Silicon cycling in Southeast-Asian paddy soils

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1 General introduction

1.1 Background – the LEGATO project

Rice (*Oryza sativa* L.) is the staple food for more than half of the world´s population (IRRI 2002) and the demand is continuously increasing (FAO 2002). More than 90 % of the world's rice is grown and consumed in Asia (Khush 2005). The project 'Land-use intensity and Ecological Engineering – Assessment Tools for risks and Opportunities in irrigated rice based production systems (LEGATO; www.legato-project.net) aims at advancing long-term sustainable development of irrigated rice cropping systems against risks arising from multiple aspects of global change (Settele et al. 2015). The focal issues are: (i) the socio-cultural and economic contexts, (ii) the link between local as well as regional land-use intensity and biodiversity, and (iii) the potential impacts of future climate and land use change. This thesis is embedded in part ii. One idea to improve long-term sustainability is to actively increase floral diversity around paddy fields in order to increase faunal diversity, and thus, natural pest control. When predator-prey relationships are brought to ecological equilibrium, the fauna feeding on rice pest insects could replace or mitigate the application of ecologically harmful pesticides. Also outbreaks of secondary pests can be avoided as populations only reach damaging levels when populations of their natural enemies are disrupted by treatments targeted toward another pest. Another or an additional possibility to decrease pesticide application while maintaining high yield levels is to increase the rice plants´ resistance against insect pests and pathogens. This can be achieved by a sufficient silicon (Si) supply to rice plants (Guntzer et al. 2012a; Haynes 2014), which is investigated in this thesis.

1.2 Silicon in rice plants

Rice accumulates up to 10 % Si in the dry mass, more than essential nutrients, such as nitrogen (N), phosphorus (P), potassium (K), or calcium (Ca) (Tsujimoto et al. 2014). However, it is only recognized as beneficial and not as essential nutrient element, mainly because there is no evidence of Si being involved in the metabolism of plants (Ma et al. 2011). Rice is a Si-accumulating plant according to the criteria of Ma and Takahashi (2002), who also recognized that Si-rich species have generally low Ca concentrations and vice versa. They proposed that plants with Si concentration over 1 % and a [Si]/[Ca] ratio > 1 are 'accumulators', plants with Si concentration below 0.5 % and a [Si]/[Ca] ratio < 0.5 are 'excluders', and plants not meeting these criteria are 'intermediates' (Ma and Takahashi 2002). Among Si accumulators are also other important crops, such as sugarcane (Savant et al. 1999), wheat (Rains et al., 2006), and maize (Mitani et al. 2009).

Rice takes up Si in the form of monosilicic acid from the soil solution passively as well as actively. The active transport is mediated by different transporters; low silicon 1 (LSi1), LSi2, and LSi6 were identified recently (Ma et al. 2006; Ma et al. 2007; Yamaji and Ma 2009); others still remain to be identified (Ma et al. 2011). In main and lateral rice roots, Si is transported by the combined action of the influx transporter LSi1 and the efflux transporter LSi2. LSi1 and LSi2 are polarly localized at the distal and proximal sides, respectively, of both root exodermis and endodermis (Yamaji and Ma 2011). LSi1 belongs to the group of aquaporins; the transporter is permeable to silicic acid in both directions and transport is driven by the Si concentration gradient. LSi2 is a putative anion transporter that actively transports silicic acid and is driven by a proton gradient. Following uptake by the roots through Lsi1 and Lsi2, Si is translocated to the shoot by transpirational volume flow through the xylem; the transporter for xylem loading of Si has not been identified yet (Ma et al. 2011). The transporter LSi6 mediates the transfer of Si from the large vascular bundles coming from the roots to the diffuse vascular bundles connected to the panicles (Yamaji and Ma 2009).

More than 90 % of Si taken up by the roots is translocated to the shoot (Ma and Takahashi 2002); 86 % of aboveground Si is stored in the stem and leaves (straw) (Klotzbücher et al. 2015b). In rice grain, silica is mostly deposited in the husk (Ma et al. 2011). The distribution of Si within shoot organs and tissue is determined primarily by the transpiration rate of the organ (Haynes 2014); when the concentration of silicic acid exceeds 2 mM in the cytosol, it polymerizes into amorphous silica ($SiO_2 \cdot nH_2O$), forming deposits called 'phytoliths' (from Greek 'plant stones') (Ma et al. 2011). In rice leaves, silica is deposited beneath the cuticle to form a cuticle-Si double layer (Figure 1.1) and in dumbbell-like vascular bundles cells, the bulliform motor cells (Ma et al. 2011). Silica can also accumulate in the vascular system and the endodermis of roots (Mitani and Ma 2005).

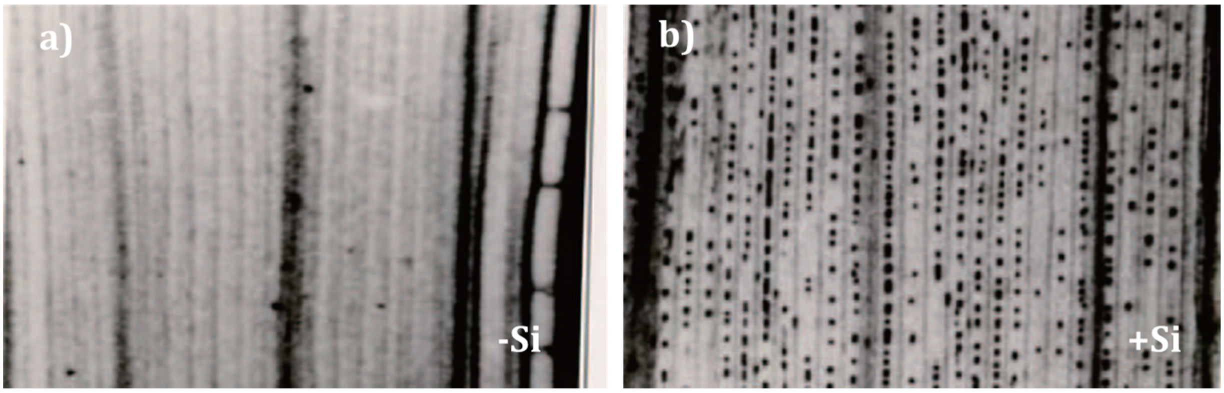

Figure 1.1 Soft X-ray image of rice leaves a) without deposition of Si and b) with deposition of Si; black dots are phytoliths (Ma et al. 2011)

Phytoliths give the plant strength and rigidity. Below a critical level of 5 % Si in dry mass, rice leaves are soft and loopy (Figure 1.2), mutual shading is high and photosynthetic activity and yields are lower (Dobermann and Fairhurst 2000). Silicon uptake by rice increases the plants´ tolerance against abiotic stresses, such as drought, lodging, salinity, high radiation and temperature, and freezing (Ma 2004). The mechanisms behind are (i) physiological, such as modulation of transpiration rates, increased photosynthesis, and decreased uptake of sodium and chlorine ions, and (ii) biochemical, such as improved antioxidant defences and osmotic adjustment with organic solutes (Haynes 2014). Silicon supply can also decrease the toxicity of the metals aluminum (Al), manganese (Mn), iron (Fe), cadmium (Cd), lead (Pb), and zinc (Zn) (Haynes 2014) and decrease the uptake of the toxic metalloid arsenic (As), as Si and As share the same uptake pathway in rice (Bogdan and Schenk 2008; Ma et al. 2008). Also biotic stresses are decreased by sufficient Si supply. The cuticle-Si double layer can mechanically impede penetration by fungi and insect pests, and thereby, avoid the infection process (Epstein 1994; Ma et al. 2011). It is also a physical barrier to sucking insects and leaf-eating caterpillars. Soluble Si in plants can act as a modulator of host resistance to pathogens through physiological and biochemical/molecular mechanisms. Furthermore, Si plays a role in the induction of chemical defenses against herbivores (Haynes 2014). Due to these benefits, increased Si supply can increase rice yields while decreasing the demand for pesticides (Guntzer et al. 2012a).

Figure 1.2 Rice plants grown in hydroponics with low (-Si) and high (+Si) Si supply; credit: Martin Hinrichs, Institute of Plant Nutrition, Leibniz University Hannover

1.3 The biogeochemical silicon cycle in rice paddies

The main Si pools in soils are the litho-/pedogenic mineral pool (lithogenic primary and pedogenic secondary minerals) and the biogenic pool (phytoliths and microorganisms). Silicon cycling in rice paddies is affected by transformation processes (weathering, mineral formation, decomposition of organic material), translocation processes within the soil-plant system (e.g. bioturbation, plant uptake), inputs (irrigation, dust, and fertilization), and exports (drainage, leaching, and removal of harvested products) (Sommer et al. 2006) (Figure 1.3).

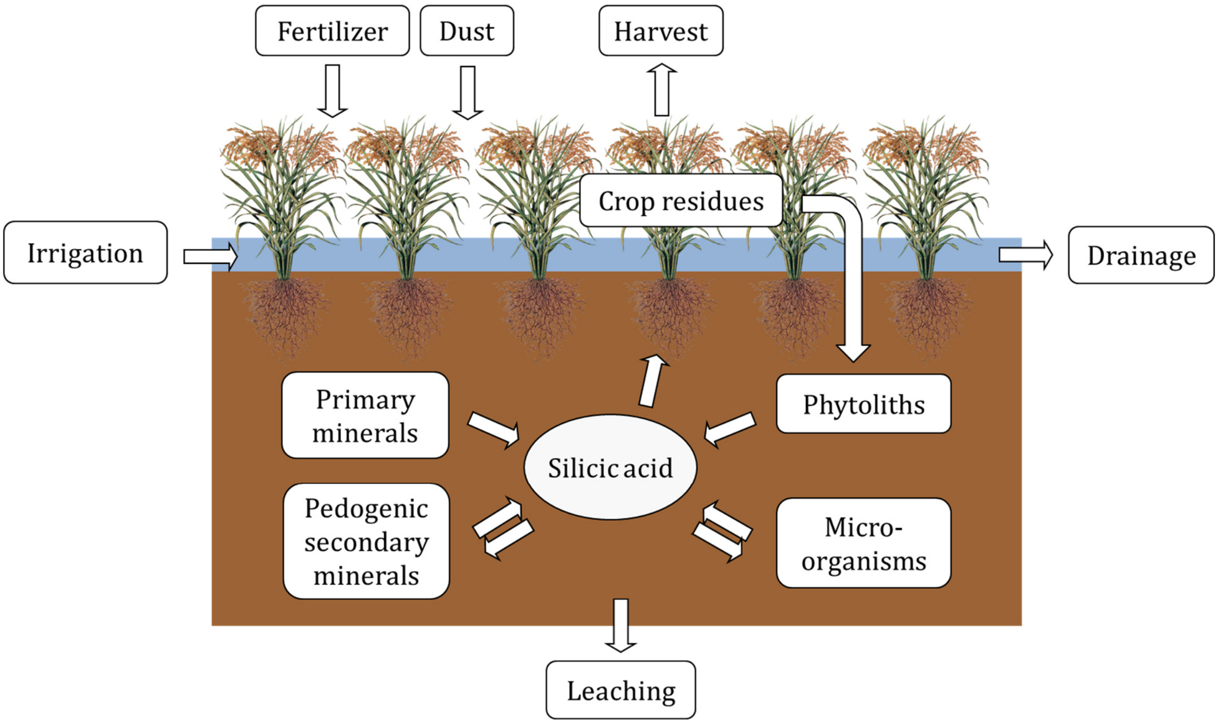

Figure 1.3 Scheme of the biogeochemical Si cycle in paddy fields

Silicon fluxes in soils are mainly mediated through water (Sommer et al. 2006). Dissolved Si in the soil solution is mostly present in the form of monomeric silicic acid (H_4SiO_4), which dominates over a wide pH range and can be transformed into polymeric silicic acid, becoming stable at pH > 10 (Dietzel 2000). Silicon concentrations in soil solutions mostly range between 0.1 and 0.5 mmol l^{-1} (Sommer et al. 2006).

Silicon is the second-most abundant element in the earth crust (28.8 weight %) after oxygen; more than 90 % of all minerals are silicates (Wollast 1983). Primary minerals are the original source of Si in the environment and release Si during weathering. Dissolved Si may either exit the soil system (by plant uptake, leaching, or drainage) or be re-deposited in crystalline phases (pedogenic secondary minerals, mainly clay minerals), poorly crystalline aluminosilicate phases (e.g. imogolite and allophane), and amorphous phases (e.g. opal) (Sommer et al. 2006). It can also precipitate as almost pure, amorphous silica phases on mineral surfaces, forming amorphous siliceous shells and covers, or can adsorb onto organic compounds, carbonates, or iron (Fe) and aluminium (Al) (hydr-)oxides. The affinity of Si to adsorb to Fe and Al (hydr-)oxides is high and sorption is related to amount, type, size, and crystallinity of the mineral (Sommer et al. 2006). Silicon might also be occluded in Al and Fe (hydr-)oxides by co-precipitation (Sommer et al. 2006).

Iron (hydr-)oxides play a key role in the interaction between the solid and liquid Si phases in paddy soils (Sommer et al. 2006). As paddies are periodically flooded, they are subject to cyclic changes in redox potential. Flooding of the field at the beginning of a cropping season induces reduced availability of oxygen in the topsoil. Thus, microorganisms start using alternative electron acceptors to oxygen, causing decreasing redox potential (Kögel-Knabner et al. 2010). Quantitatively, Fe^{3+} is the most important oxidant in paddy soils (Yao et al. 1999). Thus, Fe (hydr-)oxides increasingly dissolve during prolonged submergence, and thereby release associated Si. Drainage of the field shortly before harvest leads to aeration of the topsoil and to increasing redox potential. In result, Fe (hydr-)oxides re-precipitate and can thereby adsorb or occlude dissolved Si.

The biogenic Si sources in paddy soils consist mainly of phytoliths originating from crop residues, but also of microorganisms. Silicon can be released from biogenic sources through mineralization/dissolution (Sommer et al. 2006). Phytoliths may dissolve, be stored, or become structurally or chemically altered in soil (Barão et al. 2014; Sommer et al. 2006). The solubility of phytoliths increases with pH in the range of pH 3 to pH 12 (Fraysse et al. 2006). However, there is contradicting information in literature concerning the role of phytoliths in Si cycling. On the one hand, phytoliths have been extracted from archaeological sites (Santos et al. 2010; Piperno 2014), suggesting that they cycle slowly in soils and can be preserved for centuries. On the other hand, a number of recent studies suggest that fresh phytoliths are among the most important sources of Si in soil solution and Fraysse et al. (2009) showed in laboratory experiments that phytoliths extracted from different plants are 100-10,000 times more soluble than clay minerals, primary mafic silicates, or feldspars. It is still uncertain, what is the main source of plant-available Si in soils. Further constituents of the biogenic Si pool in soils are organisms originating from marine environments, such as diatoms, which build their skeletons from SiO_2, and siliceous sponge spicules (Clarke 2003; Struyf et al. 2009). Also testate amoebae take up Si to build their shells (Aoki et al. 2007). In general, knowledge about size, properties, and transformation of biogenic Si is very scarce (Sommer et al. 2006).

Inputs of Si into the soil-plant system can occur via irrigation. Irrigation water may contain solid Si particles as well as silicic acid in large amounts, depending on its origin, and thus, may be a significant source for plant-available Si (Tsujimoto et al. 2014; Klotzbücher et al. 2015b). Klotzbücher et al. (2015b) reported for Philippine paddies that inputs of dissolved Si by irrigation varied between 10 % and 94 % of plant Si uptake, whereby also dissolved Si losses by leaching and drainage were very high. Silicon particles can further be transported into the system via atmospheric deposition (Sommer et al. 2006). Silicon fertilization to rice is applied in the USA (Datnoff et al. 1997), China, and Japan (Haynes 2014). There are a few naturally occurring mineral materials such as wollastonite, olivine, and diatomaceous earth that can be mined from the earth's surface and used as fertilizer. More commonly used are industrial byproducts, mainly Ca and Mg silicate slags (Haynes 2014).

Exports of Si from the soil-plant system can occur via drainage and leaching. A simulation has shown that vertical Si transport results in potential loss of up to 10 Mg Si ha^{-1} from Vietnamese paddy soils with two annual rice cropping cycles; a loss that is approximately one order of magnitude greater than the amount of Si returned through incorporation of the crop residues (Nguyen et al. 2016). Advanced desilication due to high weathering stage of soils is most pronounced in humid tropical environments (Haynes 2014). Furthermore, Si is exported from the system with harvested products which can severely deplete soils of their phytogenic Si pool (Keller et al. 2012).

It is still uncertain if the main supply of dissolved Si in soil solution is of litho-/pedogenic or of phytogenic origin. Even if it was shown in laboratory experiments that phytoliths are by a multiple more soluble than litho-/pedogenic minerals, no field experiments on Si release of rice straw were conducted yet. Knowledge of phytolith turnover times would be important for farmers, who could actively influence plant-available Si by their crop residue management. Silicon inputs by irrigation water can hardly be managed by farmers as sources and amounts of irrigation water are mostly determined by availability and demand of irrigation water. Another option for farmers to increase Si availability to plants might be Si fertilization.

1.4 Objectives

The overarching goals of this thesis were to contribute to an improved understanding of the Si cycle in rice production systems and to generate recommendations on how the Si supply to rice plants might be improved in regions with low Si availability. The three specific aims of the thesis were to

(i) identify relationships between Si forms in soils and Si supply to rice plants by collecting and evaluating data across large geographic scales,
(ii) test the role of recycling rice straw and rice straw ash for Si supply to plants and biomass production, and to
(iii) test the effects of Si fertilization on the Si supply to plants and biomass production.

To identify the main determinants on Si supply to rice plants (i), 10 paddy fields in seven regions in Vietnam and the Philippines were chosen, respectively (altogether 70 paddies). Two of the Vietnamese regions are located in the Red River Delta (Hai Duong and Vinh Phuc), one in the Northern Vietnamese mountains (Lao Cai), and one in the Mekong Delta Tien Giang); the Philippine regions are located on the largest Philippine island Luzon, two of them in the lowlands (Laguna and Nueva Ecija) and one in the mountains in the North of Luzon (Ifugao). A screening of the different forms of reactive Si in topsoils was conducted using common soil extraction methods. Silicon concentrations in rice plants and biomass production were measured in order to examine relationships between reactive Si pools in soils and Si uptake by rice. Soil and plant data of the 70 paddies are presented in Chapter 2.

Interviewing farmers of the Legato study fields showed that some of them remove part of the straw from the fields after harvest (Klotzbücher et al. 2015). We were interested in the question whether this might be one reason for low plant Si availability observed at some of the Vietnamese fields (Chapter 2). To test the role of recycling rice straw for Si cycling (ii), straw was allowed to decompose in a laboratory pot experiment. Straw Si release and subsequent uptake by rice plants during decomposition were examined (Chapter 3). Also data obtained from a field experiment allowed to discuss possible effects of the straw management on Si cycling (Chapter 4). In particular, effects of Si release of burned rice straw on Si uptake by rice plants are discussed.

Use of Si fertilizers might be an option to improve the Si supply to plants in some rice production areas. To test the effects of Si fertilization on Si cycling (iii), two regions with inherently low Si supply to plants were chosen and field plot experiments were conducted applying silica gel, a readily soluble Si source. The first experiment was conducted during one single cropping season in the Red River Delta (Vinh Phuc); a low and a very high Si rate were applied to test for the effects of Si uptake by plants, biomass production and yield. Furthermore, the produced straw of different Si concentrations was used in the laboratory experiment (Chapter 3) to test the effects of increasing Si concentration in rice straw on its decomposability and Si availability for plants. The second Si fertilization experiment was conducted during two cropping seasons in the Mekong Delta (Tien Giang) in Vietnam. Silica gel was applied at three rates; changes in concentrations of dissolved Si, plant-Si-uptake, biomass production and yield were tracked (Chapter 4).

2 Silicon cycle in rice paddy fields: insights provided by relations between silicon forms in topsoils and plant silicon uptake

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Author contributions:
T. K. wrote the manuscript; T. K. and A. M. conducted soil sampling and analyzed the data, A. M. coordinated plant sampling; D. V. initialized plant sampling; all authors designed the study together and commented on the manuscript

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2.1 Abstract

Silicon (Si) enhances the stress resistance of rice plants. Silicon cycling in paddy fields is, however, still poorly studied. We examined relationships between Si forms in topsoil and plant Si uptake for 4 Vietnamese and 3 Philippine regions (10 fields per region). Mean rice straw Si concentrations within regions ranged from 3.0 to 8.4 %. For most of the Vietnamese fields they were lower than the critical value of 5.0 %, suggesting Si limitation of plant growth. For fields with low Si availability, straw Si concentrations were positively related to acetate-extractable Si in topsoil (i.e., dissolved and adsorbed Si). Such a relationship was not found for fields with high Si availability, presumably due to a maximum Si uptake capacity of rice plants. Mean annual Si uptake by rice within regions ranged from 0.31 to 1.40 Mg Si ha^{-1} year^{-1}. They are determined by the continuous supply of plant-available Si during the cropping season and by aboveground biomass production. Weatherable silicate minerals mainly determine spatial differences in supply of plant-available Si. Concentrations of alkaline carbonate-extractable Si in topsoil (an estimate of amorphous Si) largely differed between regions; (regional means of 2.2 to 16.7 g Si kg^{-1}). The differences in concentrations and amounts in topsoil are not related to phytolith (i.e., amorphous Si in straw) input, presumably due to other yet uncertain factors on carbonate-extractable Si in soil (e.g., differences in phytolith solubility or contribution of non-phytolith sources to Si in the extracts).

2.2 Introduction

Silicon (Si), the second most abundant element of the earth`s crust, has long been neglected by ecologists, presumably since not considered an essential nutrient for plants (Epstein 1999). However, recent studies showed strong beneficial effects of Si for plant growth. It enhances their resistance against pests, pathogens, and abiotic stresses, such as salts, drought, and storms (Cooke and Leishman 2011; Guntzer et al. 2012a).

Rice plants absorb Si as dissolved silicic acid (dSi) through a combination of two transporters (Lsi1 and Lsi2), localized at the distal and proximal site of root exo- and endodermis. The specific spatial arrangement of Lsi1, a Si permeable channel with a distinct selectivity (passive transport driven by concentration gradient), and Lsi2, an efflux Si transporter requiring a proton gradient (active transport) (Ma and Yamaji 2015), enables rice to accumulate Si in higher amounts than many other cereals (Sakurai et al. 2015). The dSi precipitates in the plant forming amorphous Si dioxide (ASi) bodies, the 'phytoliths'. Phytolith formation enhances the strength and rigidity of the plant. Rice straw Si concentrations can make up to 10 % of the dry mass; they typically are several-fold larger than concentrations of major nutrients such as nitrogen (N), phosphorous (P) and potassium (K) (Tsujimoto et al. 2014).

Traditional theory presumed that dSi in soil is primarily controlled by the abiotic weathering of silicate minerals, but more recent studies demonstrated that vegetation (i.e., plant-Si-uptake and recycling of phytoliths) also plays a significant role. Estimates suggest that the annual fixation of dSi by terrestrial vegetation is 10–40 times more than the yearly export of dSi from terrestrial ecosystems into coastal environments (Struyf and Conley 2012). Furthermore, it is now well established that vegetation affects the storage of reactive Si in soil, which potentially contribute to the Si supply to plants (e.g., Barão et al. 2014; Cornelis et al. 2011; Vandevenne et al. 2015). Humans strongly impact the biogeochemical Si cycle by altering land-use and by agricultural exports of Si in plant material (e.g., Clymans et al. 2011; Vandevenne et al. 2012).

What are the most reactive Si fractions in soil? Si readily available to plants comprises dSi and Si adsorbed to mineral surfaces, especially to surfaces of Fe- and Al-(hydr-)oxides (Sauer et al. 2006; Haynes 2014). Silicon might also be occluded in poorly-crystalline Fe-hydroxides (Sommer et al. 2006; Cornelis et al. 2011). In paddy soil, this Si might be released into soil solution when the fields are flooded during the cropping season, soil conditions become anoxic, and the Fe-hydroxides dissolve. In turn, precipitation of Fe-hydroxides when conditions become oxic again might `trap` some of the dSi. Phytolith dissolution is thought to be an important source of dSi (Haynes 2014). Laboratory tests show that the solubility of phytoliths increases from pH 3 to pH 12 (Fraysse et al. 2006). Under flooded conditions, the pH in paddy soil solution typically is neutral (Kögel-Knabner et al. 2010), and in this pH range phytoliths should be much more soluble than common crystalline silicate minerals (Fraysse et al. 2009; Guntzer et al. 2012b). Besides phytoliths, other forms of ASi can be present in soil, including shells of microorganisms (Puppe et al. 2015) and pedogenic forms such as ASi coatings on mineral surfaces (Sommer et al. 2006). The relative importance of these forms for Si availability is hardly studied yet.

The present study is part of the interdisciplinary LEGATO project, which aims at advancing sustainable rice cultivation in Southeast Asia (Settele et al. 2015). A core aim of the project is to identify strategies for reducing the input of harmful pesticides while maintaining high yield levels. Making use of the stress resistance that Si provides to rice plants might be a key factor in the development of sustainable cultivation systems. However, in order to achieve and maintain an optimal Si supply, our basic knowledge on the Si cycle in irrigated paddy fields needs to be improved. In the LEGATO project, altogether 70 paddy fields in Vietnam and the Philippines are studied. A first assessment of field characteristics showed that the concentrations of readily available Si in topsoil (estimated by extracting Si from soil with acetate solution) were significantly larger for Philippine than for the Vietnamese regions (Klotzbücher et al. 2015a). Presumably, a larger pool of weatherable primary silicates in Philippine soils is the main reason for the finding. A detailed study on relationships between Si fluxes (inputs/exports of Si via water fluxes and harvesting), forms of reactive Si in soil and plant-Si-uptake was conducted in one Philippine region (Laguna region; herein denoted as PH_1; Klotzbücher et al. 2015b). In this region, the total Si uptake by plants considerably differed between paddy fields, but it was not related to concentrations of reactive Si forms in topsoil, presumably as the Si uptake was not limited by Si availability. The topsoils showed high concentrations of carbonate-extractable Si (several times higher than concentrations reported for other types of ecosystems in literature), suggesting an accumulation of ASi. This finding was explained by interaction of a high input of plant-available dSi by irrigation and mineral weathering, high plant Si uptake and recycling of phytolith-rich rice straw to topsoil.

The relationships described in Klotzbücher et al. (2015b) might be typical for regions with high Si availability; consequently, they could be largely different in regions where availability is lower. Herein we examine relationships between reactive Si in topsoils and plant-Si-uptake for all seven LEGATO regions. Forms of reactive Si are estimated by commonly used soil extraction techniques. We use data on acetate-extractable Si ($Si_{acetate}$) presented in Klotzbücher et al. (2015a) for the discussion. Furthermore, we present results on oxalate-extractable Si ($Si_{oxalate}$) and carbonate-extractable Si ($Si_{carbonate}$). Data on $Si_{oxalate}$, $Si_{carbonate}$ and plant Si uptake for the Laguna region are taken from Klotzbücher et al. (2015b); data for the other six regions were not yet published. A limitation of the extraction techniques is that they are not selective for a particular form of Si in soil. Hence, the contribution of different forms to the extracted Si needs to be discussed. Furthermore, we will discuss the following questions: Which factors determine the concentrations/amounts of different forms of reactive Si in topsoil? What is their importance as Si source for plants? Which are the major factors determining Si concentrations in plants as well as the total amounts of Si taken up by the plants?

2.3 Material and methods

2.3.1 Study sites

Research of the LEGATO project focuses on seven study ‘regions’ of 15x15 km. The three regions in Luzon Island (Philippines) are denoted as PH_1 to PH_3, the four regions in Vietnam as VN_1 to VN_4 (Klotzbücher et al. 2015a). VN_3 and PH_3 are located in mountain areas, where rice is grown on terraces. Two regions are located in the lowland of Luzon Island (Philippines), two regions are located in the Red River area (Northern Vietnam) and one is located in the Mekong Delta (Southern Vietnam). The research of LEGATO focuses on altogether ten rice fields per region (see Appendix 1 for general information on sampling date, relief and location of sampled fields).

A detailed description of the characteristics of the study regions can be found in Klotzbücher et al. (2015a). Briefly, the climate of Luzon Island and Southern Vietnam is classified as monsoonal tropical, and in Northern Vietnam as warm humid subtropical. Luzon Island is dominated by extrusive rocks and sedimentary rocks containing andesitic-basaltic lavas and pyroclasts. The geology of our study regions in the Red River delta (VN_1 and VN_2) is dominated by silty and loamy sediments. In the Vietnamese areas upstream of the Red River, granites, gneisses, schists, sandstones and limestone dominate. In VN_3, Mesozoic sandstones dominate. The Mekong Delta in Southern Vietnam is filled with quaternary sediments of complex composition. The soils of the paddy fields belong to the units of Hydragric or Irragric Anthrosols (IUSS Working Group WRB 2014) but have developed from a wide range of other soil units. The dominant soils outside the paddy fields in PH_1 are Gleyic Cambisols, Orthic Luvisols and Eutric Nitisols; in PH_2 Gleyic Cambisols, Dystric Nitosols and Pellic Vertisols; in PH_3 Dystric Nitosols, Orthic Acrisols, Leptosols, Umbrisols and Cambisols; in VN_1 Eutric Gleysols; in VN_2 Orthic, Gleyic and Ferric Acrisols; in VN_3 Orthic Acrisols; in VN_4 Eutric Gleysols, and Dystric and Thionic Fluvisols.

The number of rice crops per year range between one in the mountains (PH 3, VN 3) to three in the Mekong Delta (VN 4). Most of the farmers in the other regions grow two rice crops per year. On 16 of the 70 study fields, farmers practice crop rotation, i.e., one additional fruit or vegetable crop is grown per year besides rice. The crop residue management differs from field to field. Some of the farmers return the straw untreated, while others burn the straw and return the ash to the fields. Some farmers permanently export part of the straw after harvest; this practice is most common in Northern Vietnam. However, no quantitative information is available on the amounts of exported straw. All of the farmers apply chemical nitrogen fertilizer, and most of them apply also chemical phosphorous and potassium fertilizers (Klotzbücher et al. 2015a).

2.3.2 Plants: sampling, calculations and analyses

Plants were sampled at harvest stage. The sampling procedure differed between fields depending on the seeding method. Direct seeding was applied in VN_4, while in all other regions the transplanting method was applied. In VN_4, we sampled plants within 1 m^2 areas that were assessed using a wooden frame (n=3 areas per field). In the other regions, four neighbouring `hills` of plants (one hill consists of 3-4 individual plants) were sampled instead of a 1 m^2 area (n=3 per field). Hill densities were measured at three random locations per paddy by counting hills within a frame of 1m^2 area.

The plant materials were dried at 65°C, the straw was separated from the kernels, and the weight of the different plant parts was determined. For samples from VN_4, we estimated the oven-dried weight from data on air-dried plant material (presuming the water content of air-dried material was 14 %, and of oven-dried material 3 %; Dobermann and Fairhurst 2000). The Si concentration in the different plant parts was determined by wave length-dispersive X-ray fluorescence analysis (WDXRF). Further details on the methodology are given in Klotzbücher et al. (2015b).

For some of the sampling campaigns, we were not able to obtain plant data for all 10 fields per regions (i.e., data for only 6-9 fields are available). When the farmers decided on harvesting in the short-term, it was not possible to arrange sampling in time.

When plant data for the different cropping seasons of a year were available (e.g., dry season and wet season), we were able to calculate the annual uptake of Si into aboveground biomass. This was the case for six to nine fields in all regions. Table 2.1 provides an overview on cropping seasons for which data are available.

2.3.3 Soils: sampling, calculations and analyses

We sampled soils from all of the ten paddy fields in each of the seven regions. Samples were taken from the surface to the top of the plough pan (Ap+Arp horizons), thus sampling depth varied between 10 and 30 cm. Samples were taken with a plastic corer of 7.5 cm diameter (n=9 cores per field). All soil core samples were air-dried and then shipped to the soil laboratories of the Martin-Luther-University in Halle (Saale), Germany, where they were oven-dried (40°C), pooled to obtain one sample per paddy field (same dry mass of soil was taken from all of the cores per field) and sieved (< 2mm) for laboratory analysis. A subsample of soil was dried at 105°C in order to determine the total water content.

Basic soil properties including pH (measured using a 1 M KCl solution), organic carbon (C_{org}) concentrations (determined using combustion analysis), particle size distribution, total reserve of bases, and concentrations of total Si and acetate-extractable Si ($Si_{acetate}$) were determined within the study of Klotzbücher et al. (2015a) and are given in Appendix 2.

For the present study, $Si_{oxalate}$ was determined by ammonium-oxalate extraction, a commonly used method to assess amorphous Fe- and Al-oxides according to the protocol of Schwertmann (1964), Cornelis et al. (2011). Data on oxalate-extractable Fe and Al are given in Appendix 2 on basic soil properties.

We furthermore applied the sodium carbonate extraction method according to DeMaster (1981). Silicon concentrations in carbonate extracts were determined after 1h, 2h, 3h, 4h, and 5h of extraction. We used the correction proposed by DeMaster (1981) to estimate the contribution of crystalline Si forms to $Si_{carbonate}$.

Data on amount of dry soil (105°C) of <2mm diameter in the sampling tubes with known diameter (bulk density), sampled soil depth and concentrations of $Si_{carbonate}$ in soil were used to calculate the stock of Si forms stored in soil above the plough pan.

Dissolved Si, Fe and Al in extracts were analysed using inductively coupled plasma optical emission spectrometry (ICP-OES, Ultima 2, Horiba Jobin-Yvon, Longjumeau, France). The extracted solutions were filtered (pore size: 0.45 µm) before analysis.

2.3.4 Statistics

The Sigmaplot 11.0 software was used for statistical analysis. Kruskal-Wallis one-way ANOVA on ranks followed by Dunn`s method for multiple comparison was used to test for statistically significant differences in concentrations of Si in straw, total plant Si uptake, concentrations and amounts of $Si_{oxalate}$, and concentrations and amounts of $Si_{carbonate}$ in soil between regions (this type of ANOVA was used because the assumptions of the standard ANOVA procedure were violated). Regression analysis was used to evaluate relations between $Si_{acetate}$ in soil and plant Si uptake and between biomass production and plant Si uptake.

2.4 Results

2.4.1 Rice plant Si uptake

Mean Si concentrations in rice straw differed significantly between the regions (data of all fields and seasons combined; Figure 2.1a). In general, they were larger in the Philippines than in Vietnam. The highest regional mean value of 8.4 % was found for PH_1 (with individual values in the range of 5.4 to 10.3 %), while the lowest mean value of 3.0 % was found for region VN_4 situated in the Mekong Delta (range of 2.2 to 4.2 %). Within the two countries, the regional mean values did not significantly differ (Figure 2.1a; Table 2.1).

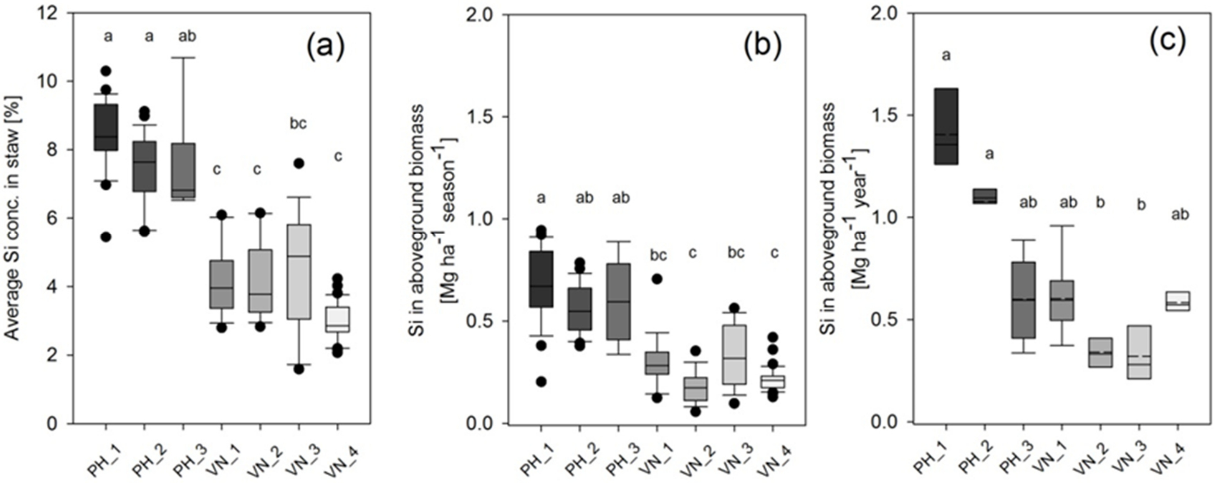

Figure 2.1 Si concentration in straw (a) and total Si uptake by rice plants per cropping season (b) and per year (c) for the seven LEGATO research regions (the solid line within boxes shows the median, the dashed line shows the mean; different letters indicate significant differences between regions); raw data are given in Appendix 3

Regional means of aboveground biomass production by rice plants within one cropping season ranged from 6.1 to 13.9 Mg ha^{-1} (Table 2.1). The amounts of Si uptake within a season ranged from 0.14 Mg Si ha^{-1} (VN_2), to 0.76 Mg Si ha^{-1} (PH_1). They were generally higher for Philippine than for Vietnamese fields, mainly because of the higher Si concentrations in the Philippine plants (Figure 2.1b). The regional means for annual Si uptake by rice plants were between 0.31 Mg Si ha^{-1} year^{-1} and 1.40 Mg Si ha^{-1} year^{-1}. The annual Si uptake was significantly larger for PH_1 and PH_2 than for VN_2 and VN_3, while no significant differences were found between the other regions (Figure 2.1c). In PH_3 and VN_3, the mountainous regions, only one rice crop is planted per year (2-3 crops are planted in lowland regions), and this explains the relatively low annual Si uptake. Potential amounts of Si recycled in straw range from 0.27 (VN_2) to 1.15 (PH_1) Mg Si ha^{-1} year^{-1}; the calculation bases on the assumption that all of the straw or the ash of the straw is returned to the fields, which is not the case for some of our study fields, where unknown quantities are not returned in some of the cropping seasons.

2.4.2 Oxalate- and carbonate-extractable Si in topsoils

Regional means of Si$_{\text{oxalate}}$ concentrations ranged from 0.04 g Si kg^{-1} (VN_2) to 1.42 g Si kg^{-1} (PH_3). In most comparisons between a Vietnamese and a Philippine region, concentration was significantly higher in the Philippine region, while no significant regional difference was found within one country (Figure 2.2). A similar pattern was found for amounts of Si$_{\text{oxalate}}$ stored in soil above the plough pan, for which regional means ranged from 0.06 Mg Si ha^{-1} (VN_2) to 0.57 Mg Si ha^{-1} (PH_1). However, note that the differences in amounts between Philippine and Vietnamese regions are generally less drastic than the differences in concentration (Figure 2.2). This is due to a lower storage of soil (<2mm) above the plough pan in the Philippines. Regional means of soil masses above the plough pan were 834 (PH_1), 1110 (PH_2), 702 (PH_3), 1851 (VN_1), 1406 (VN_2), 1564 (VN_3), and 1137 Mg ha^{-1} (VN_4).

Concentrations of Si$_{\text{carbonate}}$ were considerably larger than those of Si$_{\text{oxalate}}$. Regional means ranged from 2.2 g Si kg^{-1} (VN_1) to 16.7 g Si kg^{-1} (PH_1). They were significantly larger for PH_1 and PH_3 than for the Vietnamese regions, but no significant differences between PH_2 and the Vietnamese regions were found (Figure 2.2). Average amounts of Si$_{\text{carbonate}}$ stored above the plough pan ranged from 3.7 Mg Si ha^{-1} (VN_4) to 14.7 Mg Si ha^{-1} (PH_1). They were significantly larger for PH_1 than for the other regions except PH_3. No significant differences between the other regions were found (Figure 2.2).

Table 2.1 Aboveground biomass production, Si concentrations in straw and amounts of Si transferred to aboveground biomass by rice plants in the seven LEGATO regions; raw data are given in Appendix 3

Region	Season	No. of fields	Rice plant aboveground biomass Mg ha^{-1}	Si in straw %	Si in straw Mg ha^{-1}	Si uptake aboveground biomass Mg ha^{-1}
PH_1	Dec 11-May 12 (dry season)	8	12.9 (1.6)	9.1 (0.6)	0.63 (0.11)	0.76 (0.14)
	May 12-Nov 12 (wet season)	7	12.4 (2.1)	8.6 (0.8)	0.61 (0.13)	0.71 (0.14)
	Dec 12–May 13 (dry season)	8	11.2 (3.2)	7.6 (1.0)	0.45 (0.15)	0.56 (0.20)
PH_2	Jan 12–Apr 12 (dry season)	8	12.7 (1.6)	8.1 (0.8)	0.48 (0.09)	0.63 (0.09)
	Jun 12–Oct 12 (wet season)	9	10.3 (1.3)	7.8 (0.6)	0.42 (0.09)	0.51 (0.08)
	Jan 13–Apr 13 (dry season)	8	13.9 (2.5)	6.3 (0.8)	0.45 (0.15)	0.55 (0.16)
PH_3	Jan 13–Sep 13	9	10.2 (3.4)	7.6 (1.4)	0.55 (0.19)	0.60 (0.20)
VN_1	Feb 12–Jun 12 (dry season)	10	9.4 (2.5)	4.1 (0.9)	0.18 (0.07)	0.23 (0.06)
	Jun 14 – Oct 14 (wet season)	9	10.8 (2.3)	4.0 (1.0)	0.31 (0.13)	0.37 (0.14)
VN_2	Feb 12–Jun 12 (dry season)	9	6.1 (2.2)	4.3 (1.1)	0.10 (0.07)	0.15 (0.07)
	Jun 14–Oct 14 (wet season)	9	7.5 (2.0)	4.0 (1.1)	0.17 (0.07)	0.21 (0.07)
VN_3	May 12–Oct 12	9	9.9 (2.5)	4.8 (1.8)	0.23 (0.13)	0.28 (0.14)
	May 14–Oct 14	8	12.3 (2.3)	4.4 (1.7)	0.33 (0.14)	0.39 (0.15)
VN_4	Feb 12–Jun 12	10	12.2 (1.6)	3.0 (0.5)	0.17 (0.03)	0.24 (0.05)
	Jun 12–Sep 12	9	11.1 (1.8)	3.0 (0.6)	0.16 (0.06)	0.23 (0.07)
	Dec 12–Feb 13	8	10.9 (1.1)	2.8 (0.5)	0.13 (0.02)	0.17 (0.03)
	Feb 13–May 13	6	10.9 (1.1)	3.2 (0.7)	0.15 (0.04)	0.20 (0.04)

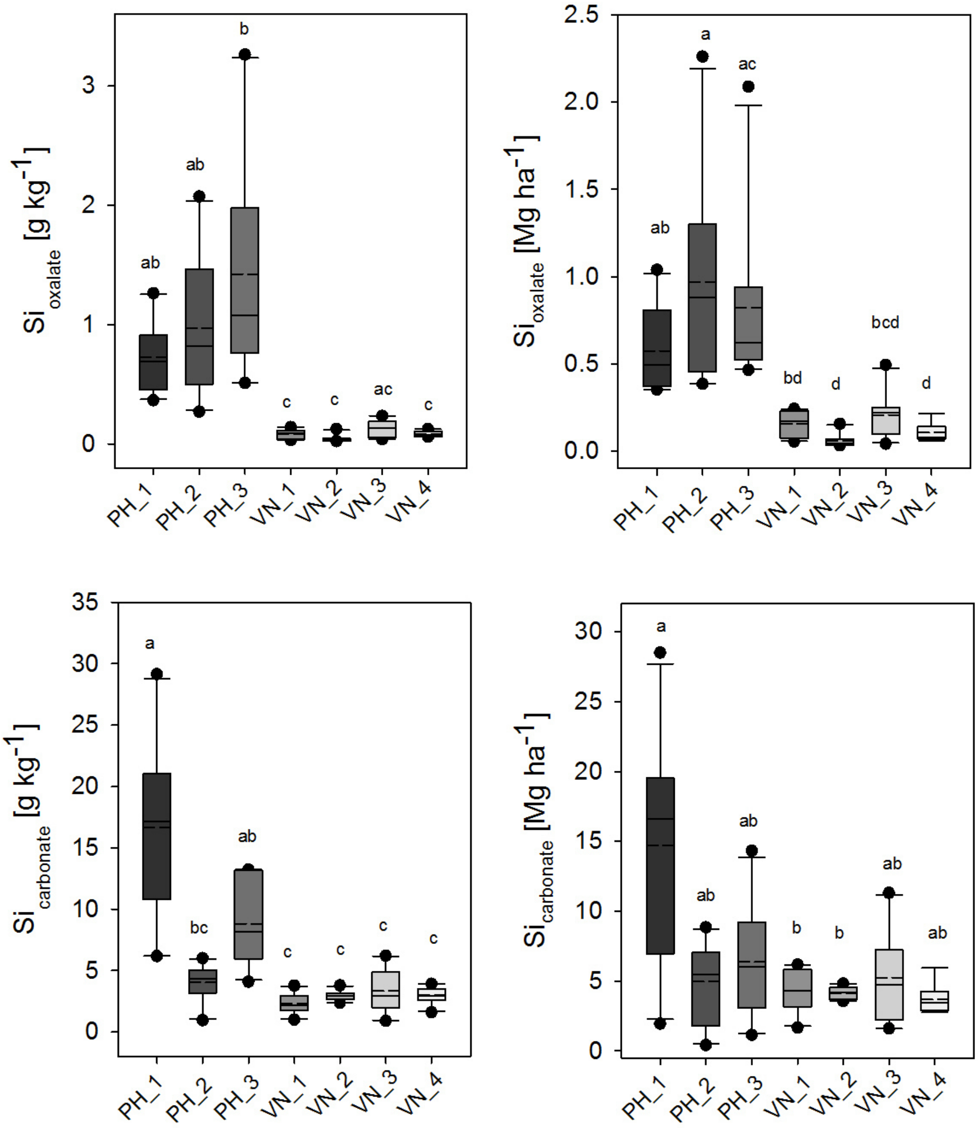

Figure 2.2 Concentrations and total amounts of Si$_{oxalate}$ and Si$_{carbonate}$ in soil stored above the plough pan of the seven LEGATO study regions (the solid line within boxes shows the median, the dashed line shows the mean; different letters indicate significant differences between regions), raw data are given in Appendix 4

2.5 Discussion

2.5.1 Possible Si limitation of rice plant growth in Vietnam

The Si concentrations in straw are indicative for how well the rice plants are supplied with Si. We showed that they can differ largely between regions. Dobermann and Fairhurst (2000) proposed a critical value of 5 %; lower concentrations typically cause soft and loopy leaves, increase mutual shading and reduce photosynthetic activity and yields. For 39 of the 40 Vietnamese fields, we found lower values for at least one cropping season. This finding supports recent reports suggesting that Si-limitation in rice production is a widespread phenomenon, i.e., critical straw Si concentrations were found for 35 of 97 rice fields in Louisiana, USA (Kraska and Breitenbeck, 2010) and 67 of 99 fields across different African regions (Tsujimoto et al. 2014).

We found no relationship between Si concentrations in straw and aboveground biomass or grain biomass production for our Vietnamese fields (not shown). However, the biomass production should also be strongly affected by other unknown factors (e.g., level of biotic stress, rice variety, other nutrients), and so our field data are not suited to directly test whether growth of the Vietnamese rice plants was limited by Si supply. Evidence for a Si limitation in Vietnam was, however, presented in Marxen et al. (2016). Here, a field experiment conducted in Vinh Phuc region (VN_2) showed that application of easily soluble silica gel to paddy topsoil increased Si concentrations in rice straw as well as grain biomass production.

2.5.2 Drivers of plant Si uptake

According to Haynes (2014), three parameters should be important for plant availability of Si in soil: (i) intensity (i.e., concentration of dSi in soil solution), (ii) capacity (the `reserve` supply of Si; for irrigated paddies, this should be mainly inputs of dSi with irrigation and dissolution of solid soil particles during the cropping season; Desplanques et al. 2006, Klotzbücher et al. 2015b), (iii) retention capability (Si adsorption capacity). For fields with straw Si concentrations of ~8 % and smaller, we found positive relationships between straw Si concentrations and concentrations of $Si_{acetate}$ in topsoil (Figure 2.3 above). It is presumed that the acetate extraction technique extracts dSi and some of the Si adsorbed to mineral surfaces (Sauer et al. 2006), hence, Si that is readily available to plants. $Si_{acetate}$ concentrations should thus be affected by intensity and retention capability. Relationships between similar indicators of readily soluble Si in soils and Si concentrations in plants were also found by others (Sauer et al. 2006; Tsujimoto et al. 2014; Haynes 2014). They can be used as a rough estimate on how well the plants are supplied by Si. Hence, they provide a basis for Si fertilizer recommendations. However, the one-time $Si_{acetate}$ analyses are not indicative for the total amounts of Si taken up by plants during a cropping season, which were on average 5.0 times larger than amounts of $Si_{acetate}$ stored in the topsoil at the date of soil sampling (Figure 2.3). The amounts of Si taken up by the plants should firstly be driven by capacity (i.e., the dSi inputs during the cropping season, which continuously `renew` Si readily available to plants) and secondly by aboveground biomass production, which considerably differed between fields (the correlations between Si uptake amounts and biomass production are shown in Figure 2.4; they were found when Vietnamese fields and Philippine fields were considered separately). The capacity is driven by weatherable primary minerals. We previously reported that the total reserve of bases, an indicator of weatherable primary silicate minerals, is larger for the Philippine than Vietnamese topsoils (Klotzbücher et al. 2015a). Primary mineral weathering might enhance the Si supply to plants by various mechanisms. It can directly provide dSi to soil solutions and plants, and thus also enhance production and recycling of soluble phytoliths. Furthermore, primary minerals in rocks and soils might determine dSi concentrations in irrigation water, which mainly derives from regional river and groundwater resources. Our data are in line with other recent studies indicating that the storage of weatherable minerals in soils is a major factor for spatial differences in continuous dSi inputs (Husnain et al. 2008; Tsujimoto et al. 2014).

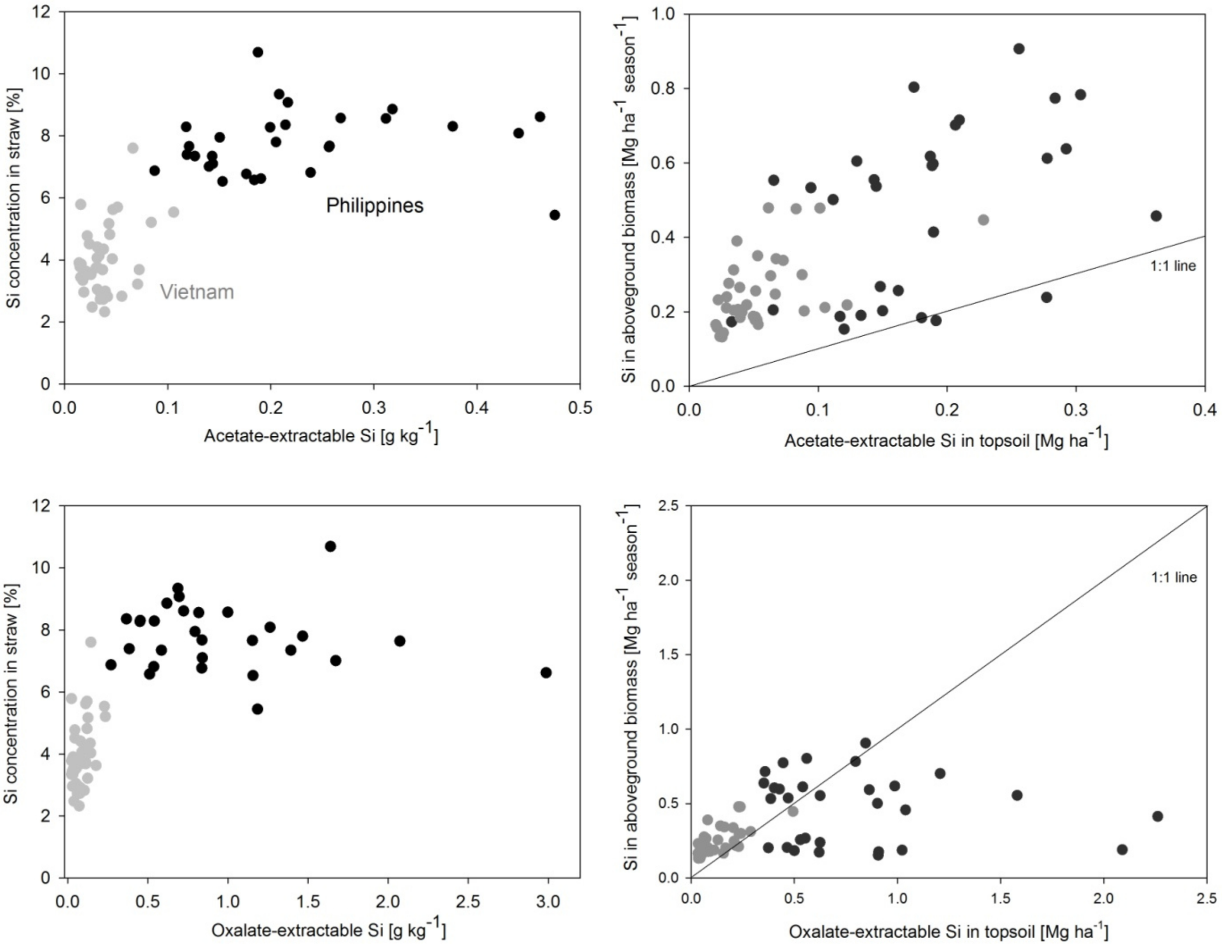

Figure 2.3 Relations between concentrations and amounts of $\text{Si}_{\text{acetate}}$ or $\text{Si}_{\text{oxalate}}$ ($\text{Si}_{\text{acetate}}$ data from Klotzbücher et al. 2015a) in soil stored above the plough pan and Si uptake by plants at harvest stage for Vietnamese and Philippine study fields (data for Si concentrations in straw and seasonal Si uptake are mean values calculated from data for the different cropping seasons; see Table 2.1 for information on cropping seasons, for which data are available)

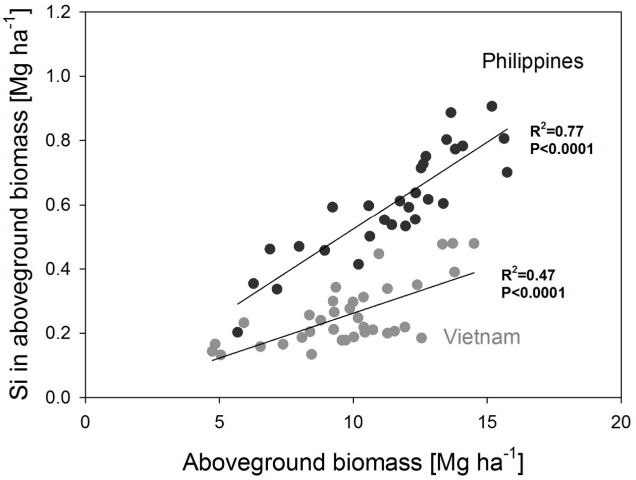

Figure 2.4 Relations between rice plant biomass production and total Si uptake per cropping season for Vietnamese and Philippine study fields (data for Si uptake are mean values calculated from data for the different cropping seasons; see Table 2.1 for information on cropping seasons, for which data are available)

The positive relationship between $Si_{acetate}$ concentrations and Si concentrations in straw was only perceived when all available data from fields of largely different Si availabilities were plotted (Figure 2.3). For instance, no relationship was found when data from the two countries were considered separately. On the Philippines, differences in straw Si concentrations between fields are relatively small despite large differences in $Si_{acetate}$ concentrations (Figure 2.3). We thus assume that the Si uptake was limited by a maximum uptake capacity of rice plants, which occurs once straw-Si concentrations of 8-10 % are reached. In accordance, other authors reported similar maximum Si concentrations in rice straw (Kraska and Breitenbeck 2010; Tsujimoto et al. 2014). Hence, in the Philippines, plants probably did not use all of the Si potentially available to them. In Vietnam, large differences in straw Si concentrations despite relatively small differences in $Si_{acetate}$ concentrations were found. This suggests other unknown factors besides Si availability in soil to play a crucial role for Si concentrations in straw.

The relationship of $Si_{oxalate}$ concentrations to Si concentrations in straw was similar to the one of $Si_{acetate}$ concentrations (Figure 2.3). However, the concentrations of $Si_{oxalate}$ were on average 3.7 times higher than the concentrations of $Si_{acetate}$. Furthermore, in many Philippine fields, the amounts of $Si_{oxalate}$ present in topsoil were larger than the amounts of

Si transferred to aboveground biomass during one cropping season (Figure 2.3). Both extraction methods assess Si adsorbed onto mineral surfaces, and possibly the oxalate method is more effective and extracts a larger share of this fraction. It furthermore is thought to effectively dissolve poorly crystalline Al-hydroxides, Fe-hydroxides, and poorly-crystalline/amorphous aluminosilicates such as allophone and imogolite (e.g., Cornelis et al. 2011). Regional means of the ratio between oxalate-extractable Fe and Al (Fe_{ox}/Al_{ox}) were between 2.7 in VN_3 and 11.0 in PH_3 (not shown) suggesting that poorly crystalline Fe-hydroxides were quantitatively more important than amorphous/poorly-crystalline Al-hydroxides and aluminosilicates. Hence, a large fraction of $Si_{oxalate}$ might comprise Si associated (adsorbed and occluded) with poorly crystalline Fe-hydroxides. The availability of this Si fraction might be tightly coupled to dissolution and re-precipitation of Fe-hydroxides during the redox cycles. Detailed quantitative studies on Fe-Si interactions are, however, not yet available.

2.5.3 Limits of data availability and uncertainties about other potential drivers

So far we discussed the most apparent relations between soil properties and plant Si uptake. This provided insight into likely drivers of the Si cycle. One needs to keep in mind that our study sites can largely differ in other potential drivers such as climate, water management, straw residue management and agricultural intensification. What about their role in spatial differences of plant Si uptake? Few details and quantitative data on these factors are currently available, and so we can only present a qualitative and more speculative discussion on possible impacts.

The mountain regions (PH_3, VN_3) differ from the lowland regions in many aspects. The first one to mention is climate. Temperatures are lower and precipitation is higher in the mountains (PH_3, VN_3) (Klotzbücher et al. 2015a). Climate should exert effects on Si cycling. For instance, it should determine dSi transport via water fluxes (irrigation inputs, plant transpiration etc.). The climate impact on Si availability presumably is highly complex and still poorly studied. Mountain and lowland regions furthermore differ in \`intensity\` of rice production, i.e., in lowlands farmers plant 2-3 rice crops per year, and in the mountains only one. Recently, Carey and Fulweiler (2015) hypothesized that intensification of rice cultivation enhances phytolith production. The correlation between amounts of plant Si uptake and aboveground biomass production presented herein (Figure 2.4) supports the assumption. The authors furthermore hypothesized that an increased phytolith recycling might enhance the transfer of dSi from terrestrial ecosystems to rivers and oceans because of a high solubility of phytoliths in soil. However, they also indicate that this effect typically is not observed, presumably due to a large export of phytoliths from crop fields upon harvest. On the `broad` geographic scale, we found primarily differences in plant Si uptake between Vietnam and the Philippines. This suggests that the collective effect of potential other factors is overshadowed by above discussed effect of weatherable minerals.

Silicon balances of paddy fields should strongly depend on straw residue management (Savant et al. 1997). Herein, straw contained in average 79 % of the Si transferred to aboveground biomass. A part of the interviewed Vietnamese farmers reported that they do not completely recycle the straw, while all of the Philippine farmers do (Klotzbücher et al. 2015a). Hence, straw removal might be another cause for low Si availability in Vietnam. Unfortunately, detailed historical and quantitative records on straw management practices are missing for our study sites. Hence, it is currently uncertain whether farmers in Vietnam really remove more Si from fields in the long term. In the Philippines, it is common that the straw is burnt on a pile, and the ash is not evenly spread on the field (Dobermann and Fairhurst 2002), which may cause large spatial differences of Si recycling within fields.

The plant Si uptake can also considerably differ within regions (Figure 2.1). This might be due to small scale differences in soil properties, straw management and/or water management. Our detailed assessment of the Si cycle in PH_1 showed that even within regions, water management can largely differ between fields (Klotzbücher et al. 2015b). For the other regions, data on water fluxes are missing. Studies directly addressing water management effects on Si availability are not yet available. Water management should affect inputs/exports of dSi as well as soil chemical processes including the dissolution of Si containing minerals. In particular in regions with low availability such as in Vietnam, more detailed research is necessary on how agricultural practices can affect Si availability.

2.5.4 Relations between $Si_{carbonate}$ in topsoil and plant Si uptake

Alkaline Na_2CO_3-extraction has been commonly used to estimate ASi amounts in soil. Recent work highlighted the limitations of the approach: a significant portion of $Si_{carbonate}$ may derive from poorly crystalline aluminosilicates and clay minerals (Barão et al. 2014; Meunier et al. 2014; Vandevenne et al. 2015), and Meunier et al. (2014) showed that only fresh phytoliths are effectively extracted, while aged phytoliths stored in topsoil are only partly extracted. Previously, we hypothesized that the high $Si_{carbonate}$ concentrations in topsoil of PH_1 might be due to high phytolith recycling (Klotzbücher et al. 2015b). However, the concentrations found for the other regions are lower (Figure 2.2). Regional differences in both, concentrations and amounts of $Si_{carbonate}$ in topsoil were not related to phytolith production (which can be estimated from data on plant Si uptake), i.e., they cannot be related to differences in potential amounts of phytolith input. The potential phytolith input should be much larger in PH_2 than in the Vietnamese regions, while no difference was found for $Si_{carbonate}$ concentrations and amounts between these regions. The finding might be explained by differences in phytolith solubility in soil; however, it may also be due to above discussed limitations of the analytical method. For instance, the contribution of non-phytolith sources to $Si_{carbonate}$ might differ between regions.

2.6 Summary and conclusions

Our data provide further evidence that Si limitation is a widespread phenomenon in rice cultivation systems. They suggest that the decisive determinant causing clear-cut differences in rice straw Si concentrations between Vietnamese and Philippine fields were differences in input of Si available to plants. These differences seem to be largely driven by weathering status of the parent materials in soil. On the broad geographical scale, this factor seems to mask the collective effect of other potential factors such as climate and agricultural practices. Amounts of Si taken up by plants within the countries are furthermore determined by plant growth parameters. In the Philippine regions with high input of Si available to plants, maximum Si concentrations in rice plants were reached, suggesting that at some fields not all of the potentially available Si was taken up by plants. The total amounts of Si transferred into aboveground biomass are driven by aboveground biomass production. Agricultural intensification in the last decades hence should have caused increasing phytolith production. Future research should address implications of this trend for Si availability and balances of rice fields. In particular in regions with low Si availability, a more precise knowledge about how human activity drives Si cycling is necessary.

2.7 Acknowledgements

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3 Interaction between silicon cycling and straw decomposition in a silicon deficient rice production system

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Author contributions:
A. M. wrote the manuscript and conducted the laboratory experiment; A. M., T. K., and N. V. S. conducted the field experiment; A. M., T. K, R. J, and D. V. designed the experiments; A. S. handled the litter bags and chose the fauna for the laboratory experiment; all authors commented on the manuscript

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3.1 Abstract

Background and aims Rice plants (*Oryza sativa* L.) contain large quantities of silicon (Si) in form of phytoliths, which increase their resistance to abiotic and biotic stresses. The Si cycle through rice fields is hardly studied. We tested how increasing Si availability affects rice growth and the decomposability of the straw. Secondly we tested the role of straw recycling for Si availability.

Methods In a field experiment, we applied three levels of silica gel during one rice cropping season. In a follow-up laboratory experiment, we used straw produced in the field experiment, having different Si concentrations, and studied straw decomposition, straw Si release, and Si uptake by plants.

Results Silicon fertilization increased Si contents, biomass production, and grain yield of rice plants. Increased Si uptake by rice decreased concentrations of C and some essential nutrients (N, P, K, Ca, and Mg) in the straw, and increased straw decomposability and Si release.

Conclusions Fertilization with silica gel is an option to improve Si supply to rice plants growing on weathered soils with low levels of plant-available Si. Phytoliths from fresh rice straw dissolve fast in soil, thus, recycling of rice straw is an important source of plant-available Si.

3.2 Introduction

Rice (*Oryza sativa* L.) is the staple food for more than half of the world's population and the demand for rice is continuously increasing (De Datta 1981; IRRI 1997). Silicon (Si) is a beneficial element for rice plants, usually taken up in larger amounts than essential nutrients, such as nitrogen (N), phosphorus (P), potassium (K), and calcium (Ca) (Ma and Takahashi 2002). Recent research revealed that Si increases plant resistance to biotic stresses, such as fungal and insect pests, as well as to abiotic stresses, such as strong rain, wind, and salinity (Guntzer et al. 2012a). Rice plants take up Si in the form of monosilicic acid from the soil solution, involving active and passive transport (Ma et al. 2006; Ma et al. 2007; Yamaji and Ma 2009). Within the plant, Si is transported with the transpiration stream and precipitates near evaporating surfaces in cell walls, cell lumina, or intercellular spaces, forming amorphous SiO_2 bodies, called phytoliths (Jones and Handreck 1967; Epstein 1999). Plant-available monosilicic acid in paddy soils originates from irrigation water, desorption from the soil matrix and weathering of Si-containing soil minerals (Klotzbücher et al. 2015b). Rice straw contains about 86 % of Si taken up by rice plants (Klotzbücher et al. 2015b). Some rice farmers remove part of the straw after harvest permanently from the field; others leave it in the field (Klotzbücher et al. 2015a). Deposition of crop residues is a crucial factor for Si balance of rice fields (Klotzbücher et al. 2015b). The effects of rice straw input on Si availability in soil should strongly depend on the solubility of the phytoliths, a process that is still not well understood.

Phytoliths have been extracted from archaeological sites and used to date back land-use changes (Santos et al. 2010; Piperno 2014). This suggests that phytoliths cycle slowly in soils and can be preserved for centuries. Phytoliths can contain considerable quantities of carbon (C) (e.g., 1–13 %; Parr and Sullivan 2011). Phytolith cycling is, thus, discussed as mechanism for long-term sequestration of C in soils (Parr and Sullivan 2011). By contrast, a number of recent studies suggest that fresh phytoliths are among the most important sources of Si in soil solution. Fraysse et al. (2009) showed in laboratory experiments that phytoliths extracted from different plants (larch, elm, fern, horsetail) are 100–10,000 times more soluble than clay minerals, primary mafic silicates, or feldspars. Few data are available on the Si release during rice straw decomposition. They suggest that decomposition produces considerable amounts of plant-available Si (Hossain et al. 2001; Ma and Takahashi 2002; Watanabe et al. 2013), implying that phytoliths are relatively soluble. It is not clear how the contrasting findings can be explained. Possibly, the solubility of phytoliths decreases during litter decomposition in soils by yet unknown mechanisms.

In regions with soils of low Si availability, Si fertilization might be an alternative or additional option to recycling of rice straw. Various authors reported positive effects of the addition of Si sources on rice growth and grain yields (reviewed by Guntzer et al. 2012a). The consequences of Si fertilization for the ecosystem are, however, not yet well explored. Changing Si availability may, for instance, affect the cycling of C and nutrients by altering (i) biomass production, (ii) plant nutrient uptake (Guntzer et al. 2012a) and (iii) re-mineralization of nutrients during litter decomposition.

Rates of litter decomposition depend on climate, litter quality, and the structure of the decomposer community (e.g., Cornwell et al. 2008; Strickland et al. 2008). Schaller and Struyf (2013) showed for the common reed (*Phragmites australis*) that an increased Si availability during plant growth affects nutrient composition of the plant tissue, which in turn caused changes in decomposability. In addition, Si concentrations in litter can affect fungal growth (Schaller et al. 2014) and the activity of invertebrate decomposers (Schaller and Struyf 2013), which play a crucial role in controlling rice straw decomposition rates (Schmidt et al. 2015a). The phytoliths may also act as a physical barrier hindering fungal hyphae to penetrate the litter surface and insects to feed on the litter (Schaller and Struyf 2013; Schaller et al. 2014). The mechanisms linking Si in the litter to growth and activity of decomposers have, however, not yet been studied in detail. In particular, effects of Si concentrations on decomposition and recycling of nutrients in rice fields have not been tested so far.

Using a combined field and laboratory experiment, we tested the effects of increasing Si availability on rice growth and decomposition of the resulting straw. In addition, we tested the role of straw recycling for Si supply to rice plants (Figure 3.1). Finally, the study also examined some of the consequences of increasing Si availability for the system.

Following questions were addressed:

Q1 Does Si fertilization increase Si uptake, biomass production, and yield of rice in soils with low levels of plant-available Si?

Q2 How do increased Si concentrations in rice straw affect its decomposition by microorganisms and mesofauna?

Q3 Are phytoliths readily dissolvable and does therefore recycling of rice straw increase Si availability in soils and Si uptake by rice plants?

Fertilization effects (Q1) were tested in the field experiment. Straw with different Si concentrations produced in the field experiment was then used in the follow-up laboratory experiment. Here, straw poor in Si and straw rich in Si were used to test for decomposition effects (Q2), as well as for Si release and Si uptake by rice plants (Q3).

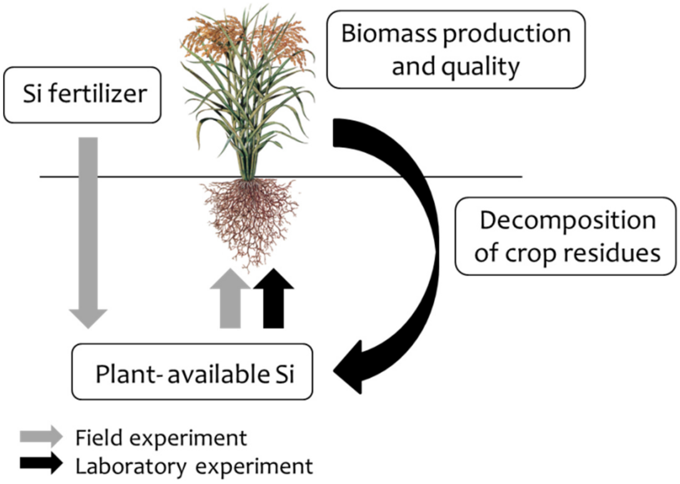


Figure 3.1 Scheme of the study concept

3.3 Material and methods

3.3.1 Field experiment

The field plot experiment was conducted in the Northern Vietnamese Vinh Phuc province (21°21’8.33^N 105°42’26.90^E), where plant-available Si concentrations in soils are low (Klotzbücher et al. 2015a). The experiment was conducted during the dry season in 2013 (February-June) on a hydragric Anthrosol (Dystric, Siltic); basic soil parameters are given in Table 3.1. We used silica gel for Si fertilization, applying Si at three levels: 17.3 Mg Si ha^{-1}, 0.4 Mg Si ha^{-1}, and a control without Si application. The very high Si application rate of 17.3 Mg Si ha^{-1} was applied to produce Si-rich straw for the laboratory experiment. The low Si application rate of 0.4 Mg Si ha^{-1} was used for testing the effects of an application rate that would be feasible for farmers to apply in economic terms. Five neighbouring paddies (farmers’ fields) were selected, and one replicate of each treatment was established in each paddy. The control plot was established at the edge of water inflow; next to it the plot with the low Si application rate, followed by the plot with the high Si application rate. This arrangement of plots was chosen in order to minimize redistribution of applied Si with the inflowing water. Plot size was 2 m×2 m; plot areas were marked with bamboo sticks at the corners. Industrial-grade silica gel of 2–3 mm grain size (TTL Phú Lương, Hanoi, Vietnam) was homogeneously distributed in the plots and mixed into the topsoil using a spade before flooding the fields. Soil tillage, fertilization with N and K, and pesticide application were carried out by the farmers according to their common practice. Soil was ploughed by a machine 8 to 12 days after Si application (dates varied between the five fields); 12 to 14 days after Si application, soil was ploughed again by buffalo directly before rice (*Oryza sativa* L. cv. Khang Dan 18) seedlings were transplanted. Four months later, rice plants from the core of each plot (inner 1.5 m×1.5 m) were harvested in two steps: first, the upper part of all plants in a core plot was cut (one third to a half of the plant’s height), then the lower part was cut directly above the soil surface. Grains were separated from straw (stems and leaves). Afterwards, hulls were separated from grains using forceps.

Table 3.1 Basic soil parameters of the hydragric Anthrosol (Dystric, Siltic) (IUSS Working Group 2014), horizons and texture were classified according to FAO (2006), TOC = total organic carbon, CEC = cation exchange capacity, BS = base saturation

Depth [cm]	Horizon	Texture	pH	TOC $[\text{g kg}^{-1}]$	C/N	CEC 3)	Ca^{2+} $[\text{mmol}_c\ \text{kg}^{-1}]$	Mg^{2+}	K^+	Na^+	BS [%]
Composite sample for laboratory experiment											
0-20	Arp	SiL	4.4 1)	19	11	67	19.6	2.6	0.4	≤ 0.1	34
Soil profile											
0-20	Arp	SiL	5.7 2)	16	11	60	15.7	≤ 1.4	0.9	0.2	30
20-27	Ardp	SiL	5.2 2)	9	11	43	10.1	≤ 0.2	0.8	0.2	26
27-50	Bg	SiCL	5.4 2)	3	10	92	16.3	2.5	0.8	0.4	22
50-80	Bg	SiCL	n.a.	2	7	82	12.4	3.4	0.8	0.3	21

1) Laboratory measurement using KCl
2) Field measurement using $CaCl_2$
3) Extraction with ammonium acetate at pH 7

3.3.2 Laboratory pot experiment

Straw produced in the field experiment was used in the laboratory experiment. Therefore, the lower part of straw from the control plots and from the 17.3 Mg Si ha^{-1} plots of the field experiment were pooled, respectively. These samples are referred to as Si-poor straw (control in the field experiment) and Si-rich straw (17.3 Mg Si ha^{-1} in the field experiment).

The experiment was conducted in a climate chamber with 11/13 h light/dark cycle at air temperature of 28 °C/25 °C, air humidity of 70 %, and light intensity of 350 µmol m^{-2} s^{-1}.

The experiment had three factors:

(i) Kind of Si source: We used straw with different Si concentrations (Si-poor straw and Si-rich straw) to study the effect of increased Si uptake by rice plants on their decomposability, Si release and availability. We also applied a control without Si application and a treatment with silica gel application to compare Si release and availability to the treatments with straw.

(ii) Addition of mesofauna: For both types of straw (Si-poor straw and Si-rich straw), we applied treatments with (+Fauna) and without (−Fauna) the addition of individuals of three decomposer groups (see below) in order to study the effect of increased Si concentration in rice straw on decomposition by those invertebrates.

(iii) Rice growth: Rice seedlings (*Oryza sativa* L. cv. IR 64) were transplanted to all treatments with straw to study Si uptake. The treatment with silica gel and the control without Si application were run with (+Plant) and without (−Plant) rice plants to study the effect of Si uptake by plants on Si release and availability.

The approach resulted in eight treatments (Figure 3.2) replicated five times. The experiment was divided in two phases: a litterbag incubation phase of 33 days and a rice growth phase of 30 days, resulting in an entire experimental period of 63 days.

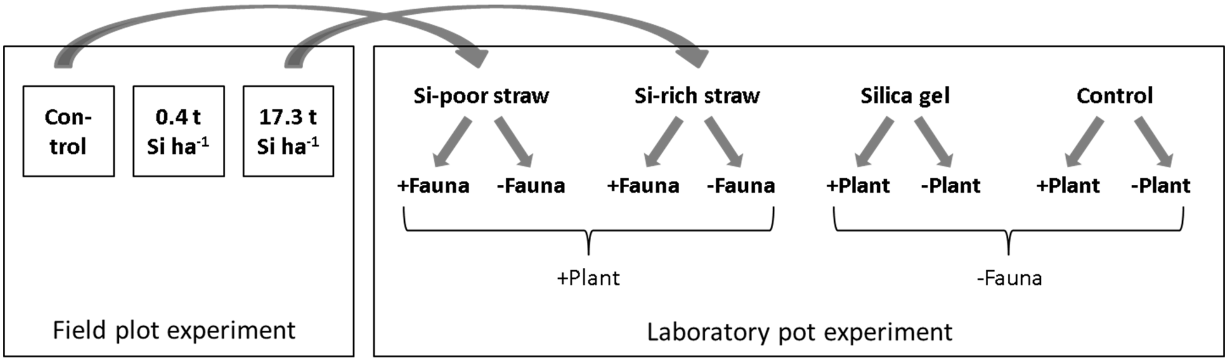


Figure 3.2 Scheme of the treatments in the field and in the laboratory experiment

Pots of 2 l volume were filled with 1700 g of topsoil from Vinh Phuc province; basic soil parameters are given in Table 3.1. For the treatments with straw, 2 g of straw, out of 12 g per treatment in total were packed in litterbags and the remaining 10 g were mixed with the soil (straw was cut in pieces of 2–7 cm length). The straw application equaled about 20 Mg ha^{-1}, roughly the equivalent of straw produced in five cropping seasons. We decided to use such a large amount of straw to (i) achieve a relatively large ratio of straw mixed with soil to straw in the litterbags, thus, to keep the portion of the straw removed with litterbags after 33 days small, and (ii) to maintain a sufficient amount of straw residues after 33 days in the litterbags for nutrient analyses. Litterbags had a size of 10 cm×10 cm and were made of nylon net of 5 mm×5 mm mesh size. Litterbags were retrieved on day 33. For the treatments with silica gel, soil was mixed with 2.85 g of silica gel of 70–200 µm grain size (Fluorochem Ltd, Hadfield, UK). This corresponded to the amount of Si added with the Si-rich straw based on the initial analyses of straw samples from the field plots using XRF spectroscopy (see analysis below).

Fauna was added to the particular treatments at the beginning of the experiment, directly after submergence of the soils. Around 200 individuals (0.6 g dry weight) of *Lumbriculus variegatus* (Annelida, Lumbricidae), around 2000 individuals (0.6 g of dry weight) of *Tubifex tubifex* (Annelida, Naididae), and around 900 larvae (0.7 g dry weight) of *Chironomus plumosus* (Arthropoda, Chironomidae) were added. Individuals of the same species were packed in bags containing 90 ml of nutrient solution and were ordered from www.interaquaristik.de. We have chosen those species as annelids and chironomid larvae are among the most abundant groups of invertebrate decomposers in flooded rice fields (Schmidt et al. 2015b). Most earthworm species, like *Lumbriculus variegatus* are edaphic litter dwelling organisms feeding on dead organic matter. *Chironomus plumosus* and *Tubifex tubifex* rather indirectly contribute to the decomposition of rice straw, e.g., by grazing on the straw surface which promotes microbial reproduction and colonization rates and therefore their decomposition activity.

At the beginning of the second phase (day 33), immediately after litterbag retrieval, rice seedlings (*Oryza sativa* L. cv. IR 64) were transplanted to the pots. Seeds had been incubated 15 days for germination, 2 days in an oven at 58 °C, 1 day at room temperature, 1 day soaking in distilled water, 3 days in a moist tissue in an incubator with 14/10 h light/dark cycle at air temperature of 30 °C, and 8 days on vermiculite in the incubator. After transplanting to the pots, plants grew for 30 days, and then rice shoots were cut above the soil surface. We kept the soils submerged with distilled water during the entire experiment. Supernatant water was only allowed to evaporate at the end of both experimental phases, before litterbag retrieval and before plant harvest.

Soil solution was sampled every 2–5 days, using permanently installed suction cups (Rhizon SMS, Rhizosphere research products, Wageningen, The Netherlands) that consisted of a 5 cm long porous part with an outside diameter of 2.5 mm, a pore size of 0.12–0.18 µm, and a 60 cm PE/PVC tube. Up to 2 ml of soil solution were sampled per pot at a suction of 40 kPa for determination of Si; sample vials contained 40 µl of HNO_3 (65 %) to prevent co-precipitation of dissolved Si and Fe oxides and sorption of dissolved Si onto Fe oxide-surfaces (Sauer et al. 2006). Additional samples were taken at the same dates for pH measurement using empty vials.

For continuous measurement of the soil redox-potential, one pot of each treatment was equipped with a redox electrode and a reference electrode (Ag/AgCl) connected to a logger. The reference electrode was in contact with the soil solution via a salt bridge constructed according to Ackermann et al. (2008) to avoid ion transfer to the soil solution.

3.3.3 Analyses

For determination of Si, P, K, Ca, and Mg in plant samples of the field experiment, XRF spectroscopy (S4 PIONEER, Bruker-AXS, Karlsruhe, Germany) was applied. To do so, three grams of ground and dried (85 °C) samples were mixed with 650 mg wax; then 32 mm pellets were prepared by pressing with a force of 12 Mg. The XRF measurements were performed using a wavelength-dispersive XRF spectrometer (S4 PIONEER, Bruker-AXS, Karlsruhe, Germany), equipped with a 4 kW-Rh X-ray tube (75 µm Be window), 60 kV generator, and an eight-position crystal changer. The spectrometer operating conditions were vacuum, 23-mm collimator mask and 0.46° collimator in conjunction with the analyzing crystal PET, and 30 kV at current of 80 mA. Calibration was performed using a plant matrix standard addition method: a dried and ground grass sample was mixed with different amounts of SiO_2 (2–14 % with an increment of 2 %), pressed to pellets and measured under above described conditions.

For determination of Si in plant samples of the laboratory experiment (Si-poor straw, Si-rich straw, straw residues from the litterbags, and harvested rice shoots), samples were dried at 65 °C for 48 h, ground, and extracted using a microwave-assisted digestion method (Haysom and Ostatek-Boczynski 2006). To do so, 100 mg of a sample (two repetitions) were subjected to nitric acid/peroxide oxidation in a low-pressure microwave digestion system (MARS 5 Xpress, CEM, Kamp-Lintfort, Germany). Then, the residue was dissolved in 10 % sodium hydroxide at 180 °C with maximum energy input of 800 W using a microwave-system (MARS 5 Xpress, CEM, Kamp-Lintfort, Germany). The extracts were neutralized and filtered (0.45 µm) before Si was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (Ultima 2, Horiba Jobin-Yvon, Longjumeau, France). Silicon in soil solutions was also determined by ICP-OES.

We used different methods for determining Si in plant samples of both experiments, because sample masses were too low to allow XRF spectroscopy in the laboratory experiment. XRF spectroscopy requires lower effort (time and chemicals), but more sample material (3 g of dry matter) than alkaline digestion; it was used in the field experiment as well as in a field survey (Klotzbücher et al. 2015a, b). We tested the comparability of the two methods by analysing 13 plant samples (originating from different studies) with Si concentrations covering the range of our samples. Results were 1.4±0.4 times higher when samples were analysed by XRF spectroscopy.

For determination of P, K, Ca, and Mg in Si-poor straw, Si-rich straw and straw residues from the litterbags, samples were subjected to digestion with HNO_3 in a pressure unit; the extracts were analyzed by ICP-OES. Concentrations of C and N were measured using a dry combustion analyzer (Vario EL, Elementar, Hanau, Germany).

3.3.4 Data analysis

Analyses of variance (ANOVA) were performed using SigmaPlot software version 12.0 (Systat Software Inc.). If required, Tukey’s HSD test was performed as posthoc analysis. Results are given in the tables and figures presenting the analysed data.

3.4 Results

3.4.1 Field experiment

Silicon concentrations in rice straw increased upon the application of Si gel in the field (Figure 3.3a). The increase averaged 28 % (addition of 0.4 Mg Si ha^{-1}) and 120 % (addition of 17.3 Mg Si ha^{-1}) compared to the control, respectively. Likewise, Si concentrations in rice hulls increased by 34 % (0.4 Mg Si ha^{-1}) and 72 % (17.3 Mg Si ha^{-1}), respectively (Figure 3.3b). Silicon concentration in rice grains was ≤0.1 in all treatments (data not shown).

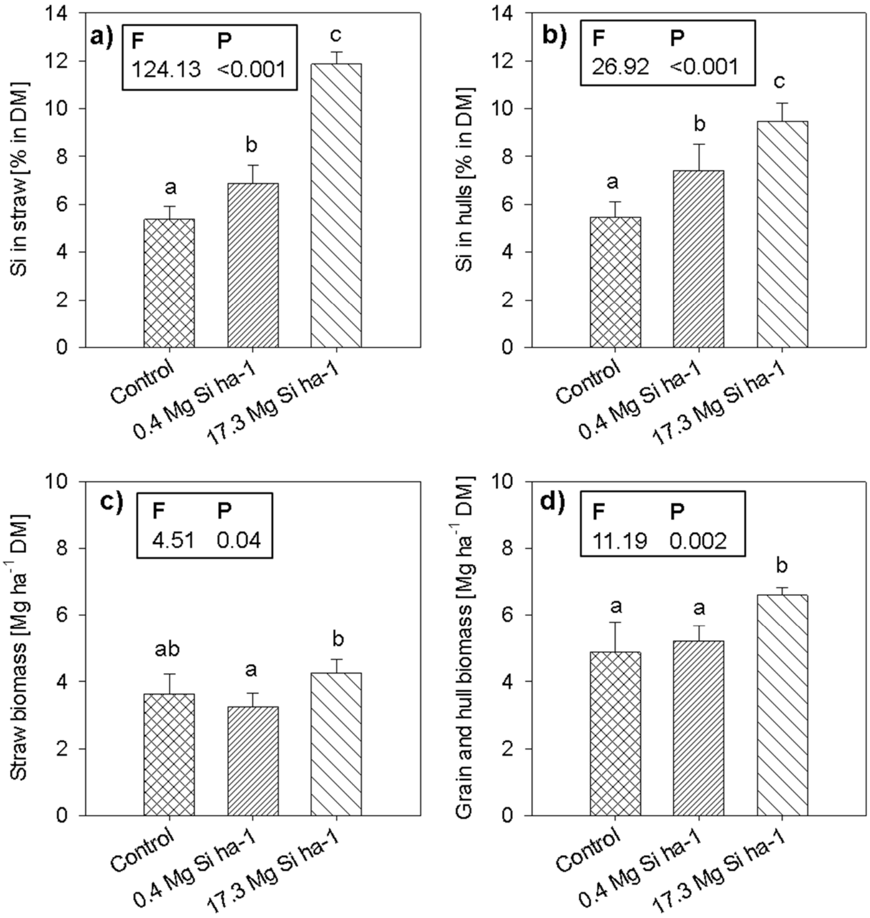


Figure 3.3 Impact of fertilization with silica gel on Si concentrations a) in rice straw and b) in rice hulls at harvest stage, and on c) straw biomass production and d) grain and hull biomass production in the field experiment; error bars represent standard errors; results of one way ANOVA are given in the legends, results of Tukey's HSD test ($P < 0.05$) are given by small letters

Biomass production of straw was not affected by Si application (Figure 3.3c), but grain yield increased by 35 % upon the high Si application rate (17.3 Mg Si ha^{-1}) (Figure 3.3d). Total Si uptake by rice shoots (including straw, hulls, and grains) increased by 37 % (application of 0.4 Mg Si ha^{-1}) and 126 % (application of 17.3 Mg Si ha^{-1}) compared to the control (Table 3.2); the increased uptake corresponds to 10 % (application of 0.4 Mg Si ha^{-1}) and 1 % (application of 17.3 Mg Si ha^{-1}) of the applied Si. Total uptake of P was increased and total uptake of Ca was decreased due to the high Si application rate (17.3 Mg Si ha^{-1}) (Table 3.2); N, K, and Mg uptake were not affected by Si application (Table 3.2).

Table 3.2 Impact of Si fertilization on total nutrient uptake of rice aboveground biomass [kg dry matter ha^{-1}] in the field experiment; numbers in parentheses are standard errors, results of one way ANOVA are given below, results of Tukey's HSD test ($P< 0.05$) are given by superscripted letters

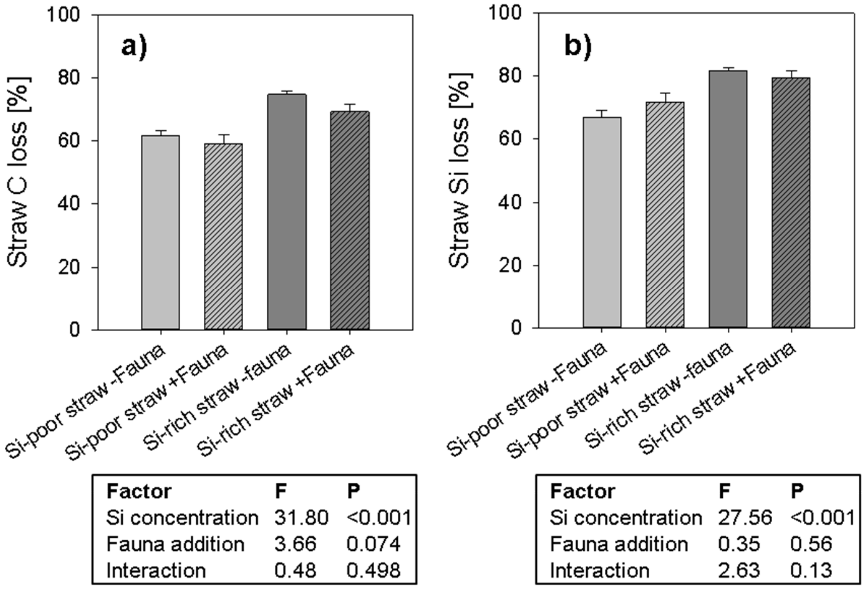
Treatment	Si	N	P	K	Ca	Mg
Control	107 (3) ^{a}	79.0 (4.2) ^{a}	21.4 (1.4) ^{a}	45.0 (3.5) ^{a}	7.75 (0.22) ^{a}	9.29 (0.48) ^{a}
0.4 Mg Si ha^{-1}	146 (9) ^{b}	78.1 (2.5) ^{a}	22.0 (1.0) ^{ab}	42.1 (2.6) ^{a}	7.62 (0.22) ^{a}	9.05 (0.28) ^{a}
17.3 Mg Si ha^{-1}	241 (5) ^{c}	89.3 (4.0) ^{a}	25.9 (0.8) ^{b}	44.9 (2.8) ^{a}	6.52 (0.21) ^{b}	10.0 (0.29) ^{a}
ANOVA results						
F-value	138.04	0.97	4.38	0.31	8.92	1.53
P-value	< 0.001	0.494	0.043	0.740	0.006	0.263

3.4.2 Laboratory pot experiment

Initial nutrient composition of the straw samples used for incubation is given in Table 3.3; initial C/N ratios were the same for Si-poor straw and Si-rich straw. During 33 days of incubation, relative C loss was larger for Si-rich straw than for Si-poor straw (Figure 3.4a). Also, relative Si loss was larger from Si-rich straw than from Si-poor straw (Figure 3.4b), thus absolute Si release increased with Si concentration in the straw. Fauna affected neither relative C loss nor relative Si release from straw.

Table 3.3 Initial nutrient concentrations [mg g^{-1} dry matter] in the straw samples used for incubation in the laboratory experiment

Treatment	Si	C	N	P	K	Ca	Mg
Si-poor straw	36.9	357	8.65	2.35	26.1	5.38	3.14
Si-rich straw	80.8	309	7.29	1.97	19.0	2.69	1.67



Factor	F	P
Si concentration	31.80	<0.001
Fauna addition	3.66	0.074
Interaction	0.48	0.498

Factor	F	P
Si concentration	27.56	<0.001
Fauna addition	0.35	0.56
Interaction	2.63	0.13

Figure 3.4 Impact of initial straw Si concentration and mesofauna on a) C loss and b) Si loss from straw in litterbags during 33 days of incubation; error bars represent standard errors; results of two way ANOVA are given in the legends

Redox potential in all pots decreased within the first 6 days to~−160 mV (data not shown). Soil solution Si concentration reflected application of silica gel already at the first sampling time (day 1; Figure 3.5a). Without plants, Si concentration in soil solution of the silica gel treatment (Silica gel -Plant) increased steadily, while it was constant in the control treatment (Control -Plant). In the treatments with straw (Si-poor straw -Fauna and Si-rich straw -Fauna; Figure 3.5b), Si concentration was initially similar to the control treatments (Control -Plant and Control +Plant). After a few days, Si concentration started to increase at a faster rate than in the treatments with silica gel (Silica gel -Plant and Silica gel +Plant).

The concentrations levelled off after around 25 days; the plateau was on a higher level for Si-rich straw (Si-rich straw -Fauna) than for Si-poor straw (Si-poor straw -Fauna). In all treatments with plants, Si concentration started to decrease a few days after transplanting; the decreases were faster and ended up at a lower level in the treatments with straw than in the treatment with silica gel.

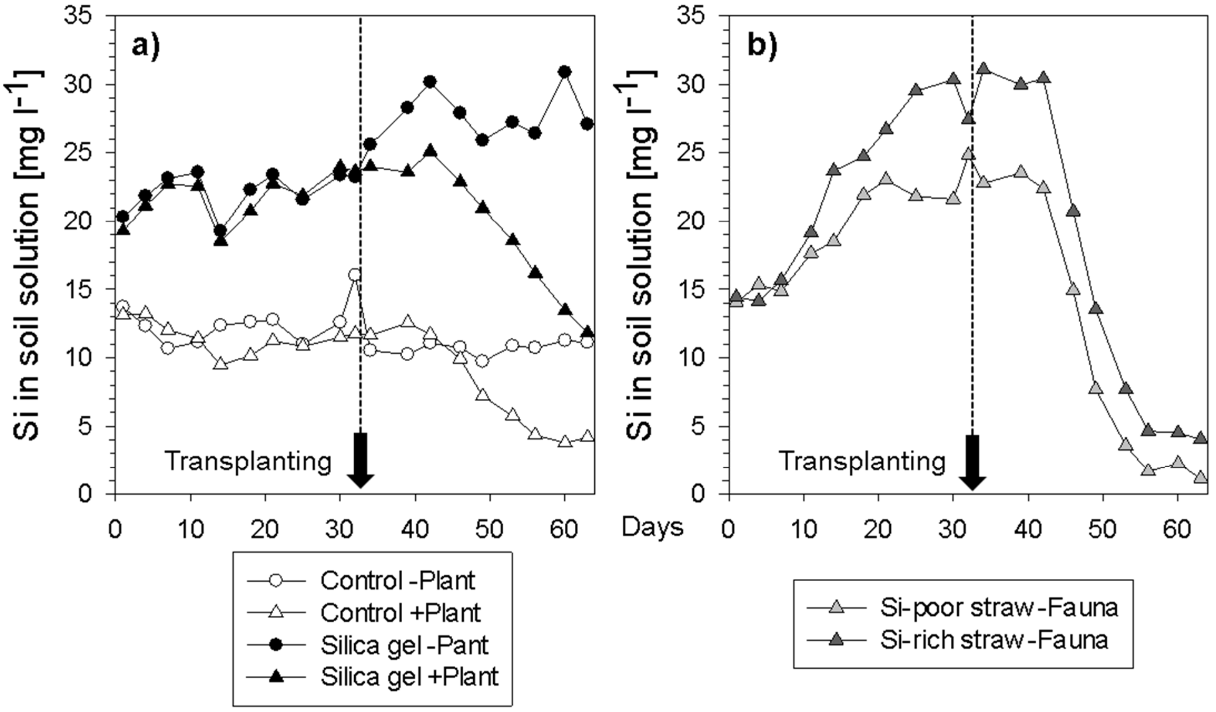


Figure 3.5 Si concentration in the soil solutions during the experimental time of 63 days a) for the control treatments and silica gel treatments, and b) for the straw treatments with plants and without fauna

3.5 Discussion

3.5.1 Effect of Si fertilization on Si uptake and growth of rice (Q1)

Increasing Si availability in the soil resulted in increased Si uptake by plants. Hence, Si uptake is limited by Si availability in soil. Straw from the control plots had 5.4 % Si in the dry matter (measured by XRF spectroscopy), thus only little more than the critical value of 5 % proposed by Dobermann and Fairhurst (2000). A lower concentration is thought to indicate Si limitation to rice growth, meaning that the plants' leaves are soft and droopy, and the plants' resistance against abiotic and of >8 % (Dobermann and Fairhurst 2000) were only achieved by a very high application rate of silica gel (17.3 Mg ha^{-1}). In this treatment, also biomass production and grain yield increased, which suggests that Si availability is indeed a limiting factor to plant growth in the study region.

Application of Si fertilizers may, thus, be an option for farmers to increase rice yields. We found that the additional Si uptake equaled 10 % of the applied Si in the treatment with the low application rate of silica gel (0.4 Mg Si ha^{-1}) and only 1 % of the applied Si in the treatment with the high application rate of silica gel (17.3 Mg Si ha^{-1}). These data suggest that dissolution of silica gel limited Si uptake by rice in the treatment with the low Si application rate, while for the treatment with the high Si application rate, the availability of Si was likely higher than the plants' demand. Si concentration in the soil solution of the 17.3 Mg Si ha^{-1} treatment increased faster and to a greater extent than in the 0.4 Mg Si ha^{-1} treatment. Therefore leaching of Si might be more important in the treatment with the high Si application rate.

3.5.2 Decomposability of rice straw as a function of straw Si concentration (Q2)

Increased Si availability during rice growth increased the decomposability of the produced straw (i.e., increased the relative loss of organic C during 33 days; Figure 3.4a). The same observation was made in similar experiments using litter of the common reed (*Phragmites australis*) (Schaller and Struyf 2013; Schaller et al. 2014). The reason for an altered decomposability might be changes in the quality of the organic matrix of the straw upon increased Si availability. Raven (1983) proposed that the formation of structural C compounds, such as cellulose, lignin, or polyphenols decreases upon increased Si availability during plant growth. Silicon seems to perform similar functions in plants than structural C compounds, including cell strength and tissue support, defence against insects and diseases, and alleviation of abiotic stresses (Cooke and Leishman 2011). Hence, phytolith formation following Si uptake could be an energetically cheaper alternative to the synthesis of structural C compounds (Raven 1983). In line with this hypothesis, Schoelynck et al. (2010) found negative relationships between lignin and Si concentration for wetland species. Lignin is generally assumed to be among the most degradation-resistant organic litter components; lignin concentrations are frequently negatively related to litter decomposition rates (Aerts 1997; Cornwell et al. 2008). Increasing Si uptake, however, changed also other potential controls on straw decomposition rates such as the concentrations of essential nutrients in straw (Table 3.3). In addition, altered Si and phytolith concentrations in straw could affect its decomposability. The current opinion, however, suggests that increased phytolith concentration might rather decrease straw decomposition by the microbial community (Schaller et al. 2014), a view that is not supported by our data. In summary, the mechanisms linking changes in Si availability and straw decomposability are currently uncertain. Detailed studies on this issue are necessary, as Si concentration in the straw can affect a number of decomposition controls.

Added fauna did neither affect decomposability of straw nor Si release from straw (Figure 3.4). An explanation for this finding might be that microbial processes were dominant in straw decomposition in our experiment. Based on field data, we used three decomposer species representing abundant groups of secondary decomposers in rice fields which stimulate the decomposition process by grazing on the microflora on pre-decomposed organic material. Often, their effect is less obvious than the effect of primary decomposers (which ingest litter material directly). Further, even though the soil was dried before the experiment, a number of indigenous mesofauna emerged from the substrate in all treatments (mainly ostracods) which also may have alleviated treatment differences. Other studies demonstrated positive effects of invertebrate grazers on decomposition in aquatic environments but also could not show a mediating effect of Si concentration in litter

(Schaller 2013).

3.5.3 Release of Si during straw decomposition (Q3)

We found particularly fast losses of Si in the straw decomposition experiment. The increased Si uptake of rice plants in the treatments with straw addition compared to the control (Table 3.4) clearly shows that Si released during straw decomposition is plant-available. The amounts of Si taken up by plants were much larger than the decrease of dissolved Si in the soil solution (Table 3.4); Si concentration in the soil solution of the control without plant remained nearly constant during the whole experimental period, indicating that these systems were in equilibrium. These data suggest that the plant-Si-uptake accelerated the release of dissolved Si by weathering of phytoliths in straw and soil minerals (i.e., phytoliths, primary and secondary silicates); decreased Si concentrations in soil solutions might be the reason for the accelerated weathering.

Table 3.4 Change of Si dissolved in the soil solution [mg] during plant growth (day 34 to day 63; water content of 0.9 l per pot was assumed for the saturated soils) and total Si uptake [mg] by the plant in the laboratory experiment

Treatment	Si change in soil solution	Si uptake by plant
Control -Plant	1	-
Control +Plant	-7	33
Silica gel -Plant	1	-
Silica gel +Plant	-11	65
Si-poor straw -Fauna	-19	76
Si-poor straw +Fauna	-24	68
Si-rich straw -Fauna	-17	103
Si-rich straw +Fauna	-20	86

The temporal changes in Si concentrations in the soil solution show that Si release rate and pattern for rice straw and silica gel differed. In the treatments with silica gel, Si was rapidly released and Si concentration in the soil solution was already increased 1 day after start of the experiment (Figure 3.5). Decomposing rice straw started to release Si after 5 days of incubation. We assume that Si concentrations in the soil solution increased only when the organic matrix surrounding the phytoliths was decomposed and the surface of the phytoliths became exposed to soil solution. The finding that Si concentrations in the straw residues were similar to the initial Si concentrations (Figure 3.4) suggests high rates of phytolith losses during the first 33 days (as high as the organic C losses). We calculated that, on average, 2–2.5 % of the added phytoliths dissolved per day during the first 33 days of the experiment (pH in the soil solutions varied between 6.6 and 7.0). Assuming constant dissolution rates, it would take around 50 days until the phytoliths added with the straw completely dissolved. Fraysse et al. (2009) found comparably high dissolution rates in a laboratory experiment with phytoliths extracted from horsetail; the dissolution rates at 25 °C were ~0.6 % of phytolith-Si per day at pH 6 and ~3 % of phytolith-Si per day at pH 8.6.

The increases in soil solution Si concentrations upon straw addition mainly occurred during the first 25 days; thereafter the concentrations levelled off (Figure 3.5). The temporal changes in Si release into soil solution might be linked to the decomposition rates of the organic matrix, which typically decreases over time, and the decrease is particularly strong in the first days (e.g., Klotzbücher et al. 2011). Another explanation might be that the solubility of phytoliths decreases with aging in soil. Processes causing such decreases in solubility have not been studied but deserve further attention, because they should strongly determine phytolith storage in soils and, more generally, the Si cycle and balance in rice production systems. 'Stabilization' of at least some of the phytoliths in soil would be in line with the proposed existence of old phytoliths in soils (Santos et al. 2010; Piperno 2014). This could mean that the dissolution rates measured in short-term laboratory experiments are not fully applicable for explaining the long-term fate of phytoliths in soil. In our experiment, initial Si concentrations in the soil solutions were low, promoting phytolith dissolution. High Si concentrations in the soil solution slowing Si release would probably promote phytolith stabilization in soil.

The Si budgets of the pots revealed large gaps. The sum of the increased Si uptake by the plants relative to the control and the Si dissolved in soil solution equaled only 10%of the Si added with Si-poor straw and 7%of the Si added with Si-rich straw, respectively. However, assuming the straw mixed with the soil released Si at the same rate as the straw within the litterbags, 67 % of Si from the Si-poor straw and 82 % of Si from the Si-rich straw were released already during 33 days. One explanation for the gap in the budgets might be adsorption of Si to soil particles. Another explanation might be that Si from the soil solution was consumed by algae growing in the pots. At the end of the experiment, some algae were collected and analysed; Si concentrations of about 6 % were measured. However, it was not possible to completely separate algae from the soil, and thus, to quantify algae mass.

3.6 Conclusions

Increasing Si availability in a soil with originally low plant-available Si increases Si uptake by rice plants and plant productivity (total aboveground biomass and grain yield) as well as the decomposability of the produced straw. Increased phytolith formation probably substitutes the formation of hardly-degradable cell wall components, thus, more energy is invested in the production of biomass. Consequently, biomass production increases, whereby also the portion of labile components in the biomass and the decomposability of the straw increase. Our study, thus, adds to increasing awareness that Si cycling plays a significant role in cycling of C and essential nutrients through rice production systems.

The loss of Si during straw decomposition equaled the loss of the organic matrix. This suggests that phytolith dissolution occurs rapidly after exposure of phytoliths to soil solution. Thus, phytoliths from fresh rice straw are strongly soluble and might have high turnover rates. However, decreasing Si release rates from the straw suggest that phytolith solubility decreases over time in soil. This together with the fact that geologically old phytoliths occur in soils might be explained by stabilization of (at least some of the) phytoliths during aging in the soil. However, the mechanisms inducing stabilization are still unknown.

3.7 Acknowledgements

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4 Effects of Si fertilization on Si in soil solution, Si uptake by rice (*Oryza sativa* L.), and resistance of rice to biotic stresses in Southern Vietnam

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Author contributions:
A. M. wrote the manuscript; A. M. and T. K. installed the field experiment; L. D. X., L. Q. C., and H. V. C. conducted the field experiment; R. J., D. V., T. K., and A. M. designed the experiment; C. S. commented on an early version of the manuscript

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4.1 Abstract

Silicon (Si) mitigates abiotic and biotic stresses for rice plants (*Oryza sativa* L.). Here, we test relationships between Si cycling, plant growth, and pest and fungal attacks in rice agroecosystems. We conducted a plot experiment on Si fertilization in a Southern Vietnamese paddy, where plant-available Si was inherently low. For two cropping seasons, we investigated the temporal dynamics of Si in the soil solution, plant Si uptake, and the occurrence of leaf folders (*Cnaphalocrocis medinalis*) and rice blast caused by the fungus *Magnaporthe oryzae*. Silicon application increased Si concentration in soil solution, which was furthermore affected by recycling of phytoliths with rice straw ash and plant-Si-uptake. Silicon concentrations in rice leaves at tillering stage increased with increasing Si application. However, no relationship between Si in soil solution and Si concentration in straw at maturity stage or amounts of Si uptake were found. Furthermore, we found no significant effect of Si application on biomass production. The occurrences of leaf folders and rice blast disease were mitigated by increased Si uptake. Our study contradicts assumptions that the Si uptake by rice is mainly determined by Si availability in soil; also differences in weather conditions between cropping seasons seem to play a prominent role.

4.2 Introduction

Rice plants (*Oryza sativa* L.) accumulate up to 10 % silicon (Si), mainly in the form of amorphous Si dioxide particles (Jones and Handreck 1967; Ma and Takahashi 2002). These so-called phytoliths enhance the plants´ strength and rigidity and improve defense against abiotic stresses (such as strong rain, wind, salinity, and drought) and biotic stresses (such as attacks by insect pests and fungi) (Guntzer et al. 2012a; Meharg and Meharg 2015). Hence, Si fertilization in paddy fields with inherently low plant-available Si might be an option to increase rice yields (Marxen et al. 2016) and at the same time to decrease the demand for application of pesticides (Guntzer et al. 2012a).

Silicon availability in paddy soils can differ greatly between rice production regions; weathering status of the soil seems to be the major reason for these differences (Klotzbücher et al. 2015a; Tsujimoto et al. 2014). Weathering of soil minerals and irrigation are the two main sources of plant-available dissolved Si (dSi) in paddies, while significant losses can occur due to water percolation and drainage of flooded fields before harvest (Nguyen et al. 2016; Desplanques et al. 2006; Klotzbücher et al. 2015b). Other main factors determining Si cycling in paddies are plant-Si-uptake, removal of Si due to plant harvest, and recycling of phytoliths via the rice straw (Seyfferth et al. 2013; Klotzbücher et al. 2015b; Marxen et al. 2016). Hence, Si cycling and availability are determined by both natural soil conditions and agricultural practices.

A number of Si fertilizer experiments were conducted under field conditions (reviewed by Guntzer et al. 2012a and Haynes 2014). In these studies, Si was applied in the form of calcium (Ca) or magnesium (Mg) silicate, a residue from blast furnace of industrial phosphorous mining (slag), which is highly soluble and releases plant-available Si. The addition of these materials typically enhances plant growth, an effect ascribed to the benefits of Si. From a researcher's point of view, the use of such materials has the disadvantage that the effects of enhanced Si availability cannot be studied directly, as they might be superimposed by effects of Ca^{2+} and Mg^{2+} on plant growth. Furthermore, slags might contain considerable amounts of heavy metal contaminants and their dissolution releases $(OH)^-$ ions causing increasing soil pH (Haynes 2014).

An alternative Si source that can be used to directly address effects of Si availability on plant growth is silica gel (SiO_2), which does not affect soil solution pH. We used silica gel as fertilizer in an experiment in Northern Vietnam, where plant-available Si was inherently low as soils are strongly weathered and desilified. We found that rice yields were increased by 34 % for the extremely high application rate of 17.3 Mg Si ha^{-1} (Marxen et al. 2016). For a low application rate of silica gel (0.4 Mg Si ha^{-1}), yield was not affected, but Si uptake still increased. However, the experiment only lasted one cropping season and we did not assess if increased Si uptake increased the plants' resistance against biotic stresses like pests and diseases.

A common pest in rice cultivation is the leaf folder (*Cnaphalocrocis medinalis*) which damages rice crops during its larval stage. The larva folds a leaf blade longitudinally with silk strands and feeds on mesophyll tissue inside the folded leaf, thereby creating longitudinal white and transparent streaks on the blade, disturbing photosynthesis and growth and ultimately reducing rice yield (Han et al. 2015 and references therein). High Si concentration in rice plants is assumed to cause mandibular wear of leaf folder larvae (Reynolds et al. 2009). Han et al. (2015) showed in a pot experiment that increased Si concentration in rice decreased the net reproduction rate of the rice leaf folder population and enhanced the resistance of rice plants to leaf folders because of reduced food quality and food conversion efficiencies, although consumption increased with Si concentration.

Also, the rice blast fungus (*Magnaporthe oryzae)* is common in rice cultivation and occurs mainly as leaf blast or neck blast (Bonman et al. 1989; Webster and Gunnell 1992). Leaf blast can cause severe damage before plants reach the productive growth phase while neck blast is the most destructive in terms of yield loss (Ou 1985; Bonman et al. 1989). The fungus *M. oryzae* enters the plant via appressorial penetration through the epidermis. It was often shown in field experiments that Si mitigates rice blast disease (Datnoff et al. 1997; Seebold et al. 2000; Seebold et al. 2004) while the mechanism is still uncertain. It might be a physical effect, i.e., silicified cells in the leaf epidermis or the cuticle-Si double layer may act as physical barrier for appressorial penetration. Another explanation might be that Si mediates physiological changes of rice plants to confer disease resistance (Seebold et al. 2004).

The present study was motivated by the shortage of field data on relationships between Si cycling, plant growth, and pest and fungal attacks in rice agroecosystems. We conducted a field plot experiment over the course of two cropping seasons in a paddy field in Southern Vietnam, where plant-available Si is low (Klotzbücher et al. 2015a). By applying easily soluble silica gel, we manipulated the release of potentially plant-available dSi. Our aims were to test how dSi concentrations ([dSi]) change during rice production cycles, and how the changes in Si availability are related to uptake of Si and essential nutrients and plant growth. Furthermore, we tested Si fertilization effects on occurrence of leaf folders, leaf blast and neck blast, which commonly cause problems in the study region.

4.3 Material and methods

4.3.1 Set-up of field plot experiment

The experiment was installed on a farmers' paddy field (10°26'39.76"N 106° 3'32.24"E) in Tien Giang province in Southern Vietnam. The soil was classified as hydragric Anthrosol (Eutric, Clayic, Amphigleyic); basic soil parameters are given in Table 4.1. Industrially-graded silica gel of 2-3 mm grain size (Anh Duc Co. Ltd, Vietnam) was applied to the plots once in the beginning of the first cropping season on 28th of November 2013 at three levels: 0.1 Mg Si ha^{-1}, 0.4 Mg Si ha^{-1}, and 1.5 Mg Si ha^{-1}; additionally a control (i.e., no silica gel) was established. All four treatments were spatially replicated five times. The plots had a size of 8 m × 8 m, but all samplings were done within an inner core of 6 m × 6 m in order to avoid `edge effects`. Plots were arranged in a randomized block design and margined by bunds (Figure 4.1) to minimize Si transport from/to the surroundings by the flood water. Silica gel was homogeneously distributed in the moist plots and mixed into the topsoil using a spade; directly afterwards, rice (*Oryza sativa* L. cv. IR 50404) was seeded by hand which is the locally common practice. Nine days later, the plots were flooded for the first time. They were flooded two additional times during the cropping season in order to maintain continuous submerged soil conditions until they were drained 10 days before harvest. Fertilization was done by the farmer according to the locally common practice; 80 kg N ha^{-1}, 14 kg P ha^{-1}, and 73 kg K ha^{-1} were applied during the cropping season. Pesticides were not applied to the experimental field but to the surrounding paddies (active substances are provided in the Appendix 8). The first cropping season lasted 85 days. After harvest, the rice straw was returned to the respective plots (except for a small amount, which was kept for analyses; see paragraph on plant sampling and analyses) and burned within the plots as rice straw burning is the common practice in the study area. After a fallow period of 10 days, the new rice crop (*Oryza sativa* L. cv. IR 50404) was seeded. Flooding and drainage of the experimental plots were carried out in the same way as during the first cropping season. Fertilizer amounts equaled 95 kg N ha^{-1}, 16 kg P ha^{-1}, and 65 kg K ha^{-1} during the second cropping season. The second rice crop was harvested after a growth period of 82 days; Figure 4.2 shows rice in the experimental field at maturity stage.

Table 4.1 Basic soil parameters of the hydragric Anthrosol (Eutric, Clayic, Amphigleyic) (IUSS Working Group 2014); horizons and texture were classified according to FAO (2006); TOC = total organic carbon; CEC = cation exchange capacity (extracted with ammonium acetate at pH 7); BS = base saturation; C = Clay; SiC = Silty Clay

Depth [cm]	Horizon	Texture	pH$_{KCl}$	TOC [g kg^{-1}]	C/N	CEC	Ca^{2+}	Mg^{2+} [mmol$_c$ kg^{-1}]	K$^+$	Na$^+$	BS [%]	Fe$_{oxalate}$ g kg^{-1}
0-22	Arp	C	3.1	38	11	300	117	79	2	6	68	5.7
22-33	Ardp	SiC	3.1	12	16	190	86	77	3	6	90	2.6
33-66	Brl1	SiC	3.5	13	15	199	58	73	2	6	70	2.1
66-90	Brl2	SiC	3.5	16	18	223	57	74	3	6	63	2.5
>90	Brl3	SiC	3.4	10	15	204	56	78	3	7	70	2.1

Figure 4.1 Picture of the experimental field after plot installation

Figure 4.2 Picture of rice in the experimental field at maturity stage

4.3.2 Soil solution sampling and analyses

We sampled soil solution using permanently installed suction cups (Rhizon SMS, Rhizosphere research products, Wageningen, The Netherlands). Five days after seeding (DAS) in the first experimental cropping season, three suction cups were installed in each core plot, one in the centre and two in opposite corners. The suction cups were inserted horizontally into the topsoil to a depth of 15 cm. They consisted of a 5 cm long porous part made of polyethersulfone with an outside diameter of 2.5 mm and a pore size of 0.12-0.18 µm and were connected to a 60 cm PE/PVC tube with female/male luer lock system at the end of the tube. During both cropping seasons, a syringe was connected to the end of the tube above the soil surface to remove 5 ml of soil solution every ten days. The three samples taken per plot were combined into a vial that contained 300 µl of nitric acid (65 %) to prevent co-precipitation of dSi and iron (Fe) oxides and sorption of dSi onto Fe oxide surfaces (Sauer et al. 2006). Silicon was determined by inductively coupled plasma optical emission spectrometry (ICP-OES; Ultima 2, Horiba Jobin-Yvon, Longjumeau, France).

4.3.3 Plant sampling and analyses

At tillering stage, i.e., 28 DAS and 34 DAS in the first and second cropping season, respectively, rice leaves were sampled in all core plots to determine the plants' nutritional status at a critical growth stage. Sampling was conducted by cutting the youngest fully developed leaf from several random plants until a sample size of 50 g fresh mass was obtained (Dobermann and Fairhurst 2000). Samples were dried in an oven at 65 °C for 48 hours, shipped to Germany, and ground for analysis.

At maturity stage, i.e., 85 DAS and 78 DAS in the first and second cropping season, respectively, straw production and grain yield were measured. Three samples were taken per core plot by randomly choosing a 4 m^2 area, respectively (altogether 12 m^2) and harvesting all enclosed plants by cutting them directly above the soil surface. Grains with hulls were separated from the straw and both fractions were weighed. Subsamples (150 g of straw and 100 g of grains for each sample) were air dried until constant weight was reached, weighed, and shipped to Germany. The three samples of the same plant fraction and plot were pooled, respectively, and samples were ground for analysis.

X-ray fluorescence (XRF) spectroscopy was applied to determine concentrations of Si, phosphorous (P), potassium (K), Ca, and Mg in plant material. Ground samples were dried at 85 °C for 48 hours and 3 g of each sample were mixed with 650 mg of wax; then 32 mm pellets were prepared by pressing with a force of 12 Mg. The XRF measurements were performed using a wavelength-dispersive XRF spectrometer (S4 PIONEER, Bruker-AXS, Karlsruhe, Germany), equipped with a 4 kW-Rh X-ray tube (75 µm Be window), 60 kV generator, and an eight-position crystal changer. The spectrometer operating conditions were vacuum, 23-mm collimator mask and 0.46 ° collimator in conjunction with the analysing crystal PET, and 30 kV at current of 80 mA. Calibration was performed using a plant matrix standard addition method: a dried and ground grass sample was mixed with different amounts of SiO_2 (2–14 % with an increment of 2 %), pressed to pellets and measured under above described conditions.

Concentrations of carbon (C) and nitrogen (N) were determined using a dry combustion analyzer (Vario EL cube, Elementar, Hanau, Germany).

4.3.4 Pest and disease assessment

During the first cropping season neither leaf folders nor the rice blast disease appeared in the field, thus leaf folders, leaf and neck blast were only assessed during the second cropping season.

Leaf folders were assessed according to the standard protocol used by the Southern Regional Plant Protection Center (SRPPC) in Tien Giang province, Southern Vietnam. A wooden frame of 0.2 m^2 area was placed in each core plot at tillering stage (41 DAS in the second cropping season) at five random locations (altogether 1 m^2 area per plot), counting the number of leaf folder larvae feeding on rice plants and the number of damaged leaves within the enclosed area.

Leaf and neck blast were assessed at tillering stage (34 DAS in the second cropping season) and ripening stage (74 DAS in the second cropping season), respectively. Severity of leaf blast was estimated by randomly assessing 3 leaves of 25 different tillers (altogether 75 leaves) per core plot. Severity of neck blast was estimated by randomly selecting 50 panicles of different plants per core plot. Severities of leaf and neck blast were evaluated according to the scoring system developed by the International Rice Research Institute (IRRI 1996).

4.3.5 Statistics

Data were analysed using SigmaPlot software version 12 (Systat Software Inc.). All data were tested for normality distribution and equal variances to choose the appropriate analysis. Seasonal means of [dSi] were calculated for each individual plot. These data were used to test treatment effects on [dSi] by applying the Kruskal-Wallis ANOVA on ranks followed by Dunn's HSD test for pair wise comparisons between the treatments. In order to test for differences in [dSi] between the two cropping seasons, we applied paired t-tests on data for each of the treatments. To analyze treatment effects on nutrient concentrations in leaves and straw, production of straw and grains, total Si uptake, and the severity of leaf and neck blast, the Kruskal-Wallis ANOVA on ranks was used; when the differences were significant, Dunn's test for pair wise comparisons between the treatments was applied. To compare the production of straw and grains and total Si uptake between the two cropping seasons, we used the Mann-Whitney rank sum test instead of the t-test because the data were not normally distributed. To analyze the data on leaf folders and damaged leaves, One Way ANOVA followed by Tukey's HSD test was used. Results were considered to be significant for $P \leq 0.05$.

4.4 Results

4.4.1 Dynamics of dSi in the soil solution

Means of [dSi] values in the first cropping season were 4.3, 4.6, 5.7, and 6.6 mg Si l^{-1} in the control, the 0.1, 0.4, and 1.5 Mg Si ha^{-1} treatment, respectively. Concentrations significantly differed between the control and the 1.5 Mg Si ha^{-1} treatment and between the 0.1 Mg Si ha^{-1} and the 1.5 Mg Si ha^{-1} treatment (Figure 4.3a). The temporal course of [dSi] was similar for all treatments. Means of [dSi] in the second cropping season were 7.6, 8.3, 11.4, and 16.3 mg Si l^{-1} in the control, the 0.1, 0.4, and 1.5 Mg Si ha^{-1} treatment, respectively. Concentrations only differed between the control and the 1.5 Mg Si ha^{-1} treatment. For all treatments we found significantly higher [dSi] in the second than in the first cropping season (Figure 4.3a). The temporal course of [dSi] followed the same pattern like in the first cropping season in all treatments.

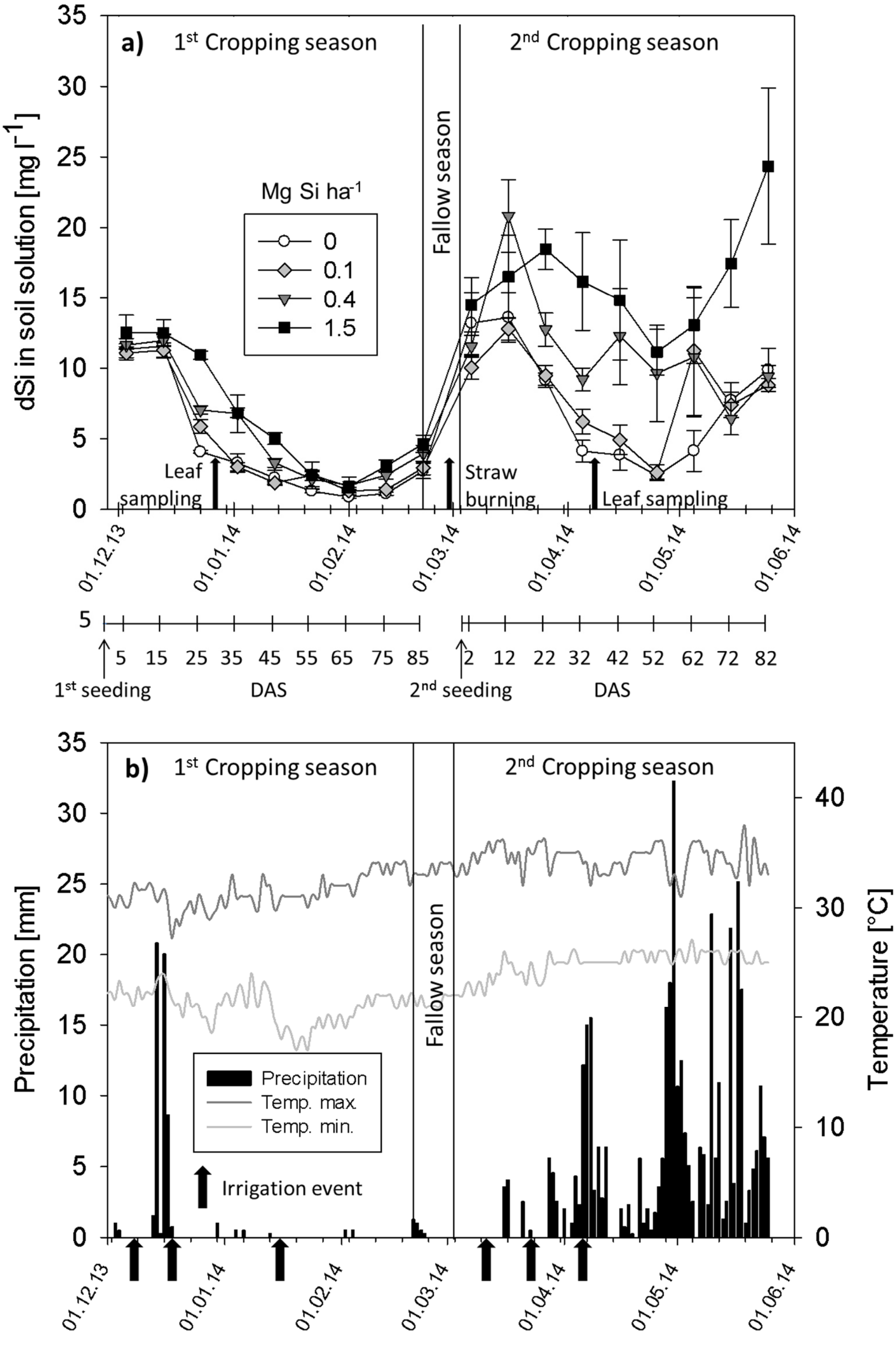

Figure 4.3 Dissolved Si concentration [dSi] in soil solution (± SE); additional x-axes below show individual sampling dates in days after seeding (DAS) and b) daily precipitation and temperature during the first and second cropping season (data taken from www.accuweather.com in August 2015); times of irrigation are plotted in the graph; amounts of irrigation were not measured

4.4.2 Si uptake and biomass production

The Si concentrations in rice leaves at tillering stage were positively related to amounts of Si application. However, when compared to the controls, the increases were only significant for the 1.5 Mg Si ha^{-1} treatment in both cropping seasons (Figure 4.4). In the first cropping season, application of 1.5 Mg Si ha^{-1} also caused significant increases in straw Si concentrations at maturity stage, while no significant treatment effects were found in the second cropping season (Figure 4.5).

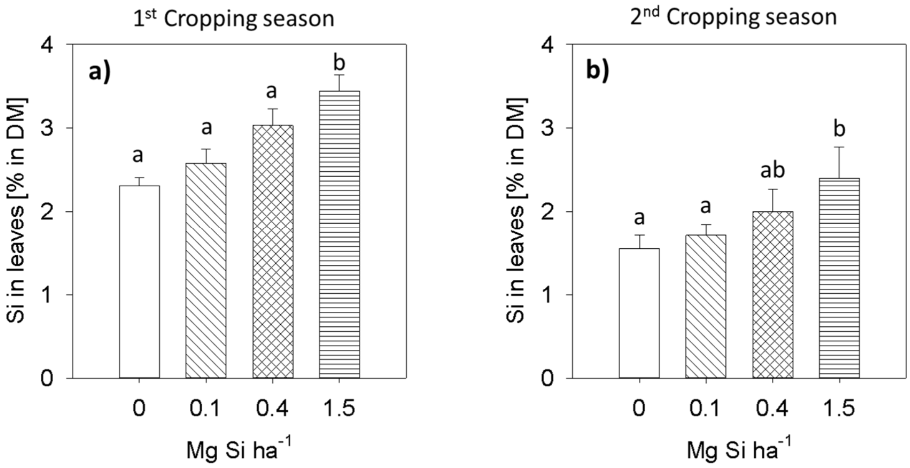

Figure 4.4 Si concentration in rice leaves at tillering stage a) in the first cropping season at 28 DAS and b) in the second cropping season at 34 DAS; error bars represent SE; letters give significant differences (P≤0.05)

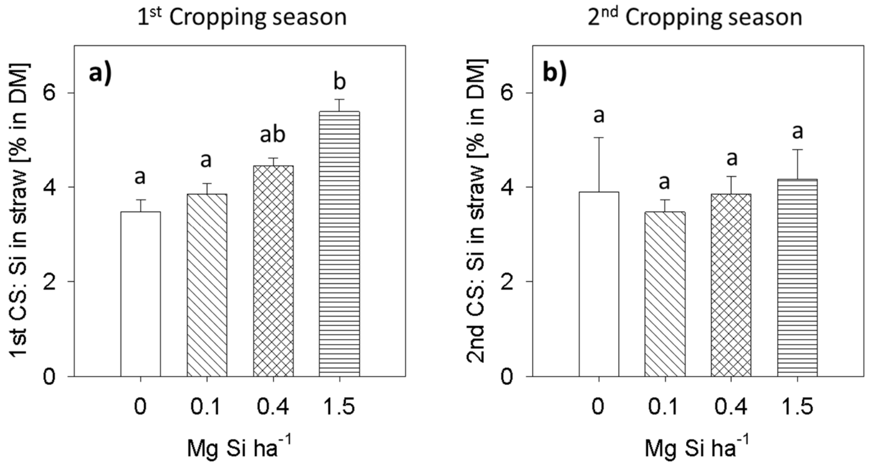

Figure 4.5 Si concentration in rice straw at maturity stage a) in the first cropping season and b) in the second cropping season; error bars represent SE; letters give significant differences (P≤0.05)

In the first cropping season, straw production and grain yield did not differ between the treatments. In the second cropping season, they both increased slightly but not significantly with increasing Si application, except for straw production in the control treatment (Table 4.2). In the second cropping season, straw production was significantly higher and grain yield was significantly lower than in the first cropping season. Total Si uptake by the plants increased slightly with increasing Si application in both cropping seasons, except for the control treatment in the second cropping season with a very high standard error (SE); when compared to the controls, the increase was only significant for the highest Si application rate in the first cropping season (Table 4.2).

Table 4.2 Straw biomass production, grain yield, and total Si uptake by aboveground biomass during the first and second cropping season; SE in brackets; letters give significant differences within one season ($P \leq 0.05$)

Treatment	Straw Mg DM ha^{-1}	Grains with hulls Mg DM ha^{-1}	Si uptake kg ha^{-1}
	1st Cropping season (dry season)		
0 Mg Si ha^{-1}	9.6 (0.4)^{a}	6.7 (0.3)^{a}	398 (15)^{a}
0.1 Mg Si ha^{-1}	9.3 (0.3)^{a}	6.7 (0.4)^{a}	420 (11)^{a}
0.4 Mg Si ha^{-1}	9.3 (0.3)^{a}	7.1 (0.3)^{a}	484 (20)^{ab}
1.5 Mg Si ha^{-1}	9.3 (0.4)^{a}	6.6 (0.1)^{a}	592 (34)^{b}
	2nd Cropping season (wet season)		
0 Mg Si ha^{-1}	11.2 (0.6)^{a}	4.8 (0.2)^{a}	485 (69)^{a}
0.1 Mg Si ha^{-1}	11.0 (0.3)^{a}	5.0 (0.1)^{a}	427 (05)^{a}
0.4 Mg Si ha^{-1}	12.2 (0.3)^{a}	5.1 (0.1)^{a}	518 (17)^{a}
1.5 Mg Si ha^{-1}	12.9 (0.8)^{a}	5.3 (0.2)^{a}	595 (66)^{a}

4.4.3 Concentrations of essential nutrients in plant tissue

In both cropping season, Si application did not influence the concentrations of C, N, P, K, Ca, and Mg in rice leaves (Table 4.3). In the first cropping season, concentrations of C and Mg in rice straw slightly decreased with increasing Si application; when compared to the control, the decrease was only significant for the highest Si application rate (Table 4.4). Concentrations of N, P, K, and Ca in straw did not differ between the treatments. In the second cropping season, Si application did not influence the concentrations of C, N, P, K, Ca, and Mg in straw (Table 4.4).

Table 4.3 Nutrient concentrations [g kg^{-1}] in rice leaves at tillering stage in the first cropping season at 28 DAS and in the second cropping season at 34 DAS; SE in brackets; there were no significant differences between the treatments within one cropping season for any nutrient

Treatment	C	N	P	K	Ca	Mg
			1st Cropping season (dry season)			
0 Mg Si ha^{-1}	409 (5)	41.4 (1.2)	3.92 (0.07)	27.1 (1.0)	4.49 (0.21)	2.46 (0.09)
0.1 Mg Si ha^{-1}	409 (2)	41.6 (1.0)	3.95 (0.05)	26.7 (1.0)	4.38 (0.22)	2.37 (0.08)
0.4 Mg Si ha^{-1}	401 (3)	41.6 (0.7)	4.08 (0.10)	27.4 (0.8)	4.27 (0.20)	2.24 (0.07)
1.5 Mg Si ha^{-1}	398 (1)	40.9 (0.7)	3.99 (0.10)	26.7 (0.7)	3.86 (0.08)	2.11 (0.07)
			2nd Cropping season (wet season)			
0 Mg Si ha^{-1}	432 (1)	27.0 (1.0)	2.95 (0.13)	22.0 (1.1)	3.82 (0.28)	2.29 (0.17)
0.1 Mg Si ha^{-1}	429 (2)	27.0 (0.7)	3.04 (0.14)	23.9 (1.3)	4.21 (0.36)	2.46 (0.13)
0.4 Mg Si ha^{-1}	427 (3)	26.5 (0.5)	2.88 (0.13)	23.7 (1.1)	4.16 (0.43)	2.29 (0.16)
1.5 Mg Si ha^{-1}	423 (4)	27.8 (0.5)	2.85 (0.09)	23.7 (2.1)	3.76 (0.48)	2.20 (0.16)

Table 4.4 Nutrient concentrations [g kg^{-1}] in rice straw at maturity stage in the first and second cropping season; SE in brackets; letters give significant differences within one cropping season ($P \leq 0.05$)

Treatment	C	N	P	K	Ca	Mg
			1st Cropping season (dry season)			
0 Mg Si ha^{-1}	387 (4)^{a}	5.81 (0.37)^{a}	1.34 (0.11)^{a}	19.7 (0.2)^{a}	3.53 (0.15)^{a}	2.06 (0.12)^{a}
0.1 Mg Si ha^{-1}	383 (2)^{a}	6.01 (0.19)^{a}	1.43 (0.03)^{a}	20.0 (0.3)^{a}	3.75 (0.21)^{a}	2.00 (0.02)^{a}
0.4 Mg Si ha^{-1}	375 (2)^{ab}	5.80 (0.17)^{a}	1.33 (0.05)^{a}	19.5 (0.6)^{a}	3.39 (0.14)^{a}	1.81 (0.05)^{ab}
1.5 Mg Si ha^{-1}	363 (1)^{b}	6.13 (0.19)^{a}	1.39 (0.07)^{a}	19.2 (0.2)^{a}	3.14 (0.08)^{a}	1.54 (0.05)^{b}
			2nd Cropping season (wet season)			
0 Mg Si ha^{-1}	387 (8)^{a}	7.41 (0.14)^{a}	1.69 (0.08)^{a}	18.3 (0.3)^{a}	3.00 (0.20)^{a}	1.65 (0.09)^{a}
0.1 Mg Si ha^{-1}	397 (2)^{a}	8.05 (0.10)^{a}	1.74 (0.06)^{a}	17.8 (0.8)^{a}	2.89 (0.13)^{a}	1.70 (0.08)^{a}
0.4 Mg Si ha^{-1}	393 (2)^{a}	8.05 (0.22)^{a}	1.66 (0.02)^{a}	18.8 (0.7)^{a}	2.77 (0.09)^{a}	1.55 (0.05)^{a}
1.5 Mg Si ha^{-1}	389 (4)^{a}	7.89 (0.37)^{a}	1.57 (0.08)^{a}	19.5 (0.3)^{a}	2.77 (0.19)^{a}	1.61 (0.07)^{a}

4.4.4 Resistance of rice against leaf folders, leaf blast and neck blast

The number of leaf folder larvae at 42 DAS in the second cropping season was significantly higher in the control than in the treatments with Si application (Figure 4.6a). Likewise, the number of damaged leaves was slightly but not significantly higher in the control (Figure 4.6b). The maximum observed damage was 20 % of leaf area.

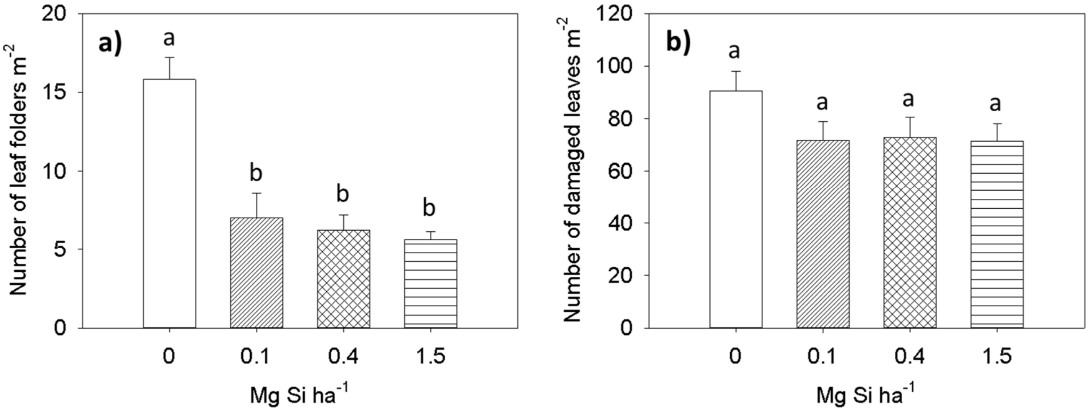

Figure 4.6 Number of (a) leaf folders and (b) damaged leaves per m^2 in the second cropping seasons at 41 DAS; error bars represent SE; letters give significant differences (P≤0.05)

Leaf blast severity at 34 DAS in the second cropping season slightly but not significantly decreased with increased Si application (Figure 4.7a). Likewise neck blast severity at 75 DAS slightly decreased with increased Si application; when compared to the control, the increase was significant for the 0.4 and 1.5 Mg Si ha^{-1} treatments (Figure 4.7b).

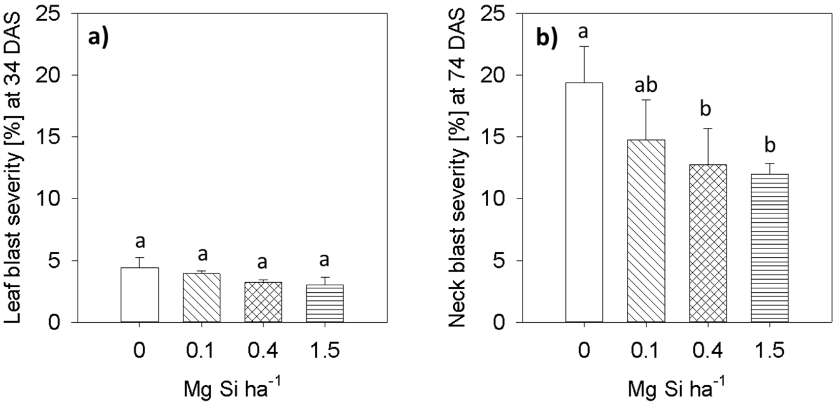

Figure 4.7 Severity of (a) leaf blast at 34 DAS and (b) neck blast at 74 DAS according to the scoring system of the International Rice Research Institute (1996) in the second cropping season; error bars represent SE; letters give significant differences (P≤0.05)

4.5 Discussion

The temporal courses of [dSi] reflect relationships between the rates of both dSi inputs and exports. Besides the application of silica gel, inputs of dSi occur by irrigation (while rain water typically shows very small or no [dSi] according to Klotzbücher et al. 2015b) and by release of Si from the soil matrix and plant residues. Exports occur by losses of water (percolation and drainage) as well as by plant Si uptake.

During the period with highest biomass gain throughout the cropping seasons, the export rates exceeded the input rates, and thus [dSi] decreased (starting at 15/12 DAS and ending at 65/52 DAS in the first/second cropping season; Figure 4.3a). Potentially, dilution of the flood water with rain water could decrease [dSi] in soil solution because [dSi] in rain typically is very low (Klotzbücher et al. 2015b). However, in our study temporal changes in [dSi] cannot be explained by the water inputs. This is firstly indicated by the finding that the decrease in [dSi] during the first cropping season was as distinct as the decrease in the second cropping season, although the rain fall in the first cropping season was very low (59 mm and 389 mm total rainfall in the first and second cropping season, respectively, Figure 4.3b). Furthermore, precipitation was highest in the last third of the second cropping season, a period when [dSi] in soil solution increased. Also irrigation events showed no clear association with [dSi] in soil solution (Figure 4.3).

We thus assume that the [dSi] decrease in the middle of the cropping seasons (that was seen for all treatments) was mainly due to Si uptake by rice plants. Decreasing [dSi] due to plant-Si-uptake was also shown for paddy soils in California (Seyfferth et al. 2013) and Japan (Mihara et al. 2016). In contrast, [dSi] remained constantly high throughout a cropping season in the Philippine paddies investigated by Klotzbücher et al. (2015b). Differences in [dSi] between the Philippine system and the system studied herein might be related to different rates of dSi regeneration by mineral dissolution. The Philippine soils contain high amounts of weatherable silicate minerals (Klotzbücher et al. 2015a), thus dSi was regenerated at a higher rate. The average [dSi] in the Philippine soils was five times higher than at our study site where the soil is strongly weathered. The decreases in [dSi] suggest that the rates of plant Si uptake exceed the rates of [dSi] input by weathering of soil minerals at our study site. In the last third of both cropping seasons, [dSi] increased presumably as plant-Si-uptake rates decreased. In this period, the plants primarily produce the grains, which typically contain very low concentrations of Si (Klotzbücher et al. 2015b).

According to the common practice by farmers in the study region, the straw of the first cropping season was scattered in the respective plot after harvest and then burned. Only five days after burning (two days after the second seeding), [dSi] was three to five times higher than at the end of the first cropping season. We relate this finding to the fast Si release from phytoliths in rice straw ash. Accordingly, the large differences in [dSi] between the treatments in the second cropping season might in part be due to differences in amounts of recycled phytoliths. The high solubility of phytoliths in rice straw ash was demonstrated in the laboratory by Nguyen et al. (2014). Also unburned rice straw was shown to be a significant source of plant-available Si in a field study by Seyfferth et al. (2013) and in many laboratory studies (Hossain et al. 2001, Watanabe et al. 2013, Marxen et al. 2016). Our results emphasize the importance of recycling crop residues for the Si supply to rice plants especially in regions with strongly weathered soils.

A further reason for the larger differences in [dSi] between the treatments in the second compared to the first cropping season (Figure 4.3a) might be that the dissolution rate of the silica gel increased during the experimental time. This might be related to the increasing average temperature (26.2 °C vs. 29.7 °C in the first and second cropping season, respectively; Figure 4.3b) as the solubility of silica gel is known to increase with temperature (Gunnarsson and Arnórsson 2000).

Silicon concentrations in straw at harvest stage as well as total Si uptake by the plants increased with increasing average [dSi] in the first cropping season (although the effect was not always statistically significant). In the second cropping season, Si concentrations in the straw did not differ significantly between the treatments although [dSi] significantly increased due to Si application. Average [dSi] values were generally higher in the second than in the first cropping season; however, total Si uptake did not differ between the cropping seasons. Taken together, these observations suggest that [dSi] in soil solution was not related to Si concentration in rice straw at harvest stage or to total Si uptake by the plants. They contradict observations from laboratory experiments, in which [dSi] typically determines plant-Si-uptake (Fleck 2013, Gocke et al. 2013, Marxen et al. 2016). How can the discrepancies between our results and those from laboratory experiments be explained? In the field, a suite of poorly studied factors of plant Si uptake might have played a role. One factor might have been differences in weather conditions (precipitation and temperature; Figure 4.3b). The effect of temperature on Si cycling was tested by Calatayud et al. (2016) for maize plants grown on different altitudes. The authors reported that Si fertilization had lower effect on plant-Si-uptake at higher altitudes with lower temperature than vice versa. This would contradict our results. However, a limitation of the study by Calatayud et al. (2016) is that [dSi] was not measured and it cannot be excluded that decreased dissolution rate of the Si fertilizer at lower temperatures explains their finding. We are not aware of any other study addressing weather effects on Si cycling in paddies.

Previous work showed that differences in Si availability can affect the uptake of other nutrients by plants (reviewed by Guntzer et al. 2012a). Silicon fertilization showed no significant effect on the concentrations of other elements in the rice plants, except for Mg and C. Magnesium concentration in the straw at harvest stage decreased with increased Si uptake in the first cropping season (Table 4.4). As straw production did not differ between the treatments, the decrease in Mg concentration might be an effect of the reduced plant mass that does not consist of phytoliths. Carbon concentrations in rice straw at harvest stage decreased with increased Si concentration in the first cropping season (Table 4.4). This is in accordance with the result of our field experiment in Northern Vietnam (Marxen et al. 2016) and might be explained by a decreased formation of structural C compounds (cellulose or polyphenols) due to increased formation of phytoliths as proposed by Raven (1983). Both plant constituents seem to perform similar functions, including cell strength and tissue support, defence against insects and diseases, and alleviation of abiotic stresses (Cooke and Leishman 2011). Hence, phytolith formation following Si uptake could be an energetically cheaper alternative to the synthesis of structural C compounds (Raven1983).

Silicon application caused decreasing numbers of leaf folders as well as a decreased severity of neck blast (Figures 4.5, 4.6). Our study thus confirms literature showing that increased Si uptake by rice plants mitigates damage by rice blast (Datnoff and Snyder 1994; Seebold et al. 2000; Seebold et al. 2004) and leaf folders (Han et al. 2015). However, despite these effects that should support plant health and growth, we found no effects of Si application on straw production and grain yield. The reason for that might be that the level of biotic stress was in general low during our study period. In the surrounding of our experiment, farmers applied pesticides, which potentially were transported to our experimental fields by wind and water (pesticide application dates and active substances are provided in Appendix 8). This could be the reason for the low occurrence of the analysed pests and diseases.

4.6 Conclusions

We have shown that [dSi] in paddy topsoil with inherently low plant-available Si are subject to strong temporal changes. Our results confirm previous studies showing that Si uptake by plants is a major factor causing decreasing concentrations of dissolved Si, while recycling of phytoliths with rice straw ash increases dissolved Si in the soil solution. Water inputs (irrigation, rain) were not related to temporal changes in dissolved Si. A surprising finding was that the total plant-Si-uptake during a cropping season was not related to differences in dissolved Si in soil solution. Hence, the relationship between Si availability and plant-Si-uptake in systems of generally low Si availability is not as straight forward as suggested by previous laboratory studies that showed positive relationships between the parameters. Obviously, there are other important factors determining plant-Si-uptake under field conditions. We assume that differences in weather conditions between the seasons played a role. These relationships are, however, poorly studied yet, thus deserve further research attention.

4.7 Acknowledgements

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5 Synthesis

5.1 Discussion

5.1.1 Si nutritional status of rice linked to reactive Si fractions in soils

Results presented in this thesis show that the Si levels in rice plants can largely differ between regions. Regional averages in straw Si concentrations differed by factors of up to 3 (PH_1 vs. VN_4). In comparison, the differences in concentrations of essential nutrients (N, P, K, Ca, and Mg) in straw are rather small (Table 5.1). Moreover, for these nutrients, differences in regional averages within one country were oftentimes similar or higher than the differences between the countries, while for Si clear differences between the countries were found. As discussed in Chapter 2, the differences in Si supply between Vietnam and the Philippines might primarily be due to differences in weatherable minerals in soils. Strongly weathered soils, such as Ferralsols, are widespread in (sub-)tropical regions due to intense climatic conditions, i.e. high temperature and precipitation (Blume et al. 2009). Thus, Si limitation to rice plants might be a widespread phenomenon in the (sub-)tropics.

Table 5.1 Elemental concentration [%] of rice straw at maturity stage in the study regions; SE in brackets; means of 2 years are given where only one annual rice crop was grown (PH_3 and VN_3), means of one dry and one wet season are given where two annual rice crops were grown (PH_1, PH_2, VN_1, and VN_2), and means of three annual rice crops are given for VN_4; harvests from 2012 to 2014 were considered; n=15 in PH_1, n=17 in PH_2, n=18 in PH_3, n=19 in VN_1, n=18 in VN_2, n=17 in VN_3, and n=27 in VN_4; detailed information on the regions is given in Chapter 2

Region	Si	N	P	K	Ca	Mg
PH_1	8.90 (0.19)	0.74 (0.05)	0.13 (0.01)	2.14 (0.16)	0.24 (0.01)	0.13 (0.01)
PH_2	7.97 (0.17)	0.71 (0.04)	0.14 (0.01)	2.21 (0.11)	0.32 (0.02)	0.18 (0.01)
PH_3	8.04 (0.32)	0.59 (0.04)	0.11 (0.01)	1.45 (0.19)	0.28 (0.02)	0.13 (0.01)
VN_1	4.06 (0.21)	0.72 (0.04)	0.14 (0.01)	2.31 (0.12)	0.40 (0.02)	0.18 (0.01)
VN_2	4.13 (0.25)	0.77 (0.04)	0.18 (0.01)	2.40 (0.10)	0.48 (0.02)	0.17 (0.01)
VN_3	4.59 (0.41)	0.72 (0.07)	0.11 (0.02)	2.32 (0.15)	0.44 (0.03)	0.20 (0.02)
VN_4	2.92 (0.10)	0.79 (0.02)	0.13 (0.01)	2.14 (0.07)	0.33 (0.01)	0.18 (0.01)

In accordance with literature, concentration of acetate-extractable Si in topsoil was found to be a suitable parameter for estimating how well the plants are supplied with Si (Chapter 2). Acetate extracts Si dissolved in the soil solution and some of the Si adsorbed to mineral surfaces (Sauer et al. 2006). In general, concentrations of acetate-extractable Si were not related to clay contents, suggesting that they were not determined by availability of sorption sites. Total Si uptake by plants during one cropping season was on average 5 times higher than the amounts of Si extracted by the acetate method from topsoil. A one-time assessment of acetate-extractable Si thus does not provide a measure for total amounts of Si available to rice plants. In Laguna (Philippines), amounts of acetate-extractable Si did not even decrease during a rice cropping season (Klotzbücher et al. 2015b; in Vietnam, the temporal course of acetate-extractable Si during a cropping season was not yet examined). Taken together, these facts indicate that acetate-extractable Si is continuously renewed by inputs of dissolved Si (i.e., due to mineral weathering, irrigation water, and/or phytolith dissolution). The rate of dissolved Si inputs seem to determine both, concentrations of acetate-extractable Si in topsoil, as well as the total amounts of Si that can be taken up by plants.

Acetate-extractable Si in topsoils correlates with Si in rice up to plant Si concentrations of 8–10 % that were only reached in some Philippine paddies, where Si uptake was probably limited by a maximum uptake capacity of rice (Chapter 2). Also other authors reported similar maximum Si concentrations in rice straw (Kraska and Breitenbeck 2010; Tsujimoto et al. 2014). In Vietnam, rice growth might be limited by Si as plant Si concentrations are below a critical value of 5 % proposed by Dobermann and Fairhurst (2000) (Chapter 2). In accordance with this view, Si fertilization increased Si uptake, biomass production and yield of rice (Chapter 3).

Also oxalate-extractable Si correlates with Si concentration in plants. Oxalate extracts adsorbed Si (probably more effective than acetate does) and additionally dissolves poorly crystalline Al and Fe (hydr-)oxides and poorly-crystalline/amorphous aluminosilicates (e.g., Cornelis et al. 2011). In the study regions, poorly crystalline Fe (hydr-)oxides were quantitatively more important than Al (hydr-)oxides and aluminosilicates as suggested by the ratios of oxalate extractable Fe/Al (Chapter 2). The oxalate-extractable Si fraction was on average 3.7 times higher than the acetate-extractable Si fraction. Hence, a large fraction of oxalate-extractable Si might comprise Si associated with poorly crystalline Fe (hydr-) oxides that dissolve and re-precipitate during redox cycles. However, it is still uncertain, which portion of the Si associated to Fe (hydr-)oxides is released during anoxic phases in the paddies and if Fe (hydr-)oxides may act as Si sink on the long-term.

The carbonate extraction method has been applied to estimate phytolith pools in soils. However, recent literature questions whether it is a suitable parameter as it probably only effectively extracts fresh phytoliths (Vandevenne et al. 2015; Meunier et al. 2014) and a significant portion of carbonate-extractable Si may derive from poorly crystalline aluminosilicates and clay minerals (Barão et al. 2014; Meunier et al. 2014). Herein, concentrations and amounts of carbonate-extractable Si in topsoil were the only parameters not generally higher in the Philippines than in Vietnam. Carbonate-extractable Si in topsoil was not correlated to phytolith production, and thus it was not correlated to potential amounts of phytolith input. It is currently not clear whether these findings are due to the limitations of the extraction method. A more detailed analysis on the sources of carbonate-extractable Si in different soil samples would be necessary for further insight into relationships between amorphous Si in topsoil and phytolith production. More reliable results on the role of phytoliths for Si supply to rice plants was obtained from a laboratory experiment (Chapter 3), which is discussed in Chapter 5.1.3.

5.1.2 Uncertain climatic effect on Si supply to plants

Climate might be another 'natural factor' determining Si cycling. Its influence probably is highly complex (it determines water fluxes, biogeochemical cycles of other elements and plant growth parameters). Hardly any research has been conducted on the effect of climate on the Si cycle in rice paddies yet. Climatic conditions differ mostly between the mountain and lowland regions, with lower temperature and higher precipitation in the mountains (Klotzbücher et al. 2015a). However, not only climate but also agricultural practices effecting Si cycling differ between the regions, such as intensity (only one annual cropping season in the mountains and 2-3 in the lowlands), crop residue management, NPK fertilization, and rice varieties (Klotzbücher et al. 2015a). Hence, it was not possible to unravel potential effects of climate on Si forms and fluxes by comparing the seven study regions in Vietnam and the Philippines.

We found considerably different results on relationships between dissolved Si in topsoil and the Si uptake by plants between two cropping seasons at the Si fertilization experiment in Southern Vietnam (Chapter 4). Weather conditions (temperature, precipitation) differed between the cropping seasons, and so we hypothesized that this might be one explanation for the finding. Future research should address the hypothesis. Uncertainties e.g., exist concerning the questions whether temperature affects the amounts of Si taken up by plant and whether temperature affects the rates of dissolved Si produced by mineral weathering in topsoil of paddy fields.

5.1.3 The role of recycling rice straw for Si cycling

It was not possible to get valuable historical data on crop residue management at the study sites by interviewing the farmers. The main problem is that many farmers do not know about the agricultural practices of their forefathers. Own field observations showed that straw management can differ from field to field within regions. The straw management practices presumably cause small-scale spatial differences in Si return to paddy fields. For example, some farmers make one pile of the straw originating from many fields in the corner of one field, burn it and don´t distribute the ash homogenously. Others return only part of the straw to the fields and use the other part for various purposes, such as for cooking fire, for animal housing, or as animal fodder.

Due to these uncertainties about spatial and temporal differences, it was not possible to analyse possible effects of straw residue management on plant Si uptake in the study sites. Also data obtained from the carbonate extraction of the 70 paddy topsoils presented in Chapter 2 were not reliable concerning the role of phytoliths on Si supply to rice plants as mentioned above. Therefore, a laboratory experiment on straw recycling was conducted

(Chapter 3). Results showed that recycled rice straw is an important Si source for rice plants in regions with low plant-available Si, which confirmed the results of a field study by Seyfferth et al. (2013) and of laboratory studies (Hossain et al. 2001; Watanabe et al. 2013). Phytoliths from fresh straw released up to 82 % of Si contained within the first month of incubation indicating high solubility of fresh phytoliths. As Si release rates decreased within the first month after straw incorporation, phytoliths might underlie stabilization in soil during ageing, which would also explain the occurrence of old phytoliths in soils, which are used by archaeologists to reconstruct past vegetation (Santos et al. 2010; Piperno 2014). The mechanisms behind the formation of old phytoliths are, however, still unknown. They might include decreasing specific surface area of the phytoliths during ageing (Fraysse et al. 2006) and/or changes in chemical composition of the phytoliths' surfaces. It has been shown that sorption of di- and tri-valent cations decrease the rates of dissolved Si release from phytoliths (reviewed by Haynes 2014).

Just like fresh straw, also straw ash was shown in a field experiment to rapidly release dissolved Si (Chapter 4), which is in line with results from a laboratory experiment by Nguyen et al. (2014). However, burning of rice straw causes air pollution and is therefore prohibited by many governments. Furthermore, the effect of burning on populations of enemies of pest insects is uncertain and killing of spiders and insects during burning might disturb the ecological equilibrium of predators and preys.

5.1.4 Effects of Si fertilization on Si cycling

In the field experiments on Si fertilization presented in Chapters 3 and 4, silica gel was used as Si source. Rather than commonly used silicate slags, silica gel does not contain any other nutrients or heavy metals; thus, fertilization effects can be more reliably referred to changes in Si availability. The experiments gave mixed results. In Northern Vietnam, silica gel application resulted in increased Si uptake by rice plants, straw production, and grain yield (Chapter 3). In Southern Vietnam, with originally even smaller Si concentrations of plants and despite increased concentrations of dissolved Si in soil solutions, such positive effects were not observed (Chapter 4). No general relationship between dissolved Si in topsoil and plant-Si-uptake was found when both cropping seasons were considered. The reasons for this finding are still uncertain but may include weather conditions that differed between the seasons. Furthermore, increased Si concentrations in rice straw within one of the cropping seasons did not affect biomass production or grain yield. This might be related to a low level of biotic and abiotic stresses during the cropping season. Increased biomass production due to increased Si uptake by rice is generally thought to be related to mitigation of stress factors (Guntzer et al. 2012a). To test this, long-term fertilization experiments covering a large span of biotic and abiotic stresses would be necessary.

The question remains if Si fertilization would be economically feasible for farmers. In Vietnam, the price of silica gel is 30.000 VND kg^{-1} (roughly 1.35 US$), which is three times the price of urea (10.000 VND kg^{-1}, equaling 0.45 US$), with both substances containing 46 % of Si and N, respectively. Increasing demand for silica gel for potential large-scale fertilizer application would probably decrease the cost as silica gel is currently only produced for industrial use. Another Si fertilizer that does not contain any other nutrients or any metals is diatomaceous earth; however, it is much more expensive than silica gel (about 4.4 US$ kg^{-1}).

5.1.5 Coupled Si and C cycling

There were indications that the Si cycle in paddy fields is coupled to cycling of organic matter. It has long been known that the cycles of Si and C are coupled through (i) weathering processes of primary silicates consuming CO_2 and (ii) Si fluxes into the oceans promoting CO_2 fixation by diatoms; the larger the Si fluxes into oceans, the higher the export flux of C within diatoms to marine sediments and the more CO_2 is finally removed from the atmosphere (Sommer et al. 2006). Also, the Si release rates of phytoliths in soil were found to be linked to the decomposition rates of the surrounding organic straw matrix (probably phytoliths start releasing Si only once their surface becomes exposed to the soil solution) and both increases with increasing Si concentration (Chapter 3). This is attributed to the decreased synthesis of structural C compounds (such as cellulose and lignin) with increased formation of phytoliths as the latter is the energetically cheaper alternative for plants to gain stability (Raven 1983; Cooke and Leishman 2011). Accordingly, Schaller and

Struyf (2013) found higher microbial decomposition rates for higher Si concentration and lower cellulose and phenol concentrations in litter of the common reed (*Phragmites australis*). Increased Si uptake by rice might also increase biomass production (Chapter 3).

The question remains: What might be the overall long-term effect of increased Si availability (e.g. due to Si fertilization) on coupled cycling of Si and C in paddy fields? So far, one can only speculate on this question, as long-term studies are missing. Central processes of the C and Si cycle seem to be accelerated at higher Si availability, including biomass production, phytolith production, decomposition of the organic straw matrix and the Si release during straw decomposition (Figure 5.1). Hence, Si and C fluxes might be higher, but the storage of phytoliths and organic C in topsoil may not necessarily change. Enhanced input of labile organic matter to soil upon Si fertilization might enhance microbial activity and decomposition processes in soil, causing loss of older organic matter (Kuzyakov et al. 2000). Also Si leaching might be affected. On the one hand, fast Si release from phytoliths might promote leaching and subsequent transfer of dissolved Si from terrestrial to riverine and marine ecosystems as hypothesized by Carey and Fulweiler (2015). On the other hand, the authors also indicate that this effect is typically not observed for agricultural systems with high phytolith production, presumably due to a large export of phytoliths from crop fields upon harvest. Even if crop residues are recycled, high leaching losses might be prevented by fastened plant Si uptake, depending on the residence time of Si in soil solution. It will be important to study the effects of increased Si availability on Si leaching, especially as leached amounts of Si control diatom production in oceans and lakes, and thus, C fixation and storage therein.

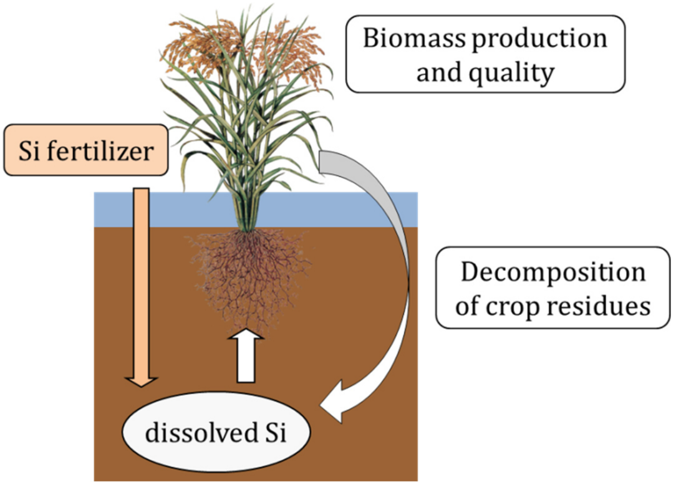

Figure 5.1 Effects of increased plant-available Si in paddy fields on biomass production and decomposition

Intensification of rice production might also exert strong effects on Si and C cycling. Biomass production correlates with total Si uptake by rice plants within Vietnam as well as within the Philippines (Chapter 2). This might suggest that plant Si uptake accelerates the release of dissolved Si from phytoliths and soil minerals by weathering (Chapter 3). Also Carey and Fulweiler (2015) hypothesized that intensification of rice cultivation enhances phytolith production. Unfortunately, it was not possible to identify the effect of intensification by comparing the study regions. Production intensity differs at most between the mountain regions with one annual cropping season and the lowlands with 2-3 annual cropping seasons. However, as already mentioned above, the regions also differ in many other factors influencing Si cycling.

5.2 Conclusions

Silicon limitation is a widespread phenomenon in rice cultivation systems. On a large geographical scale, the main determinants on plant-available Si in paddy soils are parent rock material and weathering stage of the soils. On a smaller scale, especially in regions with low plant-available Si, also agricultural practice can affect concentrations of dissolved Si. In Vietnam, where Si might limit rice growth, farmers can actively increase Si supply to plants by recycling rice straw.

Increased Si concentrations in rice plants increase the decomposability of organic matter and Si release of the produced straw. Herein, the first evidence for this effect in rice straw decomposition has been provided. Results suggest that Si availability is a control of organic matter turnover in paddy rice systems, but long-term consequences of increasing Si availability for major parameters of the organic matter cycle such as storage of organic C in soil are still uncertain.

Fertilization of Si with silica gel might be an option to increase the Si supply to plants. Long-term benefits of Si fertilization for the plants were, however, not yet studied. Combining observations from field experiments on Si fertilization and laboratory experiments on Si release from rice straw suggest that a valuable approach to maintain high levels of Si and high turnover rates could be sporadic Si fertilization in combination with frequent straw recycling. Thus, the overall cost for Si fertilization might be less expensive than the cost for other frequently applied nutrients although the price for silica gel is high.

5.3 Outlook

The effects of climate on inputs of dissolved Si into paddy soils and the Si uptake by plants need to be investigated. A valuable approach could be to identify temperature and precipitation gradients and to measure dissolved Si in soil solutions and plant Si uptake in paddy fields along these gradients.

Phytolith turnover rates need to be tested in longer term studies than in the presented laboratory experiment. It is still uncertain how ageing of phytoliths affects their solubility. Knowledge about this question is central for an evaluation of the effects of straw management on Si availability. One promising research approach might be to recycle rice straw in a field experiment and to measure ratios of Si isotopes in soil solutions over a few cropping seasons to test the origin of Si. Estimating the dissolved Si amounts released from rice straw and relating it to Si uptake by rice plants would give valuable information on turnover of phytoliths.

Furthermore, effects of Si fertilization in combination with straw recycling on C cycling must be investigated over a longer time span. Therefore, litterbags could be used for quantification of C loss during decomposition as in the presented laboratory study. Additionally, the amounts of structural C compounds in straw should be quantified to prove the hypothesized effect of increased Si on organic matter quality. To estimate the effects on C storage in soil, total C in the produced straw, C input to soil via straw recycling and C loss of straw during decomposition need to be balanced.

Long-term field studies on Si fertilization in combination with straw recycling are needed also to address the following aspects: (i) The potential of Si fertilization to increase biomass production and yield might be related to mitigation of biotic or abiotic stresses. Levels of stress occurrence might strongly differ between cropping seasons. Hence, in order to test relationships between stress occurrence and plant Si uptake, long-term experiments are necessary. (ii) Suitable Si application rates must be tested. (iii) Possible negative effects of Si fertilization need to be identified, such as adaption of pest insects to higher Si concentrations in rice, colonization by unknown pest communities, or effects on cycling of other nutrients.

Summary

Silicon (Si) is a beneficial nutrient for rice (*Oryza sativa* L.) plants, which take up silicic acid passively as well as actively from the soil solution. Within the plant tissue, amorphous Si dioxide particles precipitate; these so-called phytoliths enhance the plants´ strength and rigidity and improve its resistance to abiotic stresses (such as strong rain, wind, and salinity) as well as biotic stresses (such as pest attacks and fungal diseases). The overarching goal of this thesis was to contribute to an improved understanding of the Si cycle in rice production systems and to generate recommendations on how the Si supply to rice plants might be improved in regions with low Si availability. The three specific aims of the thesis were to

(i) identify relationships between Si forms in soils and Si supply to rice plants by collecting data across large geographic scales,
(ii) test the role of recycling fresh and burned rice straw for Si supply to plants and biomass production, and to
(iii) test the effects of Si fertilization on the Si supply to plants and biomass production.

i) Ten paddy fields in seven regions in Vietnam and the Philippines were chosen, respectively, and Si status of soils and plants were screened. Si levels in rice plants largely differed between regions by factors of up to 3. Concentrations of Si in rice straw were generally higher in the Philippines than in Vietnam. This can be explained by differences in weatherable minerals in soils. Acetate-extractable Si was found to be a suitable parameter for estimates about how well the plants are supplied with Si, i.e., the concentrations of acetate-extractable Si in topsoil correlated with the Si concentrations in straw. Acetate extracts Si dissolved in the soil solution and some of the Si adsorbed to mineral surfaces. In Vietnam, rice growth might be limited by the low Si availability. In 39 of 40 rice fields studied in Vietnam, the straw Si concentrations were below the critical value of 5 % determined by researchers of the International Rice Research Institute.

ii) It was shown in a laboratory experiment that recycled rice straw is an important Si source for rice plants in regions with low plant-available Si. Increased Si concentrations in rice plants increase the decomposability of organic matter and Si release of the produced straw. Within the first month of incubation, 82 % of the Si contained in fresh straw was released into soil solution, suggesting rapid phytolith dissolution. Similarly, a rapid Si release from rice straw ash was found in a field experiment. As Si release rates decreased within the first month after straw incorporation into soil, it is assumed that the solubility of phytoliths decreases during ageing. The mechanisms behind the solubility changes are, however, still unknown.

iii) Two field experiments on Si fertilization with silica gel were conducted. At a Northern Vietnamese site, the application of rapidly dissolvable silica gel resulted in increased Si uptake by rice plants, straw production, and grain yield. At a Southern Vietnamese site, silica gel application increased concentrations of dissolved Si in soil solution, but there was no relationship between dissolved Si and plant-Si-uptake considering the two cropping seasons under study. The reasons are still uncertain, but may include differences in weather conditions between the seasons. Furthermore, increased Si concentrations in rice straw upon silica gel application (only found in one of the two cropping seasons) did not affect biomass production or grain yield. This might be related to a low level of biotic and abiotic stresses during the cropping season.

In conclusion, the present thesis shows that Si limitation of rice growth might be a widespread phenomenon in rice cultivation on weathered (sub-)tropical soils. Farmers might be able to improve the Si supply to rice plants by application of Si fertilizers in combination with frequent recycling of Si-rich rice straw. The thesis also revealed gaps in knowledge about the biogeochemical Si cycle. Long-term solubility of phytoliths in soils is unclear; in particular, the factors causing the decrease of phytolith solubility during phytolith ageing in soil are yet uncertain. Also, longer-term Si fertilization experiments are necessary. It is not clear why the effects of Si fertilization on Si uptake and growth of rice plants differ between field experiments and between seasons. Future research should aim at relating fertilization effects to the occurrence of biotic and abiotic stresses.

Zusammenfassung

Silizium (Si) ist ein nützliches Nährelement für Reis (*Oryza sativa* L.). Reispflanzen nehmen Si in Form von Kieselsäure sowohl passiv als auch aktiv aus der Bodenlösung auf. Im Pflanzengewebe fallen amorphe Siliziumdioxid-Partikel aus. Diese sogenannten Phytolithe verleihen der Pflanze Festigkeit und Stabilität. Silizium verbessert die Resistenz der Pflanze gegenüber abiotischem Stress (wie starkem Regen, Wind und Salinität) und biotischem Stress (wie Schädlings- und Pilzbefall). Das übergeordnete Ziel dieser Arbeit war es, zu einem besseren Verständnis des Si-Kreislaufs in Nassreis-Anbausystemen beizutragen und Empfehlungen für eine Verbesserung der Si-Versorgung von Reispflanzen in Regionen mit niedriger Si-Verfügbarkeit zu geben. Im Detail waren dies die Ziele der Arbeit:

(i) Untersuchung des Zusammenhangs von Si-Formen im Boden und Si-Versorgung der Reispflanzen über einen großen geographischen Maßstab

(ii) Untersuchung des Einflusses von in den Boden eingebrachtem frischen oder verbrannten Reisstroh auf die Si-Versorgung der Pflanze und deren Biomasseproduktion

(iii) Untersuchung des Effekts von Si-Düngung auf die Si-Versorgung der Pflanze und deren Biomasseproduktion

i) Jeweils zehn Reisfelder in sieben Regionen Vietnams und der Philippinen wurden ausgewählt und bezüglich des Si-Status der Oberböden und Pflanzen verglichen. Die Si-Gehalte der Reispflanzen unterscheiden sich stark zwischen den Regionen, bis hin zu einem Faktor von 3. Generell sind die Si-Konzentrationen im Reisstroh auf den Philippinen höher als in Vietnam, was auf Unterschiede im Gehalt verwitterbarer Minerale in den Böden zurückzuführen ist. Ein gut geeigneter Parameter zur Bewertung der Si-Versorgung von Pflanzen ist Acetat-extrahierbares Si, denn die Konzentrationen an Acetat-extrahierbarem Si in den Oberböden korrelieren mit den Si-Konzentrationen im Reisstroh. Die Acetat-Extraktionsmethode erfasst gelöstes Si und ein Teil des an Mineraloberflächen adsorbierten

Si. In Vietnam könnte das Reiswachstum durch die geringe Si-Verfügbarkeit in den Oberböden limitiert sein. In 39 von 40 untersuchten Feldern liegen die Si-Konzentrationen im Stroh unterhalb eines kritischen Wertes von 5 %. Diesen Wert haben Forscher des Internationalen Reis Forschungszentrums (IRRI) ermittelt.

ii) Ein Laborexperiment hat gezeigt, dass das Recycling von Reisstroh eine wichtige Si-Quelle für Reispflanzen in Regionen mit geringer Si-Verfügbarkeit darstellt. Eine erhöhte Si-Aufnahme der Pflanze erhöht die Abbaubarkeit des produzierten Strohs sowie die Si-Freisetzung aus dem Stroh während des Abbaus. Innerhalb eines Monats wurde aus Reisstroh bis zu 82 % des enthaltenen Si freigesetzt, was auf eine sehr hohe Löslichkeit von frischen Phytolithen hinweist. In einem Feldexperiment wurde gezeigt, dass Si auch aus Reisstroh-Asche schnell freigesetzt wird. Die Si-Freisetzungsraten des Strohs sind innerhalb des ersten Monats nach Einbringung in den Boden gesunken, d. h. die Löslichkeit von Phytolithen nimmt vermutlich während ihrer Alterung im Boden ab. Die Mechanismen dahinter sind noch unklar.

iii) Zwei Feldexperimente zur Düngung mit Silikagel wurden durchgeführt. Auf einer Fläche in Nordvietnam hat die Applikation von leicht löslichem Silikagel zu einer Erhöhung der Si-Aufnahme der Pflanzen, der Biomasseproduktion und des Ertrags geführt. Auf einer Fläche in Südvietnam hat die Applikation von Silikagel eine Erhöhung der Si-Konzentration in der Bodenlösung bewirkt. Unter Berücksichtigung beider Anbauperioden innerhalb des Versuchszeitraums gibt es aber keinen Zusammenhang zwischen Si in der Bodenlösung und Si-Aufnahme der Pflanzen. Die Gründe hierfür sind unklar, aber unterschiedliche Wetterbedingungen zwischen den Anbauperioden könnten eine Rolle spielen. Außerdem hat eine Erhöhung der Si-Konzentrationen im Reisstroh in einer der Anbauperioden nicht zu einer Erhöhung der Biomasseproduktion oder des Ertrags geführt. Dies könnte auf ein niedriges Level an abiotischen und biotischen Stressfaktoren während der Anbauperiode zurückzuführen sein.

Eine Hauptschlussfolgerung der vorliegenden Arbeit ist, dass eine Si-Limitierung des Reiswachstums in (sub-)tropischen Anbausystemen auf stark verwitterten Böden weit verbreitet sein könnte. Bauern können die Si-Versorgung der Reispflanzen vermutlich verbessern, indem sie Si düngen und regelmäßig das Si-reiche Reisstroh auf das Feld zurück bringen. In der vorliegenden Arbeit werden auch wesentliche Wissenslücken in der Biogeochemie des Si-Kreislaufs aufgezeigt. Die Langzeit-Löslichkeit von Phytolithen und insbesondere die Faktoren, die eine Abnahme der Löslichkeit von Phytolithen während ihrer Alterung im Boden bewirken, sind noch nicht genau erforscht. Auch Langzeitstudien zur Si-Düngung sind erforderlich, da noch unklar ist, warum sich die Auswirkungen der Si-Düngung auf die Si-Aufnahme und das Wachstum der Reispflanzen zwischen den Feldexperimenten und zwischen den Anbauperioden unterscheiden. Ein Ziel zukünftiger Studien sollte es sein, Düngeeffekte zu testen, während die Reispflanzen biotischen und abiotischen Stressfaktoren ausgesetzt sind.

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List of Abbreviations

Al_{ox}	oxalate-extractable Al
ANOVA	Analysis of Variance
ASi	amorphous Si
asl	above sea level
BS	base saturation
CEC	cation exchange capacity
CO_2	carbon dioxide
C_{org}	organic C
DAS	days after seeding
DM	dry mass
dSi	dissolved silicon
Fe_{ox}	oxalate-extractable Fe
ICP-OES	inductively coupled plasma optical emission spectrometry
Na_2CO_3	sodium carbonate
NPK	nitrogen phosphorus potassium
SE	standard error
$Si_{acetate}$	acetate-extractable Si
$Si_{carbonate}$	carbonate-extractable Si
$Si_{oxalate}$	oxalate-extractable Si
TOC	total organic carbon
TRB	total reserve of bases
WDXRF	wave length-dispersive X-ray fluorescence
XRF	x-ray fluorescence

Danksagung

Appendix

Appendix 1 General information on land use, sampling date, relief and location of sampled fields; field numbers containing 'R' belong to paddy fields used in Klotzbücher et al. (2015a) and in Chapter 2, field numbers containing 'F' belong to fields with alternative land use and were only used in Klotzbücher et al. (2015a)

Field number	Land use 1)	Sampl. date	Slope position 2)	Slope form 2)	Sl. gradient 2)	Exposition 2)	Location 3)	m a.s.l. 2)
VN_1: North Vietnam, Hai Duong province (major land form: flood plain)								
VN_1_R_2	poorly structured	28.10.2011	plain	straight, terraced	<1%	- -	N 21.03296 E 106.35387	3
VN_1_R_1	richly structured	25.10.2011	plain	straight, terraced	<1%	- -	N 21.03488 E 106.35050	4
VN_1_F_1	tomato	25.10.2011					N 21.03488 E 106.35050	
VN_1_R_4	richly structured	26.10.2011	plain	straight, terraced	<1%	- -	N 20.99121 E 106.40790	3
VN_1_R_3	poorly structured	26.10.2011	plain	straight, terraced	<1%	- -	N 20.98842 E 106.41296	3
VN_1_F_2	banana	26.10.2011	plain	straight	<1%	- -	N 20.99073 E 106.40851	3
VN_1_R_6	poorly structured	26.10.2011	plain	straight, terraced	<1%	- -	N 20.96094 E 106.44429	2
VN_1_R_5	richly structured	26.10.2011	plain	straight, terraced	<1%	- -	N 20.96091 E 106.44228	2
VN_1_F_3	farm lane	26.10.2011	plain	straight	<1%	- -	N 20.96091 E 106.44228	
VN_1_R_7	poorly structured	27.10.2011	plain	straight, terraced	<1%	- -	N 20.94533 E 106.36392	2
VN_1_R_8	richly structured	27.10.2011	plain	straight, terraced	<1%	- -	N 20.94395 E 106.36802	4
VN_1_R_10	poorly structured	27.10.2011	lower slope	straight, terraced	2%	290° W	N 21.07937 E 106.39580	4
VN_1_R_9	richly structured	27.10.2011	lower slope	straight, terraced	3%	150° SE	N 21.08055 E 106.39358	6
VN_2: North Vietnam, Vinh Phuc province (major land form: hilly)								
VN_2_R_1	poorly structured	16.02.2012	bottom	straight, terraced	2%	180° S	N 21.34480 E 105.70945	22
VN_2_R_2	richly structured	16.02.2012	bottom	straight, terraced	3%	300° NW	N 21.34138 E 105.70935	24
VN_2_R_4	poorly structured	16.02.2012	bottom	straight, terraced	<2%	240° SW	N 21.35130 E 105.70691	26
VN_2_R_3	richly structured	16.02.2012	bottom	straight, terraced	<2%	180° S	N 21.34870 E 105.70621	23
VN_2_F_1	vegetable field	18.02.2012	bottom	straight	<2%	230° SW	N 21.34767 E 105.70515	20
VN_2_F_2	bamboo forest	18.02.2012	bottom	straight	<2%	- -	N 21.34715 E 105.70399	19
VN_2 fertilization exp.	poorly structured	01.04.2013	bottom	straight	<2%	- -	N 21.35248 E 105.70742	28
VN_2_R_5	poorly structured	17.02.2012	bottom	straight, terraced	2%	300° NW	N 21.37207 E 105.71867	40
VN_2_R_6	richly structured	17.02.2012	bottom	straight, terraced	2%	350° N	N 21.37268 E 105.72015	43
VN_2_F_3	litchi/tea	18.02.2012	lower slope		12%	320° NW	N 21.37265 E 105.72034	44
VN_2_R_7	poorly structured	17.02.2012	bottom	straight, terraced	<2%	- -	N 21.31653 E 105.73890	20
VN_2_R_8	richly structured	17.02.2012	lower slope	straight	3%	240° SW	N 21.31905 E 105.74130	21

Field number	Land use 1)	Sampl. date	Slope position 2)	Slope form 2)	Sl. gradient 2)	Exposition 2)	Location 3)	m a.s.l. 2)
VN_2_F_4	peanut field	19.02.2012	bottom	straight, terraced	<2%	- -	N 21.31602 E 105.73824	20
VN_2_F_5	forest	19.02.2012	lower slope	straight	4%	270° W	N 21.31624 E 105.74211	24
VN_2_R_9	poorly structured	17.02.2012	bottom	straight, terraced	<2%	- -	N 21.31445 E 105.73585	22
VN_2_R_10	richly structured	17.02.2012	bottom	straight, terraced	<2%	- -	N 21.31783 E 105.73450	23
VN_3: North Vietnam, Lao Cai province (major land form: mountainous, steeply dissected)								
VN_3_R_1	poorly structured	04.11.2011	lower slope	straight, terraced	40%	300° NW	N 22.41093 E 103.90205	729
VN_3_R_2	richly structured	04.11.2011	lower slope	straight, terraced	40%	280° W	N 22.41020 E 103.90220	748
VN_3_F_1	bushland	04.11.2011	lower slope	concave	30%	260° W	N 22.41053 E 103.90200	735
VN_3_R_4	poorly structured	05.11.2011	lower middle slope	straight, terraced	30%	180° S	N 22.29647 E 103.91067	979
VN_3_R_3	richly structured	05.11.2011	middle slope	convex, terraced	15%	230° SW	N 22.29853 E 103.91350	1043
VN_3_F_2	forest	05.11.2011	middle slope	straight	30%	180° S	N 22.29872 E 103.91345	1049
VN_3_R_6	poorly structured	05.11.2011	lower slope	straight, terraced	10%	40° NE	N 22.30420 E 103.88730	989
VN_3_R_5	richly structured	05.11.2011	lower middle slope	convex, terraced	15%	10° N	N 22.30205 E 103.88972	998
VN_3_F_3	bamboo forest	05.11.2011	middle slope	straight	30%	20° N	N 22.30163 E 103.88942	1010
VN_3_R_8	poorly structured	06.11.2011	middle slope	straight, terraced	30%	160° S	N 22.31800 E 103.85883	1269
VN_3_R_7	richly structured	06.11.2011	upper slope	concave, terraced	20%	20° N	N 22.31455 E 103.85820	1252
VN_3_F_4	forest	06.11.2011	upper slope to crest	convex	40%	60° NE	N 22.31448 E 103.85808	1254
VN_3_R_9	poorly structured	06.11.2011	bottom	straight, terraced	2%	- -	N 22.39314 E 103.84382	1284
VN_3_R_10	richly structured	06.11.2011	lower slope	concave, terraced	20%	280° W	N 22.39481 E 103.84445	1289
VN_3_F_5	bushland	06.11.2011	middle slope	convex	40%	300° NW	N 22.39546 E 103.84492	1302
VN_4: South Vietnam, Tien Giang province (major land form: flood plain)								
VN_4_R_8	poorly structured	28.02.2012	plain	straight	<1%	- -	N 10.37051 E 106.12852	1
NN_4_R_2	richly structured	11.11.2011	plain	straight	<1%	- -	N 10.37125 E 106.12424	2
VN_4_R_5	poorly structured	27.02.2012	plain	straight	<1%	- -	N 10.44382 E 106.05849	2
VN_4_R_4	richly structured	27.03.2012	plain	straight	<1%	- -	N 10.44085 E 106.05783	3
VN_4_R_7	poorly structured	27.02.2012	plain	straight	<1%	- -	N 10.40512 E 106.10195	2
VN_4_R_6	richly structured	27.02.2012	plain	straight	<1%	- -	N 10.40310 E 106.10335	3
VN_4_R_9	poorly structured	28.02.2012	plain	straight	<1%	- -	N 10.38010 E 106.11140	2
VN_4_R_10	richly structured	28.02.2012	plain	straight	<1%	- -	N 10.37960 E 106.11295	2
VN_4_R_11	poorly structured	28.02.2012	plain	straight	<1%	- -	N 10.40736 E 106.10760	2
VN_4_R_12	richly structured	28.02.2012	plain	straight	<1%	- -	N 10.40714 E 106.10908	3
PH_1: Philippines, Laguna province (major land form: hilly)								
PH_1_R_2	poorly structured	20.01.2012	plain	straight	<1%	- -	N 14.22875 E 121.33960	5
PH_1_R_1	richly structured	20.01.2012	plain	straight	<1%	- -	N 14.22865 E 121.33564	9

Field number	Land use 1)	Sampl. date	Slope position 2)	Slope form 2)	Sl. gradient 2)	Exposition 2)	Location 3)	m a.s.l. 2)
PH_1_F_1	fruit trees	20.01.2012	plain	straight	<1%	- -	N 14.22921 E 121.33537	10
PH_1_R_4	poorly structured	27.01.2012	lower slope	concave, terraced	6%	310° NW	N 14.11541 E 121.41048	275
PH_1_R_3	richly structured	27.01.2012	lower slope	concave, terraced	6%	310° NW	N 14.11484 E 121.41247	288
PH_1_F_2	squash field	27.01.2012	lower slope	concave	6%	330° NW	N 14.11583 E 121.41298	287
PH_1_R_6	poorly structured	30.02.2012	plain	straight	<1%	- -	N 14.21754 E 121.33509	7
PH_1_R_5	richly structured	30.02.2012	plain	straight	<1%	- -	N 14.21565 E 121.33729	8
PH_1_F_3	fruit trees	30.02.2012	plain	straight	<1%	- -	N 14.21248 E 121.33754	14
PH_1_R_8	poorly structured	31.02.2012	lower slope	concave, terraced	4%	160° S	N 14.13875 E 121.40079	187
PH_1_R_7	richly structured	31.02.2012	lower slope	concave, terraced	8%	160° S	N 14.13934 E 121.39860	190
PH_1_F_4	coconut plantation	31.02.2012	lower slope	concave	8%	160° S	N 14.13992 E 121.39901	192
PH_1_R_10	poorly structured	01.02.2012	lower slope	straight, terraced	4%	330° NW	N 14.18912 E 121.36439	18
PH_1_R_9	richly structured	01.02.2012	lower slope	straight, terraced	4%	330° NW	N 14.18725 E 121.36561	31
PH_1_F_5	coconut plantation	01.02.2012	lower slope	straight	4%	330° NW	N 14.18689 E 121.36572	32
PH_2: Philippines, Nueva Ecija province (major land form: plain)								
PH_2_R_2	poorly structured	18.01.2012	plain	straight	<1%	- -	N 15.67260 E 120.84210	45
PH_2_R_1	richly structured	18.01.2012	plain	straight	<1%	- -	N 15.67368 E 120.84324	47
PH_2_F_1	rice/vegetable	18.01.2012	plain	straight	<1%	- -	N 15.67066 E 120.84277	46
PH_2_R_4	poorly structured	19.01.2012	plain	straight	<1%	- -	N 15.66405 E 120.87556	52
PH_2_R_3	richly structured	19.01.2012	plain	straight	<1%	- -	N 15.66665 E 120.87582	55
PH_2_R_6	poorly structured	23.01.2012	plain	straight	<1%	- -	N 15.67265 E 120.92032	58
PH_2_R_5	richly structured	23.01.2012	plain	straight	<1%	- -	N 15.66865 E 120.91835	55
PH_2_R_8	poorly structured	24.01.2012	plain	straight	<1%	- -	N 15.60254 E 120.91095	44
PH_2_R_7	richly structured	24.01.2012	plain	straight	<1%	- -	N 15.60015 E 120.91115	45
PH_2_F_2	onion	24.01.2012	plain	straight	<1%	- -	N 15.59845 E 120.91125	45
PH_2_F_3	bitter gourd	24.01.2012	plain	straight	<1%	- -	N 15.57902 E 120.91120	40
PH_2_R_10	poorly structured	25.01.2012	plain	straight	<1%	- -	N 15.61690 E 120.94756	52
PH_2_R_9	richly structured	25.01.2012	plain	straight	<1%	- -	N 15.61412 E 120.94629	50
PH_2_F_4	patola	25.01.2012	plain	straight	<1%	- -	N 15.61836 E 120.94529	52
PH_3: Philippines, Ifugao province (major land form: mountainous, steeply dissected)								
PH_3_R_1	poorly structured	12.01.2012	lower slope	concave, terraced	20%	190° S	N 16.90502 E 121.07567	898
PH_3_R_6	richly structured	15.01.2012	middle slope	concave, terraced	15%	180° S	N 16.90540 E 121.06449	1075
PH_3_F_1	abandoned rice field	12.01.2012	middle slope	concave, terraced	40%	180° S	N 16.90742 E 121.07405	947
PH_3_F_7	abandoned rice field	15.01.2012	middle slope	concave	20%	180° S	N 16.90534 E 121.06454	1074
PH_3_R_2	poorly structured	13.01.2012	lower slope	concave, terraced	5%	260° W	N 16.91028 E 121.12550	851

Field number	Land use [1]	Sampl. date	Slope position [2]	Slope form [2]	Sl. gradient [2]	Exposition [2]	Location [3]	m a.s.l. [2]
PH_3_R_10	richly structured	07.02.2012	lower slope	straight, terraced	35%	320° NW	N 16.91000 E 121.12888	933
PH_3_F_3	abandoned rice field	13.01.2012	lower slope	straight, terraced	40%	320° NW	N 16.91010 E 121.12833	912
PH_3_F_2	forest	13.01.2012	lower slope	straight	35%	310° NW	N 16.90937 E 121.12612	878
PH_3_R_9	poorly structured	07.02.2012	lower slope	concave, terraced	13%	250° W	N 16.86110 E 121.09917	867
PH_3_R_4	richly structured	14.01.2012	middle slope	straight, terraced	20%	300° NW	N 16.85874 E 121.10135	933
PH_3_F_4	abandoned rice field	14.01.2012	lower slope	concave, terraced	17%	300° NW	N 16.85998 E 121.09854	871
PH_3_F_5	abandoned rice field	14.01.2012	upper slope	convex, terraced	25%	270° W	N 16.85860 E 121.10159	937
PH_3_F_6	forest	14.01.2012	upper slope	convex	25%	270° W	N 16.85850 E 121.10165	939
PH_3_R_11	poorly structured	08.02.2012	middle slope	straight, terraced	50%	60° NE	N 16.92081 E 121.05893	1089
PH_3_R_12	richly structured	08.02.2012	lower slope	convex, terraced	15%	60° NE	N 16.92075 E 121.05684	1155
PH_3_F_10	forest	10.02.2012	middle slope	straight	50%	90° E	N 16.92825 E 121.05477	1299
PH_3_R_13	poorly structured	09.02.2012	lower slope	convex, terraced	30%	40° NE	N 16.93293 E 121.13755	782
PH_3_R_8	richly structured	16.01.2012	middle slope	straight, terraced	60%	70° E	N 16.93345 E 121.13412	901
PH_3_F_9	forest	09.02.2012	middle slope	straight	30%	100° E	N 16.92994 E 121.13657	930

1) poorly structured = paddy field, surrounding dominated by paddy fields
richly structured = paddy field, surrounding dominated by other uses than paddy

2) Data derived from google maps (relief view), characterisation according to FAO 2006

3) Coordinates in WGS 84 format (measured data corrected for right position in google maps/earth

Appendix 2 Basic soil properties (regional means, standard deviation in brackets); data on pH_{KCl}, C_{org}, $Fe_{oxalate}$, and $Al_{oxalate}$ are given for each field in Appendix 4

Region	pH_{KCl}	C_{org} [%]	$Fe_{oxalate}$ [g kg^{-1}]	$Al_{oxalate}$ [g kg^{-1}]	Clay [%]	Silt [%]	Sand [%]	TRB $^{1)}$ [cmol kg^{-1}]
PH_1	4.8 (0.5)	2.7 (0.7)	5.8 (3.5)	1.5 (0.6)	39 (20)	44 (11)	17 (12)	168 (21)
PH_2	4.7 (0.8)	1.4 (0.3)	7.5 (2.2)	1.1 (0.6)	33 (9)	47 (11)	19 (11)	176 (23)
PH_3	4.1 (0.3)	2.9 (1.3)	11.0 (7.6)	2.4 (0.5)	29 (6)	47 (4)	24 (6)	167 (16)
VN_1	4.6 (0.3)	1.5 (0.2)	5.4 (1.5)	0.5 (0.1)	30 (7)	64 (6)	7 (5)	94 (9)
VN_2	4.3 (0.1)	1.6 (0.4)	2.7 (2.0)	0.6 (0.1)	14 (4)	58 (9)	27 (12)	31 (9)
VN_3	4.3 (0.3)	1.7 (0.4)	3.3 (1.8)	1.5 (0.6)	28 (8)	34 (5)	37 (10)	90 (19)
VN_4	3.6 (0.4)	3.0 (0.8)	5.5 (1.2)	1.0 (0.2)	56 (24)	32 (3)	12 (25)	89 (9)

$^{1)}$ TRB is the total reserve of bases, i.e., the sum of K, Ca, Na, and Mg contents

Appendix 3 Aboveground biomass production in the LEGATO paddies and Si concentration of different plant parts; Si was measured using x-ray fluorescence analysis; grains and hulls were separated for some samples before Si analysis, in these cases Si concentrations in grains plus hulls were calculated assuming 80 % grain mass

Field number	Season	Weather	Si in straw [%]	Yield straw [t ha^{-1}]	Si in straw [t ha^{-1}]	Si in grains [%]	Si in hulls [%]	Si in grains + hulls [%]	Yield grains + hulls [t ha^{-1}]	Si in grains + hulls [t ha^{-1}]	Yield biomass [t ha^{-1}]	Total Si uptake [t ha^{-1}]
PH_1_R_1	2011/2012	dry	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
PH_1_R_2	2011/2012	dry	9.0	7.8	0.70	0.1	9.1	1.94	5.8	0.11	13.6	0.81
PH_1_R_3	2011/2012	dry	9.3	7.8	0.72	0.1	10.8	2.28	7.3	0.17	15.0	0.89
PH_1_R_4	2011/2012	dry	10.3	7.4	0.76	0.2	12.1	2.56	7.1	0.18	14.5	0.94
PH_1_R_5	2011/2012	dry	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
PH_1_R_6	2011/2012	dry	8.8	5.7	0.50	0.1	10.4	2.19	6.3	0.14	11.9	0.63
PH_1_R_7	2011/2012	dry	8.1	6.0	0.48	0.1	9.1	1.91	4.3	0.08	10.3	0.57
PH_1_R_8	2011/2012	dry	8.8	7.4	0.65	0.1	8.2	1.73	5.0	0.09	12.4	0.74
PH_1_R_9	2011/2012	dry	9.4	7.5	0.71	0.1	10.6	2.22	6.5	0.14	14.0	0.85
PH_1_R_10	2011/2012	dry	9.5	5.5	0.52	0.1	9.8	2.07	6.1	0.13	11.7	0.65
PH_1_R_1	2012	wet	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
PH_1_R_2	2012	wet	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
PH_1_R_3	2012	wet	9.4	8.4	0.79	0.1	9.4	1.96	6.9	0.13	15.3	0.92
PH_1_R_4	2012	wet	8.6	8.8	0.76	0.1	8.1	1.69	5.1	0.09	13.9	0.85
PH_1_R_5	2012	wet	7.8	5.8	0.45	0.1	9.7	2.02	4.3	0.09	10.1	0.54
PH_1_R_6	2012	wet	8.9	6.2	0.55	0.1	11.1	2.30	5.1	0.12	11.3	0.67
PH_1_R_7	2012	wet	9.8	6.5	0.63	0.1	9.4	1.97	4.8	0.10	11.3	0.73
PH_1_R_8	2012	wet	8.2	5.8	0.47	0.1	9.6	1.99	4.7	0.09	10.4	0.57
PH_1_R_9	2012	wet	7.7	7.6	0.59	0.1	9.5	1.97	6.6	0.13	14.2	0.72
PH_1_R_10	2012	wet	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
PH_1_R_1	2012/2013	dry	5.4	3.1	0.17	- -	- -	1.40	2.6	0.04	5.7	0.20
PH_1_R_2	2012/2013	dry	8.3	7.7	0.63	- -	- -	1.60	6.3	0.10	14.0	0.73
PH_1_R_3	2012/2013	dry	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
PH_1_R_4	2012/2013	dry	8.3	6.1	0.50	- -	- -	1.93	6.0	0.12	12.0	0.62
PH_1_R_5	2012/2013	dry	8.4	3.8	0.31	- -	- -	1.61	4.1	0.07	7.8	0.38

Field number	Season	Weather	Si in straw [%]	Yield straw [t ha^{-1}]	Si in straw [t ha^{-1}]	Si in grains [%]	Si in hulls [%]	Si in grains + hulls [%]	Yield grains + hulls [t ha^{-1}]	Si in grains + hulls [t ha^{-1}]	Yield biomass [t ha^{-1}]	Total Si uptake [t ha^{-1}]
PH_1_R_6	2012/2013	dry	7.2	6.9	0.50	- -	- -	1.57	6.8	0.11	13.7	0.61
PH_1_R_7	2012/2013	dry	7.0	5.8	0.40	- -	- -	2.21	4.4	0.10	10.1	0.50
PH_1_R_8	2012/2013	dry	8.0	7.7	0.62	- -	- -	3.16	7.1	0.22	14.8	0.84
PH_1_R_9	2012/2013	dry	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
PH_1_R_10	2012/2013	dry	8.3	5.7	0.47	- -	- -	1.75	6.2	0.11	11.8	0.57
PH_2_R_1	1/2012	dry	8.3	3.9	0.33	0.1	10.0	2.10	6.3	0.13	10.2	0.46
PH_2_R_2	1/2012	dry	8.6	5.6	0.48	0.1	13.5	2.80	6.9	0.19	12.5	0.68
PH_2_R_3	1/2012	dry	8.2	6.8	0.55	0.1	9.6	2.00	7.1	0.14	13.8	0.69
PH_2_R_4	1/2012	dry	8.6	5.5	0.47	0.1	12.1	2.51	7.3	0.18	12.8	0.65
PH_2_R_5	1/2012	dry	9.1	5.4	0.49	0.1	9.8	2.06	5.5	0.11	10.9	0.61
PH_2_R_6	1/2012	dry	6.6	6.3	0.42	0.1	9.9	2.07	6.3	0.13	12.7	0.55
PH_2_R_7	1/2012	dry	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
PH_2_R_8	1/2012	dry	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
PH_2_R_9	1/2012	dry	7.4	6.8	0.51	0.1	9.8	2.04	6.8	0.14	13.7	0.65
PH_2_R_10	1/2012	dry	8.1	7.5	0.61	0.1	8.9	1.87	7.8	0.14	15.3	0.76
PH_2_R_1	2/2012	wet	7.1	3.9	0.28	0.1	7.9	1.66	5.9	0.10	9.9	0.38
PH_2_R_2	2/2012	wet	7.9	5.6	0.44	0.1	9.7	2.03	4.2	0.08	9.8	0.53
PH_2_R_3	2/2012	wet	8.1	5.4	0.44	0.1	9.3	1.95	4.4	0.09	9.8	0.53
PH_2_R_4	2/2012	wet	7.8	5.6	0.44	0.1	9.4	1.98	5.3	0.11	10.9	0.54
PH_2_R_5	2/2012	wet	8.3	4.7	0.39	0.1	7.8	1.64	4.1	0.07	8.8	0.46
PH_2_R_6	2/2012	wet	7.1	8.3	0.58	0.1	8.4	1.76	4.8	0.08	13.1	0.67
PH_2_R_7	2/2012	wet	7.7	6.3	0.48	0.1	7.2	1.52	4.9	0.07	11.2	0.55
PH_2_R_8	2/2012	wet	7.6	5.3	0.40	0.1	8.7	1.83	5.3	0.10	10.6	0.50
PH_2_R_9	2/2012	wet	9.0	3.9	0.35	0.1	7.5	1.57	4.9	0.08	8.8	0.42
PH_2_R_10	2/2012	wet	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
PH_2_R_1	1/2013	dry	5.6	5.8	0.33	- -	- -	1.67	4.7	0.08	10.5	0.41
PH_2_R_2	1/2013	dry	5.6	5.9	0.33	- -	- -	1.48	8.7	0.13	14.6	0.46
PH_2_R_3	1/2013	dry	5.9	5.3	0.31	- -	- -	1.52	5.4	0.08	10.6	0.39
PH_2_R_4	1/2013	dry	5.6	5.4	0.30	- -	- -	1.51	6.8	0.10	12.1	0.41

Field number	Season	Weather	Si in straw [%]	Yield straw [t ha^{-1}]	Si in straw [t ha^{-1}]	Si in grains [%]	Si in hulls [%]	Si in grains + hulls [%]	Yield grains + hulls [t ha^{-1}]	Si in grains + hulls [t ha^{-1}]	Yield biomass [t ha^{-1}]	Total Si uptake [t ha^{-1}]
PH_2_R_5	1/2013	dry	7.4	8.1	0.60	- -	- -	1.33	8.4	0.11	16.6	0.72
PH_2_R_6	1/2013	dry	7.0	6.9	0.48	- -	- -	1.57	7.4	0.12	14.4	0.60
PH_2_R_7	1/2013	dry	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
PH_2_R_8	1/2013	dry	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
PH_2_R_9	1/2013	dry	7.5	9.0	0.67	- -	- -	1.59	6.9	0.11	15.9	0.78
PH_2_R_10	1/2013	dry	6.1	9.1	0.55	- -	- -	1.36	7.1	0.10	16.2	0.65
PH_3_R_1	2013		6.6	6.7	0.44	0.1	8.8	1.80	1.6	0.03	8.0	0.47
PH_3_R_2	2013		6.8	4.8	0.32	0.1	8.8	1.82	1.8	0.03	6.3	0.35
PH_3_R_4	2013		6.8	10.0	0.68	0.1	8.5	1.75	2.8	0.05	12.6	0.73
PH_3_R_6	2013		6.5	11.6	0.76	0.1	8.5	1.74	2.8	0.05	15.6	0.81
PH_3_R_8	2013		- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
PH_3_R_9	2013		7.7	9.2	0.70	0.1	8.7	1.78	2.6	0.05	12.7	0.75
PH_3_R_10	2013		8.6	5.2	0.45	0.1	9.9	2.03	0.6	0.01	6.9	0.46
PH_3_R_11	2013		10.7	4.8	0.51	0.1	9.8	2.01	4.1	0.08	9.2	0.59
PH_3_R_12	2013		7.8	10.3	0.80	0.1	10.4	2.14	3.9	0.08	13.6	0.89
PH_3_R_13	2013		6.6	4.4	0.29	0.1	9.4	1.92	2.3	0.04	7.2	0.34
VN_1_R_1	2012	dry	4.1	3.4	0.14	0.1	8.3	1.74	- -	- -	8.6	- -
VN_1_R_2	2012	dry	3.8	2.5	0.10	0.1	7.0	1.50	4.9	0.07	6.5	0.17
VN_1_R_3	2012	dry	2.8	2.6	0.07	0.1	6.2	1.30	4.1	0.05	6.6	0.12
VN_1_R_4	2012	dry	4.9	5.3	0.26	0.1	6.6	1.38	2.2	0.03	11.4	0.29
VN_1_R_5	2012	dry	3.9	5.2	0.21	0.1	7.5	1.58	3.1	0.05	12.2	0.25
VN_1_R_6	2012	dry	3.5	6.9	0.24	0.1	7.2	1.52	2.8	0.04	12.8	0.29
VN_1_R_7	2012	dry	4.1	5.4	0.22	0.1	7.1	1.50	3.4	0.05	10.9	0.27
VN_1_R_8	2012	dry	4.3	5.5	0.24	0.1	7.1	1.47	2.6	0.04	11.0	0.27
VN_1_R_9	2012	dry	6.1	3.5	0.21	0.1	5.0	1.09	3.8	0.04	6.3	0.25
VN_1_R_10	2012	dry	3.4	3.6	0.12	0.1	6.5	1.37	1.6	0.02	7.7	0.14
VN_1_R_1	2014	wet	- -	- -	- -	- -	- -	- -	10.1	- -	- -	- -
VN_1_R_2	2014	wet	3.3	4.7	0.15	- -	- -	0.96	5.0	0.05	9.6	0.20

Field number	Season	Weather	Si in straw [%]	Yield straw [t ha^{-1}]	Si in straw [t ha^{-1}]	Si in grains [%]	Si in hulls [%]	Si in grains + hulls [%]	Yield grains + hulls [t ha^{-1}]	Si in grains + hulls [t ha^{-1}]	Yield biomass [t ha^{-1}]	Total Si uptake [t ha^{-1}]
VN_1_R_3	2014	wet	6.0	6.1	0.37	- -	- -	1.04	2.1	0.02	10.2	0.39
VN_1_R_4	2014	wet	4.8	4.9	0.23	- -	- -	3.62	2.2	0.08	7.1	0.31
VN_1_R_5	2014	wet	4.7	12.2	0.58	- -	- -	3.05	4.2	0.13	15.2	0.70
VN_1_R_6	2014	wet	4.0	9.1	0.36	- -	- -	1.34	3.8	0.05	12.0	0.41
VN_1_R_7	2014	wet	3.4	5.7	0.19	- -	- -	2.32	5.5	0.13	9.1	0.32
VN_1_R_8	2014	wet	3.9	8.9	0.34	- -	- -	2.20	2.7	0.06	11.5	0.40
VN_1_R_9	2014	wet	2.9	8.5	0.25	- -	- -	0.79	3.8	0.03	12.2	0.28
VN_1_R_10	2014	wet	3.3	8.3	0.27	- -	- -	1.70	3.6	0.06	9.9	0.34
VN_2_R_1	2012	dry	3.3	- -	0.00	0.1	7.7	1.62	3.5	0.06	- -	- -
VN_2_R_2	2012	dry	5.3	4.0	0.21	0.2	7.3	1.58	4.0	0.06	9.0	0.28
VN_2_R_3	2012	dry	5.4	1.5	0.08	0.1	4.4	0.97	3.1	0.03	3.6	0.11
VN_2_R_4	2012	dry	3.7	1.8	0.07	0.1	6.6	1.40	2.1	0.03	4.0	0.10
VN_2_R_5	2012	dry	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
VN_2_R_6	2012	dry	3.9	3.1	- -	0.1	5.8	1.21	- -	- -	6.9	- -
VN_2_R_7	2012	dry	4.6	3.4	0.16	0.2	6.8	1.50	2.5	0.04	8.9	0.19
VN_2_R_8	2012	dry	6.1	1.4	0.09	0.1	7.8	1.65	1.6	0.03	4.1	0.11
VN_2_R_9	2012	dry	3.4	3.6	0.12	0.1	7.1	1.50	3.9	0.06	7.4	0.18
VN_2_R_10	2012	dry	2.8	1.5	0.04	0.1	5.3	1.14	4.3	0.05	5.1	0.09
VN_2_R_1	2014	wet	3.5	4.9	0.17	- -	- -	0.77	4.7	0.04	8.4	0.21
VN_2_R_2	2014	wet	4.2	6.7	- -	- -	- -	1.02	- -	- -	10.7	- -
VN_2_R_3	2014	wet	6.2	5.1	0.31	- -	- -	0.88	4.7	0.04	8.2	0.35
VN_2_R_4	2014	wet	3.0	4.0	0.12	- -	- -	0.83	5.8	0.05	6.1	0.17
VN_2_R_5	2014	wet	3.0	2.9	0.09	- -	- -	1.07	5.4	0.06	4.7	0.14
VN_2_R_6	2014	wet	- -	- -	- -	- -	- -	- -	5.9	- -	- -	- -
VN_2_R_7	2014	wet	3.0	3.4	0.10	- -	- -	0.66	5.5	0.04	5.9	0.14
VN_2_R_8	2014	wet	4.2	4.0	0.17	- -	- -	0.89	5.8	0.05	5.6	0.22
VN_2_R_9	2014	wet	3.6	5.5	0.20	- -	- -	0.75	3.7	0.03	9.4	0.23
VN_2_R_10	2014	wet	5.0	3.6	0.18	- -	- -	1.10	4.0	0.04	7.9	0.22
VN_3_R_1	2012	summer	5.1	5.2	0.27	0.1	5.6	1.21	8.7	0.11	9.4	0.37

Field number	Season	Weather	Si in straw [%]	Yield straw [t ha^{-1}]	Si in straw [t ha^{-1}]	Si in grains [%]	Si in hulls [%]	Si in grains + hulls [%]	Yield grains + hulls [t ha^{-1}]	Si in grains + hulls [t ha^{-1}]	Yield biomass [t ha^{-1}]	Total Si uptake [t ha^{-1}]
VN_3_R_2	2012	summer	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
VN_3_R_3	2012	summer	7.6	2.4	0.18	0.1	7.5	1.57	2.1	0.03	7.1	0.21
VN_3_R_4	2012	summer	6.4	7.3	0.46	0.1	9.0	1.90	1.7	0.03	13.1	0.50
VN_3_R_5	2012	summer	5.5	6.3	0.35	0.1	7.1	1.50	5.0	0.07	11.6	0.42
VN_3_R_6	2012	summer	5.3	5.7	0.30	0.1	5.3	1.16	8.1	0.09	13.4	0.40
VN_3_R_7	2012	summer	4.5	3.4	0.15	0.1	4.9	1.08	4.5	0.05	8.9	0.20
VN_3_R_8	2012	summer	2.4	5.5	0.13	0.1	4.3	0.96	2.1	0.02	11.3	0.15
VN_3_R_9	2012	summer	1.8	3.4	0.06	0.1	3.1	0.70	5.3	0.04	7.2	0.10
VN_3_R_10	2012	summer	4.5	3.1	0.14	0.1	5.3	1.17	4.1	0.05	7.2	0.19
VN_3_R_1	2014	wet	6.2	- -	- -	- -	- -	1.06	6.1	0.06	- -	- -
VN_3_R_2	2014	wet	- -	- -	- -	- -	- -	- -	6.9	- -	- -	- -
VN_3_R_3	2014	wet	- -	9.4	- -	- -	- -	- -	7.0	- -	11.5	- -
VN_3_R_4	2014	wet	4.7	7.1	0.33	- -	- -	1.14	5.6	0.06	8.8	0.40
VN_3_R_5	2014	wet	4.9	10.0	0.49	- -	- -	0.77	5.5	0.04	15.0	0.53
VN_3_R_6	2014	wet	6.1	7.5	0.46	- -	- -	1.59	6.5	0.10	15.6	0.56
VN_3_R_7	2014	wet	3.6	7.0	0.25	- -	- -	0.90	4.9	0.04	11.5	0.29
VN_3_R_8	2014	wet	2.5	8.1	0.20	- -	- -	1.13	5.6	0.06	10.2	0.27
VN_3_R_9	2014	wet	5.5	8.4	0.46	- -	- -	0.95	7.2	0.07	13.6	0.53
VN_3_R_10	2014	wet	1.6	7.9	0.13	- -	- -	0.52	8.0	0.04	12.0	0.17
VN_4_R_2	1/2012	summer	3.7	5.5	0.20	0.1	6.7	1.38	6.3	0.09	11.8	0.29
VN_4_R_4	1/2012	summer	2.7	5.7	0.15	0.1	4.4	0.93	7.1	0.07	12.8	0.22
VN_4_R_5	1/2012	summer	2.4	5.8	0.14	0.1	4.6	0.97	7.2	0.07	13.0	0.21
VN_4_R_6	1/2012	summer	3.6	4.9	0.17	0.1	6.1	1.27	5.8	0.07	10.7	0.25
VN_4_R_7	1/2012	summer	2.7	4.9	0.13	0.1	4.9	1.03	5.7	0.06	10.6	0.19
VN_4_R_8	1/2012	summer	2.7	5.7	0.16	0.1	4.7	0.98	6.8	0.07	12.5	0.22
VN_4_R_9	1/2012	summer	2.8	5.1	0.14	0.1	5.1	1.06	5.0	0.05	10.1	0.20
VN_4_R_10	1/2012	summer	3.4	5.6	0.19	0.1	5.7	1.18	5.8	0.07	11.4	0.26
VN_4_R_11	1/2012	summer	2.3	6.5	0.15	0.1	5.0	1.04	7.5	0.08	13.9	0.23

Field number	Season	Weather	Si in straw [%]	Yield straw [t ha^{-1}]	Si in straw [t ha^{-1}]	Si in grains [%]	Si in hulls [%]	Si in grains + hulls [%]	Yield grains + hulls [t ha^{-1}]	Si in grains + hulls [t ha^{-1}]	Yield biomass [t ha^{-1}]	Total Si uptake [t ha^{-1}]
VN_4_R_12	1/2012	summer	3.3	7.1	0.24	0.1	7.4	1.51	8.3	0.13	15.4	0.36
VN_4_R_2	2/2012	autumn	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
VN_4_R_4	2/2012	autumn	2.9	4.5	0.13	0.1	5.6	1.16	6.1	0.07	10.5	0.20
VN_4_R_5	2/2012	autumn	3.2	4.6	0.15	0.1	6.1	1.27	6.4	0.08	11.0	0.23
VN_4_R_6	2/2012	autumn	2.8	4.0	0.11	0.1	6.2	1.29	4.5	0.06	8.5	0.17
VN_4_R_7	2/2012	autumn	3.2	4.5	0.14	0.1	6.7	1.39	5.5	0.08	10.0	0.22
VN_4_R_8	2/2012	autumn	2.7	4.9	0.13	0.1	4.9	1.02	5.8	0.06	10.7	0.19
VN_4_R_9	2/2012	autumn	2.9	4.9	0.14	0.1	5.7	1.18	5.9	0.07	10.8	0.21
VN_4_R_10	2/2012	autumn	2.9	4.5	0.13	0.1	6.4	1.32	5.8	0.08	10.3	0.21
VN_4_R_11	2/2012	autumn	2.1	6.7	0.14	0.1	5.1	1.07	7.1	0.08	13.8	0.21
VN_4_R_12	2/2012	autumn	4.2	7.6	0.32	0.1	7.2	1.48	6.8	0.10	14.3	0.42
VN_4_R_2	2012/2013	spring	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
VN_4_R_4	2012/2013	spring	2.2	4.8	0.10	- -	- -	0.72	6.5	0.05	11.3	0.15
VN_4_R_5	2012/2013	spring	3.0	5.5	0.17	- -	- -	0.71	6.6	0.05	12.1	0.21
VN_4_R_6	2012/2013	spring	2.2	4.4	0.10	- -	- -	0.66	4.9	0.03	9.3	0.13
VN_4_R_7	2012/2013	spring	2.8	4.5	0.13	- -	- -	0.71	5.9	0.04	10.4	0.17
VN_4_R_8	2012/2013	spring	2.8	4.8	0.13	- -	- -	0.66	6.7	0.04	11.5	0.18
VN_4_R_9	2012/2013	spring	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
VN_4_R_10	2012/2013	spring	3.4	3.8	0.13	- -	- -	0.77	5.4	0.04	9.2	0.17
VN_4_R_11	2012/2013	spring	2.5	4.7	0.12	- -	- -	0.62	7.1	0.04	11.8	0.16
VN_4_R_12	2012/2013	spring	3.5	4.5	0.16	- -	- -	0.88	7.1	0.06	11.6	0.22
VN_4_R_2	1/2013	summer	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
VN_4_R_4	1/2013	summer	3.8	4.9	0.19	- -	- -	0.75	6.6	0.05	11.5	0.24
VN_4_R_5	1/2013	summer	3.4	5.2	0.18	- -	- -	0.78	7.4	0.06	12.5	0.23
VN_4_R_6	1/2013	summer	2.7	4.4	0.12	- -	- -	0.83	5.7	0.05	10.1	0.17
VN_4_R_7	1/2013	summer	3.1	4.4	0.13	- -	- -	0.86	5.7	0.05	10.1	0.18
VN_4_R_8	1/2013	summer	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
VN_4_R_9	1/2013	summer	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -

Field number	Season	Weather	Si in straw [%]	Yield straw [t ha^{-1}]	Si in straw [t ha^{-1}]	Si in grains [%]	Si in hulls [%]	Si in grains + hulls [%]	Yield grains + hulls [t ha^{-1}]	Si in grains + hulls [t ha^{-1}]	Yield biomass [t ha^{-1}]	Total Si uptake [t ha^{-1}]
VN_4_R_10	1/2013	summer	4.0	4.4	0.18	- -	- -	0.98	5.3	0.05	9.7	0.23
VN_4_R_11	1/2013	summer	2.2	4.5	0.10	- -	- -	0.66	7.1	0.05	11.5	0.14
VN_4_R_12	1/2013	summer	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
VN_4_R_2	2/2013	autumn	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
VN_4_R_4	2/2013	autumn	2.5	4.6	0.11	- -	- -	0.75	5.7	0.04	10.3	0.16
VN_4_R_5	2/2013	autumn	2.9	4.8	0.14	- -	- -	0.76	6.1	0.05	10.9	0.19
VN_4_R_6	2/2013	autumn	2.3	4.5	0.10	- -	- -	0.87	5.5	0.05	10.0	0.15
VN_4_R_7	2/2013	autumn	2.8	4.3	0.12	- -	- -	0.78	4.8	0.04	9.1	0.16
VN_4_R_8	2/2013	autumn	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
VN_4_R_9	2/2013	autumn	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
VN_4_R_10	2/2013	autumn	2.3	5.1	0.12	- -	- -	0.67	6.2	0.04	11.3	0.16
VN_4_R_11	2/2013	autumn	2.6	5.0	0.13	- -	- -	0.61	6.7	0.04	11.7	0.17
VN_4_R_12	2/2013	autumn	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -

Appendix 4 Soil characteristics of the LEGATO fields; Si_{total} was measured by x-ray fluorescence analysis

Field number	pH_{KCl}	pH_{H2O}	EC 1) [µS cm^{-2}]	N_{total} [%]	C_{org} [%]	S [%]	C/N	Si_{total} 2) [wt. %]	$Si_{carbonate}$ [g kg^{-1}]	$Si_{carbonate}$ [t ha^{-1}]	$Si_{acetate}$ [mg kg^{-1}]	$Si_{acetate}$ [t ha^{-1}]	$Si_{oxalate}$ [g kg^{-1}]	$Si_{oxalate}$ [t ha^{-1}]	$Al_{oxalate}$ [g kg^{-1}]	$Fe_{oxalate}$ [g kg^{-1}]
PH_1_R_1	5.6	6.6	210	0.17	1.6	0.038	9	25	6.2	2.0	475	0.15	1.19	0.37	1.87	9.55
PH_1_R_2	5.2	6.2	238	0.35	4.0	0.063	11	26	12.3	7.5	461	0.28	0.72	0.45	1.15	4.12
PH_1_R_3	4.3	5.6	138	0.24	2.3	0.040	9	26	15.6	19.2	208	0.26	0.69	0.85	2.45	4.20
PH_1_R_4	4.6	5.8	164	0.30	2.9	0.058	10	27	25.4	20.5	217	0.17	0.70	0.56	2.53	1.61
PH_1_R_5	4.9	6.0	142	0.22	2.3	0.044	10	26	6.4	5.3	440	0.36	1.26	1.04	1.20	10.61
PH_1_R_6	5.4	6.3	508	0.34	3.7	0.109	11	28	17.3	13.4	376	0.29	0.45	0.35	0.94	2.36
PH_1_R_7	4.2	5.4	132	0.21	2.1	0.030	10	26	17.0	16.2	199	0.19	0.45	0.43	1.27	6.32
PH_1_R_8	4.8	5.9	156	0.29	2.8	0.042	10	26	29.2	28.5	214	0.21	0.37	0.36	1.30	2.15
PH_1_R_9	4.1	5.2	184	0.24	2.4	0.043	10	25	17.8	17.3	312	0.30	0.82	0.80	1.37	10.75
PH_1_R_10	4.6	5.6	172	0.25	2.8	0.048	11	27	19.5	17.1	318	0.28	0.62	0.54	0.86	6.10
PH_1_F_1	4.9	6.2	76	0.18	1.8	0.038	10	26	- -	- -	306	- -	1.19	- -	2.49	13.86
PH_1_F_2	4.6	6.0	72	0.21	1.9	0.030	9	24	- -	- -	139	- -	3.16	- -	9.43	11.21
PH_1_F_3	4.8	6.2	72	0.19	2.1	0.036	11	26	- -	- -	351	- -	1.15	- -	1.70	13.36
PH_1_F_4	5.3	6.4	116	0.22	2.2	0.030	10	24	- -	- -	210	- -	1.29	- -	3.53	13.44
PH_1_F_5	5.2	6.4	89	0.19	1.9	0.031	10	25	- -	- -	242	- -	0.94	- -	2.58	11.91
PH_2_R_1	4.4	6.0	83	0.12	1.3	0.018	10	27	4.3	5.9	140	0.19	1.67	2.26	1.50	8.74
PH_2_R_2	4.1	5.5	127	0.16	1.7	0.026	11	27	4.4	5.0	126	0.14	1.39	1.58	1.51	9.93
PH_2_R_3	5	6.0	89	0.13	1.3	0.013	10	33	6.0	7.3	119	0.14	0.38	0.47	0.54	7.75
PH_2_R_4	4.2	5.4	161	0.17	1.9	0.026	11	27	2.1	1.4	143	0.09	0.59	0.39	2.18	8.93
PH_2_R_5	3.8	4.8	122	0.15	1.7	0.027	11	32	5.6	8.9	118	0.19	0.54	0.86	0.46	10.55
PH_2_R_6	3.9	5.2	90	0.12	1.3	0.019	11	34	4.5	6.7	87	0.13	0.27	0.40	0.55	7.63
PH_2_R_7	5.5	6.8	181	0.09	0.8	0.011	9	29	3.5	1.9	121	0.07	1.15	0.63	1.03	3.48
PH_2_R_8	6.1	7.3	233	0.14	1.3	0.019	9	25	1.0	0.4	256	0.11	2.07	0.90	2.03	4.94
PH_2_R_9	5	6.3	134	0.15	1.5	0.021	11	29	4.1	5.1	151	0.19	0.80	0.99	0.80	6.50
PH_2_R_10	5.3	6.6	218	0.16	1.6	0.026	10	28	4.9	7.0	144	0.21	0.84	1.21	0.87	6.38
PH_2_F_1	5.0	6.2	288	0.12	1.3	0.012	11	29	- -	- -	109	- -	0.72	- -	0.93	5.67
PH_2_F_2	5.5	7.0	156	0.11	0.9	0.011	8	27	- -	- -	146	- -	2.49	- -	2.13	4.53
PH_2_F_3	5.3	6.6	147	0.07	0.5	0.007	8	28	- -	- -	70	- -	1.07	- -	1.11	2.20
PH_2_F_4	3.9	5.3	123	0.13	1.1	0.012	9	29	- -	- -	44	- -	0.54	- -	0.88	5.65

Field number	pH_{KCl}	pH_{H2O}	EC 1) [µS cm^{-2}]	N_{total} [%]	C_{org} [%]	S [%]	C/N	Si_{total} 2) [wt. %]	$Si_{carbonate}$ [g kg^{-1}]	$Si_{carbonate}$ [t ha^{-1}]	$Si_{acetate}$ [mg kg^{-1}]	$Si_{acetate}$ [t ha^{-1}]	$Si_{oxalate}$ [g kg^{-1}]	$Si_{oxalate}$ [t ha^{-1}]	$Al_{oxalate}$ [g kg^{-1}]	$Fe_{oxalate}$ [g kg^{-1}]
PH_3_R_1	4.1	5.0	623	0.33	4.0	0.112	12	25	5.7	5.5	184	0.18	0.51	0.50	2.08	5.77
PH_3_R_2	4.0	5.5	115	0.15	1.6	0.026	10	25	13.2	14.3	176	0.19	0.84	0.91	2.14	8.78
PH_3_R_4	3.7	4.8	214	0.22	2.1	0.074	10	24	8.0	9.3	239	0.28	0.54	0.62	2.07	9.48
PH_3_R_6	3.8	5.1	121	0.18	2.1	0.033	11	23	8.3	6.5	153	0.12	1.16	0.91	2.14	9.10
PH_3_R_8	4.2	5.6	96	0.12	1.2	0.014	10	22	6.1	1.2	173	0.03	3.26	0.62	3.51	10.78
PH_3_R_9	4.1	5.0	208	0.35	4.0	0.107	11	21	6.0	3.8	257	0.16	0.84	0.53	2.51	31.43
PH_3_R_10	4.8	5.9	381	0.24	2.7	0.043	11	26	4.1	2.3	268	0.15	1.00	0.55	1.81	7.34
PH_3_R_11	4.0	5.2	210	0.32	3.9	0.064	12	22	13.2	8.2	188	0.12	1.64	1.02	2.39	14.13
PH_3_R_12	4.3	5.7	127	0.19	2.2	0.028	11	23	10.5	3.3	205	0.07	1.47	0.47	2.47	6.83
PH_3_R_13	4.4	5.5	218	0.46	5.0	0.064	11	22	13.2	9.2	190	0.13	2.99	2.09	3.23	6.79
PH_3_F_1	4.3	6.1	64	0.13	1.2	0.012	9	26	- -	- -	154	- -	0.99	- -	2.58	10.13
PH_3_F_2	5.0	6.2	108	0.31	3.6	0.025	11	22	- -	- -	172	- -	2.44	- -	2.95	3.28
PH_3_F_3	4.7	6.4	74	0.17	1.7	0.016	10	25	- -	- -	169	- -	1.30	- -	2.76	9.64
PH_3_F_4	4.0	5.2	66	0.20	1.9	0.059	10	21	- -	- -	137	- -	0.53	- -	3.51	13.36
PH_3_F_5	4.2	5.6	95	0.23	2.1	0.048	9	23	- -	- -	205	- -	0.74	- -	3.55	12.77
PH_3_F_6	4.2	5.5	117	0.26	2.7	0.042	10	22	- -	- -	169	- -	0.60	- -	4.64	9.00
PH_3_F_7	3.9	5.4	79	0.15	1.6	0.016	11	24	- -	- -	95	- -	2.77	- -	3.24	10.87
PH_3_F_8	4.5	5.6	139	0.29	3.2	0.026	11	22	- -	- -	116	- -	0.87	- -	5.14	7.57
PH_3_F_9	5.0	6.2	81	0.16	1.8	0.014	11	21	- -	- -	185	- -	4.95	- -	4.34	5.47
PH_3_F_10	4.3	5.9	72	0.21	2.4	0.017	11	20	- -	- -	162	- -	6.49	- -	6.55	8.96
VN_1_R_1	4.6	5.1	772	0.14	1.6	n.a.	11	35	2.9	5.9	34	0.07	0.10	0.20	0.38	4.16
VN_1_R_2	5.0	5.7	361	0.11	1.1	n.a.	11	35	2.1	4.1	26	0.05	0.04	0.07	0.33	3.32
VN_1_R_3	4.7	5.5	186	0.15	1.5	n.a.	10	33	1.8	3.0	32	0.05	0.08	0.13	0.37	6.15
VN_1_R_4	5.2	6.1	173	0.13	1.3	n.a.	10	31	1.6	3.2	44	0.09	0.12	0.24	0.51	7.81
VN_1_R_5	4.6	5.3	548	0.16	1.5	n.a.	9	28	3.1	5.0	38	0.06	0.14	0.23	0.73	5.19
VN_1_R_6	4.5	5.3	352	0.18	1.7	n.a.	10	28	1.0	1.7	32	0.05	0.09	0.14	0.63	5.28
VN_1_R_7	4.8	5.6	336	0.12	1.4	n.a.	12	33	2.2	4.4	31	0.06	0.11	0.23	0.54	4.92
VN_1_R_8	4.5	5.1	880	0.11	1.3	n.a.	12	34	2.5	5.8	32	0.07	0.09	0.20	0.40	7.61
VN_1_R_9	4.5	5.2	297	0.13	1.7	n.a.	12	35	2.3	3.7	24	0.04	0.04	0.07	0.40	5.30
VN_1_R_10	3.9	4.6	389	0.16	1.8	n.a.	11	32	3.8	6.2	18	0.03	0.03	0.06	0.61	3.80
VN_1_F_1	4.5	5.3	n.a.	0.13	1.2	0.041	9	33	- -	- -	41	- -	0.11	- -	0.51	4.35

Field number	pH$_{KCl}$	pH$_{H2O}$	EC $^{1)}$ [µS cm^{-2}]	N$_{total}$ [%]	C$_{org}$ [%]	S [%]	C/N	Si$_{total}$ $^{2)}$ [wt. %]	Si$_{carbonate}$ [g kg^{-1}]	Si$_{carbonate}$ [t ha^{-1}]	Si$_{acetate}$ [mg kg^{-1}]	Si$_{acetate}$ [t ha^{-1}]	Si$_{oxalate}$ [g kg^{-1}]	Si$_{oxalate}$ [t ha^{-1}]	Al$_{oxalate}$ [g kg^{-1}]	Fe$_{oxalate}$ [g kg^{-1}]
VN_1_F_2	7.4	8.1	n.a.	0.09	0.8	0.010	9	32	- -	- -	141	- -	0.36	- -	0.48	3.00
VN_1_F_3	5.9	7.0	n.a.	0.13	1.0	0.019	8	29	- -	- -	97	- -	0.29	- -	0.78	4.36
VN_2_R_1	4.4	5.1	149	0.17	1.7	0.031	10	41	2.7	4.1	16	- -	0.03	0.04	0.46	0.86
VN_2_R_2	4.2	4.9	161	0.14	1.6	0.026	11	38	3.2	4.5	22	- -	0.05	0.06	0.63	3.19
VN_2_R_3	4.2	5.0	165	0.15	1.5	0.027	10	42	2.6	3.7	16	0.02	0.02	0.03	0.38	1.95
VN_2_R_4	4.4	5.2	125	0.16	1.7	0.031	11	26	3.0	4.3	18	0.03	0.02	0.03	0.37	1.50
VN_2_R_5	4.0	4.8	122	0.13	1.1	0.019	8	38	2.7	3.9	19	0.02	0.03	0.04	0.55	2.55
VN_2_R_6	4.2	5.0	168	0.15	1.4	0.021	9	39	3.8	4.8	16	0.03	0.03	0.04	0.64	2.21
VN_2_R_7	4.3	5.1	88	0.16	1.4	0.024	9	39	3.2	4.3	15	0.03	0.02	0.03	0.61	1.16
VN_2_R_8	4.4	5.0	183	0.23	2.4	0.036	11	33	2.9	3.6	43	0.02	0.13	0.16	0.67	7.76
VN_2_R_9	4.5	5.3	187	0.24	2.2	0.034	9	38	3.1	4.8	23	0.02	0.05	0.08	0.74	3.41
VN_2_R_10	4.3	5.1	193	0.14	1.3	0.024	9	40	2.4	3.6	14	0.05	0.03	0.05	0.62	2.09
VN_2_F_1	n.a.	n.a.	n.a.	0.06	0.6	0.007	10	43	- -	- -	30	0.03	0.05	- -	0.29	0.94
VN_2_F_2	n.a.	n.a.	n.a.	0.07	0.7	0.006	10	42	- -	- -	7	0.02	0.04	- -	0.27	1.55
VN_2_F_3	n.a.	n.a.	n.a.	0.14	1.6	0.014	12	38	- -	- -	15	- -	0.08	- -	1.19	4.34
VN_2_F_4	n.a.	n.a.	n.a.	0.09	0.8	0.011	9	39	- -	- -	12	- -	0.04	- -	0.51	1.77
VN_2_F_5	n.a.	n.a.	n.a.	0.10	1.3	0.012	14	39	- -	- -	7	- -	0.02	- -	1.01	1.18
VN_3_R_1	4.1	5.1	39	0.14	1.6	n.a.	12	28	1.2	1.7	47	0.07	0.11	0.16	1.52	2.49
VN_3_R_2	4.1	5.2	34	0.06	0.8	n.a.	14	29	0.9	1.6	28	0.05	0.06	0.10	0.90	2.07
VN_3_R_3	4.7	5.8	155	0.10	1.2	n.a.	12	25	4.0	6.3	66	0.11	0.15	0.23	1.11	2.31
VN_3_R_4	4.7	5.8	74	0.13	1.6	n.a.	12	27	4.6	9.9	106	0.23	0.23	0.49	1.46	4.17
VN_3_R_5	4.1	5.1	63	0.20	2.5	n.a.	13	24	6.2	6.1	84	0.08	0.24	0.23	2.04	7.07
VN_3_R_6	4.1	5.0	60	0.15	1.9	n.a.	13	32	5.7	11.3	51	0.10	0.12	0.24	1.21	3.02
VN_3_R_7	4.8	5.5	158	0.16	2.0	n.a.	13	24	2.6	3.7	46	0.07	0.14	0.21	2.43	4.58
VN_3_R_8	4.6	5.5	56	0.13	1.8	n.a.	13	31	2.3	2.4	27	0.03	0.04	0.04	1.02	4.24
VN_3_R_9	4.3	5.4	53	0.15	1.8	n.a.	12	37	3.4	5.5	21	0.03	0.18	0.29	2.23	0.44
VN_3_R_10	4.1	5.2	79	0.13	1.6	n.a.	12	32	2.5	4.0	32	0.05	0.05	0.08	0.91	2.80
VN_3_F_1	4.0	5.2	n.a.	0.22	2.6	0.026	12	26	- -	- -	35	- -	0.10	- -	2.30	2.79
VN_3_F_2	3.9	4.9	n.a.	0.25	2.8	0.035	11	24	- -	- -	36	- -	0.14	- -	2.68	5.81
VN_3_F_3	4.0	4.9	n.a.	0.26	3.0	0.032	11	26	- -	- -	60	- -	0.21	- -	2.54	7.29
VN_3_F_4	4.0	4.9	n.a.	0.27	3.9	0.041	14	24	- -	- -	24	- -	0.07	- -	3.81	9.15

Field number	pH$_{KCl}$	pH$_{H2O}$	EC [1] [µS cm^{-2}]	N$_{total}$ [%]	C$_{org}$ [%]	S [%]	C/N	Si$_{total}$ [2] [wt. %]	Si$_{carbonate}$ [g kg^{-1}]	Si$_{carbonate}$ [t ha^{-1}]	Si$_{acetate}$ [mg kg^{-1}]	Si$_{acetate}$ [t ha^{-1}]	Si$_{oxalate}$ [g kg^{-1}]	Si$_{oxalate}$ [t ha^{-1}]	Al$_{oxalate}$ [g kg^{-1}]	Fe$_{oxalate}$ [g kg^{-1}]
VN_3_F_5	3.9	4.8	n.a.	0.21	3.3	0.025	16	25	- -	- -	18	- -	0.07	- -	4.19	6.49
VN_4_R_2	4.2	4.9	n.a.	0.32	3.1	0.192	10	27	3.0	- -	73	- -	0.11	- -	0.87	5.20
VN_4_R_4	3.5	4.0	1952	0.40	4.4	0.316	11	25	2.9	2.8	42	0.04	0.06	0.06	1.08	4.28
VN_4_R_5	3.3	3.6	2200	0.38	4.0	0.302	11	26	3.9	4.4	40	0.04	0.06	0.07	1.32	4.57
VN_4_R_6	3.3	3.7	2350	0.23	2.3	0.239	10	28	3.9	5.9	35	0.05	0.06	0.09	0.92	4.03
VN_4_R_7	3.2	3.6	2700	0.23	2.2	0.259	10	26	2.6	3.7	35	0.05	0.08	0.11	1.13	6.38
VN_4_R_8	3.4	3.8	2950	0.37	3.8	0.362	10	26	3.4	3.4	38	0.04	0.08	0.08	0.91	5.47
VN_4_R_9	4.1	4.7	1506	0.27	2.5	0.153	9	41	2.6	4.1	56	0.09	0.10	0.17	1.06	5.20
VN_4_R_10	4.2	4.9	1106	0.22	2.1	0.119	9	27	1.6	2.8	71	0.12	0.13	0.22	0.82	7.64
VN_4_R_11	3.3	3.7	2700	0.32	3.2	0.327	10	26	3.1	3.2	39	0.04	0.07	0.07	1.19	4.73
VN_4_R_12	3.4	4.0	1530	0.25	2.4	0.174	10	27	3.0	3.0	37	0.04	0.08	0.08	1.17	7.35

1) EC = electrical conductivity

2) Si$_{total}$ measured by XRF analysis

Appendix 5 Elemental concentrations [mg kg^{-1}] of LEGATO topsoils measured by x-ray fluorescence analysis; data for Si are given in Appendix 4

Field	Na	Mg	Al	P	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Rb	Sr	Zr	Pb	Sn	Ba
PH_1_R_1	8910	7280	89420	1380	8120	17470	5860	187	22	2971	72320	13	134	119	5	64	226	139	15	4	546
PH_1_R_2	6020	4560	79930	480	3230	15320	4630	191	27	1237	49520	11	111	90	3	11	211	119	15	3	357
PH_1_R_3	18230	12970	99370	1540	8920	39260	5170	159	67	499	37770	28	68	131	3	28	558	139	21	4	595
PH_1_R_4	17380	11500	92990	1240	8480	36500	4740	140	61	454	28260	25	64	79	3	27	537	129	18	3	562
PH_1_R_5	7080	4880	83700	640	5910	13330	5330	194	24	1436	64280	13	111	95	3	32	188	130	13	3	485
PH_1_R_6	9130	4760	75020	550	4380	21290	3810	148	23	650	42530	8	79	76	2	14	269	99	12	3	334
PH_1_R_7	17640	12040	94300	1030	8550	37310	4870	226	79	527	51130	25	57	84	3	30	524	122	16	3	568
PH_1_R_8	17750	11050	93620	820	7960	38380	4560	148	92	387	35320	21	54	96	<2	25	551	121	19	3	538
PH_1_R_9	9200	7620	93050	1340	6040	19240	6210	209	64	540	64420	25	131	164	3	30	276	131	18	4	453
PH_1_R_10	9300	5580	83490	590	5820	17960	5160	193	64	522	49030	21	95	88	<2	21	266	119	15	3	393
PH_1_F_1	3790	3400	109570	430	14060	3450	4490	65	21	213	34480	11	7	48	3	47	97	238	13	3	592
PH_1_F_2	790	11190	100960	690	20440	1410	6670	128	120	677	62390	55	35	74	3	114	38	273	15	6	374
PH_1_F_3	4430	3460	104110	590	19070	2940	10520	160	114	369	46860	50	45	66	2	97	182	272	28	5	624
PH_1_F_4	100	960	116940	310	2630	420	6080	113	19	131	53160	13	9	57	2	17	19	247	24	4	82
PH_1_F_5	340	7460	97520	380	28450	360	5960	124	103	159	59940	28	22	42	3	95	22	291	10	7	531
PH_2_R_1	18800	12930	86180	520	4800	22790	4500	186	165	1040	53510	40	46	89	<2	11	146	75	2	2	109
PH_2_R_2	18510	12080	87120	500	4470	21290	4480	189	179	957	51620	41	47	82	2	13	138	78	2	3	113
PH_2_R_3	9760	6070	61450	450	4010	13310	5190	165	100	888	40570	20	29	56	2	14	104	116	4	2	91
PH_2_R_4	12260	7800	89540	410	4330	14570	5340	199	87	509	55400	30	59	83	3	16	125	98	3	<2	131
PH_2_R_5	7150	3290	56720	670	1230	12030	4860	265	83	1116	59730	21	48	56	4	4	108	131	7	5	207
PH_2_R_6	6190	2790	56870	350	990	9060	5090	223	89	834	51830	19	38	39	5	4	86	156	5	<2	124
PH_2_R_7	22010	17520	78830	720	6120	36250	4560	178	85	991	48820	29	41	70	<2	12	229	72	<2	2	123
PH_2_R_8	15630	23350	91810	1030	6560	29080	5010	196	82	1476	64910	39	79	114	3	14	197	80	<2	2	127
PH_2_R_9	19790	11530	76660	400	4180	29080	4930	178	87	914	47490	24	42	73	<2	12	192	86	3	<2	124
PH_2_R_10	19930	12220	78340	670	4670	29430	4960	169	80	1007	48190	27	46	77	<2	14	193	79	3	2	132
PH_2_F_1	19110	11470	73450	740	5190	26850	4130	174	173	1163	46650	32	35	73	<2	12	169	73	<2	<2	100
PH_2_F_2	20320	18480	84010	750	6430	32860	4880	186	86	1139	53790	32	52	80	<2	13	230	78	3	<2	122
PH_2_F_3	21840	16960	76390	610	5820	38410	4720	186	81	961	50220	24	35	65	<2	12	229	72	<2	2	109

Field	Na	Mg	Al	P	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Rb	Sr	Zr	Pb	Sn	Ba
PH_2_F_4	20610	10970	72580	900	4470	31100	4940	178	90	1052	45530	22	36	83	<2	11	198	82	5	2	111
PH_3_R_1	7490	12450	95380	410	6130	17360	3560	135	12	482	37490	11	64	94	4	14	250	62	7	4	264
PH_3_R_2	12870	16210	97770	270	3830	25380	4810	196	<10	828	54210	6	58	102	<2	8	428	44	3	2	295
PH_3_R_4	3120	11200	114100	860	13380	9090	5100	241	29	440	45740	16	107	94	5	40	364	121	17	3	525
PH_3_R_6	6210	13070	109900	550	5920	14330	4430	191	16	817	56580	15	78	124	2	15	309	56	5	3	395
PH_3_R_8	11860	15800	107870	1500	13870	30390	4860	243	20	1509	67780	15	93	92	<2	31	730	68	6	3	395
PH_3_R_9	960	8760	117110	850	4550	6260	5560	240	25	1387	64560	14	89	97	7	15	143	116	10	3	295
PH_3_R_10	10520	12730	90570	550	7460	23990	3850	162	13	705	46580	11	59	94	3	16	296	60	5	<2	274
PH_3_R_11	7850	17700	97640	560	6950	22960	4600	235	25	1106	64420	13	70	80	3	14	354	44	<2	<2	254
PH_3_R_12	9260	19160	105000	690	8230	25450	3880	186	27	669	54350	16	92	104	<2	18	388	47	4	<2	259
PH_3_R_13	8420	16710	98270	1210	13390	28700	4260	228	37	943	52250	21	105	82	<2	28	515	60	6	<2	368
PH_3_F_1	9210	13480	93020	490	8850	19660	3780	157	13	640	50150	10	55	88	3	19	265	67	5	<2	240
PH_3_F_2	9260	12750	87550	520	6250	21370	4290	162	17	1397	58470	12	66	81	3	17	240	67	2	<2	178
PH_3_F_3	11570	16080	91900	510	5820	26400	4020	172	15	1141	55610	12	63	95	4	13	364	51	4	<2	282
PH_3_F_4	1310	8540	126240	1250	6740	5440	6090	282	31	594	57070	16	97	131	8	25	200	125	15	3	285
PH_3_F_5	2950	11030	111000	1000	13520	8710	4890	241	28	678	52530	15	111	98	6	45	374	124	16	2	522
PH_3_F_6	3500	12240	108760	1070	14470	9660	4860	260	28	944	57070	15	109	92	7	48	393	115	16	2	523
PH_3_F_7	11040	13540	102900	490	6720	20100	4360	189	14	803	57910	11	81	144	<2	16	410	53	4	<2	418
PH_3_F_8	2830	13990	99770	580	4030	8000	6160	266	18	1815	78130	14	46	95	3	16	175	72	2	<2	210
PH_3_F_9	7880	21390	101830	1090	14400	32230	5070	278	26	1570	77500	19	90	85	<2	34	685	66	2	3	339
PH_3_F_10	3780	20180	104820	560	9050	21110	5460	332	52	1779	87430	25	87	94	<2	20	528	45	<2	2	276
VN_1_R_1	3610	3410	55910	790	14420	3130	5420	82	68	143	16510	20	34	69	6	86	66	337	34	7	377
VN_1_R_2	3640	3520	55760	380	14760	2490	5570	89	61	229	25040	20	27	57	10	88	63	332	31	6	375
VN_1_R_3	4400	6100	64400	670	17960	3340	5210	98	76	259	32380	31	36	91	12	107	74	315	35	7	430
VN_1_R_4	4810	8220	71250	1390	20790	4520	5180	101	82	576	39030	39	54	121	19	124	80	270	50	10	464
VN_1_R_5	4270	10000	89720	630	24280	3170	5480	133	92	630	49030	48	46	112	22	147	78	209	41	7	518
VN_1_R_6	4080	10000	92940	530	25180	3050	5450	134	95	453	48820	47	43	115	19	154	79	200	44	7	521
VN_1_R_7	4610	5490	69160	600	18530	3170	5650	106	76	222	31680	28	38	89	11	117	79	299	36	7	437
VN_1_R_8	5050	4910	57280	810	17800	3720	4820	78	62	275	27700	24	31	84	10	107	80	345	28	5	415
VN_1_R_9	1020	2350	51690	550	11630	1960	5280	85	59	62	27140	14	27	42	15	79	42	323	32	6	284
VN_1_R_10	1280	3100	70770	550	14310	2120	5860	113	72	62	23920	19	27	46	14	95	53	301	42	6	338

Field	Na	Mg	Al	P	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Rb	Sr	Zr	Pb	Sn	Ba
VN_1_F_1	3570	4440	71680	510	17670	2730	5490	93	73	256	25810	27	34	84	9	110	70	308	33	5	408
VN_1_F_2	4900	8820	73970	600	20850	8040	5090	100	80	794	39660	39	35	93	16	122	80	292	33	6	463
VN_1_F_3	4560	9840	87560	630	23240	4060	5400	118	88	913	47000	44	42	111	23	141	80	232	40	7	514
VN_2_R_1	440	290	20720	450	2420	1000	3530	33	20	45	5880	8	9	25	<2	19	15	396	13	3	81
VN_2_R_2	400	490	40190	480	3610	990	4420	49	25	80	17000	9	14	35	5	32	17	519	16	5	97
VN_2_R_3	350	310	20160	320	2350	800	3930	31	21	52	6090	7	9	23	<2	18	16	372	11	3	83
VN_2_R_4	2970	6980	109670	900	19530	4190	4890	120	87	162	36090	36	31	97	11	145	88	175	30	5	402
VN_2_R_5	1190	540	40810	730	6750	890	4780	55	41	86	19230	12	21	42	18	46	35	406	23	3	182
VN_2_R_6	1230	480	34300	910	6400	1080	4720	62	37	90	16230	10	17	37	16	41	34	398	25	3	181
VN_2_R_7	1050	490	34570	390	5740	810	4900	56	38	89	13990	12	18	34	8	40	32	351	16	3	175
VN_2_R_8	2200	770	61880	630	10160	1290	5190	93	64	397	40710	15	33	65	5	71	54	302	25	4	294
VN_2_R_9	1280	560	38590	820	6370	1320	4270	60	40	139	13570	14	21	47	6	44	37	353	17	3	192
VN_2_R_10	790	450	30490	720	4480	1040	4080	52	34	90	11610	10	15	32	7	32	27	367	16	3	153
VN_2_F_1	320	280	15510	290	1510	1300	3660	50	20	86	7270	6	7	20	3	13	13	499	9	3	52
VN_2_F_2	790	320	21700	270	4230	440	2910	38	36	327	16440	12	14	33	5	30	20	261	14	3	117
VN_2_F_3	1050	450	39260	540	5550	690	5030	64	43	174	21680	11	20	29	42	42	29	419	55	5	161
VN_2_F_4	1020	450	33160	370	5350	680	4710	56	36	197	19020	11	17	35	11	41	30	414	14	4	157
VN_2_F_5	490	400	38480	230	3980	420	4570	62	39	96	21260	10	14	27	4	32	15	398	12	5	107
VN_3_R_1	890	2770	100090	470	11300	1130	5490	79	31	106	33080	12	11	48	2	48	39	338	13	3	486
VN_3_R_2	11290	8410	100520	280	23420	3210	3910	57	12	324	28750	7	8	64	<2	79	129	219	10	4	932
VN_3_R_3	3890	28130	86880	680	27040	11830	6100	128	98	688	55400	43	37	130	<2	125	101	212	15	5	654
VN_3_R_4	2390	10620	93170	480	15070	5590	5810	132	40	681	49310	21	22	83	<2	72	106	242	14	4	868
VN_3_R_5	1410	2570	105980	970	16700	1520	12300	177	110	329	61690	46	61	95	2	90	123	313	31	6	592
VN_3_R_6	2000	1330	74450	380	18850	1490	7070	78	65	75	22240	20	15	43	<2	79	186	321	33	5	758
VN_3_R_7	440	3490	121830	450	8840	1030	5400	102	19	280	43850	19	12	76	<2	60	46	221	32	4	262
VN_3_R_8	700	2730	74130	690	14760	1240	5920	165	66	137	46160	18	37	31	4	73	18	346	14	6	586
VN_3_R_9	4950	2620	42140	380	10080	3300	5300	46	30	103	11120	5	6	22	<2	32	102	362	14	4	630
VN_3_R_10	660	4150	64990	520	17410	1040	5580	101	86	88	37980	18	13	28	3	78	31	405	11	5	427
VN_3_F_1	3790	3400	109570	430	14060	3450	4490	65	21	213	34480	11	7	48	3	47	97	238	13	3	592
VN_3_F_2	790	11190	100960	690	20440	1410	6670	128	120	677	62390	55	35	74	3	114	38	273	15	6	374
VN_3_F_3	4430	3460	104110	590	19070	2940	10520	160	114	369	46860	50	45	66	2	97	182	272	28	5	624

Field	Na	Mg	Al	P	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Rb	Sr	Zr	Pb	Sn	Ba
VN_3_F_4	100	960	116940	310	2630	420	6080	113	19	131	53160	13	9	57	2	17	19	247	24	4	82
VN_3_F_5	340	7460	97520	380	28450	360	5960	124	103	159	59940	28	22	42	3	95	22	291	10	7	531
VN_4_R_2	3260	6050	107160	430	20420	3450	5300	131	84	141	26300	36	37	76	12	146	105	173	36	5	432
VN_4_R_4	2330	6330	115620	470	19390	3570	4780	113	87	201	24410	43	34	86	8	143	98	158	34	5	371
VN_4_R_5	2540	5700	106770	510	18720	3050	4920	109	81	171	24410	36	28	72	8	137	101	161	30	5	367
VN_4_R_6	2710	5810	105800	350	19280	3040	5060	125	79	207	26440	35	55	80	9	136	79	188	34	6	390
VN_4_R_7	2830	6330	103530	570	19620	3210	5110	118	90	267	49100	33	25	82	12	143	81	174	32	5	372
VN_4_R_8	3370	6020	105190	670	19970	4030	5130	120	81	184	26580	41	30	88	11	141	101	161	33	7	394
VN_4_R_9	560	400	23260	520	3210	1000	4560	35	25	81	7550	7	14	31	<2	23	21	432	14	5	107
VN_4_R_10	3000	6820	105940	850	19630	4090	4990	118	83	307	40010	39	28	88	10	147	85	179	32	6	392
VN_4_R_11	2560	6400	111040	600	20110	3700	5050	123	86	286	34200	36	26	83	11	151	87	164	33	6	367
VN_4_R_12	2640	5920	107960	680	19970	2840	5230	122	87	197	37280	34	24	90	12	142	80	173	34	6	373

Appendix 6 Elemental concentrations [%] of rice straw at maturity stage and leaf blades at a critical growth stage around 45 days after transplanting/seeding in the LEGATO paddies, Si concentrations of straw are given in Appendix 3

Field	Season	Weather	Straw						Leaf blades						
			N	C	Mg	P	K	Ca	N	C	Mg	Si	P	K	Ca
PH_1_R_1	2011/2012	dry	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
PH_1_R_2	2011/2012	dry	0.57	34.99	0.17	0.06	1.66	0.21	- -	- -	- -	- -	- -	- -	- -
PH_1_R_3	2011/2012	dry	0.42	34.19	0.10	0.12	2.28	0.22	- -	- -	- -	- -	- -	- -	- -
PH_1_R_4	2011/2012	dry	0.61	33.77	0.15	0.11	2.03	0.21	- -	- -	- -	- -	- -	- -	- -
PH_1_R_5	2011/2012	dry	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
PH_1_R_6	2011/2012	dry	0.69	35.56	0.12	0.07	1.87	0.27	- -	- -	- -	- -	- -	- -	- -
PH_1_R_7	2011/2012	dry	0.82	36.24	0.15	0.18	2.39	0.19	4.14	39.89	0.16	5.77	0.35	2.82	0.19
PH_1_R_8	2011/2012	dry	0.60	34.58	0.17	0.16	2.15	0.27	3.29	40.21	0.15	5.37	0.35	2.35	0.24
PH_1_R_9	2011/2012	dry	0.78	34.10	0.12	0.16	2.64	0.25	- -	- -	- -	- -	- -	- -	- -
PH_1_R_10	2011/2012	dry	0.64	34.41	0.13	0.15	1.78	0.29	- -	- -	- -	- -	- -	- -	- -
PH_1_R_1	2012	wet	- -	- -	- -	- -	- -	- -	3.04	38.49	0.14	5.43	0.23	2.97	0.23
PH_1_R_2	2012	wet	- -	- -	- -	- -	- -	- -	3.30	39.06	0.19	5.80	0.29	2.07	0.25
PH_1_R_3	2012	wet	0.66	33.24	0.16	0.12	1.53	0.21	2.99	38.01	0.22	6.18	0.34	2.67	0.24
PH_1_R_4	2012	wet	0.74	33.22	0.16	0.12	2.44	0.22	2.92	37.74	0.19	6.62	0.27	2.85	0.23
PH_1_R_5	2012	wet	0.73	35.75	0.06	0.08	1.77	0.26	2.95	39.04	0.12	5.37	0.25	2.55	0.27
PH_1_R_6	2012	wet	0.85	32.01	0.15	0.18	3.73	0.28	2.49	39.37	0.14	5.26	0.27	1.98	0.28
PH_1_R_7	2012	wet	1.24	32.58	0.16	0.17	1.33	0.33	4.00	43.34	0.17	5.03	0.34	2.10	0.24
PH_1_R_8	2012	wet	0.85	35.11	0.11	0.12	1.74	0.21	3.17	40.02	0.15	5.13	0.27	2.37	0.23
PH_1_R_9	2012	wet	0.84	34.71	0.10	0.09	2.80	0.25	3.00	38.13	0.18	5.93	0.33	2.82	0.28
PH_1_R_10	2012	wet	- -	- -	- -	- -	- -	- -	2.52	39.50	0.13	5.30	0.29	1.99	0.29
PH_1_R_1	2012/2013	dry	- -	- -	0.10	0.09	1.81	0.19	2.95	37.47	0.15	6.00	0.21	2.54	0.26
PH_1_R_2	2012/2013	dry	- -	- -	0.15	0.14	2.04	0.29	3.63	36.37	0.15	5.26	0.26	1.90	0.23
PH_1_R_3	2012/2013	dry	- -	- -	- -	- -	- -	- -	4.27	39.14	0.14	5.27	0.37	2.12	0.22
PH_1_R_4	2012/2013	dry	- -	- -	0.11	0.08	2.63	0.20	4.04	37.50	0.13	5.18	0.36	2.26	0.19
PH_1_R_5	2012/2013	dry	- -	- -	0.10	0.04	2.14	0.21	2.93	38.25	0.11	4.54	0.24	1.98	0.30
PH_1_R_6	2012/2013	dry	- -	- -	0.11	0.11	2.36	0.27	2.51	37.63	0.10	5.85	0.19	2.00	0.27
PH_1_R_7	2012/2013	dry	- -	- -	0.12	0.09	2.29	0.20	3.60	39.93	0.14	4.05	0.29	2.54	0.20

Field	Season	Weather	Straw						Leaf blades						
			N	C	Mg	P	K	Ca	N	C	Mg	Si	P	K	Ca
PH_1_R_8	2012/2013	dry	- -	- -	0.14	0.21	2.30	0.23	3.39	39.09	0.17	3.90	0.29	2.51	0.18
PH_1_R_9	2012/2013	dry	- -	- -	- -	- -	- -	- -	3.54	37.63	0.13	4.63	0.33	2.56	0.18
PH_1_R_10	2012/2013	dry	- -	- -	0.11	0.19	2.58	0.27	4.01	36.99	0.14	5.95	0.34	2.01	0.28
PH_2_R_1	1/2012	dry	0.51	34.91	0.17	0.13	2.08	0.38	- -	- -	- -	- -	- -	- -	- -
PH_2_R_2	1/2012	dry	0.54	34.83	0.15	0.15	2.40	0.29	- -	- -	- -	- -	- -	- -	- -
PH_2_R_3	1/2012	dry	0.56	34.77	0.18	0.11	2.63	0.26	2.82	38.31	0.12	6.86	0.24	1.63	0.28
PH_2_R_4	1/2012	dry	0.67	34.86	0.17	0.13	2.49	0.36	- -	- -	- -	- -	- -	- -	- -
PH_2_R_5	1/2012	dry	0.54	33.84	0.13	0.09	3.03	0.21	- -	- -	- -	- -	- -	- -	- -
PH_2_R_6	1/2012	dry	0.73	37.17	0.15	0.18	1.61	0.33	- -	- -	- -	- -	- -	- -	- -
PH_2_R_7	1/2012	dry	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
PH_2_R_8	1/2012	dry	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
PH_2_R_9	1/2012	dry	0.76	35.71	0.23	0.18	2.24	0.40	3.19	40.25	0.20	5.29	0.26	1.70	0.49
PH_2_R_10	1/2012	dry	0.70	34.78	0.22	0.22	2.90	0.33	2.74	39.67	0.19	5.23	0.30	1.96	0.32
PH_2_R_1	2/2012	wet	0.99	35.94	0.20	0.18	2.43	0.31	2.58	39.92	0.17	4.73	0.26	1.92	0.33
PH_2_R_2	2/2012	wet	0.96	35.06	0.17	0.21	1.71	0.29	2.37	37.80	0.21	5.42	0.43	2.92	0.51
PH_2_R_3	2/2012	wet	0.87	34.46	0.19	0.13	2.61	0.29	2.74	38.84	0.15	6.63	0.27	2.06	0.54
PH_2_R_4	2/2012	wet	0.79	34.34	0.15	0.12	1.83	0.24	2.83	38.83	0.22	6.41	0.24	1.89	0.40
PH_2_R_5	2/2012	wet	0.90	34.48	0.17	0.16	1.98	0.27	2.88	39.86	0.17	4.86	0.29	2.09	0.37
PH_2_R_6	2/2012	wet	0.61	36.15	0.13	0.14	1.35	0.28	2.29	40.81	0.13	4.03	0.23	1.58	0.33
PH_2_R_7	2/2012	wet	0.64	35.48	0.19	0.09	2.09	0.27	2.37	38.54	0.19	5.90	0.27	1.99	0.29
PH_2_R_8	2/2012	wet	0.59	35.12	0.18	0.11	2.05	0.33	2.56	38.58	0.21	5.87	0.25	2.30	0.30
PH_2_R_9	2/2012	wet	0.74	31.96	0.19	0.11	2.18	0.52	2.63	40.16	0.13	4.88	0.26	1.50	0.35
PH_2_R_10	2/2012	wet	- -	- -	- -	- -	- -	- -	2.89	39.43	0.18	4.95	0.32	2.34	0.36
PH_2_R_1	1/2013	dry	- -	- -	0.09	0.13	1.95	0.23	1.60	35.04	0.13	6.40	0.21	1.85	0.41
PH_2_R_2	1/2013	dry	- -	- -	0.11	0.09	1.78	0.30	2.15	37.06	0.11	6.33	0.20	1.31	0.59
PH_2_R_3	1/2013	dry	- -	- -	0.14	0.09	1.88	0.26	2.04	34.68	0.09	7.30	0.18	1.93	0.34
PH_2_R_4	1/2013	dry	- -	- -	0.11	0.16	2.07	0.29	2.81	38.50	0.13	5.75	0.28	1.43	0.34
PH_2_R_5	1/2013	dry	- -	- -	0.13	0.11	2.98	0.25	3.50	33.65	0.21	8.53	0.32	1.57	0.36
PH_2_R_6	1/2013	dry	- -	- -	0.11	0.12	2.56	0.33	2.78	38.52	0.15	5.69	0.27	1.59	0.32

Field	Season	Weather	Straw						Leaf blades						
			N	C	Mg	P	K	Ca	N	C	Mg	Si	P	K	Ca
PH_2_R_7	1/2013	dry	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
PH_2_R_8	1/2013	dry	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
PH_2_R_9	1/2013	dry	- -	- -	0.21	0.17	1.69	0.42	2.59	37.55	0.25	6.18	0.27	1.64	0.50
PH_2_R_10	1/2013	dry	- -	- -	0.20	0.29	2.44	0.30	3.76	39.98	0.19	4.57	0.34	1.83	0.45
PH_3_R_1	2012		- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
PH_3_R_2	2012		- -	- -	- -	- -	- -	- -	3.17	39.77	0.14	5.57	0.18	2.18	0.33
PH_3_R_4	2012		- -	- -	- -	- -	- -	- -	4.08	40.81	0.16	4.68	0.49	2.45	0.24
PH_3_R_6	2012		- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
PH_3_R_8	2012		- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
PH_3_R_9	2012		- -	- -	- -	- -	- -	- -	4.11	41.07	0.20	4.44	0.41	1.75	0.26
PH_3_R_10	2012		- -	- -	- -	- -	- -	- -	3.71	39.29	0.17	5.54	0.25	2.80	0.36
PH_3_R_11	2012		- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
PH_3_R_12	2012		- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
PH_3_R_13	2012		- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
PH_3_R_1	2013		0.95	36.31	0.11	0.16	1.26	0.17	2.52	39.63	0.13	4.33	0.24	2.06	0.30
PH_3_R_2	2013		0.35	35.84	0.10	0.04	1.33	0.27	1.78	38.58	0.12	5.30	0.19	1.76	0.40
PH_3_R_4	2013		0.67	34.97	0.16	0.19	2.69	0.15	3.04	38.25	0.15	5.13	0.38	3.37	0.42
PH_3_R_6	2013		0.49	35.83	0.14	0.16	2.18	0.19	3.77	39.76	0.12	4.11	0.41	2.81	0.28
PH_3_R_8	2013		- -	- -	- -	- -	- -	- -	2.84	39.56	0.10	4.68	0.28	2.48	0.25
PH_3_R_9	2013		0.86	35.30	0.16	0.18	1.44	0.28	3.19	39.95	0.17	3.88	0.36	2.58	0.33
PH_3_R_10	2013		0.59	32.89	0.10	0.17	1.32	0.24	1.53	36.87	0.10	6.98	0.18	1.47	0.30
PH_3_R_11	2013		0.35	31.13	0.09	0.02	0.17	0.40	2.12	39.24	0.10	5.57	0.16	1.56	0.22
PH_3_R_12	2013		0.31	34.88	0.11	0.03	1.54	0.18	3.81	40.19	0.11	4.03	0.34	2.67	0.19
PH_3_R_13	2013		0.42	36.38	0.09	0.13	1.17	0.29	2.77	38.46	0.12	5.62	0.25	2.09	0.30
PH_3_R_1	2014		0.71	35.85	0.13	0.08	0.65	0.41	- -	- -	0.152	4.20	0.39	2.80	0.24
PH_3_R_2	2014		0.61	34.50	0.13	0.08	0.28	0.39	1.62	39.30	0.112	4.41	0.14	1.63	0.24
PH_3_R_4	2014		0.64	32.93	0.14	0.14	1.16	0.27	3.67	39.92	0.157	3.85	0.37	2.86	0.25
PH_3_R_6	2014		0.81	31.42	0.19	0.20	3.41	0.23	2.05	38.59	0.105	5.12	0.22	1.94	0.23
PH_3_R_8	2014		- -	- -	- -	- -	- -	- -	2.36	38.23	0.094	5.35	0.24	2.57	0.30

Field	Season	Weather	Straw						Leaf blades						
			N	C	Mg	P	K	Ca	N	C	Mg	Si	P	K	Ca
PH_3_R_9	2014		0.54	35.32	- -	- -	- -	- -	1.49	41.10	- -	- -	- -	- -	- -
PH_3_R_10	2014		0.48	37.39	0.11	0.08	0.75	0.39	1.55	40.21	0.087	3.88	0.15	1.99	0.25
PH_3_R_11	2014		0.52	34.58	0.12	0.06	1.48	0.27	2.22	39.11	0.109	4.60	0.19	2.34	0.27
PH_3_R_12	2014		0.70	31.53	0.09	0.13	2.23	0.37	- -	- -	- -	- -	- -	- -	- -
PH_3_R_13	2014		0.62	34.89	0.22	0.10	1.57	0.36	- -	- -	0.186	5.51	0.32	1.88	0.42
VN_1_R_1	2012	dry	0.59	38.61	0.13	0.19	3.26	0.26	2.17	40.50	0.23	3.62	0.27	2.27	0.51
VN_1_R_2	2012	dry	0.57	39.23	0.18	0.16	2.88	0.36	2.66	41.73	0.21	3.19	0.22	2.25	0.63
VN_1_R_3	2012	dry	0.73	40.52	0.17	0.22	2.75	0.49	2.12	41.57	0.20	3.36	0.34	2.17	0.49
VN_1_R_4	2012	dry	0.55	36.63	0.16	0.11	3.05	0.44	2.45	40.14	0.17	4.62	0.26	2.33	0.61
VN_1_R_5	2012	dry	0.76	38.82	0.21	0.11	2.85	0.36	3.17	42.31	0.23	2.63	0.26	1.93	0.44
VN_1_R_6	2012	dry	0.54	40.05	0.18	0.11	2.56	0.32	2.60	41.64	0.23	3.05	0.21	2.12	0.53
VN_1_R_7	2012	dry	0.59	39.81	0.15	0.14	2.14	0.40	2.24	42.25	0.16	2.96	0.28	1.87	0.39
VN_1_R_8	2012	dry	0.57	39.04	0.18	0.12	2.12	0.31	2.33	41.29	0.20	3.43	0.27	2.05	0.39
VN_1_R_9	2012	dry	0.96	37.63	0.25	0.11	2.65	0.41	2.07	41.28	0.22	2.92	0.25	1.93	0.47
VN_1_R_10	2012	dry	0.51	40.83	0.11	0.18	2.18	0.44	2.52	41.98	0.29	2.91	0.30	1.81	0.75
VN_1_R_1	2014	wet	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
VN_1_R_2	2014	wet	0.99	38.84	0.24	0.19	2.12	0.46	3.66	40.40	0.24	3.51	0.28	2.50	0.49
VN_1_R_3	2014	wet	1.02	37.02	0.14	0.12	1.75	0.41	3.98	40.18	0.22	3.83	0.37	2.01	0.56
VN_1_R_4	2014	wet	1.05	37.17	0.23	0.15	2.76	0.53	3.89	39.61	0.27	3.70	0.30	2.47	0.83
VN_1_R_5	2014	wet	0.64	38.47	0.16	0.08	1.93	0.44	1.94	41.55	0.21	2.70	0.22	1.62	0.43
VN_1_R_6	2014	wet	0.54	39.83	0.18	0.07	1.22	0.35	2.35	42.18	0.18	2.13	0.19	1.42	0.45
VN_1_R_7	2014	wet	0.75	39.55	0.17	0.16	1.77	0.28	3.36	39.94	0.22	3.90	0.28	2.39	0.50
VN_1_R_8	2014	wet	0.71	38.78	0.15	0.14	1.98	0.22	2.97	40.17	0.19	3.90	0.26	2.17	0.40
VN_1_R_9	2014	wet	0.66	39.63	0.23	0.08	2.01	0.56	3.15	39.81	0.27	3.38	0.26	2.47	0.78
VN_1_R_10	2014	wet	0.94	38.99	0.20	0.14	1.99	0.56	3.24	40.14	0.30	3.19	0.31	2.33	0.89
VN_2_R_1	2012	dry	0.71	39.65	0.12	0.14	3.51	0.46	2.47	42.03	0.16	3.18	0.34	1.75	0.65
VN_2_R_2	2012	dry	0.78	37.29	0.21	0.24	2.59	0.54	1.79	40.89	0.15	4.54	0.22	1.76	0.72
VN_2_R_3	2012	dry	0.61	38.99	0.14	0.15	1.97	0.49	2.81	42.70	0.19	2.42	0.37	1.79	0.58
VN_2_R_4	2012	dry	0.56	39.54	0.23	0.19	2.55	0.66	2.72	40.82	0.09	5.12	0.31	1.55	0.79

Field	Season	Weather	Straw						Leaf blades						
			N	C	Mg	P	K	Ca	N	C	Mg	Si	P	K	Ca
VN_2_R_5	2012	dry	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
VN_2_R_6	2012	dry	0.54	40.27	0.11	0.13	2.22	0.40	2.38	42.04	0.15	2.78	0.32	2.44	0.39
VN_2_R_7	2012	dry	0.57	37.38	0.20	0.17	2.43	0.55	2.12	42.26	0.20	2.60	0.31	1.88	0.63
VN_2_R_8	2012	dry	0.93	37.90	0.20	0.24	1.88	0.56	2.46	40.11	0.21	5.17	0.33	1.57	0.58
VN_2_R_9	2012	dry	0.79	40.65	0.24	0.18	2.08	0.54	2.38	41.14	0.14	3.90	0.35	2.18	0.54
VN_2_R_10	2012	dry	0.60	40.40	0.17	0.10	2.91	0.52	2.53	42.43	0.14	2.95	0.29	1.81	0.77
VN_2_R_1	2014	wet	0.86	39.23	0.17	0.20	2.17	0.38	2.33	40.74	0.18	2.84	0.23	2.17	0.68
VN_2_R_2	2014	wet	0.77	38.73	0.23	0.12	1.86	0.43	2.07	39.35	0.20	3.86	0.20	2.17	0.72
VN_2_R_3	2014	wet	0.72	35.70	0.15	0.10	2.72	0.38	2.09	40.54	0.22	2.99	0.30	2.16	0.81
VN_2_R_4	2014	wet	1.09	40.12	0.21	0.27	2.02	0.50	2.21	40.39	0.18	3.22	0.30	2.09	0.76
VN_2_R_5	2014	wet	0.83	39.20	0.18	0.24	2.55	0.48	1.97	39.90	0.23	3.14	0.30	2.31	0.89
VN_2_R_6	2014	wet	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
VN_2_R_7	2014	wet	0.87	39.59	0.17	0.15	2.08	0.52	1.76	40.65	0.22	2.45	0.22	2.00	0.79
VN_2_R_8	2014	wet	0.77	38.35	0.16	0.22	2.16	0.48	2.67	38.07	0.15	5.16	0.28	2.59	0.59
VN_2_R_9	2014	wet	0.84	38.64	0.11	0.23	2.99	0.48	2.19	40.46	0.14	3.05	0.29	2.35	0.76
VN_2_R_10	2014	wet	0.98	37.51	0.12	0.12	2.57	0.37	2.18	39.97	0.17	3.14	0.26	2.49	0.80
VN_3_R_1	2012		0.47	38.95	0.14	0.07	2.67	0.34	3.94	41.97	0.10	3.69	0.19	2.74	0.40
VN_3_R_2	2012		- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
VN_3_R_3	2012		0.60	35.17	0.17	0.07	3.56	0.45	2.95	39.33	0.18	5.47	0.27	1.97	0.67
VN_3_R_4	2012		0.55	37.52	0.15	0.08	2.85	0.34	2.70	39.90	0.17	4.89	0.22	2.23	0.45
VN_3_R_5	2012		0.52	37.51	0.10	0.26	3.34	0.23	2.54	40.72	0.15	3.70	0.24	2.74	0.46
VN_3_R_6	2012		1.16	39.25	0.26	0.26	1.57	0.44	3.04	41.05	0.21	3.86	0.21	1.57	0.57
VN_3_R_7	2012		1.35	37.53	0.29	0.10	2.64	0.66	3.54	43.06	0.22	1.70	0.21	1.96	0.64
VN_3_R_8	2012		0.61	41.11	0.23	0.05	2.03	0.48	2.39	41.69	0.26	2.69	0.15	1.78	0.62
VN_3_R_9	2012		0.61	42.51	0.25	0.07	1.16	0.47	2.66	42.97	0.25	1.58	0.18	1.66	0.58
VN_3_R_10	2012		0.54	39.45	0.20	0.14	2.01	0.44	2.28	40.63	0.15	3.89	0.24	1.71	0.45
VN_3_R_1	2014		0.69	36.62	0.10	0.09	2.14	0.38	3.37	40.09	0.16	4.15	0.15	2.66	0.55
VN_3_R_2	2014		- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
VN_3_R_3	2014		- -	- -	- -	- -	- -	- -	3.62	40.29	0.14	4.13	0.14	2.33	0.64

Field	Season	Weather	Straw						Leaf blades						
			N	C	Mg	P	K	Ca	N	C	Mg	Si	P	K	Ca
VN_3_R_4	2014		0.85	38.35	0.15	0.08	2.73	0.52	2.85	39.48	0.18	4.34	0.31	2.40	0.53
VN_3_R_5	2014		0.46	37.70	0.13	0.13	2.26	0.27	2.42	38.34	0.08	4.84	0.18	2.93	0.55
VN_3_R_6	2014		0.60	36.61	0.14	0.04	2.15	0.48	2.97	39.85	0.18	4.16	0.21	2.13	0.64
VN_3_R_7	2014		1.27	38.41	0.33	0.09	2.64	0.71	3.74	42.43	0.26	1.65	0.22	2.40	0.64
VN_3_R_8	2014		0.68	40.91	0.30	0.11	1.64	0.36	3.03	40.90	0.29	2.60	0.17	2.05	0.73
VN_3_R_9	2014		0.57	36.40	0.21	0.10	2.43	0.47	2.50	39.54	0.23	3.83	0.28	2.10	0.86
VN_3_R_10	2014		0.76	41.74	0.26	0.08	1.63	0.43	2.20	42.05	0.23	1.44	0.19	2.31	0.62
VN_4_R_2	1/2012	autumn	0.85	36.01	0.16	0.12	2.27	0.25	3.53	42.53	0.26	2.37	0.42	2.17	0.28
VN_4_R_4	1/2012	autumn	0.62	38.78	0.13	0.14	2.47	0.35	2.55	42.74	0.20	2.71	0.26	1.49	0.47
VN_4_R_5	1/2012	autumn	0.84	39.33	0.16	0.15	2.15	0.34	3.30	43.06	0.25	2.59	0.27	1.46	0.61
VN_4_R_6	1/2012	autumn	0.95	36.60	0.13	0.15	2.84	0.27	2.71	42.49	0.34	2.27	0.38	2.23	0.71
VN_4_R_7	1/2012	autumn	0.72	38.75	0.17	0.16	2.15	0.28	2.11	41.97	0.33	2.28	0.37	2.49	0.45
VN_4_R_8	1/2012	autumn	0.96	38.64	0.18	0.16	1.99	0.34	3.98	42.53	0.32	2.81	0.32	2.20	0.31
VN_4_R_9	1/2012	autumn	0.95	39.53	0.19	0.14	1.82	0.31	- -	- -	- -	- -	- -	- -	- -
VN_4_R_10	1/2012	autumn	0.86	38.16	0.14	0.11	2.51	0.26	3.29	42.04	0.23	2.92	0.36	2.31	0.25
VN_4_R_11	1/2012	autumn	0.96	39.70	0.26	0.16	2.68	0.31	3.57	41.79	0.47	2.81	0.30	2.38	0.73
VN_4_R_12	1/2012	autumn	0.98	39.20	0.22	0.13	2.27	0.33	3.42	42.03	0.36	3.50	0.39	2.02	0.69
VN_4_R_2	1/2012	spring	- -	- -	- -	- -	- -	- -	3.12	41.03	0.31	3.97	0.38	1.96	0.54
VN_4_R_4	2/2012	spring	0.74	38.58	0.15	0.10	2.52	0.40	3.00	42.37	0.17	2.56	0.31	1.68	0.41
VN_4_R_5	2/2012	spring	0.60	38.16	0.12	0.10	2.61	0.34	3.28	43.12	0.19	2.52	0.27	1.72	0.40
VN_4_R_6	2/2012	spring	0.77	38.88	0.14	0.13	2.47	0.33	3.64	43.84	0.21	1.65	0.36	1.87	0.31
VN_4_R_7	2/2012	spring	0.79	38.65	0.17	0.15	2.20	0.31	3.48	43.38	0.36	1.32	0.40	1.74	0.38
VN_4_R_8	2/2012	spring	0.94	39.01	0.20	0.13	1.59	0.34	3.65	43.47	0.27	2.01	0.42	1.61	0.39
VN_4_R_9	2/2012	spring	0.71	38.73	0.16	0.10	2.31	0.30	3.49	42.87	0.27	2.00	0.34	1.97	0.32
VN_4_R_10	2/2012	spring	0.89	39.74	0.17	0.11	2.18	0.31	3.17	42.79	0.20	2.26	0.34	2.19	0.32
VN_4_R_11	2/2012	spring	0.80	39.00	0.35	0.16	2.07	0.40	3.11	41.64	0.36	1.81	0.37	2.67	0.47
VN_4_R_12	2/2012	spring	0.73	38.42	0.23	0.18	2.13	0.34	3.50	40.98	0.31	3.04	0.40	2.51	0.45
VN_4_R_2	2012/2013	summer	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
VN_4_R_4	2012/2013	summer	0.62	39.25	0.13	0.08	1.67	0.35	- -	- -	- -	- -	- -	- -	- -

Field	Season	Weather	Straw						Leaf blades						
			N	C	Mg	P	K	Ca	N	C	Mg	Si	P	K	Ca
VN_4_R_5	2012/2013	summer	0.64	38.29	0.18	0.07	1.70	0.38	--	--	--	--	--	--	--
VN_4_R_6	2012/2013	summer	0.84	39.32	0.22	0.14	1.68	0.42	--	--	--	--	--	--	--
VN_4_R_7	2012/2013	summer	0.68	38.80	0.19	0.14	1.56	0.34	--	--	--	--	--	--	--
VN_4_R_8	2012/2013	summer	0.70	39.89	0.20	0.10	1.38	0.39	--	--	--	--	--	--	--
VN_4_R_9	2012/2013	summer	--	--	--	--	--	--	--	--	--	--	--	--	--
VN_4_R_10	2012/2013	summer	0.77	39.31	0.12	0.13	2.26	0.35	--	--	--	--	--	--	--
VN_4_R_11	2012/2013	summer	0.74	40.11	0.20	0.09	1.94	0.38	--	--	--	--	--	--	--
VN_4_R_12	2012/2013	summer	0.82	38.92	0.13	0.09	2.24	0.33	--	--	--	--	--	--	--
VN_4_R_2	1/2013	autumn	--	--	--	--	--	--	--	--	--	--	--	--	--
VN_4_R_4	1/2013	autumn	0.62	36.54	0.15	0.10	2.60	0.43	--	--	--	--	--	--	--
VN_4_R_5	1/2013	autumn	0.64	38.41	0.14	0.08	2.29	0.36	--	--	--	--	--	--	--
VN_4_R_6	1/2013	autumn	0.88	40.67	0.19	0.13	2.34	0.39	--	--	--	--	--	--	--
VN_4_R_7	1/2013	autumn	0.81	38.57	0.15	0.12	2.22	0.35	--	--	--	--	--	--	--
VN_4_R_8	1/2013	autumn	--	--	--	--	--	--	--	--	--	--	--	--	--
VN_4_R_9	1/2013	autumn	--	--	--	--	--	--	--	--	--	--	--	--	--
VN_4_R_10	1/2013	autumn	0.68	38.24	0.14	0.10	2.60	0.32	--	--	--	--	--	--	--
VN_4_R_11	1/2013	autumn	0.77	39.66	0.17	0.13	1.96	0.35	--	--	--	--	--	--	--
VN_4_R_12	1/2013	autumn	--	--	--	--	--	--	--	--	--	--	--	--	--
VN_4_R_2	2/2013	spring	--	--	--	--	--	--	--	--	--	--	--	--	--
VN_4_R_4	2/2013	spring	0.72	40.52	0.13	0.12	2.23	0.27	--	--	--	--	--	--	--
VN_4_R_5	2/2013	spring	0.78	40.18	0.13	0.09	2.32	0.28	--	--	--	--	--	--	--
VN_4_R_6	2/2013	spring	0.71	41.23	0.11	0.12	2.04	0.21	--	--	--	--	--	--	--
VN_4_R_7	2/2013	spring	0.76	41.12	0.12	0.12	2.04	0.23	--	--	--	--	--	--	--
VN_4_R_8	2/2013	spring	--	--	--	--	--	--	--	--	--	--	--	--	--
VN_4_R_9	2/2013	spring	--	--	--	--	--	--	--	--	--	--	--	--	--
VN_4_R_10	2/2013	spring	0.74	40.61	0.11	0.11	1.95	0.26	--	--	--	--	--	--	--
VN_4_R_11	2/2013	spring	0.75	39.04	0.15	0.14	2.54	0.30	--	--	--	--	--	--	--
VN_4_R_12	2/2013	spring	--	--	--	--	--	--	--	--	--	--	--	--	--

Appendix 7 Elemental concentrations [%] of rice grains and hulls in the LEGATO paddies; grains and hulls were separated for some samples before nutrient analysis, in these cases Si concentrations in grains plus hulls were calculated assuming 80 % grain mass; Si concentrations of straw are given in Appendix 3

Field	Season	Weather	Grains						Hulls						Grains + hulls						
			N	C	Mg	P	K	Ca	N	C	Mg	P	K	Ca	N	C	Mg	P	K	Ca	
PH_1_R_1	2011/2012	dry	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	
PH_1_R_2	2011/2012	dry	1.44	41.2	0.16	0.31	0.25	0.01	0.64	35.8	0.11	0.15	0.61	0.11	1.28	40.1	0.15	0.28	0.32	0.03	
PH_1_R_3	2011/2012	dry	1.22	40.7	0.21	0.49	0.32	0.01	0.35	34.3	0.08	0.14	0.33	0.08	1.05	39.5	0.18	0.42	0.32	0.03	
PH_1_R_4	2011/2012	dry	1.41	40.8	0.21	0.46	0.31	0.01	0.46	34.0	0.09	0.13	0.38	0.08	1.22	39.4	0.18	0.39	0.33	0.03	
PH_1_R_5	2011/2012	dry	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
PH_1_R_6	2011/2012	dry	1.33	40.7	0.18	0.42	0.29	0.01	0.47	35.1	0.08	0.13	0.40	0.08	1.16	39.6	0.16	0.36	0.32	0.02	
PH_1_R_7	2011/2012	dry	0.58	40.9	0.20	0.44	0.31	0.01	0.79	35.3	0.13	0.23	0.70	0.07	0.62	39.8	0.19	0.40	0.38	0.02	
PH_1_R_8	2011/2012	dry	1.14	40.9	0.19	0.40	0.29	0.01	0.62	36.6	0.11	0.20	0.56	0.07	1.03	40.0	0.17	0.36	0.34	0.02	
PH_1_R_9	2011/2012	dry	1.43	41.0	0.20	0.46	0.29	0.01	0.46	34.2	0.08	0.15	0.52	0.07	1.23	39.6	0.18	0.40	0.33	0.02	
PH_1_R_10	2011/2012	dry	1.34	40.9	0.21	0.45	0.28	0.01	0.54	34.9	0.09	0.19	0.36	0.09	1.18	39.7	0.19	0.40	0.29	0.03	
PH_1_R_1	2012	wet	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	
PH_1_R_2	2012	wet	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	
PH_1_R_3	2012	wet	1.23	40.4	0.14	0.34	0.25	0.01	0.40	36.2	0.06	0.09	0.39	0.05	1.07	39.6	0.13	0.29	0.28	0.02	
PH_1_R_4	2012	wet	1.21	40.5	0.14	0.32	0.23	0.01	0.50	37.1	0.06	0.13	0.47	0.04	1.07	39.8	0.12	0.28	0.28	0.02	
PH_1_R_5	2012	wet	1.15	40.5	0.14	0.32	0.25	0.01	0.33	36.0	0.04	0.07	0.37	0.05	0.98	39.6	0.12	0.27	0.27	0.02	
PH_1_R_6	2012	wet	1.52	40.7	0.16	0.40	0.26	0.01	0.39	35.4	0.05	0.09	0.33	0.06	1.30	39.6	0.14	0.34	0.28	0.02	
PH_1_R_7	2012	wet	1.71	40.7	0.18	0.40	0.28	0.01	0.65	34.5	0.09	0.16	0.40	0.07	1.50	39.4	0.16	0.35	0.30	0.02	
PH_1_R_8	2012	wet	1.33	40.5	0.16	0.35	0.24	0.01	0.51	36.0	0.09	0.16	0.46	0.06	1.17	39.6	0.14	0.31	0.28	0.02	
PH_1_R_9	2012	wet	1.30	40.6	0.16	0.41	0.30	0.01	0.48	35.7	0.06	0.14	0.38	0.06	1.14	39.6	0.14	0.35	0.32	0.02	
PH_1_R_10	2012	wet	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	
PH_1_R_1	2012/2013	dry	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	0.10	0.26	0.34	0.02	
PH_1_R_2	2012/2013	dry	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	0.12	0.30	0.33	0.02	
PH_1_R_3	2012/2013	dry	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	
PH_1_R_4	2012/2013	dry	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	0.12	0.30	0.31	0.03	
PH_1_R_5	2012/2013	dry	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	0.11	0.24	0.27	0.02	
PH_1_R_6	2012/2013	dry	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	0.13	0.33	0.31	0.04	

Field	Season	Weather	Grains						Hulls						Grains + hulls					
			N	C	Mg	P	K	Ca	N	C	Mg	P	K	Ca	N	C	Mg	P	K	Ca
PH_1_R_7	2012/2013	dry	--	--	--	--	--	--	--	--	--	--	--	--	--	--	0.12	0.28	0.32	0.03
PH_1_R_8	2012/2013	dry	--	--	--	--	--	--	--	--	--	--	--	--	--	--	0.13	0.33	0.31	0.03
PH_1_R_9	2012/2013	dry	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
PH_1_R_10	2012/2013	dry	--	--	--	--	--	--	--	--	--	--	--	--	--	--	0.12	0.33	0.30	0.03
PH_2_R_1	1/2012	dry	1.31	40.7	0.19	0.48	0.33	0.01	0.54	35.4	0.09	0.21	0.60	0.11	1.16	39.7	0.17	0.42	0.38	0.03
PH_2_R_2	1/2012	dry	1.27	40.7	0.17	0.42	0.31	0.01	0.35	32.0	0.07	0.12	0.59	0.09	1.09	38.9	0.15	0.36	0.37	0.03
PH_2_R_3	1/2012	dry	1.26	40.1	0.17	0.37	0.28	0.01	0.56	34.0	0.10	0.18	0.58	0.09	1.12	38.9	0.15	0.33	0.34	0.03
PH_2_R_4	1/2012	dry	1.40	40.8	0.19	0.43	0.30	0.01	0.42	34.1	0.09	0.14	0.61	0.12	1.20	39.5	0.17	0.37	0.36	0.04
PH_2_R_5	1/2012	dry	1.39	41.0	0.18	0.40	0.29	0.01	0.54	34.1	0.10	0.18	0.71	0.07	1.22	39.6	0.16	0.35	0.37	0.02
PH_2_R_6	1/2012	dry	1.31	40.1	0.18	0.39	0.28	0.01	0.63	35.4	0.12	0.20	0.69	0.11	1.18	39.2	0.17	0.35	0.36	0.03
PH_2_R_7	1/2012	dry	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
PH_2_R_8	1/2012	dry	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
PH_2_R_9	1/2012	dry	1.33	41.0	0.18	0.41	0.29	0.01	0.41	35.6	0.08	0.14	0.59	0.11	1.15	39.9	0.16	0.35	0.35	0.03
PH_2_R_10	1/2012	dry	1.32	41.0	0.18	0.41	0.30	0.01	0.61	35.7	0.10	0.21	0.58	0.08	1.18	39.9	0.16	0.37	0.36	0.02
PH_2_R_1	2/2012	wet	1.62	41.0	0.14	0.33	0.25	0.01	0.66	37.5	0.10	0.17	0.59	0.08	1.43	40.3	0.14	0.30	0.32	0.02
PH_2_R_2	2/2012	wet	1.34	40.8	0.15	0.35	0.25	0.01	0.44	36.3	0.07	0.13	0.42	0.07	1.16	39.9	0.14	0.30	0.28	0.02
PH_2_R_3	2/2012	wet	1.52	40.9	0.15	0.32	0.23	0.01	0.62	36.6	0.10	0.15	0.64	0.08	1.34	40.0	0.14	0.29	0.32	0.02
PH_2_R_4	2/2012	wet	1.37	40.8	0.14	0.32	0.24	0.01	0.39	36.3	0.06	0.11	0.43	0.07	1.17	39.9	0.12	0.28	0.28	0.02
PH_2_R_5	2/2012	wet	1.43	40.8	0.14	0.33	0.24	0.01	0.54	38.4	0.09	0.15	0.42	0.06	1.25	40.3	0.13	0.30	0.28	0.02
PH_2_R_6	2/2012	wet	1.20	40.8	0.13	0.30	0.24	0.01	0.44	37.1	0.07	0.14	0.46	0.06	1.05	40.0	0.12	0.27	0.28	0.02
PH_2_R_7	2/2012	wet	1.11	40.6	0.14	0.34	0.28	0.01	0.50	37.4	0.09	0.20	0.43	0.04	0.99	39.9	0.13	0.31	0.31	0.01
PH_2_R_8	2/2012	wet	1.03	40.5	0.16	0.39	0.30	0.01	0.38	33.9	0.07	0.14	0.42	0.05	0.90	39.2	0.14	0.34	0.32	0.02
PH_2_R_9	2/2012	wet	1.29	40.6	0.14	0.38	0.27	0.01	0.48	38.0	0.07	0.18	0.41	0.06	1.13	40.1	0.13	0.34	0.30	0.02
PH_2_R_10	2/2012	wet	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
PH_2_R_1	1/2013	dry	--	--	--	--	--	--	--	--	--	--	--	--	--	--	0.11	0.27	0.36	0.02
PH_2_R_2	1/2013	dry	--	--	--	--	--	--	--	--	--	--	--	--	--	--	0.12	0.27	0.30	0.02
PH_2_R_3	1/2013	dry	--	--	--	--	--	--	--	--	--	--	--	--	--	--	0.11	0.24	0.29	0.02
PH_2_R_4	1/2013	dry	--	--	--	--	--	--	--	--	--	--	--	--	--	--	0.13	0.29	0.33	0.02
PH_2_R_5	1/2013	dry	--	--	--	--	--	--	--	--	--	--	--	--	--	--	0.13	0.34	0.37	0.02

Field	Season	Weather	Grains						Hulls						Grains + hulls						
			N	C	Mg	P	K	Ca	N	C	Mg	P	K	Ca	N	C	Mg	P	K	Ca	
PH_2_R_6	1/2013	dry	--	--	--	--	--	--	--	--	--	--	--	--	--	--	0.13	0.29	0.31	0.02	
PH_2_R_7	1/2013	dry	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	
PH_2_R_8	1/2013	dry	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	
PH_2_R_9	1/2013	dry	--	--	--	--	--	--	--	--	--	--	--	--	--	--	0.13	0.29	0.32	0.03	
PH_2_R_10	1/2013	dry	--	--	--	--	--	--	--	--	--	--	--	--	--	--	0.16	0.35	0.34	0.03	
PH_3_R_1	2013	one	1.38	41.3	0.13	0.33	0.24	0.01	0.55	36.0	0.06	0.07	0.37	0.08	1.22	40.2	0.11	0.27	0.27	0.02	
PH_3_R_2	2013		1.02	40.9	0.12	0.30	0.23	0.01	0.30	35.3	0.03	0.04	0.25	0.07	0.88	39.8	0.10	0.25	0.23	0.02	
PH_3_R_4	2013		1.46	41.2	0.16	0.40	0.27	0.01	0.34	37.1	0.04	0.06	0.44	0.06	1.24	40.4	0.13	0.33	0.30	0.02	
PH_3_R_6	2013		1.26	41.1	0.11	0.30	0.25	0.01	0.31	36.7	0.03	0.02	0.55	0.04	1.07	40.2	0.09	0.24	0.31	0.01	
PH_3_R_8	2013																				
PH_3_R_9	2013		1.18	41.2	0.12	0.32	0.26	0.01	0.31	36.8	0.04	0.05	0.50	0.06	1.01	40.4	0.10	0.26	0.30	0.02	
PH_3_R_10	2013		1.33	40.6	0.15	0.39	0.27	0.01	0.32	34.9	0.03	0.044	0.26	0.06	1.13	39.5	0.12	0.32	0.27	0.02	
PH_3_R_11	2013		1.11	40.3	0.13	0.32	0.24	0.01	0.29	35.2	0.04	0.028	0.48	0.06	0.95	39.3	0.11	0.26	0.29	0.02	
PH_3_R_12	2013		1.26	41.2	0.15	0.35	0.23	0.01	0.40	35.1	0.06	0.07	0.65	0.07	1.09	39.9	0.13	0.29	0.32	0.02	
PH_3_R_13	2013		0.99	41.0	0.11	0.28	0.24	0.01	0.34	36.9	0.04	0.05	0.29	0.09	0.86	40.2	0.10	0.23	0.25	0.03	
PH_3_R_1	2014		--	--	--	--	--	--	--	--	--	--	--	--	1.03	40.5	0.11	0.24	0.22	0.03	
PH_3_R_2	2014		--	--	--	--	--	--	--	--	--	--	--	--	0.78	39.7	0.08	0.14	0.17	0.03	
PH_3_R_4	2014		--	--	--	--	--	--	--	--	--	--	--	--	1.52	41.2	0.12	0.30	0.33	0.02	
PH_3_R_6	2014		--	--	--	--	--	--	--	--	--	--	--	--	0.98	40.0	0.12	0.29	0.26	0.02	
PH_3_R_8	2014		--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
PH_3_R_9	2014		--	--	--	--	--	--	--	--	--	--	--	--	0.95	40.3	0.11	0.25	0.27	0.04	
PH_3_R_10	2014		--	--	--	--	--	--	--	--	--	--	--	--	1.06	39.2	0.12	0.32	0.29	0.05	
PH_3_R_11	2014		--	--	--	--	--	--	--	--	--	--	--	--	1.01	39.9	0.13	0.27	0.26	0.02	
PH_3_R_12	2014		--	--	--	--	--	--	--	--	--	--	--	--	1.08	40.5	0.11	0.25	0.30	0.02	
PH_3_R_13	2014		--	--	--	--	--	--	--	--	--	--	--	--	0.97	40.4	0.12	0.28	0.39	0.04	
VN_1_R_1	2012	dry	1.29	40.5	0.15	0.39	0.31	0.01	0.41	38.5	0.06	0.12	0.66	0.10	1.11	40.1	0.13	0.34	0.38	0.03	
VN_1_R_2	2012	dry	1.12	40.3	0.15	0.37	0.29	0.01	0.42	40.4	0.07	0.13	0.57	0.10	0.98	40.3	0.13	0.32	0.34	0.03	
VN_1_R_3	2012	dry	1.42	40.5	0.14	0.39	0.29	0.01	0.67	38.3	0.09	0.22	0.59	0.09	1.27	40.1	0.13	0.35	0.35	0.03	
VN_1_R_4	2012	dry	1.08	40.4	0.11	0.30	0.28	0.01	0.49	40.3	0.08	0.18	0.65	0.09	0.96	40.4	0.10	0.27	0.35	0.03	

Field	Season	Weather	Grains						Hulls						Grains + hulls						
			N	C	Mg	P	K	Ca	N	C	Mg	P	K	Ca	N	C	Mg	P	K	Ca	
VN_1_R_5	2012	dry	1.39	40.4	0.16	0.41	0.32	0.01	0.47	39.8	0.08	0.14	0.53	0.10	1.21	40.3	0.14	0.36	0.36	0.03	
VN_1_R_6	2012	dry	1.28	40.4	0.16	0.43	0.33	0.01	0.49	40.4	0.09	0.15	0.60	0.10	1.12	40.4	0.15	0.37	0.38	0.03	
VN_1_R_7	2012	dry	1.17	40.3	0.15	0.38	0.29	0.01	0.42	40.0	0.07	0.11	0.46	0.10	1.02	40.2	0.13	0.32	0.33	0.03	
VN_1_R_8	2012	dry	1.24	40.5	0.12	0.33	0.29	0.01	0.43	40.8	0.06	0.08	0.57	0.11	1.08	40.5	0.11	0.28	0.34	0.03	
VN_1_R_9	2012	dry	1.22	40.2	0.12	0.33	0.27	0.01	0.60	41.5	0.09	0.18	0.71	0.11	1.10	40.5	0.12	0.30	0.35	0.03	
VN_1_R_10	2012	dry	1.41	40.9	0.13	0.36	0.29	0.02	0.58	39.3	0.08	0.18	0.70	0.19	1.24	40.6	0.12	0.33	0.37	0.05	
VN_1_R_1	2014	wet	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
VN_1_R_2	2014	wet	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	1.22	41.2	0.13	0.33	0.33	0.04	
VN_1_R_3	2014	wet	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	1.24	40.6	0.13	0.35	0.34	0.04	
VN_1_R_4	2014	wet	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	1.34	39.7	0.14	0.36	0.49	0.09	
VN_1_R_5	2014	wet	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	1.08	40.2	0.13	0.21	0.39	0.19	
VN_1_R_6	2014	wet	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	1.21	40.7	0.12	0.26	0.28	0.07	
VN_1_R_7	2014	wet	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	1.54	40.4	0.19	0.48	0.43	0.07	
VN_1_R_8	2014	wet	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	1.48	40.5	0.19	0.50	0.45	0.04	
VN_1_R_9	2014	wet	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	1.01	41.2	0.12	0.29	0.34	0.04	
VN_1_R_10	2014	wet	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	1.38	40.7	0.15	0.39	0.45	0.10	
VN_2_R_1	2012	dry	1.26	40.7	0.12	0.34	0.30	0.01	0.52	40.2	0.07	0.15	0.68	0.15	1.11	40.6	0.11	0.30	0.38	0.04	
VN_2_R_2	2012	dry	1.38	40.6	0.18	0.47	0.35	0.02	0.59	38.8	0.08	0.18	0.72	0.14	1.23	40.2	0.16	0.42	0.42	0.04	
VN_2_R_3	2012	dry	1.39	40.7	0.12	0.32	0.27	0.03	0.65	41.9	0.09	0.18	0.81	0.14	1.24	40.9	0.11	0.29	0.37	0.05	
VN_2_R_4	2012	dry	1.25	40.4	0.16	0.41	0.31	0.01	0.50	40.2	0.09	0.16	0.73	0.19	1.10	40.3	0.15	0.36	0.39	0.05	
VN_2_R_5	2012	dry	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	
VN_2_R_6	2012	dry	1.43	40.9	0.11	0.36	0.31	0.01	0.68	39.6	0.09	0.21	0.69	0.09	1.28	40.6	0.11	0.33	0.38	0.03	
VN_2_R_7	2012	dry	1.26	40.5	0.15	0.41	0.32	0.02	0.60	39.1	0.09	0.19	0.65	0.13	1.13	40.2	0.14	0.36	0.38	0.04	
VN_2_R_8	2012	dry	1.57	40.8	0.12	0.35	0.29	0.02	0.59	38.5	0.07	0.16	0.69	0.13	1.38	40.3	0.11	0.31	0.37	0.04	
VN_2_R_9	2012	dry	1.69	40.7	0.16	0.38	0.30	0.02	0.75	38.9	0.10	0.14	0.84	0.14	1.50	40.3	0.15	0.33	0.40	0.04	
VN_2_R_10	2012	dry	1.16	40.5	0.11	0.31	0.30	0.02	0.52	41.5	0.08	0.14	0.67	0.16	1.03	40.7	0.10	0.28	0.38	0.04	
VN_2_R_1	2014	wet	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	1.14	41.1	0.13	0.33	0.40	0.03	
VN_2_R_2	2014	wet	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	1.06	41.0	0.12	0.30	0.34	0.04	
VN_2_R_3	2014	wet	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	1.13	41.1	0.12	0.33	0.39	0.04	

Field	Season	Weather	Grains						Hulls						Grains + hulls					
			N	C	Mg	P	K	Ca	N	C	Mg	P	K	Ca	N	C	Mg	P	K	Ca
VN_2_R_4	2014	wet	--	--	--	--	--	--	--	--	--	--	--	--	1.21	41.4	0.13	0.36	0.40	0.04
VN_2_R_5	2014	wet	--	--	--	--	--	--	--	--	--	--	--	--	1.41	41.5	0.15	0.43	0.40	0.05
VN_2_R_6	2014	wet	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
VN_2_R_7	2014	wet	--	--	--	--	--	--	--	--	--	--	--	--	0.98	41.5	0.12	0.29	0.38	0.03
VN_2_R_8	2014	wet	--	--	--	--	--	--	--	--	--	--	--	--	1.10	41.1	0.13	0.31	0.33	0.03
VN_2_R_9	2014	wet	--	--	--	--	--	--	--	--	--	--	--	--	1.17	41.6	0.12	0.34	0.39	0.03
VN_2_R_10	2014	wet	--	--	--	--	--	--	--	--	--	--	--	--	1.31	41.4	0.12	0.34	0.39	0.05
VN_3_R_1	2012		1.13	40.5	0.12	0.31	0.27	0.01	0.67	39.9	0.11	0.20	0.76	0.09	1.04	40.4	0.12	0.29	0.37	0.03
VN_3_R_2	2012		--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
VN_3_R_3	2012		1.27	40.5	0.12	0.30	0.24	0.01	0.47	38.6	0.09	0.13	0.59	0.07	1.11	40.1	0.11	0.27	0.31	0.02
VN_3_R_4	2012		1.30	40.5	0.14	0.35	0.30	0.01	0.50	36.8	0.06	0.10	0.55	0.09	1.14	39.7	0.12	0.30	0.35	0.03
VN_3_R_5	2012		1.31	40.5	0.11	0.31	0.31	0.01	0.67	38.3	0.08	0.19	0.60	0.08	1.18	40.1	0.10	0.29	0.37	0.03
VN_3_R_6	2012		1.85	41.1	0.13	0.31	0.25	0.03	0.90	40.4	0.11	0.19	0.77	0.10	1.66	41.0	0.12	0.28	0.35	0.04
VN_3_R_7	2012		1.88	40.8	0.19	0.38	0.25	0.01	0.83	41.3	0.11	0.15	0.65	0.12	1.67	40.9	0.17	0.33	0.33	0.03
VN_3_R_8	2012		1.44	40.6	0.13	0.32	0.28	0.01	0.74	42.0	0.09	0.14	0.65	0.12	1.30	40.9	0.13	0.28	0.35	0.04
VN_3_R_9	2012		1.21	40.6	0.11	0.26	0.23	0.01	0.70	43.0	0.14	0.20	0.64	0.13	1.11	41.1	0.11	0.25	0.31	0.04
VN_3_R_10	2012		1.11	40.5	0.14	0.34	0.26	0.01	0.63	40.7	0.14	0.23	0.72	0.12	1.02	40.6	0.14	0.32	0.35	0.03
VN_3_R_1	2014		--	--	--	--	--	--	--	--	--	--	--	--	1.14	40.5	0.11	0.28	0.27	0.03
VN_3_R_2	2014		--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
VN_3_R_3	2014		--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
VN_3_R_4	2014		--	--	--	--	--	--	--	--	--	--	--	--	1.26	41.6	0.10	0.22	0.29	0.06
VN_3_R_5	2014		--	--	--	--	--	--	--	--	--	--	--	--	1.08	41.1	0.12	0.30	0.30	0.03
VN_3_R_6	2014		--	--	--	--	--	--	--	--	--	--	--	--	1.20	40.6	0.10	0.25	0.38	0.04
VN_3_R_7	2014		--	--	--	--	--	--	--	--	--	--	--	--	1.61	41.6	0.12	0.21	0.26	0.04
VN_3_R_8	2014		--	--	--	--	--	--	--	--	--	--	--	--	1.32	41.9	0.16	0.31	0.57	0.17
VN_3_R_9	2014		--	--	--	--	--	--	--	--	--	--	--	--	0.97	41.0	0.13	0.29	0.31	0.03
VN_3_R_10	2014		--	--	--	--	--	--	--	--	--	--	--	--	1.25	42.3	0.12	0.25	0.27	0.04
VN_4_R_2	1/2012	autumn	1.4	40.4	0.15	0.37	0.28	0.01	0.56	38.2	0.08	0.08	0.50	0.08	1.20	39.9	0.14	0.31	0.33	0.02
VN_4_R_4	1/2012	autumn	1.0	40.6	0.11	0.30	0.26	0.01	0.48	39.5	0.06	0.06	0.58	0.09	0.92	40.4	0.10	0.25	0.32	0.03

Field	Season	Weather	Grains						Hulls						Grains + hulls					
			N	C	Mg	P	K	Ca	N	C	Mg	P	K	Ca	N	C	Mg	P	K	Ca
VN_4_R_5	1/2012	autumn	1.2	41.8	0.12	0.31	0.26	0.01	0.53	40.6	0.07	0.08	0.53	0.09	1.07	41.5	0.11	0.26	0.32	0.03
VN_4_R_6	1/2012	autumn	1.3	41.7	0.12	0.31	0.28	0.01	0.57	39.3	0.07	0.08	0.57	0.07	1.13	41.3	0.11	0.27	0.34	0.02
VN_4_R_7	1/2012	autumn	1.1	40.2	0.15	0.34	0.29	0.01	0.51	40.0	0.08	0.09	0.67	0.08	0.96	40.2	0.13	0.29	0.37	0.02
VN_4_R_8	1/2012	autumn	1.4	40.3	0.17	0.40	0.31	0.01	0.71	40.0	0.10	0.13	0.58	0.13	1.26	40.3	0.15	0.34	0.36	0.03
VN_4_R_9	1/2012	autumn	1.2	40.3	0.15	0.38	0.31	0.01	0.54	39.9	0.08	0.09	0.57	0.07	1.11	40.2	0.14	0.32	0.36	0.02
VN_4_R_10	1/2012	autumn	1.2	40.3	0.15	0.36	0.29	0.01	0.58	39.0	0.09	0.10	0.58	0.09	1.11	40.1	0.14	0.30	0.35	0.03
VN_4_R_11	1/2012	autumn	1.4	41.0	0.15	0.38	0.28	0.01	0.55	40.1	0.12	0.10	0.60	0.13	1.22	40.8	0.15	0.32	0.35	0.04
VN_4_R_12	1/2012	autumn	1.4	41.0	0.15	0.40	0.29	0.01	0.49	38.1	0.11	0.09	0.61	0.13	1.21	40.4	0.14	0.34	0.36	0.04
VN_4_R_2	1/2012	spring	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
VN_4_R_4	2/2012	spring	1.2	42.0	0.15	0.37	0.33	0.02	- -	- -	0.09	0.08	0.66	0.13	0.96	33.6	0.14	0.31	0.40	0.04
VN_4_R_5	2/2012	spring	- -	- -	0.15	0.37	0.33	0.02	0.46	39.7	0.08	0.07	0.61	0.11	0.09	7.9	0.14	0.31	0.39	0.04
VN_4_R_6	2/2012	spring	1.1	41.9	0.15	0.36	0.29	0.01	0.50	40.5	0.10	0.09	0.59	0.11	0.98	41.6	0.14	0.30	0.35	0.03
VN_4_R_7	2/2012	spring	1.2	41.8	0.16	0.37	0.31	0.01	0.53	40.4	0.11	0.11	0.61	0.10	1.07	41.5	0.15	0.32	0.37	0.03
VN_4_R_8	2/2012	spring	1.4	41.9	0.16	0.39	0.34	0.02	0.54	41.1	0.10	0.08	0.57	0.11	1.21	41.7	0.15	0.32	0.39	0.04
VN_4_R_9	2/2012	spring	1.2	41.9	0.14	0.35	0.28	0.01	0.50	40.4	0.10	0.08	0.59	0.09	1.05	41.6	0.13	0.30	0.34	0.03
VN_4_R_10	2/2012	spring	1.2	41.0	0.15	0.37	0.29	0.01	0.53	39.3	0.09	0.09	0.64	0.09	1.03	40.6	0.14	0.31	0.36	0.03
VN_4_R_11	2/2012	spring	1.3	42.0	0.15	0.38	0.30	0.01	0.51	40.6	0.12	0.09	0.46	0.13	1.14	41.7	0.14	0.32	0.33	0.04
VN_4_R_12	2/2012	spring	1.2	41.9	0.15	0.37	0.28	0.01	0.50	38.2	0.08	0.08	0.52	0.09	1.05	41.2	0.14	0.31	0.33	0.03
VN_4_R_2	2012/2013	summer	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
VN_4_R_4	2012/2013	summer	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	0.96	39.9	0.10	0.26	0.29	0.03
VN_4_R_5	2012/2013	summer	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	1.04	40.0	0.11	0.28	0.28	0.02
VN_4_R_6	2012/2013	summer	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	0.97	40.4	0.11	0.26	0.35	0.03
VN_4_R_7	2012/2013	summer	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	0.94	39.9	0.11	0.27	0.33	0.03
VN_4_R_8	2012/2013	summer	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	0.99	39.9	0.13	0.29	0.33	0.03
VN_4_R_9	2012/2013	summer	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
VN_4_R_10	2012/2013	summer	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	1.01	39.8	0.13	0.33	0.35	0.02
VN_4_R_11	2012/2013	summer	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	1.00	39.9	0.13	0.30	0.36	0.03
VN_4_R_12	2012/2013	summer	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	1.19	39.5	0.13	0.33	0.33	0.02
VN_4_R_2	1/2013	autumn	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -

Field	Season	Weather	Grains						Hulls						Grains + hulls					
			N	C	Mg	P	K	Ca	N	C	Mg	P	K	Ca	N	C	Mg	P	K	Ca
VN_4_R_4	1/2013	autumn	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	0.98	39.5	0.12	0.31	0.32	0.02
VN_4_R_5	1/2013	autumn	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	0.97	39.6	0.12	0.30	0.31	0.02
VN_4_R_6	1/2013	autumn	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	1.00	40.4	0.13	0.32	0.34	0.02
VN_4_R_7	1/2013	autumn	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	0.93	40.3	0.13	0.31	0.35	0.02
VN_4_R_8	1/2013	autumn	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
VN_4_R_9	1/2013	autumn	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
VN_4_R_10	1/2013	autumn	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	0.99	40.0	0.13	0.33	0.34	0.02
VN_4_R_11	1/2013	autumn	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	0.96	40.4	0.13	0.32	0.33	0.02
VN_4_R_12	1/2013	autumn	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
VN_4_R_2	2/2013	spring	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
VN_4_R_4	2/2013	spring	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	1.19	41.8	0.12	0.30	0.29	0.02
VN_4_R_5	2/2013	spring	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	1.11	41.8	0.11	0.28	0.28	0.02
VN_4_R_6	2/2013	spring	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	0.91	41.7	0.11	0.28	0.31	0.02
VN_4_R_7	2/2013	spring	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	0.94	41.9	0.10	0.28	0.31	0.02
VN_4_R_8	2/2013	spring	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
VN_4_R_9	2/2013	spring	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
VN_4_R_10	2/2013	spring	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	1.04	41.9	0.12	0.30	0.29	0.02
VN_4_R_11	2/2013	spring	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	1.07	40.4	0.14	0.34	0.31	0.02

Appendix 8 Applied pesticides in the surrounding fields of the experimental field in Tien Giang (Chapter 4)

Application date	Active substance
11/29/2013	Pretilachlor
12/18/2013	Metaldehyde, Tricyclazole, Isoprothiolane
01/03/2014	Fipronil, Chlorfluazuron
03/05/2014	Pretilachlor
03/12/2014	Metaldehyde
03/14/2014	Cyhalofop-butyl, Penoxsulam
04/02/2014	Quinalphos, Tricyclazole. Isoprothiolane
04/18/2014	Fipronil, Chlorfluazuron
04/24/2014	Azoxystrobin, Difenoconazole, Propiconazole
04/30/2014	Kasugamycin, Hexaconazole

Publikationsliste (List of publications)

Marxen A, Klotzbücher T, Jahn R, Xuan LD, Cuong LQ, Chien HV, Sann C, Vetterlein D. Effects of Si fertilization on Si in soil solution, Si uptake by rice (Oryza sativa L.), and resistance of rice to biotic stresses in Southern Vietnam (submitted to PLoS ONE)

Klotzbücher T, **Marxen A**, Jahn R, Vetterlein D (2016) Silicon cycle in rice paddy fields: insights provided by relations between silicon forms in topsoils and plant silicon uptake. Nutr Cycl Agroecosyst DOI: 10.1007/s10705-016-9782-1

Mueller-Niggemann C, Utami SR, **Marxen A**, Mangelsdorf K, Bauersachs T, Schwark L (2016) Distribution of tetraether lipids in agricultural soils – differentiation between paddy and upland management. Biogeosciences 13: 1647-1666

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Eidesstattliche Erklärung / *Declaration under Oath*

Ich erkläre an Eides statt, dass ich die Arbeit selbstständig und ohne fremde Hilfe verfasst, keine anderen als die von mir angegebenen Quellen und Hilfsmittel benutzt und die den benutzten Werken wörtlich oder inhaltlich entnommenen Stellen als solche kenntlich gemacht habe.
I declare under penalty of perjury that this thesis is my own work entirely and has been written without any help from other people. I used only the sources mentioned and included all the citations correctly both in word or content.

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