). In addition, Zn-HNO_3 explained more variation in Zn uptake and grain Zn concentrations compared to Zn in DTPA or M3 (chapter 4). However, the 0.43 M HNO_3 extraction method has been shown to overestimate the reactive Zn pool in calcareous soils (Gao et al., 2022; Groenenberg et al., 2017). Although this problem likely did not affect our results, given the low pH soils of the field trial locations, this implies that HNO_3 results may not be equally reliable for all soils. Future research should focus on the wider suitability of the HNO_3 extraction method as a proxy for Zn availability, in particular in relation to other soil properties such as pH.

Boron concentrations in hot water, 0.43 M HNO_3 and 0.01 M $CaCl_2$ generally correlated well, although discrepancies were found at lower concentrations (chapter 5). Given the issues with reproducibility of the hot water method results, the use of either 0.43 M HNO_3 or 0.01 M $CaCl_2$ for assessing B availability seems preferable. However, neither method was a good predictor of B uptake in our study. Since much is still unknown about relations between soil B tests and plant uptake or fertiliser response in maize, I consider it premature to dismiss or recommend any extraction method at this point.

4.2. Field-scale application of QUEFTS

QUEFTS is a useful tool: yield estimates can correspond well to observed yields in field trials (Das et al., 2009; Maiti et al., 2006; Sattari et al., 2014; Tabi et al., 2008) and several studies have shown that the model can be used adequately to derive balanced N, P and K fertiliser recommendations (Maiti et al., 2006; Mesfin et al., 2021; Xu et al., 2013). We showed that using site-specific M3 soil data as input for the QUEFTS model, by applying the P and K transfer functions, added limited uncertainty to the final QUEFTS

yield estimate (chapter 2). The P and K transfer functions derived in this study thus broaden the (spatial) applicability of QUEFTS when only M3 data are available.

Apart from QUEFTS, the transfer functions enable evaluation of soil P and K availability based on M3 data. The suitability of M3 for estimating P and K availability to maize grown in tropical soils, has only been demonstrated by Chilimba et al. (1999) and in combination with other soil parameters by Shehu et al. (2019). In contrast, the suitability of the P-Olsen and Exch-K methods have been proven useful for assessing availability and fertiliser response to P and K in many studies (Bai et al., 2013; Chilimba et al., 1999; Das et al., 2009; Farina et al., 1992; Maiti et al., 2006; Sattari et al., 2014; Ussiri et al., 1998). The good relation between Exch-K and K-M3 implies that critical concentrations for K in ammonium acetate can be reliably translated into K-M3 results. The P transfer function can provide a reasonably good estimate of P-Olsen values.

Several studies have reported poor validation results for QUEFTS yield predictions with field-specific data (e.g. Njoroge Kinyanjui, 2019; Shehu et al., 2019). I would like to discuss some additional findings, not presented in previous chapters, which provide insights in potential causes for the poor performance of QUEFTS yield predictions using field-specific data.

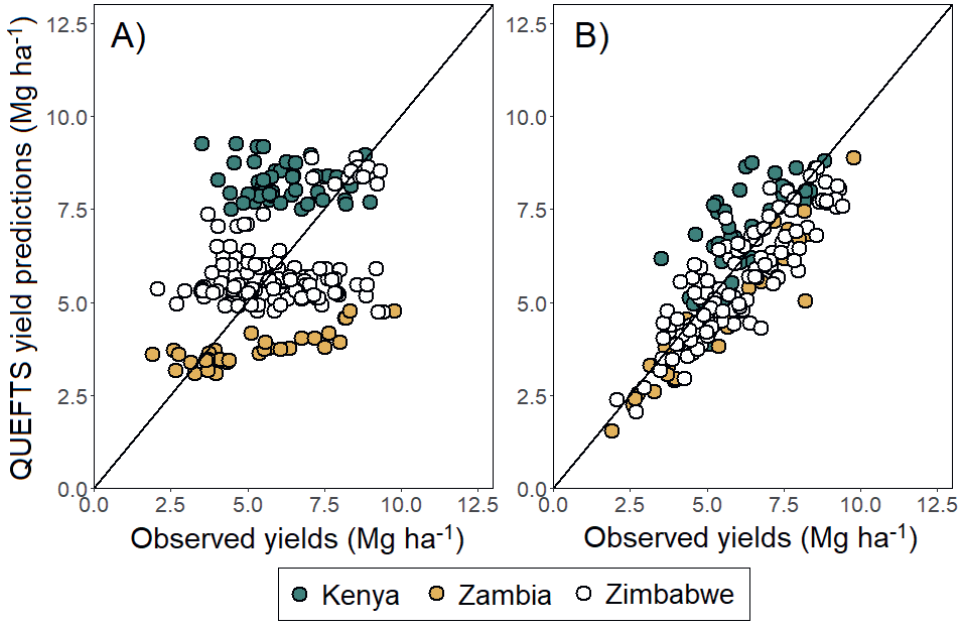


Figure 1: QUEFTS yield predictions based on (A) measured soil parameters and default fertiliser recovery fractions, and (B) measured N, P and K uptake, plotted against observed yields in the micronutrient omission trials (full and -Zn treatments; chapter 4). Lines represent the 1:1 line.

In Figure 1 (courtesy of Elise Van Eynde), QUEFTS yield predictions of the micronutrient fertiliser omission trials are compared to observed yields. In Figure 1A, QUEFTS predictions are based on soil information (i.e. pH, SOC, P-Olsen and Exch-K), as well as fertiliser gifts multiplied by the default recovery fractions (Janssen et al., 1990). Within each respective country, relations between predicted and observed yields seem absent. In Figure 1B, the measured uptake of N, P and K is used as input for QUEFTS; the first step in the QUEFTS procedure, using soil data, is skipped. In this scenario, there is good agreement between predicted and observed yields. These results are in line with Njoroge Kinyanjui (2019) and imply that either or both the supply functions and fertiliser recovery fractions cannot be applied universally.

Based on these findings, I recommend to model the recovery fractions of N, P and K fertilisers based on soil properties, as demonstrated for Zn in chapter 4. The recovery fractions show large variation in the field (e.g. Shehu et al., 2019; Tabi et al., 2008). Tailoring the recovery fractions to local conditions leads to better results compared to using default values (Ezui et al., 2016). Modelling recovery fractions based on soil properties would also benefit QUEFTS spatial fertiliser recommendations, as soil maps can be used to customise recovery fractions to specific regions. In addition, recalibrating the P supply function, which is associated with relatively large uncertainty (Tabi et al., 2008) could strongly improve the general (spatial) applicability of QUEFTS. Given the widespread availability of M3 data in SSA, deriving a P supply function based on P-M3 rather than P-Olsen data seems obvious. A P supply function based on M3 data makes the use of the P transfer function obsolete, which could reduce uncertainty in QUEFTS (spatial) predictions. For deriving future P supply functions, I recommend to test proxies for soil Al(hydr)oxide contents, as we demonstrated its relevance in the extraction of P-M3 (chapter 2).

4.3. Spatial application of QUEFTS

We demonstrated that spatial patterns in QUEFTS yield and yield-limiting nutrient predictions corresponded to predictions at the underlying point data. Application of QUEFTS to soil maps can thus provide valuable insights in spatial patterns, which can serve as a basis for further research or interventions (Arrouays et al., 2020; Giller and Zingore, 2021; Hengl et al., 2017a).

Our results show that the method chosen to develop maps with non-linear models should be selected with care. For QUEFTS, based on the Rwandan case study, the CI method seems to results in the most reliable spatial predictions of maize yields and the yield-limiting nutrient in an unfertilised situation. In order to apply the CI method, all

input data for QUEFTS and/or the transfer functions is required for each data point underpinning the maps. This implies that chemical soil analyses of all these parameters is necessary when one aims to develop maps with QUEFTS with the CI method. In case of missing data, the IC method can be an alternative. The IC method can distinguish between lower and higher yielding regions to the same extent as the CI method and could thus be used for this purpose. However, as the IC method overestimated yield predictions, maps developed with this method should be interpreted with care, in particular when used for the development of agronomic interventions.

The use of the IC method, in combination with the use of the P and K transfer functions, led to a smoothing-induced overestimation of the lowest and an underestimation of the highest spatial P-Olsen and Exch-K predictions. The use of these maps, as they are, or as input for QUEFTS, will therefore likely lead to an underestimation of P and K fertiliser requirements in certain regions and an overestimation in other regions. Although P-Olsen and Exch-K maps can serve to identify differences among regions in P and K availability, caution is required when using these maps as a basis for developing fertiliser recommendations.

4.4. **Micronutrient fertiliser recommendations**

Method of application

Our results suggest that the fertiliser use efficiency of soil applied Zn is high in soils with low pH and SOC content, common in SSA (Hengl et al., 2015). This has several implications for Zn fertiliser recommendations, mainly in regards to biofortification, as yields may not increase in most cases. First, a high fertiliser efficiency reduces the required amount of fertilisers needed to attain a similar response (Alloway, 2008). The 5 kg Zn ha^{-1} used in this study was sufficient to increase grain Zn concentrations and rates could potentially be decreased on soils with low Zn adsorption affinity. Second, as soil fertilisation has a high efficiency, no alternative methods such as foliar application are required. The foliar application of Zn has shown to be slightly more effective in increasing maize grain Zn concentrations compared to soil application, but the largest effects of foliar application are expected in calcareous, Zn fixing soils (Joy et al., 2015). However, foliar Zn application mostly affects grain Zn concentrations, but not yields (Awio et al., 2021; Joy et al., 2015). As foliar sprays require additional labour and equipment compared to soil application (Joy et al., 2015), the latter method for Zn fertilisation is preferred in non-calcareous soils.

Biofortification

Our results showed that reaching the HarvestPlus target Zn concentration of 38 mg kg^{-1} in maize grains requires development of improved Zn-accumulating varieties. Our data also suggest that relations between soil Zn availability and grain Zn concentrations could be variety-dependent. This implies that grain Zn concentrations and yield performance of improved Zn-accumulating varieties should be tested in soils with varying levels of Zn availability. Although not sufficient to reach the HarvestPlus target concentration, we showed that Zn fertilisation can raise grain Zn concentrations up to 27 mg kg^{-1}. Together with a high expected Zn fertiliser efficiency in soils with a low Zn adsorption affinity, Zn fertilisation could contribute to alleviating human Zn deficiency (Manzeke-Kangara et al., 2021). Our results furthermore suggested that providing balanced NPK fertilisation and increasing soil organic matter contents have the potential to increase grain Zn concentrations in maize. As these practises likely will also increase yields, these are economically feasible management options for increasing grain Zn concentrations. Additionally, in low Zn soils (Zn-M3 levels below ~2 mg kg^{-1}), high gifts of N(PK) may require co-application of Zn fertilisers to prevent dilution of grain Zn concentrations due to increased biomass production. Areas at risk of Zn dilution in high yielding systems, could potentially be identified based on Zn-M3 maps.

Necessity for fertilisation

The lack of a yield response to fertilisation with Zn and B, despite very low soil concentrations, demonstrated in this thesis, raises the question how problematic micronutrient deficiencies are across SSA. I hereby would like to review some of the evidence that crop micronutrient deficiencies are widespread across SSA and are limiting maize yields in particular. In chapter 4 and 5, we mentioned several studies that provided clear evidence that Zn and B availability were limiting maize yields. However, the geographical areas covered by these studies usually was limited. A few recent studies (Kihara et al., 2017; Rurinda et al., 2020; Wortmann et al., 2019) looked into the extent to which secondary and micronutrients are limiting maize yields in SSA, together covering hundreds of field trials in Ethiopia, Burkina Faso, Ghana, Kenya, Malawi, Mali, Niger, Nigeria, Rwanda, Tanzania, Uganda, and Zambia. Rurinda et al. (2020) showed that adding a combination of secondary and micronutrients to NPK, increased maize yields to a limited extent (between 0 and 0.3 Mg ha^{-1}) compared to fertilising NPK alone. In Kihara et al. (2017), secondary and micronutrients added an extra 0.8 Mg ha^{-1} (25%) to maize yields obtained with NPK fertilisation alone. Wortmann et al. (2019) showed that a combination of secondary and micronutrients increased median maize yields with 15% in Eastern and Southern Africa compared to NPK alone, but no median increase was observed in Western Africa. Although the data of Kihara et al. (2017) and

Wortmann et al. (2019) could indicate that deficiencies of Zn and B occur in maize, both studies have important limitations which hamper the conclusions that can be drawn. First of all, both studies, as well as Rurinda et al. (2020), have assessed only the effect of mixtures of secondary and micronutrients on maize yields. Although this setup provides valuable information about the extent to which a limited yield response to NPK fertilisation can be expected, the results do not provide answers as to which of the nutrients is limiting yields, and in which soils. Another important limitation of Kihara et al. (2017), although using spatially exhaustive data, is a lack of on-farm replication of the mixed secondary and micronutrient fertiliser treatment. We observed a within-farm variability of 20% in yields for a given fertiliser treatment (chapter 4 and 5). This raises the question whether individual farmers will indeed observe a clear yield increase when they apply secondary and micronutrients.

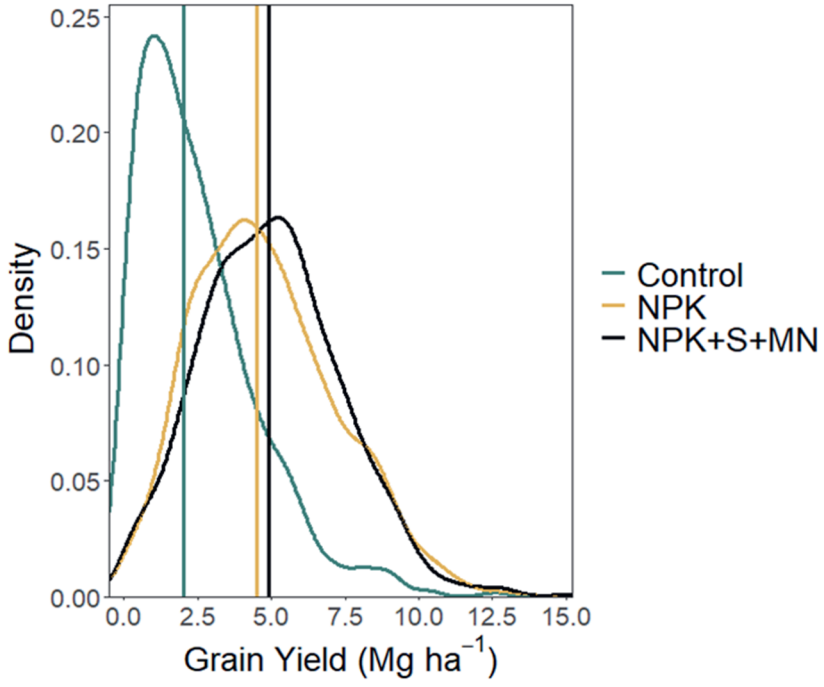


Figure 2: Density plots of maize yields in the control (no fertiliser), NPK and NPK + secondary (S) and micronutrients (MN) treatments. Data from the TAMASA (Rurinda et al., 2020) and AfSIS trials (Kihara et al., 2017). Lines represent median values.

The data of Rurinda et al. (2020) and Kihara et al. (2017), presented in Figure 2 (courtesy of Elise van Eynde), show that median maize yields increase from 2.0 Mg ha^{-1} in the unfertilised control to 4.5 Mg ha^{-1} in the NPK fertiliser treatment. Adding secondary and micronutrients further increases the median yield to 4.9 Mg ha^{-1}, which could be

considered marginal compared to the yield increase by NPK fertilisation alone. These findings are in line with the work of Awio et al. (2021), who showed that additional rice yield gains due to fertilisation with secondary and micronutrients compared to NPK alone, if present, were small. Wortmann et al. (2019) conclude that the magnitude of the median yield response to a blend of secondary and micronutrients indicates that fertilisation of these nutrients will likely not be profitable, unless well-targeted. However, as micronutrients are required in relatively small quantities, they could be easily blended in with commerically available NPK fertilisers, potentially at low (additional) cost (Joy et al., 2015). The use of such blends would address micronutrient deficiencies in case present and could improve the use efficiency and return on investment of NPK fertilisers (Vanlauwe et al., 2015). In addition, fertiliser blends containing Zn can potentially increase grain Zn concentrations (chapter 4), thereby contributing to alleviation of human Zn deficiency (Joy et al., 2015). Development and distribution of such blends could be a viable, cost-effective option for improving yields and grain Zn concentrations, until areas with micronutrient deficiencies can be clearly identified based on field trials, soil testing, models or maps.

Kihara et al. (2016) showed that application of NPK + manure leads to similar or larger yields compared to fertilising with NPK + secondary and micronutrients. Farmers owning cattle apply most of the available manure close to the homestead, whereas chemical fertilisers are spread evenly across the fields (Zingore et al., 2007b). This suggests that crop deficiencies of micronutrients in some farming systems could be alleviated through better distribution of available manure.

5. Concluding remarks

Based on the results of this thesis, I conclude that Zn and B yield-limitations in maize grown in SSA are not as widespread as earlier assumed. However, adding Zn fertilisers to maize benefits grain Zn concentrations and can potentially contribute to reducing human Zn deficiency. Based on our findings, available pH, SOC and Zn-M3 soil maps can potentially be used to identify areas associated with (i) low maize grain Zn concentrations (ii) strong grain Zn concentration responses to Zn fertilisers and (iii) an elevated risk of Zn dilution in maize grains in high yielding farming systems. This could provide a basis for targeted biofortification strategies.

The general absence of yield responses to Zn and B fertilisation, as observed in the current and literature studies, implies that increasing the use of NPK fertilisers should receive priority over micronutrient fertilisation on the short term for closing yield gaps in SSA. On the long term however, with structural applications of only chemical NPK

fertilisers, problems with Zn deficiency could emerge due to soil Zn depletion. For deriving balanced N, P and K fertiliser recommendations, the QUEFTS model can be used. The P and K transfer functions which we developed, broaden application of QUEFTS in SSA, where M3 data is widely available. Although QUEFTS spatial yield predictions were associated with large uncertainty, our findings highlighted that soil maps can be used as input for QUEFTS to identify differences in expected yields among regions. The yield-limiting nutrient was estimated correctly relatively often, indicating that QUEFTS can potentially be used for deriving regional fertiliser recommendations at low costs, based on soil maps.

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Summary

To feed the growing population in sub-Saharan Africa (SSA), yield levels currently attained in small-holder farming systems need to increase. In combination with other agronomic practices, the use of mineral fertilisers is indispensable for closing yield gaps. In order to increase yields and prevent soil nutrient mining or nutrient losses to the environment, fertilisers need to be applied in balanced ratios. Balanced fertiliser recommendations need to take into account crop nutrient requirements as well as that soils supply part of these nutrients to the crop. In SSA, fertiliser recommendations are often national or regional blanket recommendations, that do not take into account heterogeneity in soil fertility, resource availability, agro-ecological zones and/or crops. Blanket fertiliser recommendations often only include N, P and K, whereas other nutrients can also be yield-limiting. Zinc (Zn) and boron (B) are hypothesised to be yield-limiting in large areas of SSA. Zinc is not only essential for crops, but also for human health. A large part of the African population is estimated to be Zn deficient, which can partly be attributed to low soil Zn availability and consequently low Zn concentrations in crops that grow on them. Increasing grain Zn concentrations through adding Zn fertilisers is seen as a viable option to reduce human Zn deficiency.

Current blanket fertiliser recommendations are unsuitable for sustainably increasing yields across a country and do not address nutritional quality (i.e. Zn content) of yields. Site-specific, balanced fertiliser recommendations are seen as the way forward to close yield gaps. However, obtaining site-specific fertiliser recommendations based on soil testing currently is not (economically) feasible for most small-holder farmers. Therefore, cost-effective tools are needed for predicting nutrient availability and the yield response to fertilisation, taking into account interactions among several plant-essential nutrients that may limit yields.

One of such tools is the widely-used QUantitative Evaluation of the Fertility of Tropical Soils (QUEFTS) model. QUEFTS can be used to predict yields and the yield response to fertilisation. The model has two important assets. First, bioavailability of N, P and K is described as a function of multiple soil properties, rather than based on a single soil test value. As a result, these functions can theoretically be applied to a wide range of soils. Based on QUEFTS definition of bioavailability, i.e. the amount of nutrient uptake in an entire growing season when the nutrient of interest is yield-limiting, similar bioavailability models could be derived for Zn and B. Plant uptake of Zn and B would be predicted based on multiple soil parameters, thereby also bypassing analytical challenges regarding measurement of low micronutrient concentrations in tropical soils.

A second asset of QUEFTS, is that it is unique in taking interactions among nutrients into account and has proven useful for deriving balanced fertiliser recommendation of N, P and K. Available soil maps could be used as input for QUEFTS, thereby potentially refining national blanket fertiliser recommendations at low-costs.

The **general objective** of this thesis was to develop and evaluate models for predicting soil nutrient availability and to increase the understanding of the interactive effect of nutrient availability on crop yields and nutritional quality in sub-Saharan Africa. The focus of this thesis was on availability of macronutrients N, P and K as well as micronutrients Zn and B. To address the general objective, several methods were used, including soil statistical modelling, soil mapping and micronutrient fertiliser omission field trials. The QUEFTS model and its underlying principles were an important component of this thesis. The **specific research objectives** were: (1) to evaluate a spatial application of the QUEFTS model, (2) to derive generic models describing bioavailability of micronutrients zinc and boron based on soil parameters that can be measured in routine analysis and (3) to assess the effect of zinc availability, in combination with availability of other nutrients, on maize yield (quantity) and grain Zn concentrations (nutritional quality). These objectives were addressed in chapters 2-6.

Some modifications were needed for the spatial application of QUEFTS. The Mehlich 3 (M3) soil extraction method is commonly used in SSA and available soil maps are typically based on this method. However, QUEFTS requires P in an Olsen extract and exchangeable K (Exch-K) measured in an ammonium acetate extract as input, in addition to pH and soil organic carbon. In chapter 2, transfer functions were derived that relate K-M3 to Exch-K and P-M3 to P-Olsen. Soil samples from several countries in SSA were analysed for properties that could explain relations among the different extraction methods. Transfer functions for both nutrients were derived through statistical modelling. The results of this chapter show that (i) M3 can be used reliably to estimate Exch-K, likely due to similar extraction mechanisms of both methods, (ii) additional parameters are needed to translate P-M3 to P-Olsen and (iii) M3 may not be a reliable estimator for plant available P, particularly in soils with high amorphous Al contents. We showed that K transfer functions were significantly different between temperate and tropical soils, which we attributed to clay mineralogy. This highlighted the need for specific transfer functions for tropical soils. We also demonstrated that using site-specific M3 soil data as input for QUEFTS, by applying the P and K transfer functions, added limited uncertainty to QUEFTS final yield estimate when compared to using measured P-Olsen and Exch-K data. The P and K transfer functions thus broaden the applicability of QUEFTS when only M3 data is available.

In chapter 3, we applied the transfer functions and QUEFTS to digital soil maps of Rwanda, using two methods. For the first method, models were applied to data points and the final model output was spatially interpolated to develop a map of the target variable (Calculate-then-Interpolate; CI). For the second method, all model input was interpolated to develop individual soil maps, after which the models were applied (Interpolate-then-Calculate; IC). We demonstrated that (i) both methods showed strong differences in outcomes, which was attributed to the non-linear nature of QUEFTS, (ii) the IC method overestimated yields across Rwanda, due to a smoothing-induced increase in spatial predictions of soil parameters and (iii) application of QUEFTS to currently available soil maps led to spatial predictions associated with large uncertainty, irrespective of the method. Despite the uncertainty associated with the spatial yield estimates, the yield-limiting nutrient was estimated correctly in 54% (IC) and 60% (CI) of the evaluation locations. We furthermore demonstrated that spatial patterns in QUEFTS yield and yield-limiting nutrient predictions clearly corresponded to predictions at the underlying point data. This implies that spatial application of QUEFTS can be used to identify differences among regions. Our results show that the CI method is preferred when applying QUEFTS to soil maps, implying that chemical soil data for all relevant input parameters at each calibration location should be collected. The smoothing-induced overestimation of spatial P-Olsen, Exch-K and consequent yield predictions by the IC method, implies that maps developed with this method should be interpreted with care, especially when used for the development of fertiliser recommendations. Of the soil parameters, P-M3 and K-M3 maps were associated with the largest uncertainty. Improving the quality of these maps, by using covariate data at a higher spatial resolution (30-100m) than used in the current study (250m), could potentially benefit spatial P-Olsen, Exch-K and QUEFTS yield and yield-limiting nutrient predictions.

In chapter 4 and 5, using data from micronutrient fertiliser omission field trials with maize in Kenya, Zambia and Zimbabwe, we attempted to derive models describing bioavailability of Zn and B. Despite soil and plant concentrations pointing towards potential yield-limitation of both nutrients, a positive yield response to fertilisation with either Zn or B was generally absent. This shows critical soil Zn and B concentrations reported in literature, require more validation in field trials. Soil Zn and B levels, determined with the 0.43 M HNO_3 extraction method, were related with uptake of these nutrients. Zinc extracted with the 0.43M HNO_3, DTPA and M3 extraction methods was a better proxy for Zn uptake than the 0.01 M $CaCl_2$ extraction method, indicating that the capacity of the soils to buffer micronutrients was more relevant for describing bioavailability than the actually available pool of these nutrients. However, chemical soil

parameters generally described limited variation in Zn (35%) and B (21%) uptake. The weak relations likely have been caused by the fact that Zn and B were not yield-limiting, as demonstrated by a lack of yield response to fertilisation with these nutrients. Our results showed that the Zn uptake response to Zn fertilisation was high in low pH, low soil organic carbon soils, indicating that a high Zn fertilisation efficiency can be expected in soils with a low adsorption affinity for Zn. Our results provided insights into the B pool that is extracted with the hot water method, commonly used for assessing B availability. The hot water method extracted twice the amount of B compared to 0.43 M HNO_3, indicating that this method could overestimate the potentially available B pool. Our results suggest that the hot water method extracts B from undecomposed organic matter, which is not extracted by the 0.01 M $CaCl_2$ and 0.43 M HNO_3 methods.

With regards to human health, we showed that fertilising with 5 kg Zn ha^{-1} increased grain Zn concentrations in 77% of the blocks, despite not increasing maize yields (chapter 4). The average increase in grain Zn concentrations was 20% (2.4 mg kg^{-1}) compared to the situation where Zn was not fertilised. Similar to Zn uptake, high responses in grain Zn concentrations to Zn fertilisation were associated with low soil pH and organic carbon contents. In both chapter 4 and 6, we showed that soil Zn concentrations generally explained limited variation in grain Zn concentrations. We also demonstrated different relations between maize grain and soil Zn concentrations for each of the three countries where micronutrient fertiliser omission trials were executed (chapter 4). As different maize varieties were grown in each of the three countries, we could not identify whether the different relations could be attributed to a variety-effect or other agro-ecological factors. The HarvestPlus target of 38 mg Zn kg^{-1} in maize grains is considered adequate for combatting human Zn deficiency. Attaining this target, by applying Zn (chapter 4) or N fertilisers (chapter 6) to current commercially available maize varieties, is not possible without compromising yield levels. Our results also suggest that (i) higher grain Zn concentrations can be expected in soils with higher organic matter content and (ii) high availability of N, P and K, either due to fertilisation or a high native soil fertility, may mask yield-limitations by Zn. Increasing soil organic matter contents and applying balanced/optimal NPK fertilisation likely will also increase yields. Additionally, we showed that increasing yields through application of N(PK), could lead to a dilution of grain Zn concentrations on soils with low Zn availability, implying that co-application of Zn to macronutrients on these soils may be required. These findings provide a basis for developing management strategies that can increase grain Zn concentrations, as well as yields.

In chapter 7, I summarised the main findings of this thesis, discussed their limitations and provided recommendations for future research. I also discussed the practical implications of my work. I put special attention on the question whether micronutrient availability indeed is limiting (maize) yields in SSA and reviewed literature studies that have claimed this. I concluded that Zn and B yield-limitations in maize grown in SSA are not as widespread as earlier assumed, but that addition of Zn fertilisers to maize can contribute to reducing human Zn deficiency in the African population by increasing grain Zn concentrations. The general absence of yield responses to Zn and B fertilisation implies that increasing the use of NPK fertilisers should receive priority over micronutrient fertilisation to close existing yield gaps in SSA. For deriving balanced N, P and K fertiliser recommendations, the QUEFTS model can be used. The P and K transfer functions which we developed, broaden application of QUEFTS in SSA, where M3 data is widely available. Although QUEFTS spatial yield predictions were associated with large uncertainty, our findings highlighted that soil maps can be used as input for QUEFTS to identify differences in expected yields among regions. The yield-limiting nutrient was estimated correctly relatively often, indicating that QUEFTS can potentially be used for deriving regional fertiliser recommendations at low costs, based on soil maps. Additionally, based on our findings regarding Zn availability and fertiliser response, available pH, SOC and Zn-M3 maps can potentially be used to identify areas associated with (i) low maize grain Zn concentrations (ii) strong grain Zn concentration responses to Zn fertilisers and (iii) Zn dilution in maize grains in high yielding farming systems. This could provide a basis for targeted biofortification strategies.

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About the author

Mirjam S. Breure was born in Delft, the Netherlands, on the 24th of February 1990. Growing up as the daughter of a tomato grower in Westland, the love for food production was instilled at a young age. With biology as a favourite subject in secondary school, Mirjam decided to study Biology at Wageningen University in 2008. Within the first year, she switched to the more applied study of Plant Sciences. During her BSc, Mirjam discovered her passion for sustainable agriculture and food security. Following up with an MSc in Plant Sciences, she specialised in the analysis and modelling of nutrient uptake, crop growth and farming systems. As part of her MSc, Mirjam took an internship with the N2Africa project in 2013, working with smallholder farmers in South-Western Uganda. During this internship, she saw the many challenges that farmers in rural Africa have to deal with: poor soil fertility, low yields, limited (financial) access to inputs and crop failure due to irregular rainfall. Her time in Uganda increased the desire to work on issues related to food security. After a brief pause from academia, working as a junior researcher in a consultancy company, Mirjam started her PhD within the project 'Micronutrients for better yields' in 2016. This PhD provided a great opportunity to learn more about relations between soils, plants and human health and further develop data analysis, modelling and soil mapping skills. In her free time, Mirjam likes to read, garden and cook.

PE&RC Training and Education Statement

With the training and education activities listed below the PhD candidate has complied with the requirements set by the C.T. de Wit Graduate School for Production Ecology and Resource Conservation (PE&RC) which comprises of a minimum total of 32 ECTS (= 22 weeks of activities)

Review of literature (4.5 ECTS)
-Modelling micronutrient bioavailability

Post-graduate courses (9.4 ECTS)
-GIS in practice; PE&RC (2016)
-Introduction into R for statistical analysis; PE&RC (2016)
-R Specialisation data science at Coursera platform; John Hopkins University (2016)
-R for spectroscopy research and interpretation of soil spectra; Pedometrics (2017)
-Spring school; ISRIC (2017/2018)
-Farming systems and rural livelihoods; PE&RC (2018)

Invited review of (unpublished) journal manuscript (5 ECTS)
-Field Crops Research: nutrient deficiencies in maize (2016)
-Plant and Soil: effects bacteria & zinc application on productivity of wheat (2017)
-Plant and Soil: effect of soil factors on wheat grain Zn concentration (2017)
-Scientia Horticulturae: effect of soil and organic matter addition on wild versus domesticated Cichorium spp (2019)
-Frontiers in Plant Science: antagonism between phosphorus and zinc supply in Brassica spp (2019)

Competence strengthening / skills courses (3 ECTS)
-Workshop the choice; ESG (2016)
-Teaching and supervising thesis students; Educational Staff Development, Wageningen University (2017)
-The essentials of scientific writing and presenting; WGS (2017)
-Basic safety and security; Centre for Safety and Development (2018)

Scientific integrity / ethics in science activity (0.6 ECTS)
-Research integrity ethics; WGS (2016)

PE&RC Annual meetings, seminars and the PE&RC weekend (2 ECTS)
-PE&RC First years weekend (2016)
-PE&RC Day (2016)
-PE&RC Midterm weekend (2019)
-The last stretch; online; WGS (2021)

Discussion groups / local seminars or scientific meetings (4.8 ECTS)
-Plant soil interaction discussion group (2016-2017, 2020-2021)
-Sustainable intensification of agricultural systems discussion group (2017)
-Using satellite data for soil analysis, seminars at Eurofins (2017)
-Visit to Nottingham University and Rothamsted for collaboration (2018)
-Staff seminars PPS/CSA (2018-2021)
-International Symposium of Soil and Plant Analysis (2019)
-Soil cluster discussion groups (2019-2021)
-Several seminars (2020-2021): ESG lunch meetings, Wageningen student farm, Dies Natalis, Resource debates organic agriculture, Soil on one platform meetings, meeting plant-herbivore interactions, annual circular farming forum, Plant microbiome discussion meetings.

International symposia, workshops and conferences (4.7 ECTS)
-International plant nutrition colloquium; Copenhagen, Denmark (2017)
-Zinc symposium; Leuven, Belgium (2018)

Lecturing / supervision of practicals / tutorials (3 ECTS)
-Nutrient management, rewriting course material (2017)
-Soil plant interactions (2017-2020)
-Lecturing; FCE University, Zambia (2019)
-Nutrient management (2019/2022)

BSc/MSc thesis supervision (18 ECTS)
-Developing pedo-transfer functions for QUEFTS
-Low Zn soils in the Netherlands (supervision of 3 students)
-Improving a pot trial method to analyse the growth limiting nutrient
-Setting up field trials and educating non-academic students on applying science (internship)

Colofon

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