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Virtual Fertilizer Research Center

Contents

List of acronyms and abbreviations

IFDC	International Fertilizer Development Center
Se	Selenium
VFRC	Virtual Fertilizer Research Center

1 Summary

Selenium (Se) is an essential micronutrient for humans, animals and certain lower plants, and its supply in global food systems is highly variable. The variation of Se status in humans largely depends on their diet, which is strongly related to the geographical variation in soil's Se level. Selenium deficiency is regarded as a major health problem for 0.5 to 1 billion people worldwide. Whereas the global importance of selenium deficiency has been recognized for decades, strategic micronutrient interventions to overcome this deficiency are still limited. Basically, there are two groups of fortification strategies available to increase Se intake worldwide. First of all, human Se intake may be increased by supplementation of livestock, direct food fortification or supplementation with Se pills. Alternatively, agronomic strategies like plant breeding and fertilization can be used to increase Se uptake of staple food crops. We argue that the best strategy depends on the natural, societal and economic properties of local agro-ecosystems. Adapting the fortification strategy to the local properties of an agro-ecosystem is the way forward to solve Se deficiencies worldwide without resource exhaustion of the worlds' scarce Se resources and potentially harmful environmental side-effects.

An essential part of such an agro-ecosystem approach will be a robust and reliable fertilizer strategy that takes the spatial and temporal variability in climatic conditions, soil properties and cropping systems into consideration. Selecting the proper fertilizer strategy requires a mechanistic understanding of Se plant-soil-atmosphere cycling and insights in plant availability of added Se fertilizers.

The research presented in this report aims to identify when applying Se fertilizer is effective in specific agro-ecosystems based on an inventory of specific production-ecological causes for its deficiency in relation to fertilizer application. Important factors controlling Se availability and uptake are identified using meta-analysis and are integrated in a framework for a decision support tool that guides users in the selection of effective fortification strategies. This research primarily focuses on fertilization as a fortification strategy, but other strategies are briefly introduced and evaluated.

The review and meta-analysis indicate that fertilizer doses need to match crop demand with Se supply, given the capacity of soils to supply or retain Se during the growing season. Main soil properties controlling crop uptake efficiency of applied Se include acidity, redox potential, texture and organic matter. Agronomic practices such as liming, irrigation and basic fertilization (nitrogen, phosphorus and sulfur) additionally affect the crop uptake efficiency. Adapting fertilizer strategies to the local agronomic situation and soil properties can increase the crop uptake efficiency from 10% (common situation) up to 50%. Important fertilizer strategies include:

- The use of a site specific fertilizer dose: Se fertilizer use should account for the Se supply and availability in the soil and any residual effects of former Se fertilizer applications.
- The choice for a specific Se fertilizer: Selenate is about 8 times more effective on the short term than selenite and has smaller residual effects.
- Application technique: Both foliar- and soil-applied fertilizers are able to enhance Se uptake, but foliar application is more resource efficient. Seed coating can be an alternative, but the crop uptake efficiency is usually less than 10%.
- Application timing: Fertilizer application during the growing season results in higher Se levels in the crop in comparison with fertilizer applications before the growing season.

By far, the most resource-efficient way to increase the Se intake in the world's population appears to be by adding Se to food products along the production chain. The positive effects of food processing is however limited by the fact that a limited number of people have access to processed foods, particularly in developing countries.

Fortification through agronomic practices can therefore be an efficient and effective approach to increase human (and animal) Se intake through simple techniques that can be integrated in current farm management. Plant breeding for enhanced Se uptake efficiency and Se fertilization are currently the most promising agronomic strategies to increase Se status of human populations as they can deliver increased Se to a whole population safely, effectively, efficiently and in the most suitable chemical forms. These strategies might also be complementary to fortification strategies like food processing. Social and economic factors such as the availability of Se-enriched fertilizers and governmental incentives and regulations are needed to increase farmers and public acceptance of fortification programs and Se-enriched food products. The developed decision support tool integrates all these aspects in such a way that it can be applied to any agro-ecosystem.

In summary, agro-ecosystem-dependent fortification strategies are necessary to increase human Se intake without exhaustion of the worlds' scarce Se resources. The use of Se fertilizers is currently one of the most promising strategies, in particular when the fertilizer strategy (dose, formulation, application and timing) is adapted to the local properties of an agro-ecosystem.

2 Introduction

2.1 Background

Selenium (Se) is an essential micronutrient to humans, for animal health and animal product quality, with indications that it is also beneficial for crop growth and quality (Haug et al., 2007). The first clear indication that Se plays a vital role in the metabolism of biological life was obtained in the late 1950s by Swartz & Foltz (1957). Since then, numerous studies have investigated the origin, cycling and bioavailability of Se in terrestrial and aquatic ecosystems, including its effect on animal and human health (Reilly, 1996; Combs, 2001; Rayman, 2000, 2002, 2012). There is ample evidence now that Se is critical to the health of living organisms: it is a component of several major metabolic pathways including thyroid hormone metabolism, antioxidant defense systems and immune functioning (Winkel et al., 2011). The range of intake between which Se deficiency and toxicity occurs is relatively narrow, with current estimates suggesting that intakes below 40 µg day^{-1} are inadequate and those exceeding 900 µg day^{-1} are potentially harmful (WHO, 1996; Yang & Zhou, 1994). National and international agencies have therefore set dietary reference values in the range of 30-55 µg day-1 (WHO, 2004), although they may vary from 25 up to 125 µg day^{-1} depending on country or expert body (Fairweather-Tait et al., 2011; Hurst et al., 2013).

Because the world's population is expected to reach 9.1 billion (FAO, 2009) by 2050, sufficient and high quality food production is one of the most serious global challenges of humankind (Carvalho et al., 2013). Preventing widespread micronutrient malnutrition will result in positive socio-economic impacts at individual, community and national levels (Darnton-Hill et al., 2005). Currently, the vast majority of the world's population has suboptimal Se intakes, resulting in increased risk for cancer, cardiovascular diseases, viral diseases and other conditions that involve increased levels of oxidative stress (Combs, 2001). While the global importance of Se deficiency has been recognized for decades, strategic micronutrient interventions to overcome this deficiency are still limited. Basically, there are two groups of fortification strategies available to increase Se intake worldwide. First of all, human Se intake may be increased by supplementation of livestock (to increase Se levels in animal products), food fortification (addition of Se directly to food) and supplementation of individuals using Se pills. Alternatively, increased human Se intake may be achieved by agronomic strategies aimed at increasing the Se concentration in plants. These agronomic fortification strategies include plant breeding for enhanced Se accumulation and the use of Se fertilizers and seed enrichment protocols to increase Se uptake of crops.

2.2 An agro-ecosystem approach

The variation of Se status in humans largely depends on the diet. Plant foods are the major dietary sources of Se, followed by meats and seafood. This variation in turn largely depends on the geographical variation of Se levels in soil (Steines, 2009). Fortification strategies aiming to increase global Se intake should therefore take pedo-climatic differences around the world into consideration, together with differences in societal and economical drivers. For example, agronomic fortification strategies are usually preferred in developing countries where commercial food fortification may not be practical or even possible due to lack of centralized food processing plants (Miller & Welch, 2013). In addition, the world's rare Se resources need to be managed carefully so that this vulnerable resource is not squandered (Haug et al., 2007). Understanding the agronomic, economic and societal factors controlling human Se uptake (and resource efficiency) will evidently guide the strategic targeting of impactful fortification strategies. We call this an agro-ecosystem approach.

An essential part of an agro-ecosystem approach is a sound fertilizer management strategy that increases Se uptake efficiency while reducing possible environmental risks. Selecting the proper fertilizer strategy requires mechanistic understanding of Se cycling in soils and insights in plant availability of supplemented Se fertilizers. The development of an agro-ecosystem specific fertilizer strategy is stimulated by a recent call of the Virtual Fertilizer Research Center that focuses on impactful cases for micronutrient fertilizer interventions. The Nutrient Management Institute in Wageningen ultimately aims to solve this challenge by the development of a web-based decision support tool that couples the proper fortification strategy to the local properties of an agro-ecosystem (Figure 1).

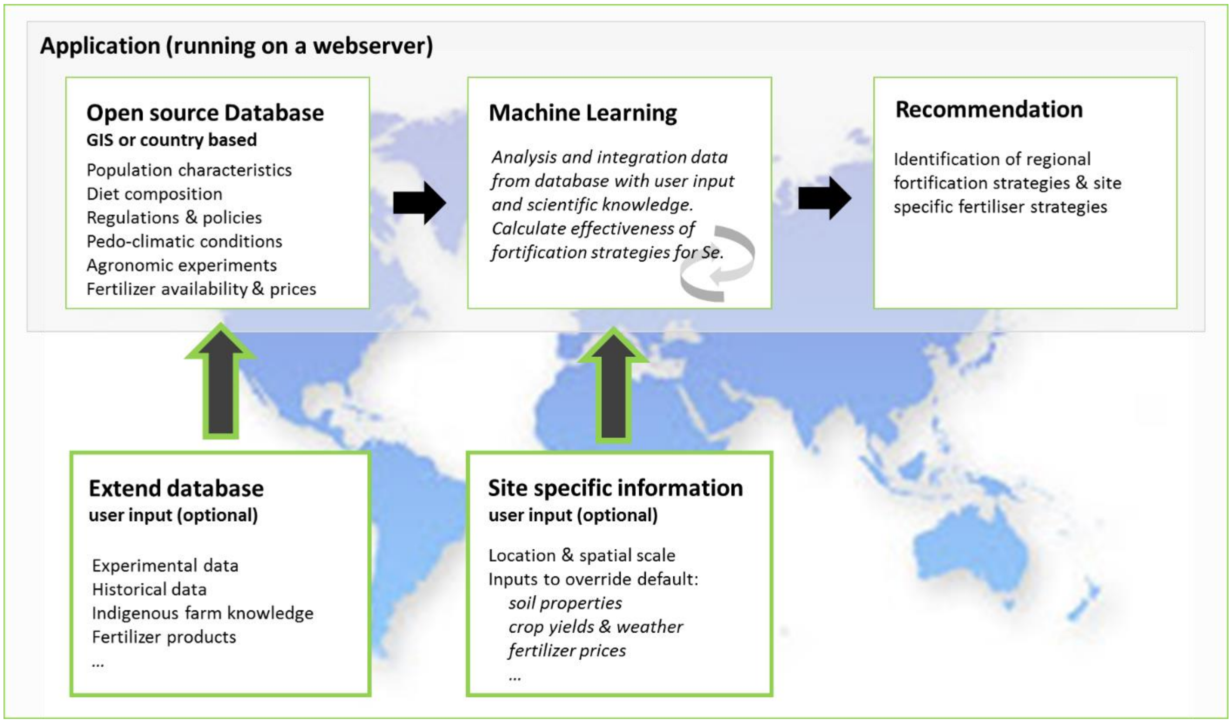

Figure 1. Conceptual framework of a decision support tool selecting best fortification strategy.

In more detail, when the pathways of Se in soils are unraveled, it might be possible to integrate the complex interactions between soil properties, weather conditions, cropping systems and fertilizer management in an on-line decision support tool. This support tool can be used to assist farmers and policymakers to underpin and optimize their fortification strategy. Basically, such a decision support tool recommends any user which strategy best fits the local conditions within any agro-ecosystem. The fertilizer strategy not only covers the required dose, but also the formulation (which Se species), timing and application techniques.

Adopting proper fortification strategies to the local conditions within and among agro-ecosystems will certainly increase crop uptake, crop recovery and finally human intake of Se without resource exhaustion of the worlds' scarce Se resources.

2.3 Objective

The research presented in this report aims to identify when applying Se fertilizer is effective in specific agro-ecosystems based on an inventory of specific production-ecological causes for its deficiency in relation to fertilizer application. Important factors controlling Se availability and uptake are identified using meta-analysis and are integrated in a framework for a decision support tool that guides users in the selection of effective fortification strategies. The results of this review and meta-analysis will also aid in understanding the relevance of a fertilizer pathway compared to alternative ways of resolving micronutrient related health problems.

3 Selenium in soils around the world

3.1 Introduction

Because geographic differences in the content and bioavailability of Se in soils have a marked effect on the Se status of crops and even entire communities (FAO, 2013), this chapter reviews the mechanisms controlling the fate of Se in soils. First of all, it describes the current variation in Se levels in the world and the main global transport routes. Additionally, it describes the processes controlling the speciation between different forms of Se in the soil and plant availability. Thirdly, the main methods used to assess the bioavailability of Se in soil are shortly introduced, after which a few comments are made regarding climatic and temporal variation in Se levels of soils.

3.2 Global inventory of Se budgets and Se levels in soils

Selenium is a rare element on our planet with an average concentration in igneous bedrock of only 0.05 mg kg^{-1}, which is less than for any other nutrient (Haug et al., 2007). Pool sizes of Se in the lithosphere, fossil fuel deposits, oceans, rivers, soils and biomass are summarized in table 1.

Table 1. Global inventories of Se in selected environmental compartments (Source: Haygarth, 1994)

Reservoir	Reservoir Mass (g)	Se Concentration (µg kg^{-1})	Se Pool (g)
Lithosphere (down to 45 km)	57 x 10^{24}	50	2.8 x 10^{18}
Soils (down to 1.0 m)	3.3 x 10^{20}	200 – 400	1.3 x 10^{14}
Fossil fuel deposits	5.6 x 10^{19}	200 – 3400	1.44 x 10^{14}
Terrestrial biomass	1.3 x 10^{18}	50 – 150	6.98 x 10^{10}
Oceans & polar ice	1.5 x 10^{24}	< 0.01 – 3000	1.31 x 10^{14}
Atmosphere*	-	-	1.3-1.9 x 10^{10}
Rivers & groundwater	3.3 x 10^{23}	< 1 – 800	1.01 x 10^{14}
Se reserves	–	–	112 x 10^{9}
Se resources	–	–	291 x 10^{9}

** No estimates of atmospheric Se pool size are available. Data represent the estimated global annual flux.*

The Se reserves that are technically and economically feasible to mine are currently estimated at 98000 tons whereas the annual mining productivity is estimated at 2000 tons per year (US Geological Survey, January 2013). The ratio between reserves in mining and production from mining can be used as an indicator of expected availability (Voortman, 2012). The most recent estimates indicate that there is sufficient Se available for about 48 years. Others indicate that Se reserves will be exhausted in 39 to 47 years (Voortman, 2012; Chardon & Oenema, 2013). Consequently, Se can be considered as a scarce nutrient which need to be used in a sustainable and resource efficient way. Any agronomic fortification strategy using Se fertilizers should therefore maximize the crop uptake efficiency of the applied Se.

In 2007, Haug et al. estimated how much Se is needed to cover the Se requirements for the world's human and livestock population. Using a recommended Se intake of 50 µg day^{-1} person^{-1} and 100 µg day^{-1} animal^{-1} they estimated that 249 tons of Se are annually required to prevent Se deficiencies worldwide. The world's annual Se production via agriculture and fisheries is about 400 tons. Hence, this amount of Se – if evenly distributed – is enough to supply 100 µg day^{-1} for each person and each head of livestock in the world, but it is not enough to prevent certain cancers (daily intake recommendations may increase up to 250 µg Se day^{-1}). As the intake is unevenly distributed throughout the world, the requirements would actually be higher than these estimates. The annual Se production via mining industries is roughly enough for the fertilization of 75% of all arable land or 40% of all pastures (with a dose of 20 g ha^{-1}). The more recent studies of Voortman (2012) and Chardon & Oenema (2013) emphasize the importance of sustainable Se fertilizer use since they conclude that current industrial production is entirely insufficient to meet the required demand from the food chain. In addition, the production is inherently difficult to increase, since Se is recovered primarily as a by-product of copper refining.

Selenium is cycled through environmental pools via both natural and anthropogenic processes (Haygarth, 1994; Nriagu, 1989; Figure 2). The main natural sources of Se are from volcanic activity and weathering of sediments and rocks (Girling, 1984). Anthropogenic Se sources arise from metal processing, fuel combustion and the use of Se-containing products like fertilizers, lime and manures.

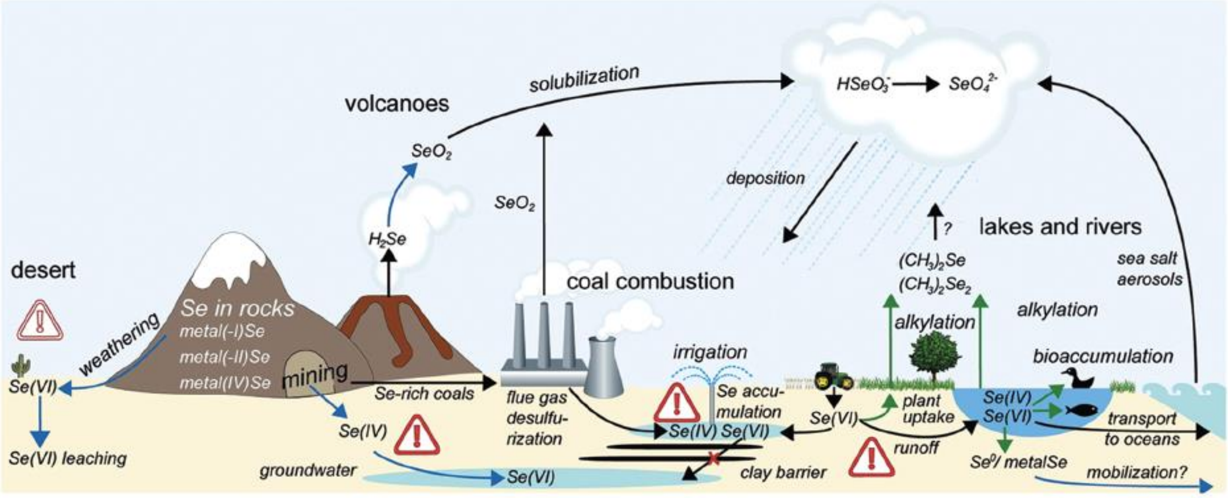

Figure 2. Schematic global cycle of Se with for the terrestrial environment (Winkel et al., 2011).

Selenium in the soil is ultimately derived from the parent material in the bedrock. Its content markedly depends on the origin and geological history of soil on the one hand, and on the other hand is controlled by mineralogical characteristics of the parent material, degree of weathering of mineral constituents and soil formation processes (Hartikainen, 2005). Selenium levels range from near zero to 1250 mg kg^{-1} soil (Oldfield, 2002) where soils in northern Europe are particular low in Se (Bitterly et al., 2010; Gupta & Gupta, 2000). Seleniferous soils are often located in relatively small hotspots derived from Se rich rocks or from irrigation with Se rich waters (Winkel et al., 2011). In general terms, high Se soils largely come from sedimentary rocks whereas low Se soils are typically derived from igneous rocks (Tamari, 1998). Clayey soils contain relatively more Se than sandy soils due to the presence of Se-enriched minerals such as biotite on the one hand, and higher levels of aluminum and iron oxides forming main components for Se sorption on the other. In organogenic soils, the native Se content varies depending on the origin of the soil (Hartikainen, 2005).

An extensive soil survey done in 1992 for 30 countries shows that mean Se levels vary from 4.0 mg kg^{-1} soil in Zambia up to 29.3 mg kg^{-1} soil in Pakistan (recalculated from Sillanpää & Jansson, 1992; AAAc-EDTA extractable

Se). The total variation within countries is usually high, with coefficients of variation ranging between 33 and 117 percent. On a global scale, Se-deficient areas are far more common than toxic ones (Hartikainen, 2005).

Marine environments are an important source of Se to the global Se cycle via transfer through the atmosphere (Wen & Carignan, 2007). According to recent estimations of the global Se budget, approximately 13,000 to 19,000 tons of Se are annually cycled through the troposphere due to evaporation of volatile Se compounds. The atmosphere is in turn a significant source of Se for the terrestrial environment via dry or wet deposition (Cooke et al., 1987; Amouroux et al., 2001; Wen & Carignan, 2007).

3.3 Selenium speciation and plant availability

It is important to note that it is not primarily the total Se content in the soils that is responsible for Se uptake in plants and organisms, but rather the bioavailable part which dictates the entrance of Se in terrestrial food chains. The bioavailability and toxicity of Se depend on the predominant chemical Se form (or speciation), which greatly depends on prevailing geochemical parameters such as pH and redox conditions, soil organic carbon, clay content and microbial activity (Martens, 2003; Lyons, 2010; Johnsson, 1991). Nevertheless, total soil Se levels are positively associated with crop Se uptake: soils with high Se levels have on average higher Se contents in harvested crop. The extensive soil survey across 30 countries (Sillanpää & Jansson, 1992) showed for example a positive relationship (r = 0.634, n = 3644) between Se levels in soil and harvested crops (Figure 3).

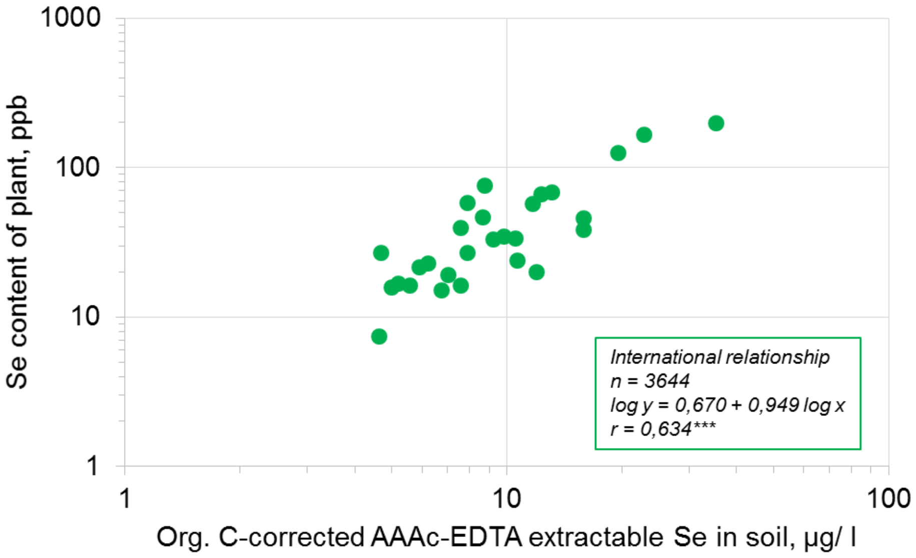

Figure 3. Relationship between soil extractable Se and the natural Se content of plants for 30 countries around the world (Source: Sillanpää & Jansson, 1992).

The plant availability of Se in soils strongly depends on its chemical speciation and prevailing soil conditions. Selenium can exist in different oxidation states varying between plus six and minus two (Russell, 1988). The different forms of Se include selenate (SeO_4^{2-}), selenite (SeO_3^{2-}), elemental Se (Se^0) and selenide (Se^{2-}). It also forms catenated species, such as volatile diselenides (Hartikainen, 2005). The Se speciation is basically controlled by three transformation mechanisms: oxidation vs. reduction, mineralization vs. immobilization, and volatilization. The rate coefficients of these transformations vary depending on Se species, microbial activity, pH-redox conditions and the properties of the soil matrix (Chasteen, 1998; Dungan & Frankenberger, 1999; Martens, 2003; Stavridou, 2012; Figure 4). Plants acquire Se predominantly as selenate, as well as selenite and organic compounds such as Se containing amino acids (Zayed et al., 1998; Hopper & Parker, 1999; Zhao et al., 2005).

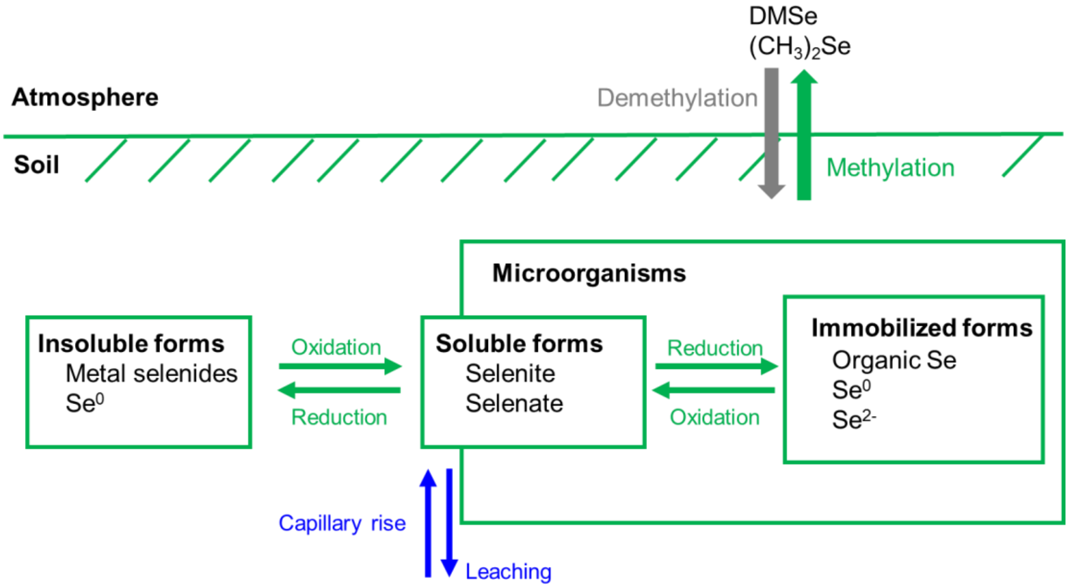

Figure 4. Schematic Se cycle in soil (adapted from Flury et al., 1997).

In more detail, inorganic Se is generally found as the anions $HSeO_4^{2-}$, SeO_3^{2-} and $HSeO_3^-$ (Figure 5) in well aerated soils. Selenate is the most common species in neutral and alkaline soils. The predominance of selenate is mainly due to a higher affinity of selenite for irreversible sorption to iron oxides, clay minerals and soil organic matter. Selenite sorption increases at low pH (due to positive surface charge of oxides) or high salt concentrations. Liming of soils is therefore a well-known strategy to increase Se availability in the soil solution (Cary et al., 1967; Gissel-Nielsen, 1971; Gupta & Winter, 1981; Neal et al., 1987). Soil texture affects the fate of Se in soil due to the presence of clay minerals and texture induced water retention properties. Clay minerals with 1:1 clays have for example a higher fixation capacity than 2:1 clays (Gissel-Nielsen, 1977). How organic matter affects the dynamics of Se is unclear. Several studies showed increased adsorption of selenite in soils with high levels of organic matter (Bisbjerg & Gissel-Nielsen, 1969; Levesque, 1974; Singh et al., 1981), suggesting a lower plant availability but studies showing increased Se availability under high organic matter levels are also present (Davies & Watkinson, 1966; Falk Ogaard et al., 2006). An increase in Se sorption due to organic matter amendments can be explained by enhanced immobilization of Se, the transformation of selenate to less available forms or by increased metal mediated sorption (Neal & Sposito, 1991; Alemi et al., 1991; Ajwa et al., 1998; Sogn et al., 2007). Furthermore, the presence of anions (sulfate, phosphate, organic anions, etc.) competing for the same sorption sites contributes to the availability of Se (Elrashidi et al.,1987; Neal 1995; Fordyce 2005; Hartikainen 2005).

Under reduced soil conditions, the predominant Se species is selenite because selenate is rapidly reduced to selenite. Elemental Se may also be present, but its contribution to the Se pool in soil solution is small (Cary & Allaway, 1969). The most common Se species in reduced natural environments however is the hydrogen selenide species, often in combination with metals. These heavy metal selenides are the most insoluble form of Se.

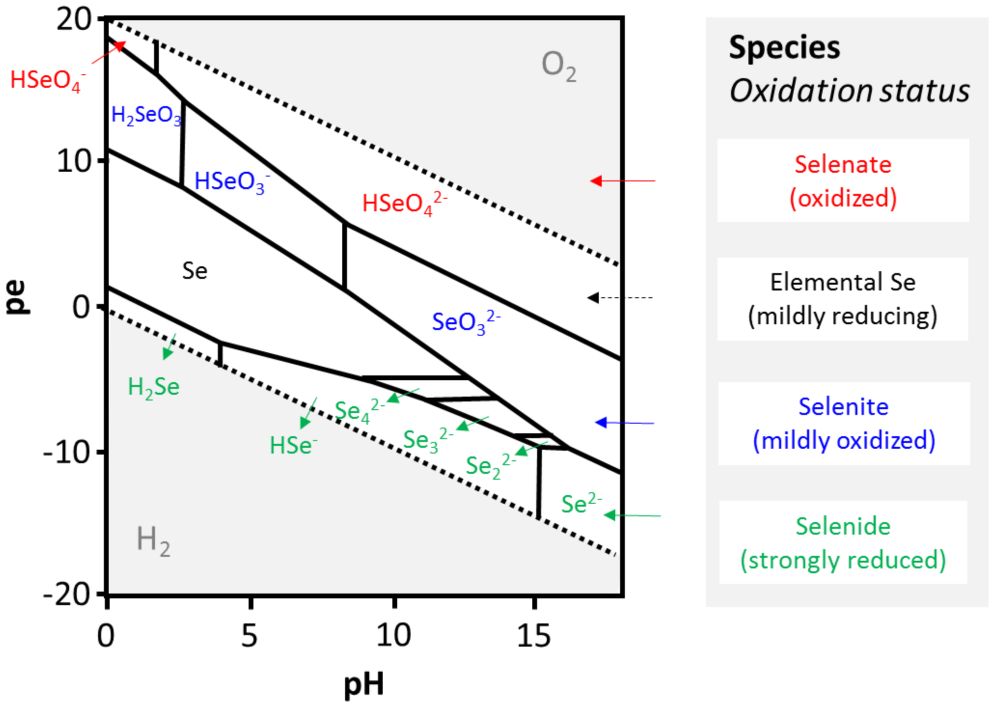

Figure 5. Speciation diagram Se in relation to pe and pH ($[Se]_{tot}=10^{-6}$ mol l^{-1}; Bruggeman, 2007).

Because chemical, biological and physical soil properties vary among agro-ecosystems, it is not surprising that the capacity of soils to supply Se is characterized by high spatial variability. Knowing the aforementioned transformation mechanisms and the Se speciation in soils, the most important soil properties controlling the supply of Se are soil acidity and aeration, texture, organic matter content and the presence of competitive ions (Mikkelsen, 1989; Sors et al., 2005; White et al., 2007). Generally, selenite is the common plant available Se species for well aerated soils with acid and neutral pH values. In neutral and alkaline soils, the selenate species predominates and is generally soluble, mobile and readily available for plants. Under reduced soil conditions, both selenate and selenite are easily plant available, but selenite predominates due to rapid reduction of selenate to selenite.

3.4 Determining soil Se supply

Because the fate of plant-available Se is governed by a complex interaction of abiotic and biotic processes, the total Se content of a soil is not a reliable indicator for the actual supply of Se for crop uptake. The distinct differences in solubility of Se species in soil have led to the development of numerous single and sequential extraction procedures aiming to extract a specific operationally defined and plant available Se fraction. Most published data are determined with relatively strong extraction methods since only recent analytical developments make it possible to quantify Se levels as present in weak extraction methods (Winkel et al., 2011). The most soluble Se forms are usually extracted with water or simple salt solutions (Keskinen, 2003; Wright et al., 2003). The main Se species measured in these weak extraction methods are selenate and Se compounds within or associated with dissolved organic matter. The weakly adsorbed pool of selenium is usually determined by extraction methods based on ligand exchange: the selenite is replaced by phosphate for example. The adsorbed Se species may also be extracted with more aggressive salt solutions such as acid ammonium oxalate or concentrated HCl. Extractions of organically bound or inorganically associated reduced selenides rely on oxidizing agents such as H_2O_2, $K_2S_2O_8$ or NaOCl. Total

Se contents in soil are usually determined after extraction with a mixture of strong acids. None of the aforementioned extraction methods is currently able to estimate the plant available Se pool in soils across different pedo-climatic regions. This might be explained by the fact that soil properties may have contrasting effects on the Se levels acquired by crops and the levels extracted by chemical methods. The applicability of various extraction methods to mimic crop uptake has therefore shown inconsistent results.

Another option to quantify the capacity of soils to supply Se is the use of multiple regression models fed with soil properties and size of Se pools in soil. Over a wide range of soil properties (usually the driving factor explaining the statistical power of such relationships) Sillanpää & Jansson (1992) reported a highly significant linear relationship between AAAc-EDTA extractable Se in soil and the Se content in maize and wheat crops. Including soil properties or environmental variables into regression models (linking soil Se levels to crop uptake) usually lead to marked improvements in the percentage explained variation (e.g. Sillanpää & Jansson, 1992; Spadoni et al., 2007). For example, Weng et al. (2010) recently showed that the Se content in grass can be predicted with the Se content of Dissolved Organic Carbon fractions in combination with available selenate, phosphorus and sulfate. Nevertheless, the model uncertainty of these statistical models is usually too high for implementation in fertilizer recommendation systems. Further up scaling, validation or simplifying of analysis methods are needed before these models can be applied on a global scale.

The buffer capacity is considered to be important to estimate the capacity of soils to supply Se: it is the capacity of a soil to sustain certain Se levels in soil solution. The buffer capacity of soil depends on the interaction between stable and bioavailable Se pools in soil, but the quantification of this interaction is still a topic of research. Due to strong variation among countries, no universal analysis protocol is currently available. Up to now, country or region specific analysis protocols need to be used in order to include an estimate of the soils' buffer capacity in fertilizer strategies. Combining soil Se levels with other driving variables in multiple regression models is currently the best option to make a robust estimate of the capacity of soils to supply Se.

Interestingly, Winkel et al. (2011) recently suggested that coupling of LC-(ICP-MS) speciation approaches (for separation and quantification) with high-resolution tandem MS (for identification) will play an essential role in future research concerning the fate of Se in the environment. Synchrotron and (high-resolution) mass spectrometry techniques give information on the kinds of species that are present and their mobility based on respectively the analyses of solid and liquid samples. They foresee that newly obtained geochemical knowledge on Se will pave the way for the development of predictive models based on both geochemical and GIS data. This consequently will result in GIS-based modeling approaches predicting Se distribution and availability on regional to global scales (Figure 6).

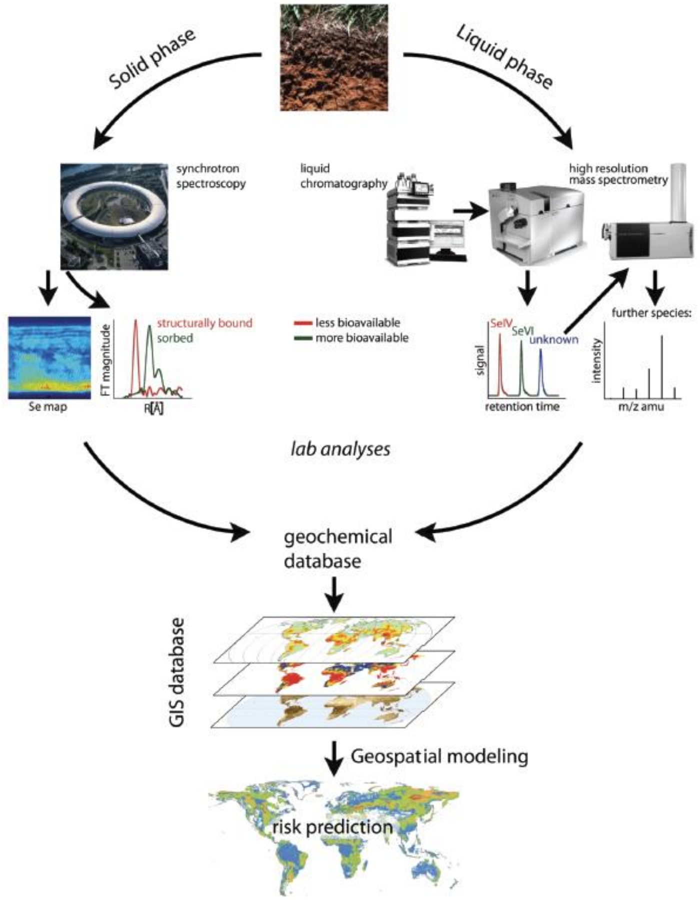

Figure 6. Schematic diagram showing the state-of-the-art analytical techniques that are available to study the behavior of Se in terrestrial environments and how these geospatial information will be integrated in spatial explicit regional models for risk prediction purposes (Source: Winkel et al., 2011).

3.5 Selenium in plants

The uptake of Se differs among crops and they are subsequently classified as accumulator, indicator or non-accumulator crops (Bitterly et al., 2010). Accumulator crops are able to grow on seleniferous soils and might accumulate Se to levels of more than 4.000 mg kg^{-1}. Most agricultural forage and arable crops are however non-accumulators and contain less than 25 mg kg^{-1}. Although there is no evidence for Se requirements in agricultural crops, there is ample evidence that Se fertilization enhances crop growth in soils with low Se availability. This positive effect on crop yield was shown for lettuce, ryegrass, potato, tea, rice, soybean and mustard (Xue et al., 2001; Hartikainen et al., 2000; Turakainen et al., 2004; Hu et al., 2003, Liu et al., 2004; Djanaguiraman et al., 2005; Stavridou, 2012). The physiological and molecular mechanisms involved are still a topic of research.

The uptake pattern of Se parallels the uptake mechanism of sulfate due to the physical and chemical similarities between both elements (Shrift & Ulrich, 1969). Selenate uptake is likely to occur by high affinity sulfate transporters in root epidermal and cortical cells (Terry et al., 2005; Sors et al., 2005). In contrast, selenite uptake mainly occurs through passive diffusion, a process that can be inhibited by phosphate. Selenite accumulation might also be mediated by proton coupled phosphate transporters (Li et al., 2008). Due to the entrances shared, sulfate and selenate and phosphate and selenite might compete for uptake. The uptake of organic Se compounds is not well known, but the permeases specific for S-containing amino acids may mediate the uptake of seleno-amino acids as well (Abrams et al., 1990). After uptake, Se is transported to the shoots via the xylem, where the distribution among plant parts differ among species, growth stages and physiological conditions.

3.6 Climatic and temporal variation

Differences in Se uptake among agro-ecosystems is not only caused by variation in soil properties but also by climatic conditions and land topography. Combining these data makes it possible to identify unique fertilizer strategies for soils sharing common geologic development, soil properties and history under specific climatic conditions (Spadoni et al., 2007).

High precipitation rates and low temperatures can reduce Se accumulation by plants (Bitterly et al., 2010). Precipitation may enhance the reduction of selenates to less available Se forms by altering redox conditions (Geering et al., 1968). High precipitation may also increase leaching and subsequently the plant available Se pool. Dry conditions may result in low Se accumulation by plants due to limited crop growth and decreased Se availability due to water shortage. Soil temperature directly controls soil dryness and favors oxidative conditions accelerating oxidation of organic matter. In his study on inter- and intra-seasonal variation of Se levels in wheat, Johnsson (1991) observed a positive relation of crop Se levels with the amount of precipitation during the growing season. This might depend on the positive relationship between precipitation and atmospheric deposition (Johnsson, 1989; Steinnes, 1984).

Gissel-Nielsen (1975) observed that Se levels in pasture strongly decreased over the growing season, suggesting a gradual depletion of plant available Se. This plant available Se pool is continuously replenished by weathering and organic matter decomposition, resulting in initial high Se levels in the beginning of the growing seasons since little or no Se was taken up during plant dormancy. With increasing crop growth rates, Se uptake from soil solution might exceed the rate of replenishment resulting in decreasing Se levels in crop. In addition, crop Se levels are diluted over time due to ongoing biomass production. The depletion of soil Se stopped towards the end of the growing season when crop growth decreased due to lower temperatures and energy inputs.

4 Selenium fertilization

4.1 Introduction

Because Se-deficient areas are more common worldwide than areas with excessive Se, considerable research has been done on fertilizer strategies to increase the Se content of crops. Selenium supplementation to crops enhances the production and quality of edible crop products, being beneficial for both crop yields and the nutritive value of foods (Haug, 2007). The most common practice to enhance Se levels in crops is through inorganic fertilization (e.g., Mikkelsen et al., 1989; Lyons et al. 2004; Broadley et al. 2006; Li et al. 2007; Schonhof et al. 2007; Omirou et al. 2009). Recently, the awareness has grown that crop management practices like catch cropping and intercropping might stimulate Se uptake in crops, an issue particularly relevant for situations with limited resources (Stavridou, 2012).

The effectiveness of Se fertilization depends on Se species used, fertilizer dose, application technique (foliar vs. soil), timing, agronomic management options and the properties of the agro-ecosystem. Understanding the fate of Se fertilizers in soil is crucial to identify and implement strategic fertilizer interventions to overcome Se deficiencies.

4.2 Selenium form

Feasible application technologies and fertilizer strategies have been studied since the 1960's (Gissel-Nielsen et al., 1984; Gissel-Nielsen, 1998). Most of the experiments focused on various selenate and selenite salts, being applied as soil fertilizers or in combination with basic nitrogen or phosphorus fertilizers. Selenite salts have been found to be effective in increasing Se contents in different crops (clover, alfalfa, mustard, sugar beet). Selenate salts increased the Se content in crops more rapidly, but the residual effects strongly diminished over time. Selenium fertilization in Finnish agricultural practice is therefore repeated every growing season. High levels of selenate application might lead to environmental losses or potentially harmful Se intake for animals. The risk of harmful Se intakes is however low in practice due to good feeding strategies and common agricultural practices. In contrast to selenate, agricultural crops seemed to be able to prevent high accumulation of selenite.

The higher crop response to selenate fertilizers is mainly due to their higher solubility and plant availability compared to selenite fertilizers. This different behavior of selenate and selenite is corroborated by numerous experiments in Denmark, Finland, Germany and the UK: the uptake of selenate can be 8 to 20 times higher than that of selenite (Bisbjerg & Gissel-Nielsen, 1969; Yläranta, 1983; Bahners, 1987). Opposite results are observed by Shand et al. (1992) and Yläranta (1990), suggesting that soil properties during the season and fertilizer strategies are as important as the Se species used. Selenate fertilizers for example result in higher uptake at alkaline pH than selenite fertilizers: Dorst & Peterson (1984) showed that selenate was rapidly removed in an acidic soil resulting in low Se levels in the crop whereas liming increased the solubility and plant uptake. In addition, Watkinson (1983) indicated that topdressing reduced the impact of soil properties depending on plant species: grasses absorb more Se via roots whereas clover had higher affinity for Se uptake via leaves.

Use of elemental Se as a long-term, slow-release fertilizer was once viewed as attractive, but different studies show that only less than 0.5% of the added elemental Se can be taken up by crops (Grant, 1965; Peterson & Butler, 1966; Gissel-Nielsen & Bisbjerg, 1970). Slightly soluble $CuSeO_4$ and $BaSeO_4$ show even a higher plant uptake than easily soluble K_2SeO_4, probably due to rapid leaching of Se from the latter during the growing season. The solubility of selenate fertilizers in water decreases in the order K_2SeO_4 > Na_2SeO_4 > $CuSeO_4$ > $CaSeO_4$ > $SrSeO_4$ > $BaSeO_4$ (Gissel-Nielsen & Bisbjerg, 1970). Similarly, K_2SeO_3 and Na_2SeO_3 are more soluble in water than $BaSeO_3$. These differences in solubility suggests that long term experiments are required to evaluate the agronomic and environmental impact of Se fertilizers: some are mainly beneficial on the short term whereas others might result in substantial residual effects. Whelan & Barrow (1994) for example showed a relatively low crop response to $BaSeO_4$ fertilization, but the response continued over a four year period. Although the plant availability of Se fertilizers is positively associated with their solubility in water, the actual Se uptake is controlled by the interaction between Se species and soil properties. For example, Bahners (1987) observed higher Se responses for selenite fertilizers based on magnesium and sodium than for fertilizers based on calcium and zinc. Mayland (1994) however found that crop uptake was not affected by the cation involved. In addition, responses determined in field experiments did not always correspond with results from pot experiments (Bahners, 1987).

4.3 Selenium dose

Since the early sixties, fertilizer trials have been performed in order to test which Se dose is necessary to reach adequate Se levels in crops. Archer (1983) for example applied sodium selenate and selenite at rates of 70 and 140 g Se ha^{-1} at ten sites in England and Wales and observed much higher (and even toxic) levels in selenate fertilized soils compared to soils fertilized with selenite. Current recommendation systems for Se have established Se doses around 7.5 up to 10 g Se ha^{-1} for grassland and arable systems. In most cases, the response of crops is linear with the Se dose applied (due to an increase in Se concentrations), even up to levels of 200 g Se ha^{-1} (Whelan & Barrow, 1994). As a consequence, the optimum fertilizer dose can be derived from crop-specific relationships between fertilizer dose and crop response.

Selenium fertilization has only minor effects on crop yields (ton dry matter ha^{-1}) and hence, an increase in Se uptake due to fertilization can mainly be explained by an increase in Se concentration. There is still some discussion on the uptake efficiency of applied fertilizers. A linear crop response to Se supplementation suggests that crops are able to take up a constant fraction of the applied Se dose, which is usually not the case for nutrients. Results from Lyons (2005) even showed that the highest uptake efficiency for wheat was obtained for treatments with the highest selenate dose (120 g ha^{-1}). If this nonlinear behavior (enhanced uptake efficiency at higher doses) occurs for all cereals, then the most efficient way to fortify cereals with Se may involve treating a relatively small area with high Se doses, then blending the Se rich grain with grains from less fertilized fields to achieve a desired Se concentration. The same principle (blending Se rich crop products from high fertilized fields with crop products form unfertilized fields) is theoretically applicable across spatial scales.

4.4 Application timing & techniques

To minimize costs, research has focused on reducing the number of application times. This requires an amount of fertilizer Se that is sufficient to maintain Se levels in soil solution during the period of crop uptake. Crop Se levels usually increase after fertilization and diminish after Se levels in soil solution decrease. Its half-life time has been estimated at 21 to 43 days in grassland ecosystems (Watkinson, 1983; Shand et al., 1992). Again, local pedo-climatic conditions and management issues affect this residual effect: Rimmer et al. (1999) observed half-life times up to 70 days whereas Bahners (1987) observed that Se levels in grass came back to background levels within two months. Several other studies found no relevant residual effects at all (Watkinson, 1983; Archer, 1983; Shand et al., 1992). Contrasting evidence was presented by Kiely & Crosse (1984) and Culleton et al. (1997) who observed a positive crop response even after three years. Gupta & Winter (1981) and Gupta et al. (1982) suggested that annual tilling could be responsible for the observation that residual effects rapidly diminish within annual crops whereas they remain visible in perennial pastures for 4 to 5 years. These results suggest that any residual effect will depend on Se species involved, soil properties, fertilizer management and climatic conditions.

From a theoretical point of view there are two contrasting possibilities based on timing to match crop demand with fertilizer supply. In the first situation, slow release fertilizers are applied in such an amount that sufficient Se is available for crop growth whereas possible losses are minimized due to low concentrations in soil solution. Annual application is not required due to high residual effects. This might be a valuable approach in particular for regions with high environmental risks. The second possibility consists of frequent use of fast release fertilizers that are applied when soil supply is not sufficient to fulfill actual crop demand. Adapting timing to crop demand surely affects plant uptake efficiency of Se fertilizers (Watkinson, 1983; Bussink, 2000; Broadley et al., 2006). Combining both approaches is also possible by smart combinations of slow and fast release Se fertilizers.

Generally, only a small portion of soil-applied Se is utilized by plants (Haug et al., 2007). Foliar application might be another approach to avoid complicated dynamics and uptake patterns in soil. Already in 1966, Davies & Watkinson showed that Se levels in clover were much higher for foliar-applied than soil-applied fertilizers. The uptake efficiency of foliar-applied Se fertilizers is affected by timing: spraying late in the season generally results in higher Se concentrations than early season applications. This can be explained by increased leaf area and dilution of incorporated Se in early sprayed crops. Mixing Se fertilizers with detergent surfactants additionally strongly increases plant uptake (Gissel-Nielsen, 1984). The efficiency of foliar fertilizers was also affected by N and S fertilization: soil amendments with sulfate reduced tissue Se levels from foliar applied Se and soil applied N fertilizers inhibited Se translocation within the plant (Gissel-Nielsen, 1975). Nitrogen might have an inhibitive effect on the translocation of Se from the leaves since Se levels increased in organs where Se was applied and decreased in the grain to which the Se is translocated when the nitrogen supply was raised. Addition of sulfate reduced the Se levels in both grain and straw, which indicated that the S status of the plants might influence the absorption of Se. Even though foliar-applied Se turned out to be taken up even several times more efficiently by plants than soil applied Se, the Se uptake efficiency strongly depends on spraying conditions and crop growth stage as well as climatic conditions during and after spraying. The solutions commonly used in foliar application contain high levels of toxic sodium selenate, and hence, health and safety precautions must be taken during on-farm application.

Another option to increase plant uptake efficiency of applied Se is seed treatment prior to planting. In seed treatment, Se amounts equal to those in soil application are needed to attain the desired Se concentration in crops. Whether this approach is suitable for all crops and will result in crop quality products with sufficient Se is still debated. Stephen et al. (1989) for example found only minor differences between seed coating, foliar application and soil applied fertilization with slightly higher Se levels in the crop for foliar applied fertilizers. Similar results are presented by Curtin et al. (2006) who showed that grain Se levels in seed enriched treatments approached those when Se fertilizer was applied at sowing. Nevertheless, only less than 5% of the applied Se was taken up by the crop whereas recoveries of about 20% were achieved for the foliar and soil applied fertilizers. Presowing treatment of barley seeds with selenite was also tested by Gissel-Nielsen (1975) and the amount of selenite needed to obtain a desirable Se concentration in the harvested grain was the same as the situation when Se fertilizer was applied by fertilizers (Gissel-Nielsen, 1998).

4.5 Agronomic circumstances

Fertilization with nitrogen, phosphorus and sulfate affect the Se content of crops due to natural Se enrichment of fertilizers, anion competition during uptake, enhanced Se retention or dilution by increased yield potential (Dhillon & Dhillon, 2000; Lee et al., 2011; Mikkelsen & Wan, 1990; Aro et al., 1995; Williams & Thornton, 1972). For example, $(NH_4)_2SO_4$ fertilizers may contain up to 36 mg Se kg^{-1} while phosphate rocks and single superphosphate can contain up to 25 to 55 mg Se kg^{-1} (White et al., 2004). Their contribution to crop Se uptake might not be overlooked, since decreasing crop Se levels during last decades are partly explained by the global replacement of single by triple superphosphate fertilizers. Triple superphosphates typically contains less than 4 mg Se kg^{-1}.

Besides this direct effect of basic fertilizers on Se supply there is also an indirect effect of macronutrient fertilization on plant availability of Se. Basic fertilization with macronutrients increases the availability of competitive ions such as SO_4^{2-} and PO_4^{3-} and subsequently affects the Se concentration in the crop (Gupta & Gupta, 2002; Severson & Gough, 1992). Similar effects occur from atmospheric deposition (Fan et al., 2008) or nutrient rich irrigation waters. The effect of macronutrients can be explained through direct antagonism or may reflect a dilution effect by altering growth rates (Mikkelsen et al., 1989; Fordyce, 2005; White et al., 2007). On average, the Se concentration in crops decreases with increasing availability of sulfate. Soil addition of phosphate is likely to increase Se crop uptake because it might release Se from sorption sites by ion-competitive behavior (Dhillon & Dhillon, 2000; Eich-Greatorex et al., 2010) or increase Se uptake due to greater root growth (resulting in a larger volume of soil to take up available Se). However, an antagonistic effect between P and Se has also been noted (Hopper & Parker, 1999; Li et al., 2008).

According to Park et al. (2011) organic waste products or manure from poultry and livestock are a good source of Se for crops. These organic amendments contain bioavailable Se forms and are a valuable form of re-utilization of an increasing “waste” product. In contrast, Bussink et al. (2000) indicated that the Se availability of animal manures remains quite low (Logan et al., 1987; Macleod et al., 1998), especially on the short-term. Consequently, it is still an open question whether the addition of organic dairy products can become an important management strategy to ensure a healthy Se content in crops (Moreno et al., 2013). Previous studies have shown that incorporation of catch crops, crop residues and manure in the soil reduced the availability of native soil Se or the Se added through fertilization (Ajwa et al., 1998; Stavridou et al., 2011). Similarly, Stavridou et al. (2012) showed no clear effect of catch crop incorporation on Se uptake by onions. In contrast, Øgaard et al. (2006) found that the addition of cattle manure together with selenate might increase Se concentrations in wheat grain. Nevertheless, organic crop residues contain considerable amounts of Se and might be beneficial as animal feed (Lyons, 2010).

Liming will affect the solubility of Se fertilizers and subsequently the crop response to Se fertilization (Bahners, 1987). In contrast, both greenhouse as well as field studies have revealed that application of gypsum reduces Se accumulation in plants by 60 up to 70% due to increased S availability (Bawa et al., 1990; Dhillon & Dhillon, 1991, 1997).

Soil compaction and irrigation in semi-arid regions might influence Se concentrations in crops (Thamas et al., 2010). Cropping systems with waterlogged/ submerged soil conditions such as paddy rice are characterized by high Se retention and leaching losses (up to 80% of the applied Se) irrespective of the Se species used (Ponnamperuma, 1972; Chen et al., 2002; Premarathna et al., 2010). Differences between selenate and selenite diminish under these conditions: both are equally available for plant uptake (Hopper & Parker, 1999; Li et al., 2008; Zhang et al., 2006).

This equality can be explained by rapid reduction rates: Sposito et al. (1991) reported removal rates less than one week for a situation without oxygen supply. The actual plant uptake efficiency also depends on the quality of the irrigation water used. For example, Zhao et al. (2007) observed lower Se levels in wheat after irrigation and explained this by increased leaching and high sulfur levels in the irrigation water.

Summarizing, the plant uptake efficiency of Se fertilizers depends on soil properties, fertilizer strategies and management options such as timing, liming, irrigation and use of organic manures and fertilizers. Algorithms correcting the fertilizer dose for these agronomic factors are not available yet.

5 Meta-analysis of scientific literature

5.1 Introduction

The efficiency of Se fertilizers is largely affected by fertilizer formulation, application strategy, weather conditions and soil type (Mikkelson et al., 1989). A study of Haug et al. (2007) for example mentioned that only 10 to 20% of added Se from fertilizers is taken up by crops in the first year after amendment. The uptake efficiency however can range between less than 1 to more than 50% due to differences in fertilizer composition, crop uptake patterns and soil properties. Up to now, more than 100 studies dealing with Se fertilization of crops have been published. There is clear evidence that Se fertilizers are able to increase Se levels in agricultural crops. Fertilizer amendment is therefore an effective way to increase Se levels in crop, animals with subsequent positive impacts on human health.

Based on the published research, it also becomes clear that local agro-ecosystem properties strongly affect plant availability and uptake of Se fertilizers. Hence, this dependency on site specific properties challenges the development of any fertilizer decision support tool to maximize plant uptake efficiency of Se. An integrative and quantitative analysis of published data might bridge the gap between published experimental data and sustainable fertilizer practices all over the world. However, a quantitative integration of all these results has not been published so far.

The research presented in this report aims to identify when applying Se fertilizer is effective in specific agro-ecosystems based on an inventory of specific production-ecological causes for its deficiency in relation to fertilizer application. Important factors controlling Se availability and uptake are therefore identified based on a meta-analysis, including a quantitative estimate of their impact on crop response (Se concentration or Se uptake) to Se fertilization.

5.2 Material and methods

A meta-analysis can be used to estimate the average response of agricultural crops to Se fertilization across a large number of studies varying in cropping systems, climatic conditions, agro-ecosystem properties, fertilizer strategies (timing, dose, Se species), and to test whether the response is significantly affected by aforementioned issues. Background information on meta-analysis can be found in the study of Gurevitch & Hedges (2001), Hedges et al. (1999), Rosenberg et al. (2000) and Ros et al. (2009; 2011). The current meta-analysis focuses on the *averaged effects across the groupings* involved (including all the variation present due to the factors not included in the grouping), and hence, the conclusions can be partly biased through indirect mechanisms or skewed distribution of specific experiments over the groupings tested. Based on this general meta-analysis, it is possible to identify the most important factors controlling the efficiency of Se fertilizers quantitatively. This analysis helps to identify the relevant agro-ecosystem properties affecting the efficiency of Se fertilizers as an agronomic fortification strategy. The most relevant factors and properties should be included in the decision support tool to be developed (see section 1). The actual development of this support tool, including the underlying algorithms accounting for main effects *and* their interactions (not included in this meta-analysis), is not part of this research.

5.2.1 Data collection

Scientific databases were searched in January 2014 using Scopus Abstracts and Google Scholar and the keywords “Selenium” in combination with “fertilizer,” “fertilization,” “amendment,” “uptake,” or “additive” over the period 1960 to 2013. In addition, a more general (without keyword “fertilizer”) and crop focused search was done using the keywords “selenium” in combination with the crops “wheat,” “cereal, “maize,” “grass,” or “rice.” A total of 218 studies published between 1960 and 2013 were identified and collected, of which 94 studies included reliable and quantitative data for a meta-analysis.

To obtain sufficient data which would allow us to use the meta-analysis approach, studies which did not report the standard deviation (SD) or standard error (SE) values were also included by using an arbitrary SD value based on a coefficient of variation (CV) of 1.25 times the average CV in the other studies (taking into account crop specific differences for field and pot experiments separately). Only studies which showed replication of the treatments were included. Error bars not identified were assumed to represent SE. If several values of the number of replicates were given, the lowest value was taken.

5.2.2 Use of response ratio

Data in a meta-analysis generally take the form of standardized metrics of an effect size and their associated sampling variances (for details on meta-analysis, see Gurevitch & Hedges, 2001). The effect size calculated for each experiment in this study was the natural log of the response ratio (R, relative difference between 2 groups). The response ratio was calculated by dividing the mean of one group by the mean of a control group (Hedges et al., 1999; Rosenberg et al., 2000). For example, the influence of fertilizer dose was determined by calculating a relative difference between Se uptake (or Se levels in crop parts) in fertilized and unfertilized soils. The mean difference between two groups among the analyzed studies was calculated as described in Gurevitch & Hedges (2001). Mean crop responses in Se uptake or Se content of experimental and control groups with their standard deviations (SDs) and replicates (n), from a large number of studies were collected.

Data were subdivided into various subgroups related to factors that could affect the concentration in or uptake of Se by agricultural crops (based on the classical review as presented in Chapters 2 and 3). The factors included were: location (country), year, basic fertilization (with N, P, K and S), soil characteristics (Se content, clay content, pH and organic C content), fertilizer properties (Se species, application form [liquid, granular, foliar]) and strategy (timing, dose) and crop properties (crop species, crop part). The response variables used were both the Se content and the Se uptake of agricultural crops. Both crop response variables are supposed to react similarly to Se fertilization because crop yield is usually not affected by Se fertilization.

5.2.3 Meta-analysis modeling

Meta-analysis was first performed on the total dataset in order to study the averaged impact of soil properties, fertilizer strategies, climatic circumstances and land uses on the crop response to Se fertilization. In addition, a specific analysis was made for grassland ecosystems. Grassland ecosystems were selected as an example because most of the data was collected from experiments in grasslands.

When the pooled within-class variance was greater than zero, a random effect model was used, whereas a fixed effect model was used when that quantity was equal to or smaller than zero. Means of response variables of different subgroups were tested for significant differences based on a model heterogeneity test (Q-test), which is tested against a chi-square distribution with n-1 degrees of freedom as implemented in MetaWin ($P \leq 0.05$).

The mean difference between two groups is significantly different (in that case the ratio is unequal to 1, indicating a significant change in crop response to Se fertilization) if both the upper and lower confidence limits were smaller or greater than one.

5.2.4 Publication bias

Publication bias (under-reporting of experiments without significant results) can lead to an over-estimation of the fertilizer response. The presence of publication bias was tested using the rank correlation tests of Kendall and Spearman (Rosenberg et al., 2000). We also calculated fail-safe numbers as suggested by Rosenthal (1979). A fail-safe number is the number of non-significant, unpublished or missing studies that would need to be added to a meta-analysis in order to change the result of the meta-analysis from significant to non-significant. If this number is large ($>5 \times n + 10$) relative to the number of observed studies (Gurevitch & Hedges, 2001), there is confidence that the observed result, even with some publication bias, is a reliable estimate of the crop response to Se fertilization.

5.3 Meta-analysis including all crops

5.3.1 Collected data

Based on 94 included papers, 243 experiments with 3865 treatments have been collected where the effect of Se fertilization was tested in comparison with an unfertilized control. Experimental details differ among the experiments in relation to the main aim of investigation: effects of pH, clay content, fertilizer dose and formulation, etc.

The majority of experiments (n = 2493 observations) have been performed in the field while the remaining (n = 1299 observations) were conducted as pot experiments in greenhouses or in growth trials using culture solutions. Most of the these experiments were performed in arable ecosystems in the northern hemisphere, including United Kingdom, USA, Denmark, Norway, Canada and New Zealand (in southern hemisphere): together 74% of the observations were derived from experiments done in these countries. On a continental scale 39% were performed in Europe, 28% in North America, 17% in Australia (particularly New Zealand) and 5 to 6% in each of Asia, South America and Africa.

The most common crops involved in these experiments were grassland (grass and clover species) and cereals (wheat, oats, barley): together they comprise 64% of the collected data. The remaining main crops include herbage crops (14%), maize (5%) and soybean and rice (4%). Given the main crops, it is not surprising that most observations are done on grains (from the cereals) and shoots (from grassland). Only 20% of the collected data was derived from crop roots and straw analyses. Crop yield is usually not given since there is a strong focus on crop quality aspects. This is corroborated by the fact that the majority of the observations (81%) are based on determined Se contents rather than on Se uptake of agricultural crops.

The most common fertilizers used in these experiments are based on selenate salts (56% of the observations) followed by selenite (35%). The remaining 9% of the observations is based on experiments with mixtures of selenate and selenite (4%), organic (waste) products, selenide and elemental Se. The fertilizer dose ranges from 0.5 to 81 kg ha^{-1} (assuming a soil density of 1350 kg m^{-3} and a soil layer of 10 cm for up-scaling). The majority gives either less than 10 g Se ha^{-1} (33% of the observations) or more than 80 g ha^{-1} (38%). Due to higher efficiency of selenate fertilizers, the fertilizer dose in selenate-based experiments is on average substantially lower than for selenite-based experiments: the median dose is about 14 g ha^{-1} for selenate and 280 g ha^{-1} for selenite.

Less is known regarding the soil characteristics involved in the experiments. In more than 50% of the observations the initial Se content of the soils is unknown. Where it was measured, it varied between < 0.3 and 4.5 mg kg^{-1} soil (usually determined by Aqua Regia extraction methods). Most of the soils (30% of the cases where data were available) had Se levels less than 0.3 mg kg^{-1}. The clay content was usually estimated from the soil texture diagram using the profile description given in the papers. The majority of soils had clay contents between 5% and 15% indicating texture classes ranging from loamy sand to silty loam. About 15% of the soils were classified as soils with clay contents between 15% and 35% (sandy clay loam, clay loam and silty clay loam) and only 7% had more than 35% clay. The soil acidity ranged from 4 to 8.5 of which 12% have pH values below 5.5, 34% with pH values between 5.5 and 6.0, 19% with pH values between 6.0 and 7.0 and about 17% with pH values above 7. Soil organic matter levels ranged from 1.0 to 551 g C kg^{-1} soil (assuming that 0.58% of the organic matter was present as carbon when only organic matter levels are given), indicating that both mineral and organic peat soils are present. Again, in almost 41% of the observations no data on organic matter levels were available.

5.3.2 Crop response to Se fertilizers

Selenium fertilizers generally resulted in a positive effect on both Se levels in crops (units: µg Se kg^{-1} crop) as well as on Se uptake (units: mass Se per surface area) ($P < 0.05$). The averaged effect was estimated as an increase of more than 600%, indicating that crops are able to take up significant amounts of added Se irrespective of the characteristics of a specific agro-ecosystem (possible differences between crop concentrations and crop uptake are quantified later). This effect may be overestimated because there was a strong bias in our dataset ($P < 0.001$), indicating that the majority of the papers showed a positive crop response to Se fertilization. This is not surprising knowing the ability of crops to take up selenate and selenite (the main fertilizer species within the dataset) under averaged circumstances. Nevertheless, the fail-safe number according to Rosenthal's (1979) method was around 0.4 billion observations and Orwin's method around 30.000 observations. In both cases the number was higher than $5 \times n + 10$, indicating that Se fertilization certainly increases the Se levels in crop.

The cumulative summary analysis is shown for the field, pot and aquatic experiments separately (Figure 7) indicating on average a positive response to fertilization. A significant positive response can be deduced from the figure for any observation (the middle of each horizontal line) where the response ratio (plotted on X-axis) and its confidence interval remains above one. Indeed, there were also numerous examples present for situations where the effect was smaller than or not significantly different from zero. This finding supports the approach that the effectiveness of Se fertilization (form, timing and dose) depends on site specific properties.

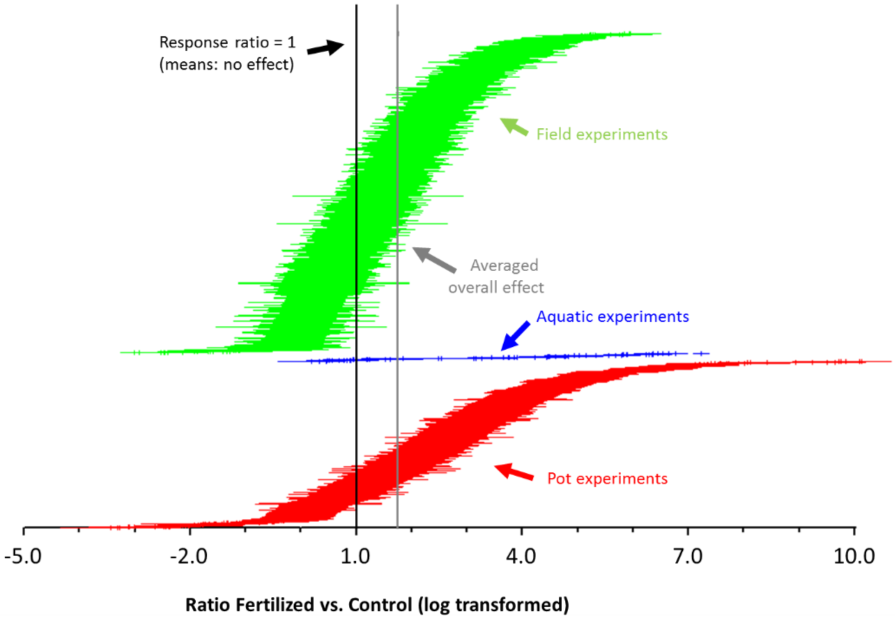

Figure 7. Cumulative summary analyses of all experimental treatments testing Se fertilizers.

Crop species had a significant impact on the observed fertilizer response (Figure 8): Se fertilization increased the crop response with approximately 400% for grassland soils (a factor 5), 650% for cereals, 610% for herbage crops, 820% for maize, 630% for soybean and 875% for remaining crops (both Se uptake and Se levels are included in this analysis). These include beet, sugar beet, herbs, tomato, radish, lucerne, beans, rape, cowpea, potato, carrots, lettuce, vetch, onion, cabbage, strawberry and canola. Highest response was present in rice based cropping systems: fertilization with Se fertilizers increased crop response by more than 1000%.

The relatively low increase for grassland ecosystems is related to the fact that most grassland experiments were done for multiple years to determine any residual long-term effects of Se fertilizers. Because the crop response to Se fertilization diminishes over time, the inclusion of long-term data decreases the averaged crop response for grassland ecosystems.

On average the effect of Se fertilizers was comparable between the Se content of the crop and crop Se uptake ($P = 0.650$; Figure 8). This corroborates with the overall finding that Se fertilization had no beneficial effect on crop yields of agricultural crops (see chapter 3). In contrast, there was on average a significant difference ($P < 0.001$) in crop response among the different crop parts analyzed (averaged over all crop species, pedo-climatic conditions, etc.). Highest response was observed in crop roots followed by grain and straw. Whether the Se will become available by mineralization for succeeding crops is still an open question and not answered with this analysis.

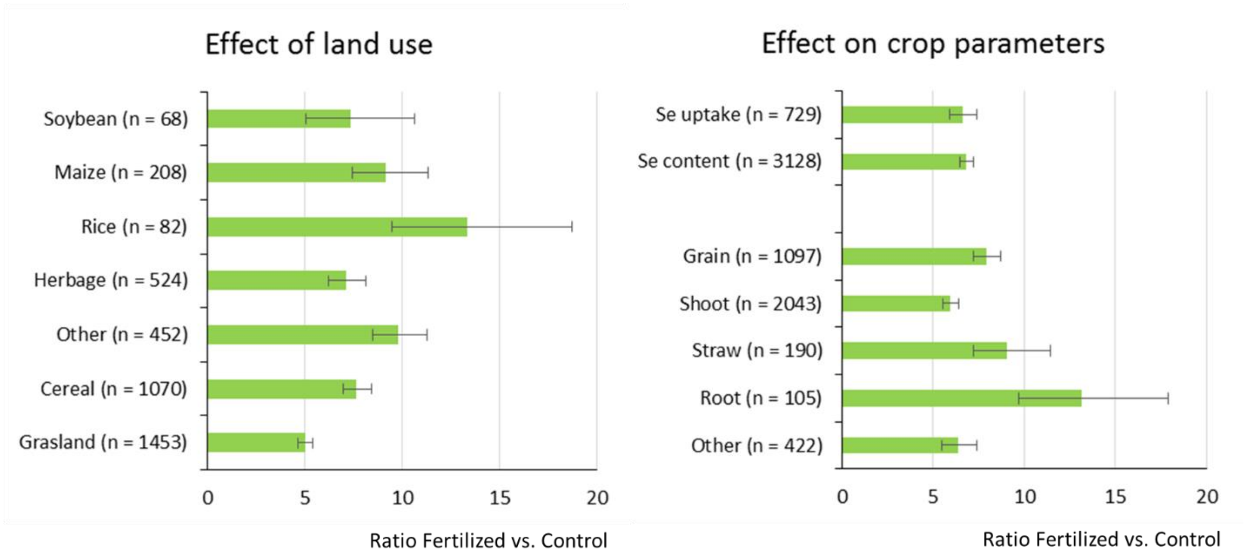

Figure 8. Averaged crop response to Se fertilizers in relation to land use and crop parameters. Error bars denote 95% confidence interval.

5.3.3 Effect of experimental design and natural Se supply

Crop response was significantly influenced by the initial Se levels in soils and the type of experiment (Figure 9). Field experiments generally resulted in a lower response than pot experiments ($P < 0.001$). This might be explained by the fact that most grassland experiments were performed on field experiments, but it might also be caused by higher leaching losses in the field and the fact that almost all environmental and nutritional factors are highly optimized in greenhouse experiments. In addition, Se doses are also substantially higher in pot than in field experiments, being partly responsible for the difference between these experimental types. These differences indicate that a robust decision support tool assisting farmers with their Se fertilization should be based on data derived from field studies to prevent any overestimation of crop responses to Se fertilization.

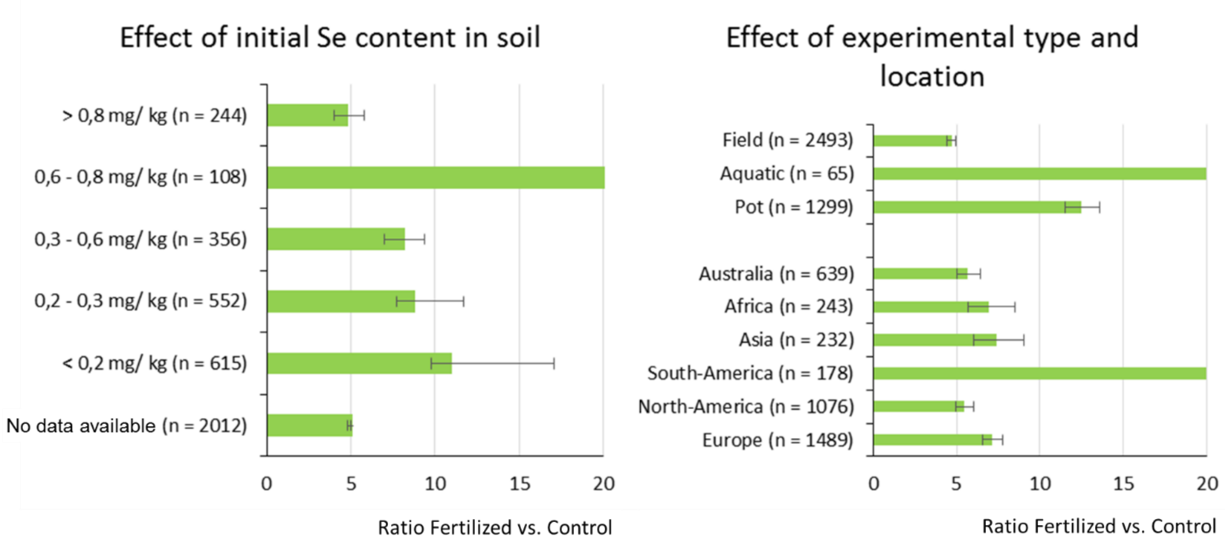

Figure 9. Averaged crop response to Se fertilizers by location, experimental type and soils Se content. Error bars denote 95% confidence interval.

The aquatic experiments are those experiments without soil which are used to unravel Se interactions with other anions on a mechanistic level without any interference from soil. The duration of these experiments is usually less than 30 days, and no Se is available for uptake in the control treatments. As a result, the response to Se fertilization might increase to unrealistic high values. In that case, the use of a response ratio is not the best way to measure an effect. The ratio is maximized at 20% for visual clarity (Figure 9). Care should be taken to extrapolate these findings from aquatic experiments to the field situation. For example, Bitterly et al. (2010) showed that plant Se levels do not depend as strongly on soil Se concentrations as they do on Se concentrations in nutrient solution. This might be due to the fact that all Se in solution is readily available for plant uptake, whereas the availability of Se in soil is controlled by biotic and abiotic mechanisms.

On average, the crop response to Se fertilization was quite similar across all continents. The explanation for this similarity across the globe is that the majority of the experiments is performed on soils relatively low in Se. The high response in South America is mainly due to a number of pot experiments with exceptional high Se doses relative to the initial Se levels: the concentration increased from approximately 10 (unfertilized) up to 800 µg kg^{-1} (fertilized) in ryegrass (Cartes et al., 2010). The influence of these pot-experiments is also visible in the soil category with Se levels between 0.6 and 0.8 mg kg^{-1}. When these data are ignored, it becomes clear that crop response shows a decreasing trend with the Se level in soil: the response increases from 400% in Se rich soils up to ~900% in soils with less than 0.2 mg Se kg^{-1} soil.

5.3.4 Fertilizer strategies

From a theoretical point of view, Se levels in crops are higher for foliar applications than for fertilizers applied to the soil due to decreasing possibilities for losses and a lower risk for growth induced Se dilution. Indeed, averaged over all crops and situations, foliar applications resulted in almost a double increase in crop response than soil applied granular fertilizers (Figure 10; both Se levels and Se uptake were included in this analysis). Nevertheless, granular fertilizers still increased crop Se response with 400%. When inorganic fertilizers were applied in liquid form, the Se uptake seemed to be substantially higher than when granular fertilizers were used: crop responses increased from 400 up to more than 1000%. This might partly depend on the timing of fertilizers: liquid fertilizers are often applied during the growing season whereas granular fertilizers are usually soil applied before the growing season starts. The possible risk of losses is thereby reduced when liquid fertilizers are used.

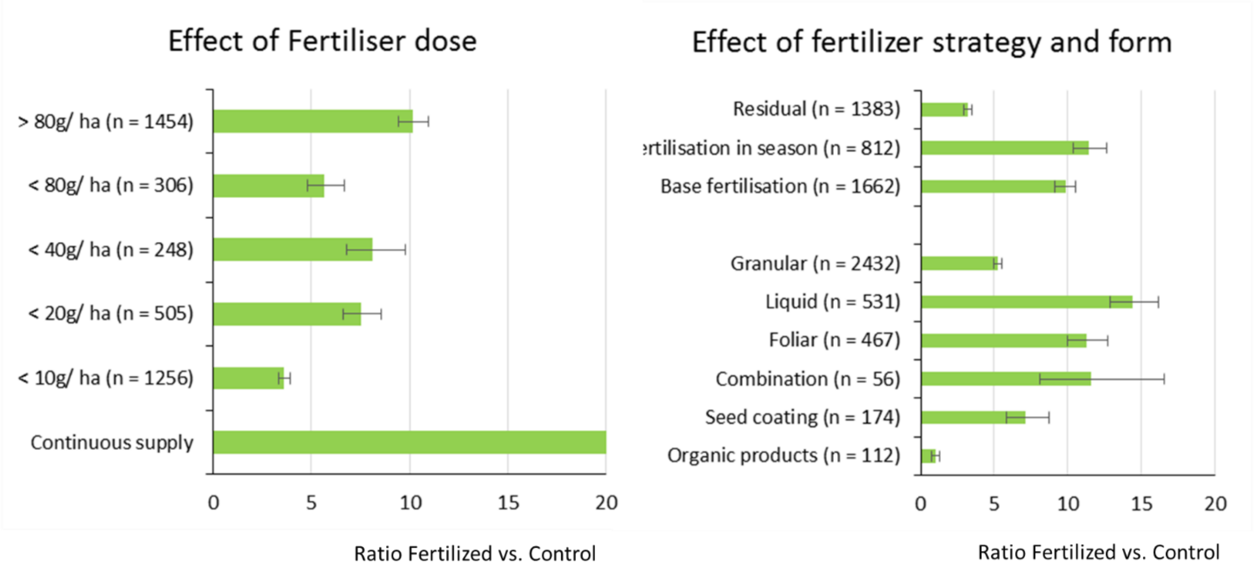

Figure 10. Averaged crop response to Se fertilizers by fertilizer dose, strategy and application form. Error bars denote 95% confidence interval.

In addition, nutrients in liquid form are directly available for crop uptake (where the availability of granular Se fertilizers depend on their solubility) and most crops already have a developed root system to take up available Se from soil solution. Surprisingly, there is also ample evidence that applied Se is beneficial for subsequent crops: Se levels in crop still increased with about 200% one (or more) years after Se fertilizer application (differences among succeeding years are neglected). Organic products are often used in seleniferous soils to reduce Se uptake from soil, and the crop response after organic amendments was indeed smaller than one. Soil amendment with organic (waste) products reduced on average the Se uptake and concentration with 35%. Surprisingly, seed coating was also quite effective, being comparable with soil application of granular fertilizers.

Again, culture solutions continuously supplied with Se showed an enormous increase in crop response to Se fertilization, partly due to the absence of Se uptake in control treatments (no Se is applied). As shown by numerous studies, the uptake of Se increased with fertilizer dose. When less than 10 g Se ha^{-1} was applied, the averaged crop response increased by 260% (Figure 10). The crop response increased up to +900% for situations where more than 80 g Se ha^{-1} was fertilized.

The effect of Se form and soil properties as organic C, pH and clay content are shown in Figure 11.

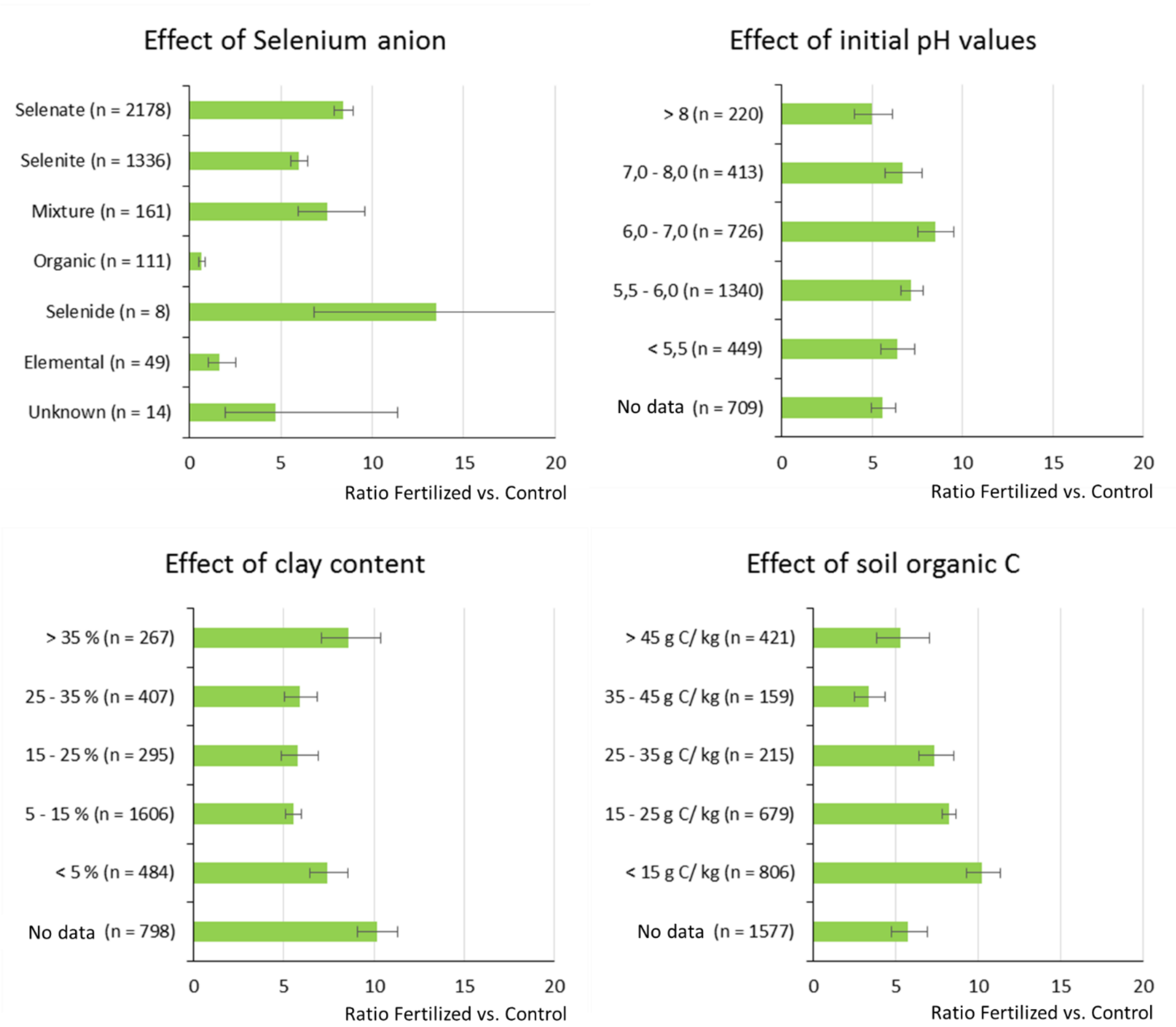

Figure 11. Averaged crop response to Se fertilizers affected by Se species and soil properties. Error bars denote 95% confidence interval.

It has been known for decades that selenate applications are usually more effective than selenite applications: crops can even take up selenate up to toxic levels whereas the uptake of selenite is more restricted by the physiology of plants. Crop response to Se fertilization indeed differed among these Se forms (Figure 11) with a stronger increase after selenate application ($P < 0.001$). When both compounds are mixed together, the crop response is somewhere in between, showing also higher variability related to variable mixture composition among experiments. The difference between the selenate and selenite fertilizers increased when Se dose is taken into account (selenite fertilizers are usually supplied at higher doses than selenate fertilizers). Selenate fertilizers increased crop Se response on average with 159% per 10 g Se ha^{-1} whereas selenite increased the crop response with 21% per 10 g Se applied per hectare (data not shown). The uptake of elemental Se is quite low although it still increased crop Se response with 65%. Use of selenide based fertilizers also seem able to result in a positive crop response, but the number of observations is too low for an accurate estimate of its averaged effect.

5.3.5 Soil properties

The effectiveness of Se fertilizers across soil pH classes resulted in quite similar crop responses over all soil groupings varying in acidity (Figure 11). This suggests that either soil pH is not a primary driver controlling use efficiencies of Se fertilizers or the selected Se fertilizers is already biased by the experimental design of the majority of experiments. In addition to the soil pH, the pH of the fertilizers themselves (e.g., MAP is acidic while urea is basic) also could influence how soluble Se would be released from them. This effect however is likely small due to high pH buffering in soils.

Differences in soil texture had a small effect on crop response to Se fertilizers, varying from 450% in loamy sandy soils up to 750% in clay soils. Surprisingly, the unclassified samples showed on average a higher crop response than any sample with known soil characteristics. Organic matter tends to decrease crop Se response in mineral soils: the response decreased from +900% in soils with low levels of organic matter down to 230% in soils with 35 to 45 g C kg^{-1} soil. The dynamics in peat soils might be slightly different since the crop response in organic rich soils (> 45 g C kg^{-1}) tends to increase up to 320%.

Summarizing, Se fertilizers significantly increased Se levels in crops. Main factors controlling the uptake efficiency are related to fertilizer strategy and management (timing, dose and formulation). A strong difference exists between pot and field experiments, indicating that robust fertilizer recommendations should be based on data obtained from field rather than pot experiments. The response to fertilizers is also crop specific, and fertilizer recommendation systems should therefore account for differences in crop uptake strategies. Selenate fertilizers are thereby more efficient than selenite fertilizers. The impact of soil properties as pH, clay and organic matter content significantly affect crop uptake. Adapting fertilizer strategy and management to soil properties will make it possible to overcome any Se deficiency in soil.

5.4 Meta-analysis grassland ecosystems

5.4.1 Selenium balance in Dutch grassland systems

In grassland systems, the supply of Se originates from atmospheric deposition, fertilizers (inorganic and organic products) and via water transport into the rooting zone (irrigation water or capillary rise). Selenium is removed from the soil by translocation via grass to cattle, being partly converted into beef, milk and manure, and via dynamic soil processes like volatilisation and leaching. The major components of the mass balance of Se in the soil plant system of grassland ecosystems are visualised in Figure 12.

For illustration purposes, we quantified the mass balance for Se in Dutch grassland ecosystems. Deposition of Se varies between 2 and 7 g ha^{-1} (Haygarth et al., 1991; 1994; Fordyce, 2005). Mineral inorganic fertilizers contain variable amounts of Se depending on the raw materials used, ranging from 0.033 mg kg^{-1} (lime) up to 25 mg kg^{-1} (rock phosphates), assuming a fertilizer dose of about 25 kg P_2O_5 ha^{-1} results in a Se supplement of about 4 mg Se ha^{-1}. Organic manure can be another important Se source because a large part of dietary Se uptake is excreted via urine and faeces. Bussink (2000) estimated the Se supply via diary excretion on about 2 g Se ha^{-1} for an average farm (self-supporting with roughage; 1.6 dairy cow ha^{-1} and some young stock). Sewage sludge might also contribute to the Se inputs in grassland systems since they have relatively high Se levels up to 10 mg kg^{-1} (Kabata-Pendias & Pendias, 1984; Sauerbeck, 1987), but application of these sludges is not allowed. It is also questionable whether this Se is available for plant uptake (Logan et al., 1987; Macleod et al., 1998). Total amount of Se supplied via sprinkling water and capillary rise has been estimated at maximally 0.36 g Se ha^{-1}. Total Se input in Dutch grassland systems can be estimated at about 4.3 g Se ha^{-1}.

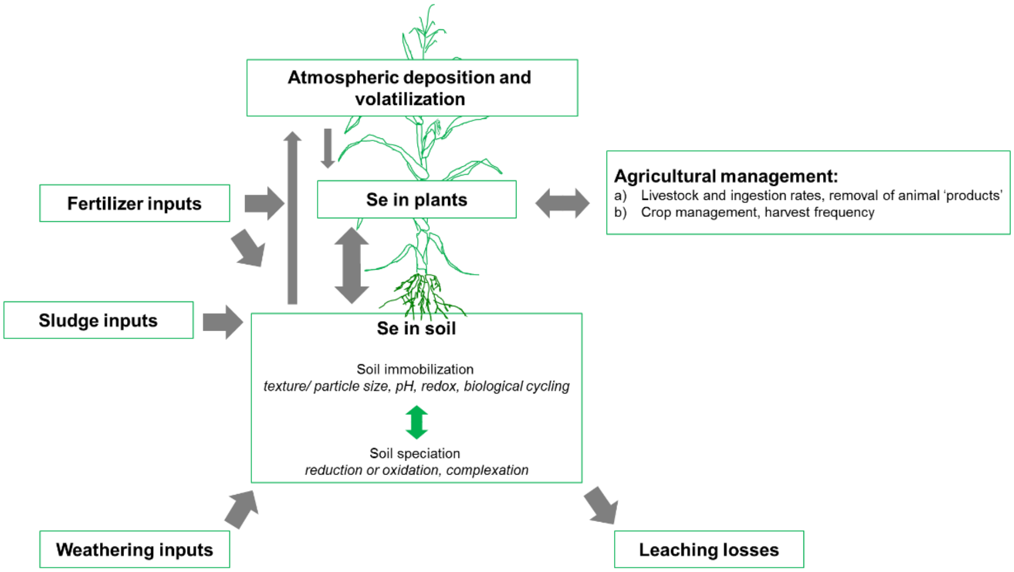

Figure 12. Major components in the mass balance of Se in soil plant system.

Losses of Se from the soil occur via uptake, volatilization and leaching. An extensive monitoring study in the Netherlands in 1999 showed that 80% to 95% of grass silages had a Se content lower than 60 µg kg^{-1} whereas Se levels in grass need to reach levels around 150 to 200 µg kg^{-1} for cows (Combs & Combs, 1986; Wattel-Koekoek, 2006). Growing awareness concerning the relevance of Se fertilization increased the Se content to the current level of 67-94 µg kg^{-1}, assuming a Se content of 90 µg kg^{-1} results in an uptake of about 1.4 g Se ha^{-1} yr^{-1} for productive grass production sites. **Volatilization** losses from pastures are estimated at 1 to 1.5 g ha^{-1} yr^{-1} (Bussink, 2000) whereas leaching losses are estimated at maximally 0.5 g Se ha^{-1} yr^{-1} (Bussink, 2000). Leaching losses are small due to strong variations in redox conditions: most of the applied Se will stay in the top layer of the soil. Hence, total losses account for 3.4 g Se ha^{-1} yr^{-1}, resulting in a small surplus of Se of about 0.7 g Se ha^{-1} yr^{-1}.

Since most of the Se in soil and organic manures is not available for plant uptake, most of the required uptake needs to be addressed by Se fertilizers.

5.4.2 Selenium availability in grassland soils

Grass production in intensive cropping systems can be as high as 18 ton ha^{-1} yr^{-1}. Optimizing Se levels for four to five cuttings (target value of 0.15 mg kg^{-1}) therefore requires knowledge of the capacity of soils to supply Se during the season. The relatively low Se levels in grass in West European countries prove that the natural capacity of soils to supply Se is not sufficient to reach the desired Se content. Selenium amendment via diary excretion (~2 g ha^{-1}) is usually unavailable for plant uptake since it is mainly present as elemental Se^0 (Bussink, 2000). Mayland (1994) noted for example that less than 1% of inorganic and organic Se species from urine and manure could be taken up by plants. Mineralization of soil organic matter might be another source of Se in soils, but the majority of Se containing amino acids are volatilized or converted to insoluble Se species. Deposition of Se via rainfall occurs mainly during winter (Haygarth, 1994) and hence, the net supply during the growing season is approximately 60% of the annual deposition flux. Nevertheless, deposition of Se might strongly contribute to the Se uptake of grasses since Haygarth (1994) showed that 33% to 82% of the Se could be derived from deposited Se. Selenium supply by groundwater flow is usually low due to a net surplus of water during winter (resulting in low soil solution concentrations in spring). Obviously, soil characteristics strongly affect sorption kinetics of Se. Selenate is, under Dutch circumstances, better available than selenite, although it may rapidly be reduced at decreasing pH values and relatively high groundwater levels. Selenite is relatively stable in soil, in particular due to high nitrate levels in soil; all nitrates are reduced before selenite due to its higher redox potential (White & Dubrovky, 1994).

An important driving factor affecting Se use efficiency is the seasonal pattern of crop production and subsequent Se uptake. In literature there is relatively little information available about this issue for grassland systems. Selenium contents in grass from native sources are lowest in spring and highest in autumn (Grant & Sheppard, 1983; Murphy & Quirke, 1997; Shand et al., 1992; Culleton et al., 1997). In a trial in Scotland the lowest concentration was obtained in the second cut (Shands et al., 1992). Similar results were obtained in an Irish trial (Culleton et al., 1997), but not in a field trial in Germany (Bahners, 1987).

5.4.3 Meta-analysis grassland ecosystems

Dataset characteristics

All observations in grassland ecosystems were analyzed using meta-analysis as described before (section 4.2). All data from experiments with aquatic solutions were excluded. The included crops were both clover (n = 346 observations) and grass species (n = 1071 observations). The majority of the observations were done in field experiments with grass and clover (n = 1097) with the remaining part as pot experiments with ryegrass (n = 320). Field experiments with grass and clover were mainly performed in Europe (42%) and New Zealand (36%); no data was available from Asia, Africa or South America. Because of the strong differences in crop responses to Se fertilization due to fertilizer management, soil pretreatment and weather conditions between field and pot experiments (P < 0.001), both subsets were analyzed separately.

Averaged over all observations, crop response was positively affected by Se fertilizers (both crop Se content and Se uptake are included). The average increase in Se content or uptake was estimated to be approximately 380%. Again, there was a strong indication of publication bias, indicating that negative crop responses to Se fertilization are not likely to be published. This can be explained by the main driver for Se-related research in grassland ecosystems: to solve possible crop deficiencies by soil and fertilizer management. This is also related to the keywords used to select relevant papers: a (strong) relationship with fertilization was required. This also limits the outcome of this analysis to non-seleniferous soils: management strategies to overcome Se toxicity are not included. Within this boundary conditions, there is strong evidence for a positive relationship between Se fertilization and crop response.

Meta-analysis results

Fertilization with Se increased the Se content of both clover and grassland species with almost 200 to 330% under field conditions (Figure 13). The positive effect of Se fertilizers was much higher in the pot experiments with increases up to 1700% for grass and > 2000% for clover.

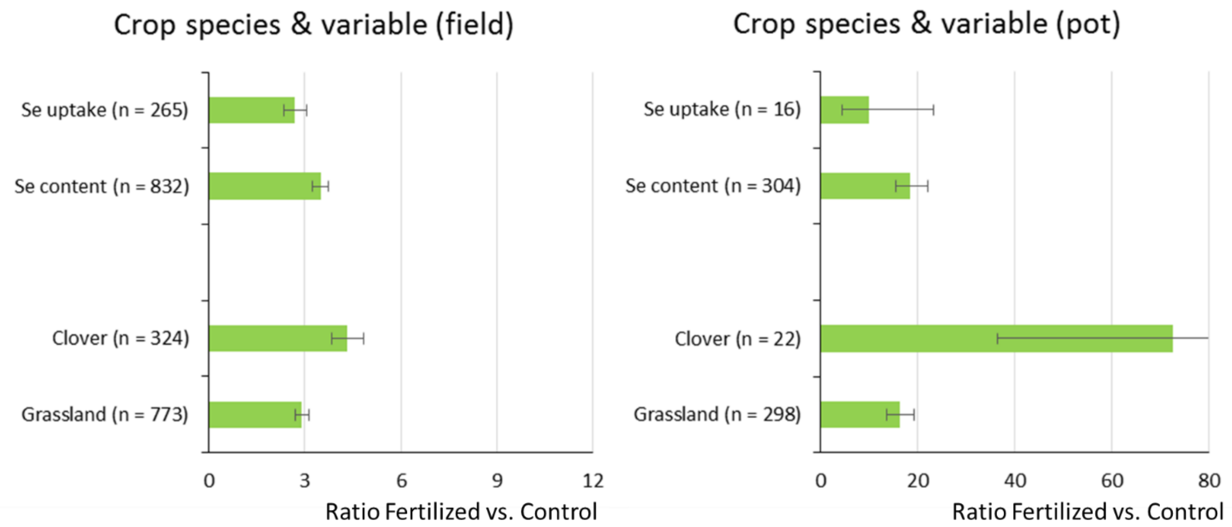

Figure 13. Averaged crop response to Se fertilizers affected by crop species and analyzed crop property for pot (right side) and field experiments (left side). Error bars denote 95% confidence interval.

Differences between pot and field experiments can be contributed to differences in growing conditions, harvested crop stage and higher Se doses. Both the Se content and the total uptake of Se were affected to a similar extent: the effect of Se fertilization on grass yield was negligible.

The crop response was affected by the fertilizer strategy used: residual effects of Se fertilizers (more than one year after application) were significantly lower than the crop response in the first year of application (Figure 13). The residual effect still accounted for a positive response of +100% (averaged over 2 to 4 years of experimentation) under field conditions. Similar findings were observed for pot experiments but the averaged effect is much higher: the response ratio is usually above a factor 10. Again, it emphasizes that results from pot experiments are not directly applicable to a field situation.

The fertilizer dose ranges from less than 10 g ha^{-1} to more than 100 g Se ha^{-1}. There was a strong and almost linear effect of the applied dose on the crop response under controlled conditions of the pot experiments ($P < 0.001$). This relationship was weakly present under field conditions: the crop response was 170% in the lowest dose and increased up to 320% when more than 80 g Se ha^{-1} was applied. Hence, fertilizer dose was less important under field conditions. Fertilization up to a dose of 80 g ha^{-1} didn't result in a significant increase in crop response.

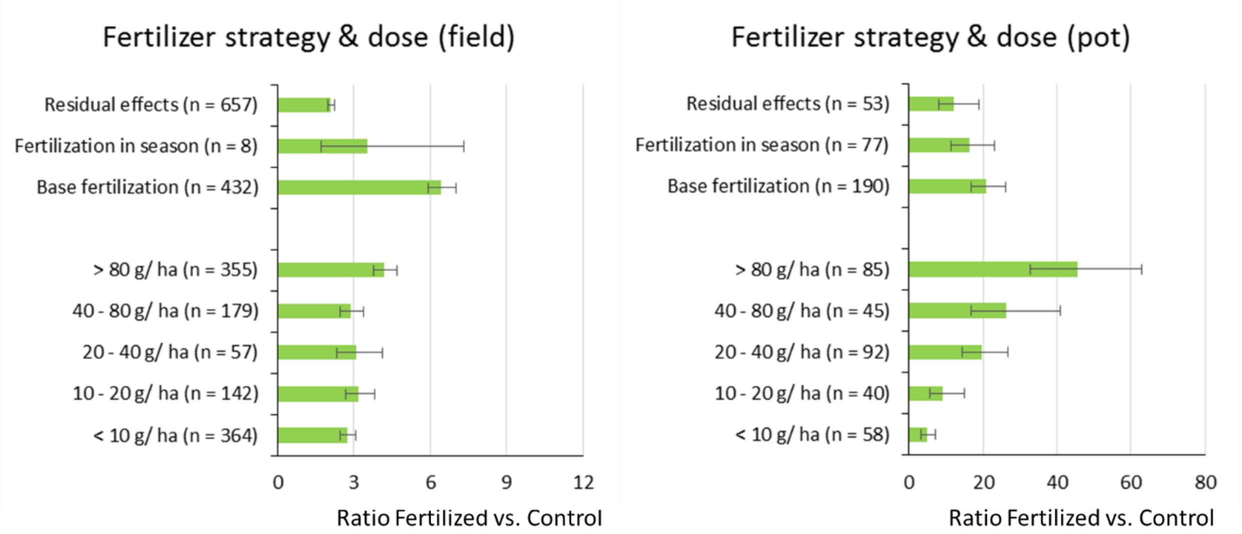

Figure 14. Averaged crop response to Se fertilizers affected by fertilizer strategy and Se dose for pot (right side) and field experiments (left side). Error bars denote 95% confidence interval.

Selenium fertilizers might have a strong residual effect over time due to the intensive rooting system of grassland ecosystems: nutrients will be taken up as long as growth is not limited by other stress factors. The crop response in the first year after application was on average 290% for organic products, 410% for selenate fertilizers and 570% for selenite fertilizers. The average effect strongly decreased to 40% for the organic products, 19% for selenate fertilizers and to 100% for selenite fertilizers during the second year after application (Figure 15). The rapid decrease levelled off after the second year, and a residual effect of 5% was still present in the third year after application. Selenite has a stronger residual effect than selenate but these differences likely diminish in the fourth year after application.

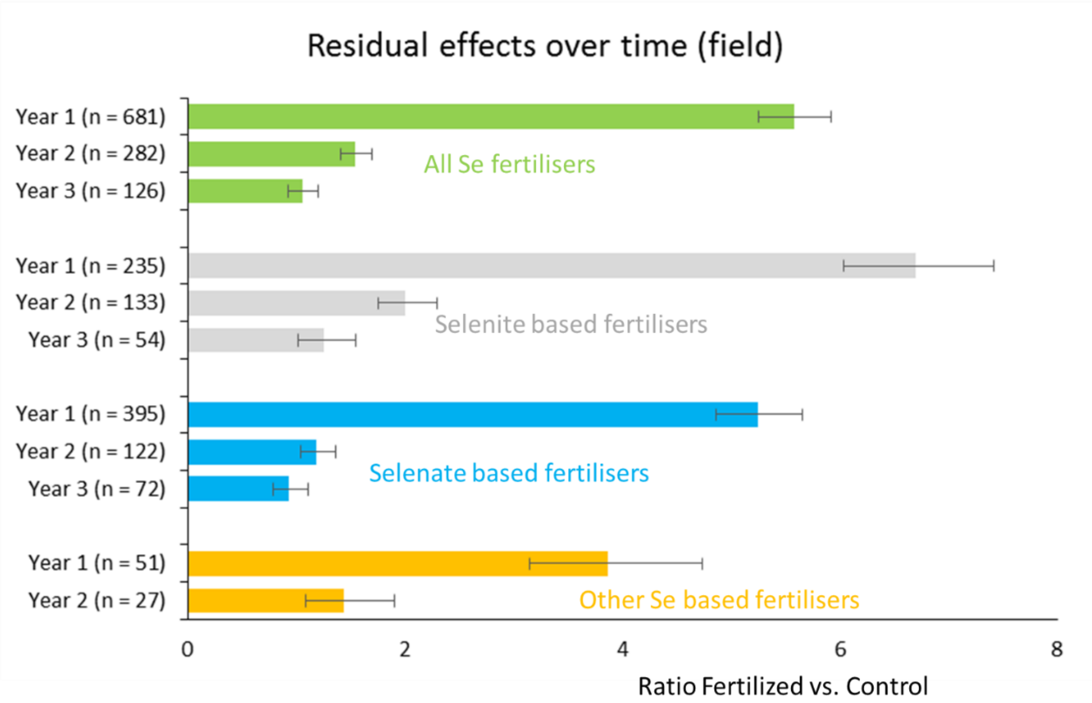

Figure 15. Averaged crop response to Se fertilizers affected by time after Se application. Error bars denote 95% confidence interval.

Both selenate and selenite had a positive effect on crop response to Se fertilization. Averaged over all conditions, selenite seems to result in a higher crop response than selenate fertilizers, but this effect is related to a higher fertilizer dose given in selenite based trials. When crop responses are corrected for fertilizer dose, it becomes visible that selenate is much more efficient than selenite. The crop response to selenate fertilizers showed on average an increase of 86% per 10 g applied Se per hectare whereas selenite fertilizers showed an increase of only 14% (data not shown).

Basic fertilization with N, P, K or S had on average no significant effect on crop responses to Se fertilization under field conditions (Figure 16). The crop response tended to increase with nitrogen and sulfate doses and to decrease with phosphate fertilization. Potassium fertilization had a variable effect with highest crop responses at low and high levels of potassium fertilization. Surprisingly, the studies without any information regarding fertilization showed on average the highest crop response.

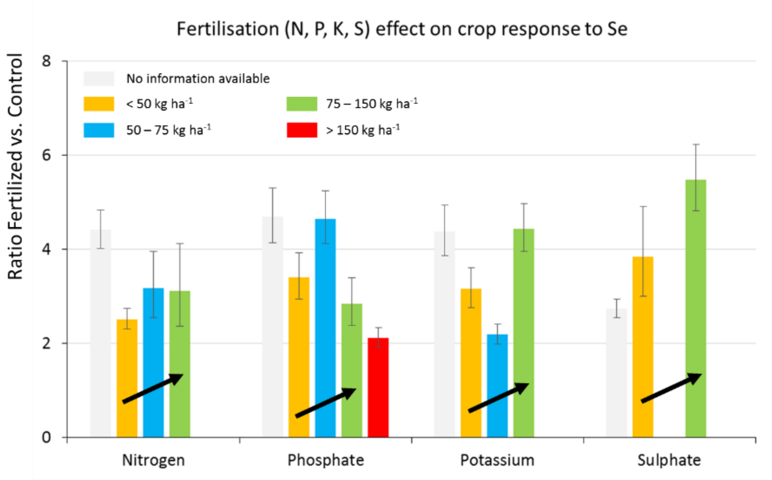

Figure 16. Averaged crop response to Se fertilizers affected by basic fertilization with N, P, K or S in field experiments (black arrows indicate an increase in fertilizer dose). Error bars denote 95% confidence interval.

Soil texture (clay content) had a significant effect on crop response with lowest values for clayey soils (Figure 17). The response decreased from 260% in the sandy soils down to 60% in soils with more than 35% clay. An effect of initial Se levels could not be quantified due to low availability of reliable soil data.

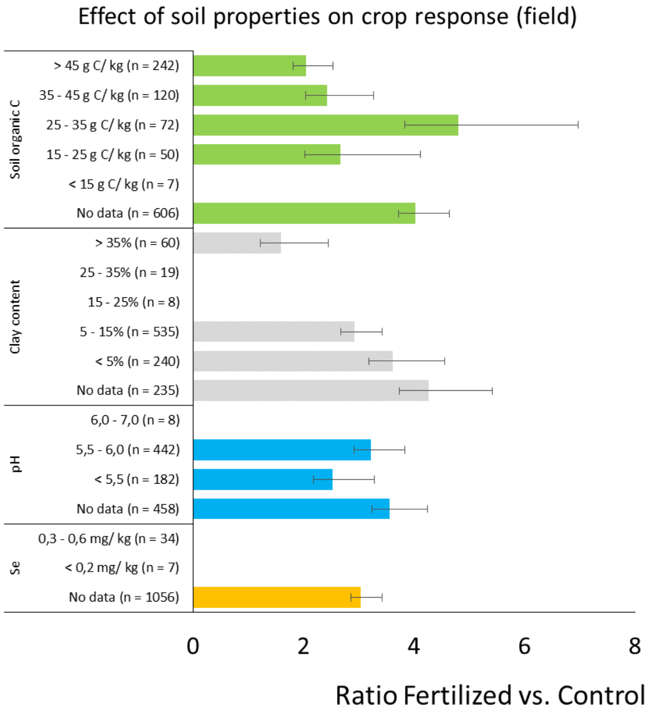

Figure 17. Averaged crop response to Se fertilizers affected by soil properties in field experiments (averaged values based on less than 40 observations were removed). Error bars denote 95% confidence interval.

Soil pH values and the organic matter content of a soil could influence the crop response: responses varied from 100% in organic matter rich soils (with more than 45 g C kg^{-1}) up to 380% in soils with 25 to 35 g C kg^{-1}. High variation within groupings indicate that fertilizer management had a higher influence on crop response of grassland than soil organic matter and pH.

6 Fertilization strategies: an agro-ecosystem approach

6.1 Introduction

Strategic micronutrient interventions to overcome Se deficiencies in agricultural ecosystems are hampered by the complex interactions among soil properties, climatic data, crop properties, application techniques and the Se fertilizers involved. An agro-ecosystem approach might boost the Se uptake by crops, animals and ultimately the human population without adverse impacts on aquatic or terrestrial ecosystems (chapter 1). The scientific review and meta-analysis done (chapters 2 to 4) creates insight in the fate of Se in soils and helps to develop a decision support system by targeting the most appropriate fertilizer strategy to local agro-ecosystem properties.

6.2 Framework decision support tool

Selenium supply from soils is usually not enough for required Se levels in nutritional crops for human intake and in grassland and herbages for animal intake. Consequently, the gap between crop ‘demand’ and Se supply need to be overcome by artificial fertilizers or crop management. The scientific review and meta-analyses showed that any Se fertilization will be beneficial for crop quality, but that substantial variation might be present due to variation in soil properties, cropping systems and fertilizer management issues like dose, timing and application technique. Matching crop demand with available Se fertilizers can be done in a user-friendly decision support system as visualised below.

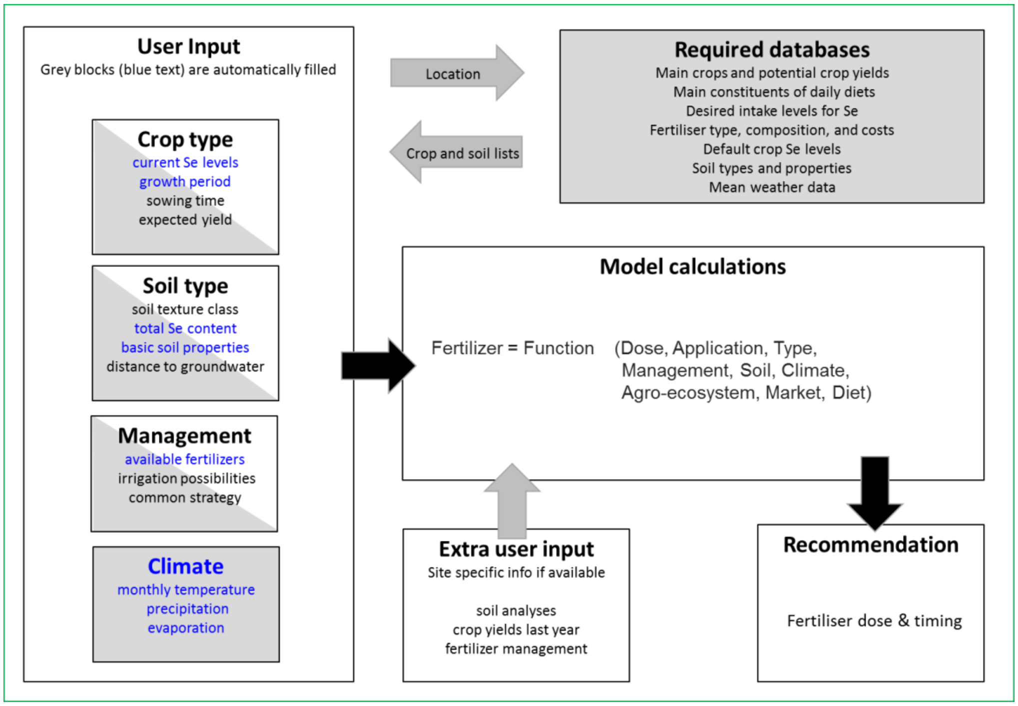

Figure 18. Schematized framework for a decision support tool optimizing Se fertilization.

The framework consists of five modules: (1) default user input, (2) required databases, (3) model calculations, (4) extra user input and (5) the recommendation. The required databases are described in section 5.2.1., the default and additional user input possibilities in sections 5.2.2., and the model calculations in section 5.2.3. Finally, this results in a recommended fertilizer strategy.

Basically, the desired Se fertilization strategy is calculated using a nutrient balance approach, taking into account the Se supply from or retention in soils, preceding fertilizers and incorporated crop residues. Basic information required for this tool can be stored in a GIS-based database containing information at country level. This information can be used to make a pre-selection of the main crops and soil types within a certain area in order to reduce user inputs as soon as the location is known. The minimum required input is ultimately reduced to location, crop type, crop yield and soil type. If more detailed information is available for specific farms or regions, this information can be used to overwrite the default assumptions regarding fertilizer prices, soil properties, irrigation possibilities and application techniques.

6.2.1 Basic databases required

A country-specific database needs to be developed containing agro-ecosystem properties affecting Se demand and crop uptake efficiency in relation to fertilizer strategies. These include:

- The main constituents of daily diets within a country, where possible specified for male, female populations and children. This information is the ultimate driver for the desired Se dose that needs to be applied for certain crops. On country level, this information can be derived from FAO databases. If this information is not available, it can be derived from the main crops growing within a country.
- All major crops available within a country including the background Se levels within these crops. For most countries around the world, this information is available (Sillanpää M & Jansson, 1992). When data is missing, estimates can be made from comparable agro-ecosystems in neighbouring countries. Crops that do not significantly contribute to daily human intake (or animal feedstock when food is used for husbandry) will not be fertilized with additional Se. Since Se content also depends on crop yield (dilution factor) a default yield potential also needs to be known (whereas this yield potential depends on the agro-ecosystem).
- All major soil types within a country or region with related basic soil properties such as Se levels, pH, soil organic matter levels and clay content.
- Monthly weather data including temperature, precipitation and evaporation based on long-term averages, available via the worlds' meteorological organization.
- Fertilizer information derived from fertilizer companies: composition, Se content, carrier, Se salt and prices.

6.2.2 User input

An agro-ecosystem dependent fertilizer strategy is ultimately driven by local and spatially explicit information. The first input required from any user is therefore the location. Within a GIS based information system, this might be derived from the exact location on earth, estimated via GPS technology or the name of the village or region of interest. When the location is known, the decision support tool creates region dependent lists of the main crop and soil types within the selected region and selects climatic data from nearby weather stations. Subsequently, the user can select the crop of interest, the main soil type and the spatial application level: policy makers and industrial companies are likely interested in information on country or regional level whereas a farmer is interested in field scale information.

Because most of the required data are taken from default databases, the required input is minimal. The minimum required input for any user is ultimately reduced to four entry fields: location, crop type, crop yield and soil type. In many cases, this information is sufficient to select the correct fertilizer formulation and application technology. If a user is interested in further optimizing fertilizer strategy (increasing the use efficiency of applied Se fertilizers), more detailed information can be used to adjust the fertilizer dose to the local conditions at field scale.

6.2.3 *Model calculations and background*

The model calculations resulting in an agro-ecosystem dependent fertilizer strategy is conceptually visualized in figure 19. Basically the fertilizer strategy optimizes the Se use efficiency by adapting the fertilizer dose, timing and application technique to the specific conditions within a certain area.

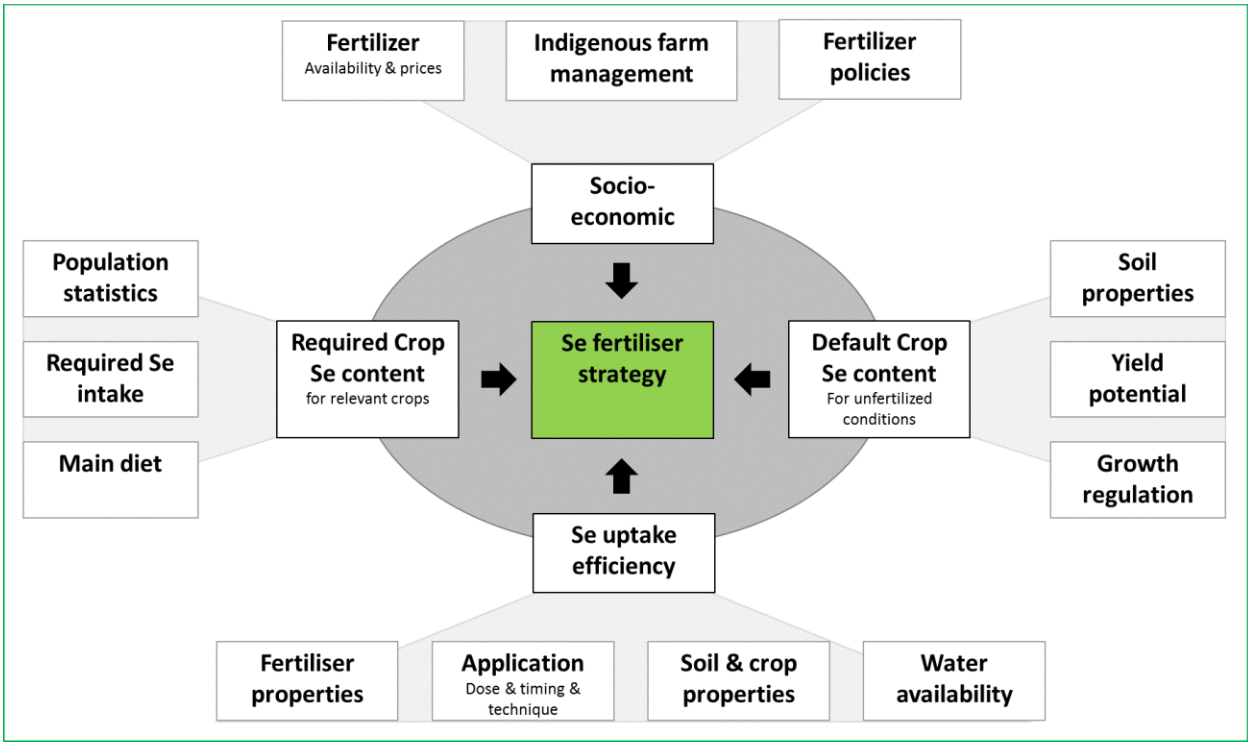

Figure 19. Framework optimizing fertilizer strategies for Se within an agro-ecosystem approach.

The required human and animal Se intake is calculated from Se levels of main diet components on region or country level in relation to the required Se intake. The large influence of dietary and geographic variables on Se status is evident from recent summaries describing national and regional differences in Se intakes (Reilly, 1996). In plant and animal tissues, Se is mostly associated with proteins, and hence, most of the human Se intake is in organic form (generally more than 80%). The most important food sources of Se are meats, seafood and cereals either due to their high protein content or high consumption rates (Levander & Burk, 2006). Drinking water analyses from public water supplies around the world show that Se levels are usually less than 10 µg l^{-1}, although it may exceed 50 µg l^{-1} in certain areas (NAS, 1976, 1977; Gore et al., 2010). Knowing the main food consumption within a certain area it is possible to select a food component of the diet that significantly contributes to human intake. The required crop Se content can then be calculated from the averaged recommended Se intake.

Selenium is an essential element, and various national and international guidelines for daily intake are available. The joint World Health Organization and Food and Agriculture Organization of the United Nations recommend intakes of 6 to 21 µg Se day^{-1} for infants and children (depending on age), 26 and 30 µg Se day^{-1} for adolescent females and males, respectively, and 26 and 35 µg Se day^{-1} for adult females and males, respectively. The United States National Academy of Sciences Panel on Dietary Oxidants and Related Compounds increased these recommendations up to 55 µg Se day^{-1} for both men and women and 70 µg Se day^{-1} for women during pregnancy and lactation. Recommended Se intakes for children are between 15 and 30 µg day^{-1}, depending on age (NAS, 2000). Comparable values are established by the United Kingdom Expert Group on Vitamins and Minerals (UK EGVM, 2002). The upper tolerable limit for Se was established at 400 µg Se day^{-1} (FAO/WHO, 1998; NAS, 2000; EGVM, 2002). Combining the recommended Se intake levels with main diet composition identifies the crop species that need to be fertilized with Se to overcome possible deficiencies.

Although the required Se levels are usually not met by natural Se sources, the Se levels in food reflects the available Se content of soils to produce this food (and the feed used to produce livestock). Accordingly, great variations in the Se content of food occurs. An optimized fertilizer strategy therefore needs to account for the capacity of soils to supply Se. Unfortunately, a robust, cheap and easy method to assess the plant available pool of Se in soil is still missing. Currently, the best option to estimate the Se supply of soils is to use the multiple regression models estimating plant available Se from extracted Se pools in combination with basic soil properties like pH and organic carbon (see chapter 2.4). A first estimate can be given by the statistical model of the global FAO study, but other country specific algorithms can be derived from the scientific publications listed in the reference list. Alternatively, existing data on Se levels in food products can be used to account for the Se supply from the natural environment. For most countries, this information is available, at least for the main wheat and maize crops. When the database is filled with known soil and plant Se levels, it is also possible to use dynamic machine learning principles to derive crop and soil related Se levels. Anyway, the recommended fertilizer dose needs to fill the gap between the desired and background Se levels in the crop.

The Se uptake efficiency is currently low, varying between 5% and 20%. Adapting the fertilizer strategy to local soil and crop conditions should be able to increase Se use efficiency up to 60% at minimum (Bussink, 2000). The meta-analysis has shown that fertilizer dose, application technology and timing has a substantial effect on Se contents in the crop. Adapting these three issues to the local conditions will certainly improve the Se use efficiency. The dataset collected can be used to derive algorithms integrating all these aspects in a quantitative way using machine learning principles or GLM modelling approaches.

In addition to these natural and environmental factors, there are also socio-economic drivers affecting the actual fertilizer strategies on farms. First of all, Se-enriched fertilizers should be available on the local market whereas their prices shouldn’t exceed the common basic fertilizers for N, P or K. This is important, because farmers are unlikely to fertilize with trace elements such as Se without incentives or government regulations that would make doing so profitable or mandatory. In addition, the available fertilizers should be manageable by farmers. When extra costs, activities or machineries are required, successful implementation of fertilizer strategies is not likely to occur. In addition, application techniques should fit within indigenous farm knowledge and management options. For example, the application of spraying technology is likely to depend on water availability, plot scale and available spraying technologies. Any field scale user of the decision support tool therefore needs a possibility to adapt the fertilizer strategy to its own local situation on a farm. For regional or national implementation, this adaptation is less relevant: fertilizer formulation and dose are in that case the main driving factors.

6.2.4 Proof of principle

Both the classical review and the meta-analysis show that it evidently helps to identify relevant fertilizer strategies based on specific production-ecological causes for micronutrient deficiencies, to assess the potential impact of micronutrient fertilization on crop production, and subsequently in improving human health and sustainability of agriculture. The developed framework for a decision support tool is not validated yet, but supporting evidence for the potential of such a DSS can be found in recent publications of Winkel et al. (2011) and Spadoni et al. (2007).

Both studies applied GIS-based modelling of agro-ecosystem properties while assessing spatial variation in crop Se uptake. Winkel et al. (2011) expect that increasing our understanding of the fate of Se in soils will result in spatially explicit models predicting distribution and availability of Se in areas where this is currently unknown. Such information would be extremely beneficial for poor rural communities that depend on local food products. They showed a successful example of this approach for arsenic on global, continental and regional scales. As an example, they have used this integrated modelling approach to identify regions in China that are likely to be Se deficient by combining soil and climate data. The created patterns visually match well with areas where Se deficient diseases occur and where soils contain low to marginal Se levels (Figure 20). This shows much promise for the development of risk map modelling and spatially explicit fertilizer strategies resulting from Se availability maps. The developed framework within our research extends this GIS-based strategy with a recommendation system adapting Se fertilizer strategies to the local properties of the agro-ecosystem.

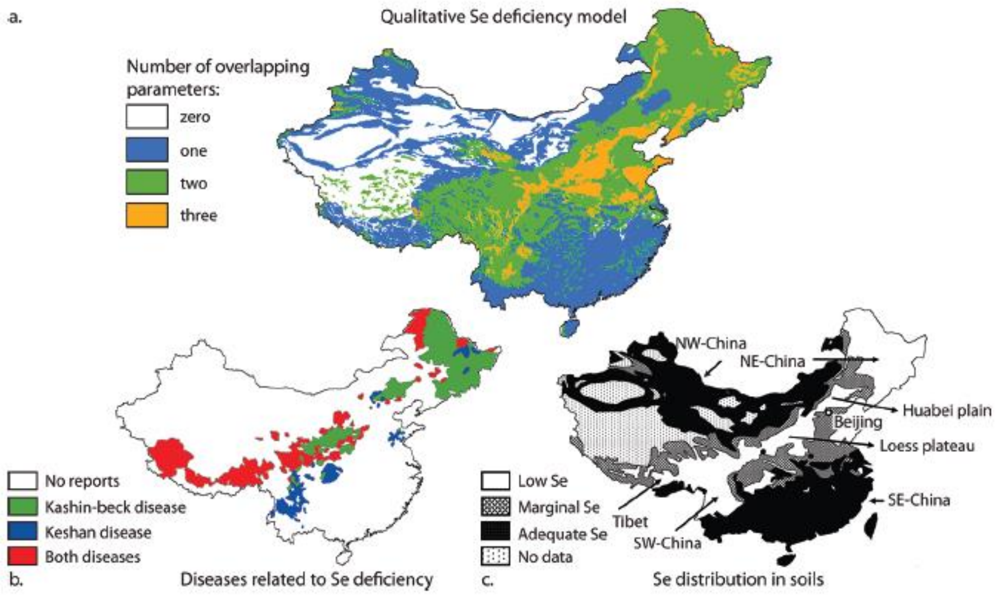

Figure 20. Comparison among selected maps of China. (a) Qualitative risk map for Se deficiency with the number of risk factors being present (ranging from zero to three). These risk factors are related to climate and soil variables. (b) (Co)occurrence of diseases that have been related to Se deficiency. (c) Se distribution in soils. Source: Winkel et al. (2011).

In another example, Spadoni et al. (2007) developed a multiple regression model based on six geochemical and pedoclimatic variables to predict the Se concentration of wheat in areas where analytical data were missing for different Italian soil regions (Figure 21). The statistical model succeeded in identifying Se enriched as well as depleted areas with an acceptable level of agreement with the biogeochemical map based on measured Se levels in wheat. This finding shows that an accurate description of plant Se availability can be made based on a combination of agro-ecosystem properties using GIS based modeling. Combining this information with appropriate fertilizer strategies derived from meta-analytical models or machine learning principles will evidently be helpful for an agro-ecosystem dependent fertilizer strategy.

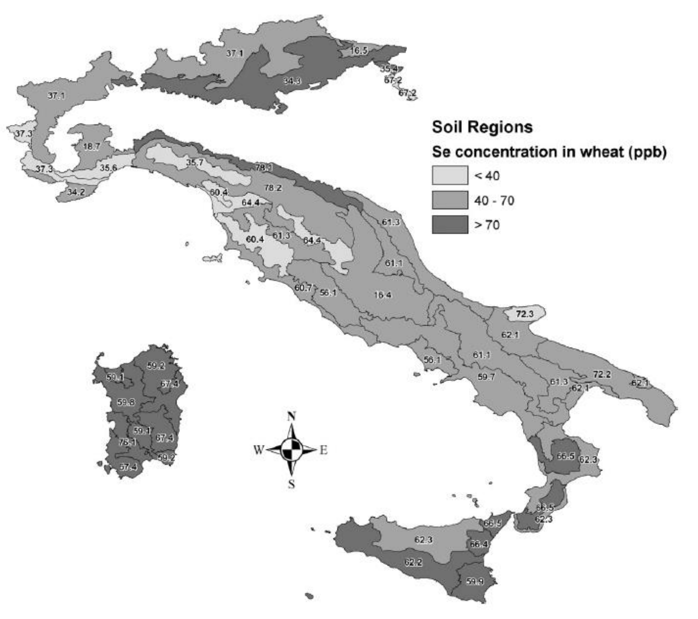

Figure 21. Selenium predicted concentrations for Italian wheat based on spatial explicit GIS modeling. Source: Spadoni et al. (2007).

6.3 SWOT analysis fortification methods

6.3.1 Introduction

Selenium deficiency is regarded as a major health problem for 0.5 to 1 billion people worldwide (Haug et al., 2007) and hence, fortification strategies increasing Se intake will have substantial positive effects on global human health. High Se containing supplements via medication, fortified food products, drinking water enrichment with Se or supplementing animal feed are possible remedies for Se undernourishment of human populations. Alternatively agronomic fortification via fertilization or breeding programmes might also be a safe way to increase Se uptake. Most common present routes to increase Se uptake are shortly evaluated below.

6.3.2 Agronomic fortification

Agronomic fortification might be an innovative strategy for addressing micronutrient malnutrition in a sustainable way (Miller & Welch, 2013). It involves the use of plant breeding, genetic plant engineering (Lonnerdal, 2003; Zhu et al., 2009) and agronomic approaches such as micronutrient fertilizer applications to increase Se levels in food crops and animal feeding (Bouis et al., 2011). For both arable and dairy ecosystems, agronomic fortification mainly focuses on optimizing the application of fertilizers and/or the improvement of the solubilisation and mobilization of Se in soil (White & Broadley, 2009). Conventional plant breeding and genetic engineering aim at improving plant varieties to acquire a higher capacity to accumulate Se in edible plant tissues and to increase their bioavailability for humans (Carvalho & Vasconcelos, 2013). Breeding for improved Se uptake and retention by crops might have potential since Combs (2001) and others (Wei, 1996; Graham et al., 1999; Lyons, 2003) argued that substantial variability exists in Se uptake within crop varieties. Agronomic fortification of pastures or forages using Se fertilizers has been widely demonstrated (Gissel-Nielsen, 1998; Gupta & Gupta, 2000, 2002). Finland, for example, started fortification with fertilizers in 1981 and obtained excellent results: Se levels of most arable and dairy food products increased and had a positive effect on human Se intake (Eurola et al., 2003). Crop and soil fertilization with Se have also had a large impacts on animal and/or human Se intake in countries such as Australia, New Zealand and France (Hartikainen et al., 1997). Compared to direct Se supplementation to food, agronomic biofortification is considered to be advantageous in that inorganic Se is assimilated into organic forms which are more bioavailable to humans. In addition, plants act as an effective buffer that can prevent accidental excessive Se intake (Hartikainen, 2005).

Agronomic fortification strategies are currently deployed in Southern hemisphere particularly targeting resource poor rural inhabitants in developing countries where commercial food fortification may not be practical or even possible (Miller & Welch, 2013). Main crops used for micronutrient fortification include rice, wheat, maize, beans, potato, cassava and pearl millet. The success of these fertilizer-based fortification strategies depends on three principles: (1) fortified crops must be high-yielding and profitable to farmers, (2) consumption of fortified crops must measurably improve the nutritional health of people and (3) socioeconomic adoption of fortified crops within farming strategies and diets.

Given a similar dose, the addition of selenate increases plant Se concentrations much more effectively than the addition of selenite (Chapters 3 and 4) due to their different sorption behaviour in soils (Gissel-Nielsen et al., 1984; Sing; 1991; Shand et al., 1992; Cartes et al., 2005). For this reason, selenate is more widely used than selenite, and is available in a range of commercial Se fertilizers (Broadley et al., 2006). Besides the use of granular fertilizers, liquid or foliar application might be an alternative method to overcome high retention in soil. Decisive criteria to select the proper Se form and application technique should account for initial Se levels in soil and the risk to Se retention and leaching (Jezek et al., 2012). Soil conditions such as pH, Eh, soil texture and the content of iron oxides and organic matter have a significant influence on plant uptake of Se (Hawkesford, 1997). Soil application of selenate is suitable to a wider extent and more variable soil conditions than selenite. The use efficiency of Se fertilizers also depends on application technique, dose and timing, and even additional soil amendments (e.g. liming) or basic fertilizers. Large variability in soil-to-plant transfer factor values and their dependence on soil, plant and other factors clearly shows that a sound understanding of the soil-plant system is necessary to make realistic use of such data in decision support systems. Some therefore argue that current data availability are unsuitable to account for spatial and temporal variation in Se limiting the use of mathematical models to match fertilizer dose to crop demand and soil supply (Bitterly et al., 2010). Others are more optimistic on the potential of GIS modelling tools (Spadoni et al., 2007; Winkel et al., 2011) or suggest alternative strategies by combining highly enriched crop products (from highly fertilized fields) with common products grown on unfertilized soils (Haug et al., 2007).

A drawback of the fertilization strategy is the frequent need for regular applications, which makes this approach costly, difficult in logistic terms and potentially negative for the environment (Carvalho & Vasconcelos, 2013). In addition, the scarce resource availability of Se might limit widespread application of Se fertilizers: Se reserves are expected to be exhausted in less than 40 years (White & Broadley, 2009) whereas the current plant uptake recovery of applied Se usually remains below 20% to 35%. So it can be argued that a sizeable proportion of the world's scarce Se resources will be lost and unavailable for future use. When Se is added to fertilizers at 10 mg per kg fertilizer about half of the world's Se production would be needed annually (Haug et al., 2007). These findings challenge the fertilizer fortification approach to create strategies that maximize the uptake efficiency of Se. Indeed, the review and meta-analysis show that fertilizer strategies can be used to increase the uptake efficiency by matching fertilizer type, dose and application to the local demand and soil supply (including residual effects of former fertilizations). In more detail, the efficiency of fertilizer Se uptake increase up to 50% as shown in the studies of Yläranta (1985; 1990), Ekholm et al. (1995), Tveitnes et al. (1996) and Eich-Greatorex et al. (2007).

Long-term fertilizer application of Se is sometimes considered as a potentially hazard to soils and water resources (Heninger et al., 1997), but extensive Finnish monitoring programs showed little evidence of Se enrichment in water ecosystems (Mäkelä et al., 1995; Wang et al., 1995). Only a few groundwater samples showed simultaneous increases in total N, P and Se concentrations that may have resulted from the leaching of Se from the fertilizers into the ground water (Mäkelä et al., 1995). Concern that the continuing use of Se-amended fertilizers might eventually lead to accumulation of toxic levels in the environment appears to be unfounded (Vuori *et al.*1994; Oldfield, 1999). In addition to the Finish data, the residual effect of Se treatments was found to be low to negligible in the following year, even when it had been applied at the high rate of 500 g ha^{-1} (Gissel-Nielsen, 1981; Ylaranta, 1983a, b, 1984; Singh, 1991; Shand *et al.* 1992; Gupta *et al.* 1993; Gissel-Nielsen & Gupta, 2001).

Another complication might be that farmers are unlikely to fertilize with trace elements that are essential for humans but not for the crop without incentives or government regulations that would make doing so profitable or mandatory (Miller & Welch, 2013).

Taking into account all the aforementioned limitations, it is important to explore more cost-effective and long-term strategies to improve Se concentrations in edible plant portions. It has been advocated that strategies of plant breeding (for enhanced Se uptake efficiency) and Se fertilization are the most desirable and most promising methods to increase Se status as they represent a fortification strategy that can deliver increased Se to a whole population safely, effectively, efficiently and in the most suitable chemical forms (Lyons, 2005). It is also easy to combine with other fortification approaches. However, in the end the viability of the fortification programs will be strongly dependent on the farmers and public acceptance as well as on the political support which will ultimately judge their costs and benefits. In addition to providing adequate quantities and forms of Se, an effective fertilization strategy must be demonstrably safe to the environment. In the longer term, it may be possible to exploit genotypic variation in Se accumulation in crops to select or breed varieties with increased Se (Lyons et al., 2004, 2005), thereby minimizing the need to use Se fertilizers in all agro-ecosystems except for situations with really low Se plant available levels. The potential of the breeding strategy has been debated (Noble & Barry, 1982; Yoshida & Yasumoto, 1987; Lyons, 2003), but it might have economic advantages over a strategy based entirely on fertilization.

6.3.3 Food processing strategies

Food processing has enormous potential to both increase dietary diversity and enhance concentrations of micronutrients in commonly consumed foods (Miller & Welch, 2013). Several types of commercial fortification programs are in place in countries around the world, including mass fortification, targeted fortification, voluntary fortification and mandatory fortification. Mass fortification is the addition of nutrients to foods that are generally consumed by all segments of the population: it is the preferred approach to reduce a particular nutrient deficiency within a country. Sometimes, only particular food products are enriched with micronutrients in order to target a particular group within a population. Both approaches can be regulated by policies and governmental regulations. Sometimes food companies voluntarily enrich food products with valuable nutrients whereas in other situation the government issues laws and regulations to fortify certain food products. The mandatory approach is typically implemented in countries where there is documented evidence of widespread nutrient deficiency diseases or low intakes of particular nutrients. The mandatory approach is usually preferred when there is a clear public health need and consumer knowledge is limited (Allen et al., 2006).

The use of high Se-containing supplements, including yeast-based formulations, appears to be an effective and safe option for human subjects (Rayman, 2004). It is generally agreed that organic forms are more bioavailable than inorganic forms of Se on the long term (Gupta & Gupta, 2002) whereas inorganic forms of Se can respond more rapidly to an acute Se deficiency (Thiry et al., 2012). Compared to agronomic fortification strategies, the production of Se enriched yeast is more manageable than the production of Se enriched crops (Dumont et al., 2006). However, supplements are relatively expensive and only a small proportion of populations are likely to take such personal intervention measures, particularly since recent EU legislation restricts the sale of such supplements (Broadley et al., 2006). In addition, large parts of Se in foodstuffs are currently still not qualified (Thiry et al., 2012), making it difficult to conclude their potential and actual health effects.

A well-known drawback of individual supplementation as a population strategy to improve nutrition is that those who are most in need tend to be the least likely to take supplements (Lyons, 2003). For example, women and children in developing countries often rely on one staple food for most of their energy and nutrient requirements and lack the money to improve their diet. The high prevalence of Fe, Zn, vitamin A, I and Se deficiencies suggest that any fortification strategy should aim to increase Se intake for whole populations (Graham & Welch, 1996; Graham *et al.* 2001). Anyway, not only technical solutions are required but education is also important to encourage people to consume appropriate amounts and proportions of different classes of healthy foods. Knowing these drawbacks, agronomic fortification is often preferred in countries in the Southern hemisphere, targeting resource poor rural inhabitants in developing countries (Miller & Welch, 2013). On the long term it might be more sustainable to breed wheat cultivars that are better at accumulating grain-Se (Lyons, 2003).

As inorganic Se has no taste, smell or colour, there is always a risk of overdosing the nutrient when adding it to food products. The mixing procedures must therefore be under strict quality control to avoid this possibility (Haug et al., 2007). This is usually the case for food industry companies in Western countries.

While food fortification is technically quite simple for most foods, it does require specialized processing equipment and trained personnel (Miller & Welch, 2013). Since the costs are ultimately paid by the consumer, the benefits of fortification needs to be addressed via educational programs whereas production costs need to be reduced by centralized food processing plants. In developing countries, food fortification is more difficult because most foods are grown locally on smallholder farms and are being processed in small scale processing operations. Capital costs for installing and maintaining equipment for adding nutrients may be prohibitive.

Food fortification has the potential to significantly benefit human population at large scale: “no other technology offers as large an opportunity to improve lives at such low costs and in such a short time” (World Bank, 1994). Food fortification requires collaboration and cooperation between industry and government agencies. To be successful, it should meet several criteria (Dary & Mora, 2002):

- The enriched food product should be widely consumed in significant and consistent quantities year round.
- The enriched food product should be processed centrally on a relatively large scale.
- The added nutrient should not alter food taste and appearance.
- The food carrier should not interfere with the bioavailability of the added nutrient.
- The nutrient should be stable in the food matrix under normal storage, transportation and food preparation conditions.
- The addition should be regulated by an appropriate government agency to prevent excessive intakes and to ensure consistent levels over time.
- A monitoring system should be in place to ensure compliance.

7 Conclusion

Whereas the global importance of Se deficiency has been recognized for decades, strategic micronutrient interventions tackling location specific situations are still lacking. This research aims to identify when applying Se fertilizers is effective in relation to agro-ecosystem properties. The identification of relevant fertilizer strategies are based on an inventory of specific production-ecological causes for Se deficiency, the potential impact of Se fertilization on crop Se uptake and the consequences for human health and the environment. Because the earth's Se resources are scarce and recycling is difficult, any fortification strategy should maximize Se use efficiencies.

Based on a classical review and two meta-analyses, we developed a framework for a web-based decision tool to guide policymakers, fertilizer producers and traders in the selection of agro-ecosystems where Se-fertilization is likely to have a large impact on product quality and human health. Basically, this tool integrates agro-ecosystem properties and fertilizer management options controlling Se use efficiency. These factors include crop type, yield potential, soil fertility, weather conditions and the availability of Se fertilizers. The focus on management strategies is relevant since fertilizer dose, fertilizer type and application strategy control the efficiency of Se fertilizers. Adapting these strategies to the local conditions of an agro-ecosystem will certainly increase the crop recovery of Se. A few examples are also given to show that integrating spatial data with modeling tools evidently helps to link Se demand (required dose) to fertilizer strategies.

In the short-term, agronomic fortification via fertilizers offers an effective means of increasing crop Se contents. In the longer term, a more sustainable approach that involves genetic crop improvement of enhanced Se accumulation would be preferable. In all cases, Se availability in soil will be a dominant factor but still difficult to determine. Other agronomic activities may also influence Se uptake by crops, such as macronutrient fertilization, soil amendments (e.g., lime, gypsum and organic matter) and soil and crop management (irrigation, compaction).

Feasible application technologies and fertilizer strategies have been studied since the 1960's in which most of the experiments focused on various selenate and selenite salts, being applied as soil fertilizers or in combination with basic nitrogen or phosphorus fertilizers. In general, selenate fertilizers proved to be more efficient than selenites in increasing plant Se levels. Elemental Se or other organic forms are rarely used due to their minor effect on crop uptake. Fertilizer application via foliar spraying and seed coating has also been explored. In general, Se fertilization by soil application of Se-supplemented NPK fertilizers was found to be a reliable, broadly applicable and cost-effective method for increasing Se levels in crops. Foliar application is a more resource efficient alternative.

By far, the most resource-efficient way to increase the Se intake in the world's population appears to be by adding Se to food products along the production chain. The positive effects of food processing is only limited by the fact that a limited number of people have access to processed foods, particularly in developing countries. The addition of Se via fertilizers might be an effective way to increase Se levels in crops on the one hand, and the intake of Se by humans and animals on the other, but large amounts of Se might be lost when fertilizers are misused.

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