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Silicon availability in Lower Austrian topsoils

Master Thesis

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Abstract

Silicon is an important plant nutrient involved in alleviation of multiple stresses. Globally increased export of silicon with harvest and utilization of crop residues for bio-refinery and bioenergy production has raised concerns about Si depletion in cultivated soils. As no information about phytoavailability of silicon in Austrian soils is available, we determined CaCl_2 -extractable (potentially plant available) and NaOH -extractable (amorphous) silicon in Lower Austrian topsoils under arable and grassland use in Lower Austria. To this end we re-sampled 95 sites for which archived soils collected between 1986 and 2000 are available. Using multiple linear regression models we show that the plant available silicon concentrations in archived non-calcareous soils are positively related to pH and clay content, and negatively with organic matter. In calcareous soils plant-available silicon was negatively related to organic matter, sand and silt content. While we found no model explaining the amorphous silicon fraction in non-calcareous soils, this fraction was related negatively to organic matter, sand and the carbonate content in calcareous soils. The amorphous silicon fraction increased in the order Fluvisols < Leptosols < Regosols < Phaeozems < Cambisols < Umbrisols, indicating accumulation of amorphous silicon with the advance of soil formation. Plant-available silicon showed a similar pattern up to the Phaeozems, however, lower values for the most developed, more acidic Cambisols and Umbrisols. The medians of the amorphous silicon fraction were similar in archived (2730 mg kg^{-1}) and re-sampled (2620 mg kg^{-1}) soils, with no relevant difference between grassland and arable soils. The medians of the plant-available silicon concentrations were 29.0 mg kg^{-1} in archived, and 20.5 mg kg^{-1} in the re-sampled soils, with concentrations only half (resampled soils) or less than half (archived soils) in grassland as compared to the corresponding arable soils. The fraction of soils below the suggested critical value for plant-available silicon (20 mg kg^{-1}) increased from 39 % in the archived to 47% in the re-sampled soils.

We conclude that a substantial, increasing proportion of Lower Austrian soils is depleted of plant-available silicon, possibly requiring fertilization and/or changes in management, even though the amorphous fraction did not change during the past 20-30 years. Further monitoring and refinement of silicon fractionation with emphasis on the biogenic pools, along with validation of the suggested critical plant-available silicon value is required to enhance our understanding of factors controlling the soil silicon status of Lower Austrian soils, and to adopt strategies for the management of silicon availability to crops.

Table of content

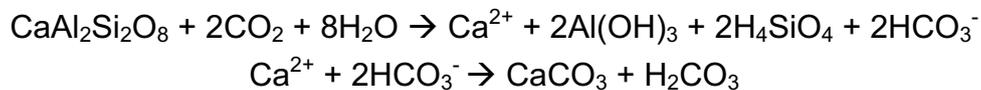
1. Introduction.....	1
1.1. Global geochemical cycle of silicon	1
1.2. Importance of silicon for plants.....	2
1.3. Silicon pools in soils and its availability for plants	3
1.4. Importance of phytoliths and impact of agriculture on their global cycle	5
1.5. Analytical methodologies to extract different silicon fractions from soil material and measurement approaches.....	6
2. Objectives and hypothesis	9
3. Materials and methods	11
3.1. Selection of soil sites and soil sampling	11
3.2. Determination of basic soil properties and climate conditions	14
3.3. Soil preparation for analytical procedures.....	15
3.4. Preliminary work for method implementation	15
3.4.1. Testing analytical procedures.....	17
3.5. Soil extraction procedures	18
3.5.1. 0.01M CaCl ₂ extraction (Haysom and Chapman, 1975)	18
3.5.2. 0.2M NaOH extraction	18
3.6. Colorimetric method.....	18
3.7. Statistics	19
3.7.1. Multiple regression analysis with environmental parameters and soil properties as determining factors for soil silicon fractions	20
4. Results and discussion	23
4.1. Current state and temporal changes of potentially plant-available silicon.....	23
4.2. Effect of principal type of land use on plant available Si concentrations.....	25
4.3. Current state and temporal changes of the amorphous silicon fraction	26
4.4. Principal type of land use as determining factor for amorphous Si concentrations differences	29
4.5. Soil Si concentrations and soil groups.....	30
4.6. Analysis on environmental parameters and soil properties as determining factors for soil silicon fractions	32
4.6.1. Multiple regression analysis results – Non-calcareous soils	32
4.6.2. Multiple regression analysis results – Calcareous soils	33
4.6.3. Discussion – Environmental factors determining plant available Si concentrations in soil	34
4.6.4. Discussion – Environmental factors determining amorphous silicon concentrations in soil	36
5. Conclusions.....	37
References	38

1. Introduction

90% of all minerals consist of silicate minerals and after oxygen, silicon is the second most abundant element on earth (Struyf et al., 2009). Even though silicon is one of the main components of the earth's crust, our knowledge on the biogeochemical behavior of this element is still limited. Scientists aim to solve some of the numerous open questions concerning silicon behavior in plants and soil, considering its importance in several field of application, from high tech industries to agricultural utilization.

1.1. Global geochemical cycle of silicon

The seven major global reservoirs of silica are: soil solution, groundwater, soil, biomass, rivers, oceans and atmosphere (Cornelis et al., 2011). Its abundance on the planet earth makes it a very important element, because of its interactions with other chemical elements and because of the multiple forms in which it is present in the environment. Special attention goes to its interaction with carbon dioxide. CO₂ is consumed during the weathering of silicates, following this reaction (Stumm, 1970):



Silicic acid is obtained, together with *gibbsite* and dissolved HCO₃⁻, from *anorthite*, water and CO₂. The consumption of CO₂ reduces its amount in the atmosphere and therefore, on geological timescales, it is influencing the global climate (Berner et al., 1983).

About 0.26 Gt C yr⁻¹ are consumed globally every year for the chemical weathering of silicates (Hartmann et al., 2009), which depends on the intensity of rainfall, runoff and temperature and the characteristics of lithology, topography and vegetation of the weathered site (Drever, 1994).

The main action of the chemical weathering towards silicon is to release it from the silicates, allowing its vertical and horizontal translocation in the terrestrial ecosystem. Plants, diatoms and microphytes can successively uptake and immobilize silicon. This silicon pool can permanently remain in this form or being again released into the ecosystem (Struyf et al., 2010).

In ocean ecosystems, silicon is particularly essential for the growth of *diatoms* (*Bacillariophyceae*), a phytoplankton which uses silicon to build its cell walls, called

“frustule” (Struyf et al., 2010). Together with silicon, diatoms also sequester carbon, inducing a carbon flux towards the sea bottom. Another kind of phytoplankton, called coccolithophores, is not a silicon accumulator, but it is characterized by calcite shells: during the formation of the shells, CO₂ is produced, because of the reaction between calcium and hydrogen carbonate (Rost et al., 2004). The presence of these two phytoplankton in the ocean environment, highly influences the net CO₂ flux (Treguér et al. 2000).

1.2. Importance of silicon for plants

Silicon has been found in high concentrations in plants, ranging between 1% to 10% (mass/mass) of the dry matter (Epstein, 1994) and its beneficial effects for them has been recognized starting from the beginning of last century (Guntzer et al., 2010). Plants uptake silicon in the form of silicic acid, which undergoes polymerization processes and it is stored as amorphous SiO₂.nH₂O in cell walls, intercellular spaces of roots, leaf cells and bracts (Mitani et al., 2005). Many empirical studies have been carried out, in order to understand silicon’s direct role in plant metabolism, but the mechanisms involved require further in-depth analysis.

Biotic and abiotic stresses may be reduced after application of silicon fertilizers: fungal attacks and diseases decreased in both wheat and rice (Rodgers-Gray and Shaw, 2004; Ma and Takahashi, 2002). The pathogen’s defense mechanisms enhanced by silicon application in plants have been proven to be both physical and biochemical: a physical barrier formed by silicon below the cuticle prevents bacteria penetration. Biochemically, silicon increases the activity of protective enzymes, the expression of genes related to defense and it changes the cell wall structure (Gutierrez-Barranquero et al., 2012, Chang et al., 2002; Diogo and Wydra, 2007).

Regarding the interaction of silicon with other nutrients, it has been shown that it can improve the availability of P for crops (Brenchley and Maskell, 1927) and the same beneficial effects have been proven with potassium, nitrogen and calcium (Mali and Aery, 2008a,b).

Plants can be highly negatively affected by the presence of pollutant metals in soils. Silicon acts in the soil and/or directly in the plant’s roots to prevent the assimilation and the consequent toxicity of Cd, Al, Fe, Cu, Zn, Mn and As (Ma and Takahashi 2002; Gu et al. 2012; Liang et al. 2007).

1.3. Silicon pools in soils and its availability for plants

Plants uptake silicon from the soil, actively or passively, mainly in the form of an uncharged monomeric orthosilicic acid (H_4SiO_4) dissolved in the soil solution (Casey et al., 2004). The concentration of silicon in soil solution varies between 0.1 to 0.6 mM (Epstein, 2001) and this amount highly depends on the supply from the silicon pools in their adsorbed or solid phases. There are several mineral and biogenic silicon pools in the soil and a complex biogeochemical cycle regulates their interactions (Sommer et al., 2006). The chemistry of silicon in soil is still not well known, especially the mechanisms that regulate the presence of silicon in the soil solution: together with the *intensity*, which is the parameter that defines silicon concentration in the soil solution, this element is also 'stored' in the solid phase (*capacity*) and adsorbed to the soil material (*retention capability*). The conditions that favor the release from the solid phase or the adsorption/desorption mechanisms are still not fully understood (Haynes, 2014).

Following Figure 1, we can briefly summarize the silicon distribution in soil, underlining those fractions that mostly affect the silicon concentration in soil solution. Starting from the right side of the figure, where the solid phase is shown, we can see the primary (quartz, mica, feldspars) and secondary minerals (clay soils), which constitute the crystalline fraction. The primary minerals are part of the sand and silt fractions of the soil and the secondary minerals are predominantly accumulated in the clay fraction (Allen and Hajek, 1989). The poorly crystalline minerals, such as microcrystalline and "short-range-ordered" silicates are present as a consequence of soil formation (Sommer et al., 2006). This last group of minerals and specifically imogolites and allophanes, contain high amount of aluminum and they are mostly formed in acidic environments (Wada, 1989; Farmer et al., 1979).

Within the amorphous forms of silica, the biogenic fraction is the one for which we are lacking more knowledge. The vegetation can store silicon as hydrated amorphous silicon dioxide ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) (Piperno, 2006) which partially constitutes the biogenic Si pool that is further subdivided into phytogenic (opal-A polymerized in leaves), microbial and protozoic silicon (Sommer et al., 2006).

The amorphous silicon can also comprise minerogenic forms, like opal-A, favored by the supersaturation of silicic acid in soil solution (Cornelis et al., 2011).

In this context, the amorphous silicon pool will deserve a detailed explanation, because it will be of great interest for our research.

The liquid phase of silicon includes complexes with organic and inorganic compounds and the dissolved monomeric and polymeric silicic acid, the latter one being able to

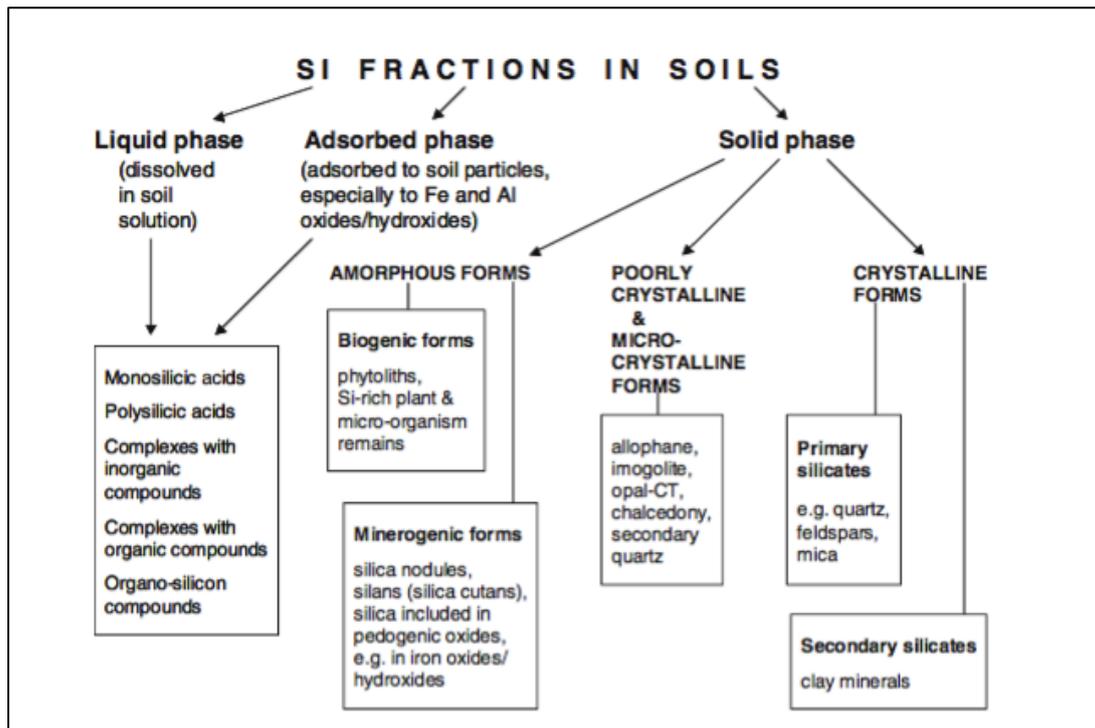


Figure 1: Silicon fractions in soils, taken from Sauer et. al. 2005, modified from Matichencov and Bocharnikova, 2001

create bonds between the soil particles, which improve soil aggregation and water holding capacity (Norton et al., 1984).

Si adsorption/desorption on various solid phases create another important pool for silicon. The amount, size and crystallinity of Fe-oxides and Al-hydroxides play an essential role, together with the pH values of the soil solution, in determining the rate of sorption of silicon to these soil colloids (Jones and Handreck, 1963). It is very difficult to estimate how strongly the adsorption of the soil colloids influences the solubility of silicon in soil solution. At high pH levels, silicic acid dissociates, changing into the anionic form $H_3SiO_4^-$, which is readily adsorbed by the Fe and Al hydrous oxides (Bowden et al., 1980). On the other hand, the relationship between pH value of the soil and Si solubility is usually positive (Fox et al., 1967) but as we just discussed, the adsorption contribution could reverse the trend.

The release process of silicon from the primary silicates is called desilication and it is caused by chemical weathering (White, 1995). Temperature, particle size, chemical composition and the presence of disrupted surface layer influence the mineral solubility (Drees et al., 1989). Humid tropical environments are characterized by higher desilication processes than temperate regions (Karathanasis, 2006) and two of the most diffused crops in the world (rice and sugarcane), mostly grow in the first type of environment. This factor could affect these two important crops and reduce the amount of up-taken silicon by the plants, with the following negative consequences for their growth performances.

1.4. Importance of phytoliths and impact of agriculture on their global cycle

Plants benefit from the accumulation of dissolved silicon, which deposits as solid amorphous silica in leaves, stems, roots and reproductive structures of plants (Kaufman et al, 1981). Once the plant dies and the litter deposits on the ground, the organic matter starts decomposing and silicon is released in the form of biogenic silica, which constitutes one of the main plant-available silicon pools in soils. It has been estimated that the main silicon transfer in soil happens between biomass and soil solution in a range from 1.7 to 5.6×10^{12} kg Si/yr globally (Conley, 2002). Many studies carried out in forested ecosystems, also show that high percentages (60-86%) of the silicon taken up by trees come directly from the phytogenic Si pool, but this strongly depends on the mineral weathering supply (Bartoli et al., 1983, Alexandre et al., 1997). Different anthropogenic soil uses can highly interfere with the silicon cycle: in arable soil, with modern agricultural techniques, a consistent amount of vegetation is periodically harvested, modifying in this way the BSi flux towards the soil. The rate of silicon removal from arable soils has been estimated worldwide, being between 210 and 224 million tons each year (Bazilevich et al., 1975, Savant et al., 1997). This high removal rate, which exceeds those of other important nutrients such as nitrogen, phosphorus and potassium (Tubana et al., 2016) is of great concern in terms of the sustainability of farming systems and its possible impacts on the global silicon cycle. The lower yields in rice production in many areas of the world could have been caused by depletion in plant-available silicon, followed by a too intense agricultural utilization of the land (Savant et al., 1997). Silicon fertilizer application could be required in the future to refurbish the soil solution of this important nutrient, since replenishment from mineral weathering in many soils can require longer periods of time (Tubana et al., 2016).

Forested lands are characterized by a continuous cycle of BSi. The vertical distribution of ASi concentrations in the soil profile shows similarities to that of organic carbon, with concentration peaks where plant litter material deposits and where roots grow. Similar pattern were observed in grazed forest and pasture soils, having however much lower (almost half) amounts of amorphous Si than continuous forest soils. On the contrary, arable soils show more evenly distributed ASi concentrations in the soil profile. The ASi concentrations in arable soils are lower than in pasture soils down to a soil profile depth of 0.1 m. Below this surface layer, the ASi concentrations in pasture soils largely decrease (Clymans et al., 2011).

1.5. Analytical methodologies to extract different silicon fractions from soil material and measurement approaches

As discussed in chapter 1.3, silicon is present in soil in different forms: from the solid fraction of the primary silicates to the dissolved one in the soil solution. In the past 50 years, many methodologies have been established to differentiate and quantify fractions of differential reactivity, and they are still being modified and improved (Sauer et al., 2006). Spectrometric methods of evaluation soon replaced the gravimetric approach, which required longer analysis time. The solubilization of silicon in the analyzed material is needed, in order to measure its amount in solution with the spectrometric methods. Possible substrates that can be investigated are: soil, plants and fertilizers. The total amount of silicon is generally obtained after fusion at high temperature with sodium hydroxide or other sodic bases (Snyder et al., 2001), but it is generally of little relevance for the plant-available fraction of silicon (Yanai et al., 2016). This is the most relevant for agriculture, because it determines if the field requires Si fertilization or not, therefore many chemical solutions have been used to extract the DSi fraction. Some are listed in Table 1, together with the extraction ratios, extraction time, the suggested critical level, below which a negative impact on crops may be expected and the references, where the extraction method is described in detail. Scientists from all over the world described and implemented these methods on different soil types and each of them is different in terms of extraction capacity, therefore a universal methodology to extract plant-available silicon has not been developed yet.

A solution of 0.01M CaCl_2 is considered as one of the weakest extractants for silicon after water (Sauer et al., 2005) and it showed a good correlation with sugar cane yield ($r^2=0.82$) in a comparison made by Haysom and Chapman (1975) between different extraction solutions, showing its capacity to quantify the plant available silicon concentration in soils. Both researches conducted by Berthelsen et al. (2003) and Miles et al. (2014) give evidence of the efficacy of the CaCl_2 extraction method in excluding the other non-plant available silicon fractions, compared to 0.005M and 0.02M H_2SO_4 and it has been recommended by Berthelsen et al. (2001,2005) as best single measure of silicon availability.

Extractant	Extraction ratio and period	Suggested critical level (mg/kg)	Reference
H ₂ O	1:10 for 4 h	< 0.90	Fox et al. (1967); Elawad et al. (1982)
0.01M CaCl ₂	1:10 for 16 h	< 20	Haysom and Chapman (1975); Berthelsen et al. (2003)
0.5M NH ₄ -Acetate (pH 4.8)	1:50 for 1 h	< 20	Fox et al. (1967)
0.5M Acetic acid	1:10 for 1 h	< 15	Snyder (1991)
0.18 Na Acetate (plus 0.87 M Acetic acid, pH 4.0)	1:10 for 5 h	< 60	Imaizumi and Yoshida (1958)
0.005M Sulfuric acid	1:200 for 16 h	< 100	Hurney (1973); Berthelsen (2003)
0.025M Sulfuric acid	1:10 for 20 min	< 40-70	Meyer and Keeping (2001); Kanamugire (2007)
0.04M Na ₂ HPO ₄ (pH 6.2)	1:10 for 24 h	< 200-300	Heinai and Saigusa (2006)

Table 1: Selected extractants with respective extraction ratio and extraction time, and the suggested critical levels of potentially plant available Si (Haynes, 2014)

Biermans and Baert (1977) developed another extraction procedure using a complexing agent, called Tiron. The full name of the chemical used by this group of scientists and by few others (Guntzer et al., 2010; Kendrick et al., 2004; Höhn et al., 2008) is *4,5-dihydroxy-1,3-benzene-disulfonic acid disodium salt*, C₆H₄Na₂O₈S₂. This substance is a nontoxic chelator of metals therefore it is used to reduce oxidative stresses in animal cells (Guntzer et al., 2010). The amorphous inorganic soil fraction targeted by the Biermans and Baert (1976) procedure is a mixture of silica and sesquioxides of iron and aluminum. They chose to use Tiron as extracting substance, because it could simultaneously increase the solution pH, which favors the silica solubilisation, and acts as a complexing agent that solubilizes the aluminum and iron oxides. Nevertheless, smectite dissolution was observed using this extraction method (Georgiadis et al., 2011), showing how the actual ability to extract amorphous silicon from soil is still not perfect and needs further development.

Guntzer et al. (2010) extended this type of extraction to plant material, because the phytoliths contained in the shoots are mainly composed by amorphous silica and they obtained promising results. They suggested that Tiron extraction of plant material is faster, safer and cheaper compared to other methods – electrothermal vaporization and high temperature lithium-metaborate digestion – and it allows a rapid extraction when dealing with many samples at the same time.

For our research, we also implemented an alkaline wet chemical dissolution technique for obtaining the amorphous silicon, because this fraction is solubilized at high pH levels. Furthermore, a surface process induces the dissolution of amorphous silica and it needs a catalyst, a hydroxyl ion, to happen. Silicic acid on the soil surface reacts

with the OH⁻ ions and produces silicate ions Si(OH)₅⁻ which are released into solution (Iler, 1979). The most utilized solution which provides the hydroxyl ions contains NaOH in various concentrations. Sodium carbonate (Na₂CO₃) solution is also widely used for amorphous silicon extraction but more often on aquatic sediments than on soil material (Sauer et al., 2006).

A well-known issue related to alkaline extraction is its low selectivity: clay minerals are also attacked to some extent by these extractants and the silicon contained in poorly ordered and crystalline minerals could be also included in the measurement, together with the amorphous fraction.

In a recent publication, Georgiadis et al. (2015) optimized the NaOH extraction, using several different substrates, temperature, soil:solution ratios and extraction times, with the aim to minimize the amount of silicon extracted from non-amorphous materials. We decided to follow Georgiadis' optimized method for determining the ASi fraction in our samples and the exact procedure will be described in detail in the *Material and methods* chapter.

2. Objectives and hypothesis

Given the relevance of silicon as a plant nutrient and in geochemical cycling, and the lack of information on the silicon status of Austrian soils, the purpose of our project was to quantify different silicon fractions in soil samples coming from the region Lower Austria in the northeastern part of Austria. As we had access to archived soil samples collected during the Austrian soil mapping campaign between the years 1986 and 2000, we re-sampled 95 sites to obtain information about the current silicon status and its change during the past 20-30 years. In this work, we addressed the following hypotheses:

- Hypothesis 1: As a consequence of silicon removal with harvest and the utilization of silicon-rich crop residues for non-food purposes (e.g. bio-refinery, biogas production), the amorphous silica content of the investigated soils has decreased considerably during the past 2-3 decades.
- Hypothesis 2: In line with hypothesis 1, the plant-available silicon measured in a CaCl_2 extract is currently below the suggested critical value for optimal plant growth and stress resilience in a substantial proportion of the analyzed soil samples. The proportion of potentially silicon-deficient soils has increased during the past 2-3 decades.
- Hypothesis 3: With advance of soil formation and weathering, amorphous silicon is accumulating in the soils. Therefore, soil groups characterized by little soil development (e.g. Leptosols) are likely to display lower amorphous silicon compared to more developed soils (e.g. Cambisols or Umbrisols).
- Hypothesis 4: Silicon fractionation in soil is the result of complex interactions between land use, climate and soil factors determining biological cycling, weathering, and leaching rates of silicon. Based soil pH, soil texture, organic matter, carbonate content, annual precipitation and mean annual temperature to be among the main controls of amorphous and plant-available silicon in soil. More specifically, we expect to find lower amorphous silicon concentrations in soils coming from colder and rainy areas, where the weathering rate is slow. Further we expect coarse soil texture to enhance leaching, slow down the weathering rate and to provide less surface area for silicon sorption, and therefore assume that amorphous silica concentrations will be higher in fine-textured soils. High carbonate contents in the parent material are expected to dilute the amount of amorphous silica while literature provides evidence for increasing concentrations of amorphous Si with increasing organic matter because of its relation to higher input of phytoliths from the vegetation. High soil pH should enhance silicon solubility and therefore the concentrations in the

CaCl₂-extractable fraction but the opposite trend is expected for amorphous silica as enhanced weathering is typically associated with a decrease in soil pH. Based on previous work (Clayman et al., 2011) we expect higher amorphous and plant-available silicon fractions in grassland compared to arable soils.

Archived soil samples and the corresponding re-sampled soils were obtained from 13 soil mapping areas of the Austrian soil map in Lower Austria (Figure 3):

- Retz (mapping area n.177);
- Laa an der Thaya Sud (213);
- Laa an der Thaya Nord (212);
- Eggenburg (171);
- Mödling (26);
- Schwechat (1);
- Scheibbs (178);
- St. Peter in der Au (163);
- Gaming (196);
- Lilienfeld (205);
- Gloggnitz (200);
- Aspang (192);
- Kirchberg an der Pielach (191).

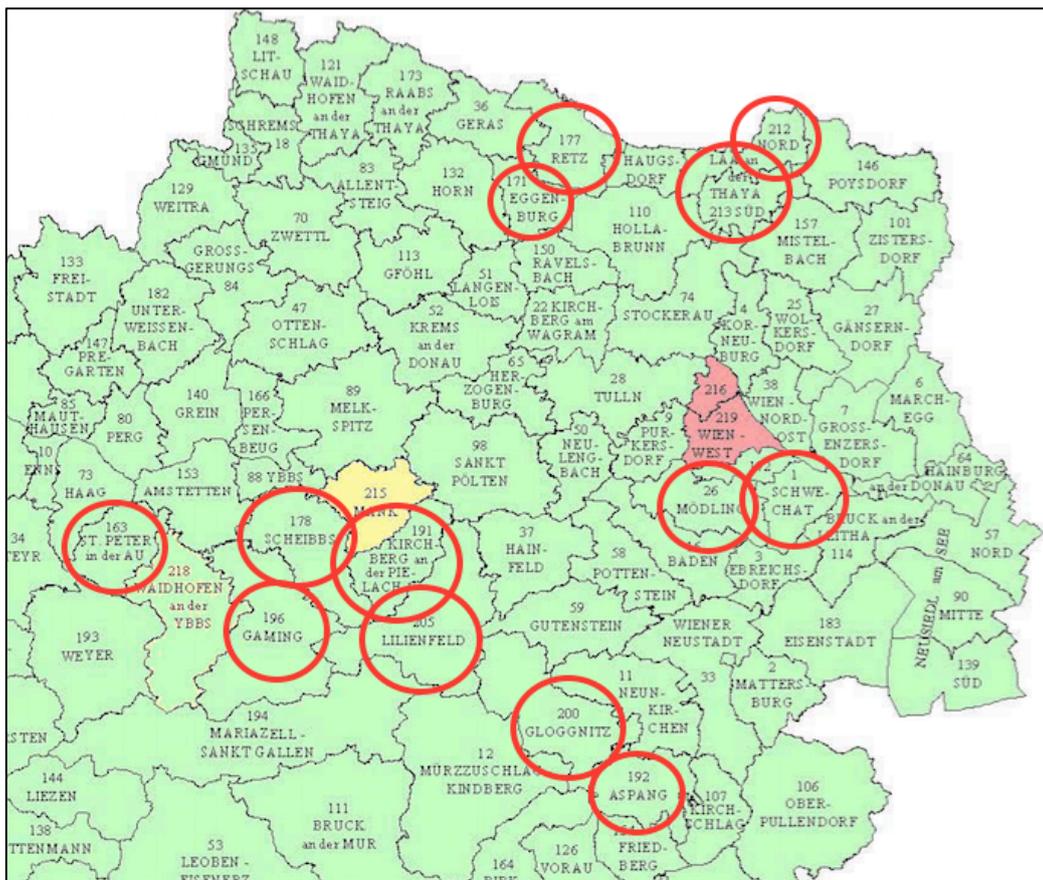


Figure 3: Soil mapping areas of Lower Austria. Mapping areas re-sampled in this study are indicated by red circles.

The selection of these specific districts was based on a list of soil samples provided by the Head of the *Institute for Land and Water Management Research*, Dr. Peter Strauss. The list contains the codes and the site information of more than 5000 soil samples, collected between the year 1986 and 2000. For most of the locations, several samples are available: one for each horizon of the profile. We selected for our sampling campaign only the sites for which the archived topsoil (A horizon) was available and we tried to collect at least three sites with the same soil type according to the Austrian soil classification system within each region. In four mapping areas, the latter condition could not be met.

We retrieved coordinates, current land use as well as site and soil descriptions along with analytical data for the archived soil samples from the online portal *eBOD* (<https://bfw.ac.at/rz/bfwcms2.web?dok=7066>). In Table A1 in the Annex, we provide for each soil the coordinates of the sampling site along with the classification according to IUSS Working Group WRB World Reference Base (2014) and the Austrian classification system.

Using as reference the Austrian soil classification system, the soil types that we selected were: Tschernosem, Auboden, Braunerde, Parabraunerde, Rendsina, Pararendsina, Felsbraunerde, Kolluvium, Feuchtschwarzerde, Kulturrehoboden, Gley, Hanggley, Pseudogley and Relikt-pseudogley. Using the soil description and analytical data we also classified the soils using the IUSS Working Group WRB (2014). Using this classification system, we obtained 8 different soil groups according to IUSS Working Group WRB (2014): Umbrisol, Cambisol, Phaeozem, Regosol, Stagnosol, Gleysol, Leptosol and Fluvisol.

In Figure 4, the number of collected samples for each soil mapping area is shown. The sampling campaign lasted for approximately 2 weeks between October and November 2015 and we collected 95 soil samples with 58 from arable land and 37 from grassland. Using a shovel, we collected between 5 to 7 kg of soil from the uppermost mineral horizon, which depth was indicated in the soil profile description in *eBOD*. We collected the soil in plastic bags and we brought them to our laboratory for further processing.

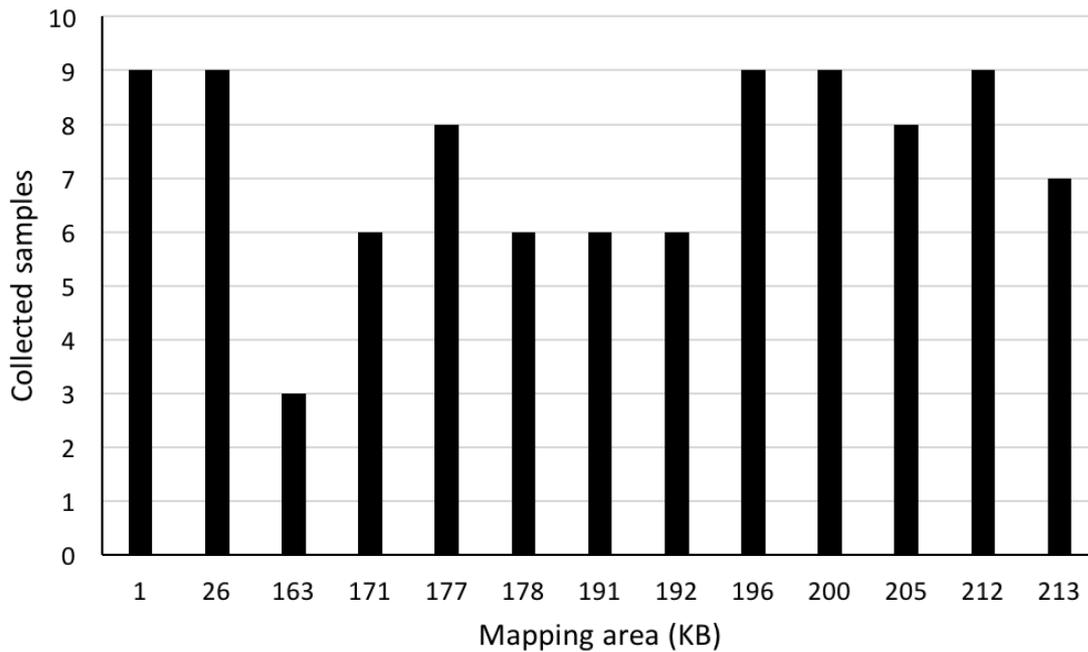


Figure 4: Number of collected soil samples for each soil mapping area

3.2. Determination of basic soil properties and climate conditions

An important part of our research was to evaluate relations between the silicon fractions, soil properties and climate conditions available for the archived samples through eBOD. These properties including soil texture, pH values, lime and organic matter content and the corresponding amounts for each soil sample are listed in Table A2 in the Annex. These properties had been measured during the Austrian soil mapping campaign of the *Bundesministerium für Land-und Forstwirtschaft* (Austrian Ministry of Land and Forestry), following the procedures as detailed below:

- The texture of the fine soil fraction (< 2mm mesh size) was determined through wet sieving, after destructing the soil crumbles with a dispersing agent containing tetrasodium pyrophosphate and after shaking. The particle's diameter intervals are defined as follows: <0.002 mm for clay, 0.002 - 0.06 mm for silt and 0.06 - 2 mm for sand;
- The organic matter content (humus) was measured using the Walkley – De Leenheer method, which oxidize through a wet combustion only the fraction of the organic substance which represents the humus;
- The lime content was measured using the volumetric method of Scheibler, which only gives information regarding the total content of carbonates, but not about their solubility or distribution;

- The pH measurement was conducted mixing the soil fine fraction in a solution of 1M KCl, at a ratio of 1:2.5. pH was measured electrometrically using a glass-electrode. To this end, 10 g of soil were mixed with 25 mL of 1M KCl for 2 hours in. After shaking gently and letting the soil deposit, we measured the pH in the KCl solution using a pH-meter (PROLAB 4000, Schott Instruments).

As we assumed that soil texture, lime and organic carbon content were relatively stable since the initial sampling, we only repeated the pH measurement in the re-sampled soils, using the same procedure as for the archived soils.

For each soil sampling, we retrieved the mean annual temperature (calculated using the annual means between 1981-2010) for the nearest climate station from the website www.zamg.ac.at (*Zentralanstalt für Meteorologie und Geodynamik* – Institute for Meteorology and Geodynamics).

The mean annual precipitation for the same period was obtained from an online portal of the *Bundesministerium für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft* (<http://ehyd.gv.at/>). As the data was reported for 6km x 6km grid areas we located our sampling sites and used the spatially averaged value of precipitation for the grid area in which they were included.

3.3. Soil preparation for analytical procedures

The soils were air-dried for 4 to 10 days, depending on the water content of the samples. We used a 2-mm sieve to separate the coarse fraction and the root material from the fine earth fraction and we stored approximately 1kg of sieved soil in plastic bags for each sample. We measured the water content of each soil sample by drying an aliquot of air-dried soil at 105°C for 20 to 24 hours. We calculated the water content as the ratio between the lost weigh during drying and the final dry amount of soil.

The archived soil samples were provided in air-dry, sieved (<2 mm) condition and stored in plastic boxes. A preliminary check of the water content of these samples showed negligible amount (<1.5%), therefore we considered these samples as completely dry for the extraction step.

3.4. Preliminary work for method implementation

We conducted three extraction procedures throughout the experiment development:

- Calcium Chloride (0.01M);
- Tiron (0.01M);
- Sodium Hydroxide (0.2M).

Several preliminary trials were conducted, before we could consider the extraction methods and the measurements reliable. Many analytical details were missing in the literature of reference, especially regarding the filtration steps. For both CaCl_2 and Tiron extraction, we compared 3 different techniques, using paper filter (Munktell Ahlstrom, grade:14/N), with and without a second filtration through syringe filters ($45\mu\text{m}$) (Beckton Dickinson BD discardit, PP/PE, 20 mL) and centrifugation (*Thermo Scientific Heraeus Multifuge X3R*, with a radius of 9.8cm) at 5000 rpm ($2739 \times g$) for 10 min + syringe filtration.

The results did not show any significant difference according to the ANOVA tests ($p=0.97$ for CaCl_2 samples and $p=18$ for Tiron) performed on the three groups of results obtained using different filtration/separation techniques and we decided to proceed using paper filters, which simplifies the work, when measuring a large number of samples.

Encouraged by the information found in the literature, we applied Tiron extraction to our soils, following the method modified by Kodama et al. (1991).

The solution was prepared dissolving 31.42g of Tiron (*Merck KGaA*, $M=332.22 \text{ g/mol}$) in 800mL high quality water (TKA Genpure water system - ThermoFisher, type: 08.2205, 90L/h Performance) – the reference pointed out that the pH would become acidic (5.5) at that point, but we measured higher values (7.5).

An aliquot of 5.3g of anhydrous Na_2CO_3 (*Merck KGaA*, $M=105.99 \text{ g/mol}$) dissolved in 100mL H_2O was then mixed to the Tiron solution while stirring. For adjusting the pH value to 10.5, we added increments of 4M NaOH and more water was added to reach the final volume of 1L.

For extraction, 30 mL of final Tiron solution was added to 25 mg ground ($<0.180 \text{ mm}$; Retsch MM2 ball mill) soil material placed in 50-mL acid washed polyethylene tubes, and shaken in a water bath for 1 hour at 80°C (Kodama et al., 1991). All extractions were done in duplicate. Throughout all the experiment's steps we only used polypropylene and polyethylene material and no glassware, in order to avoid silicon release in the Tiron solution.

The initial analysis outcome showed realistic and quite encouraging results: the calibration curve obtained after measuring with ICP-OES was linear and the silicon concentration in the blank Tiron solution was close to zero. The concentrations of silicon ranged between 1.73 and 4.38 g/kg, which is a similar interval to the one reported by Höhn et al. (2008): 0.68 to 2.38 g/kg.

The measured silicon concentrations using ICP-OES were not stable within the same series of analysis and even when measuring the same sample multiple times, the error

values between the results were too high to consider the outcome as valid. The silicon single standard Tiron solutions showed the same instability.

We attempted to solve the problem with different approaches: we destroyed the Tiron matrix, as suggested by Kodama et al. (1991), by adding 30% H₂O₂, and in other two trials, we did not add any nitric acid but an internal Yttrium single standard. Our last trial implied the substitution of the measuring device, as we will explain in detail in the next paragraph. As we did not see any improvement, we decided to replace Tiron solution by NaOH to extract amorphous Si.

3.4.1. Testing analytical procedures

At the beginning of our study, we decided to perform all measurements using the ICP-OES (*Inductively Coupled Plasma – Optical Emission Spectrometry, Perkin Elmer - Optima 8300*) for both CaCl₂ and Tiron extracts. The Si standards showed a linear calibration curve and the measured Si concentrations in CaCl₂ soil extracts were initially consistent, but then we encountered similar problems as described for Tiron solution. In the same period, we conducted the measurement of the archived soil CaCl₂ extracts and the Si concentrations were lower than for the re-sampled soils, which was completely against our predictions.

To overcome these measurement difficulties, we decided to measure silicon in the extracts using a *Varian DMS 200 UV visible spectrophotometer* (Blecker et al., 2006; Wang et al, (1986); Smith et al., (1984)). The measurement is performed after applying a *colorimetric molybdate procedure*, which is described in paragraph 3.5.

There was no sign of blue color, given by the molybdate, in the yellow Tiron matrix and in fact, the absorbance values measured with the spectrophotometer were always equal to zero. After we started to implement the molybdate colorimetric procedure to our Tiron solution extracts, we verified if the results of the CaCl₂ extracts, obtained with the ICP-OES were reliable and we repeated the measurement of some of them, using the *UV visible spectrophotometer*. As expected, the Si concentrations in the archived samples were lower than obtained with the ICP-OES.

We repeated all the CaCl₂ extracts measurement and we used it also for measuring silicon in the NaOH extracts.

3.5. Soil extraction procedures

3.5.1. 0.01M CaCl₂ extraction (Haysom and Chapman, 1975)

We used acid washed 50-mL centrifuge vials, in which we mixed 2g of sieved fresh soil with 20mL of 0.01M CaCl₂ (Merck KGaA, CaCl₂*2H₂O, M=147.01g/mol). The recently collected samples, which were air dried, still contained a relevant amount of water (mean water content: 5.8%) relative to oven-dry (105°C) conditions. Therefore, we added the weight of fresh soil, equivalent to the water contained in each sample. In this way, we could obtain the correct 2 grams of dry soil, prescribed by the procedure.

We placed these vials for 16 hours (over night) in an end-over-end shaker at a speed of 22 rpm. As described in chapter 3.3, we filtered using paper filters (14/N) and we stored the filtered solution in the fridge (4 °C), until we measured the silicon concentration using the Varian DMS 200 UV visible spectrophotometer after colorimetric procedure described in chapter 3.6.

We extracted both our archived and re-sampled soil samples in duplicates.

3.5.2. 0.2M NaOH extraction

We weighed 25mg of ground air dried soil (< 0.180 mm, Retsch ball mill MM2) adding an aliquot of soil with equivalent weight of the water contained in the 25 mg. We used 50mL plastic vials and we added the corresponding 0.2M NaOH (Merck KGaA, M=40 g/mol, pure) solution volume, in order to reach a soil (dry weigh):solution ratio of 1:400 (10mL). As we did for the CaCl₂ extraction, we considered the soil water content, only for the *new* soil samples and not for the *archived* ones.

After 120 hours of end-over-end shacking at 4rpm, we centrifuged the vials at 3000 rpm (986 x g) for 5 minutes and we filtered the supernatant with paper filters (Munktell Ahlstrom, grade:14/N).

We measured the silicon concentration using the *UV visible spectrophotometer*.

3.6. Colorimetric method

The solutions used for the colorimetric procedure were prepared following the instructions given by Morrison et al. (1963):

- Acidified molybdate solution: 89g of ammonium molybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ in 800 mL H_2O + 62 mL of 98% sulfuric acid in 100 mL of H_2O + H_2O to 1L total solution;
- Tartaric acid solution: 28% w/v;
- Reducing agent solution: 2.4g of sodium sulphite $\text{Na}_2\text{SO}_3\cdot 7\text{H}_2\text{O}$ + 0.2g of 1-amino-2-naphthol-4-sulphonic acid in 70 mL H_2O + 14g of potassium metabisulfite in 30mL H_2O .

We prepared 10mL solution for each extract:

- 0.2 mL extract;
- 8 mL water;
- 0.5 mL acidified molybdate solution;
- after 10 min., 0.5 mL tartaric acid;
- after 5 min., 0.25 mL reducing agent solution.

After each of the previous step, we gently mixed the 20mL tube in which we prepared the solution and we let it rest for one hour before measuring with the Varian DMS 200 UV visible spectrophotometer, using a flow through cuvette and a wavelength of 810 nm.

We used a silicon single standard to spike the solutions with different concentrations: 0.5, 1, 2, 5, 10 and 15 mg Si/L in 0.2M NaOH and 0.5, 2, 4, 6, 8, 10 mg Si/L in 0.01M CaCl_2 .

The final concentrations expressed in mg Si/L were converted to mg Si/kg of oven-dry soil (105°C), for both plant available Si and amorphous Si concentrations.

3.7. Statistics

We performed the statistical analysis using the software *IBM Statistics SPSS, Version 24*, with $p=0.05$. Descriptive statistics (minimum, maximum, mean, median, standard deviation, skewness and kurtosis) were employed to explore the CaCl_2 and NaOH – extractable Si concentrations, for both archived and re-sampled soils. Histograms of frequency distributions of the Si concentrations were produced using *Microsoft Office Excel*.

For evaluating a potential difference in NaOH and CaCl_2 -extractable Si between archived and re-sampled soils and between arable and grassland soils, either a parametric or a non-parametric test could be performed. In order to understand which test would be suitable, we tested our data for normal distribution using a Shapiro-Wilk

test, which confirms the null-hypothesis of normal distribution with values of significance $p > 0.05$.

The distributions of both archived and re-sampled CaCl_2 -extractable Si concentrations are not normal, according to the Shapiro-Wilk test, with values of significance respectively of 0.003 and 0, respectively. Therefore, a non-parametric Mann-Whitney u-test was performed to verify if a significant difference (with significance level $p = 0.05$) between the two groups of values exists.

We isolated the arable and grassland soil groups within the re-sampled and archived soils and presented the same descriptive statistics conducted in the previous analysis. The inspection of a possible significant difference in Si concentration between the two soil uses (arable versus grassland) was done with either a t-test or a Mann-Whitney u-test, after having checked the assumption of normality. The distributions of the arable soils Si concentrations (in both archived and re-sampled soils) are normal, with values of significance of 0.6 and 0.06. CaCl_2 -extractable Si of grassland soils in archived and re-sampled soils has a not normal distribution, with values of significance of 0. All comparisons were conducted using a Mann-Whitney u-test, except for the two groups of values which showed a normal distribution: a t-test was performed to check for temporal differences in Si concentrations within arable soils.

Both archived and re-sampled soils for NaOH- extractable Si rejected the null-hypothesis of normality with values of significance respectively of 0.02 and 0.01. A nonparametric Mann-Whitney u-test was therefore performed on these data.

Both arable and grassland Si concentration distributions for the archived soils show a normal distribution, according to the Shapiro-Wilk test, with values of significance of 0.08 and 0.16. A parametric t-test was performed to compare the mean values of these two groups.

Regarding the re-sampled soils, the arable soils Si distribution rejected the assumption of normality ($p = 0.04$), while it was confirmed for the grassland soils ($p = 0.049$). In this case, we performed a non-parametric Mann-Whitney u-test.

For both comparisons within the two soil use's groups, between archived and re-sampled soils' Si concentrations, we conducted a Mann-Whitney u test.

3.7.1. Multiple regression analysis with environmental parameters and soil properties as determining factors for soil silicon fractions

We applied a standard multiple regression model to quantify how much unique variance in the dependent variable each of the independent variable explains. The two explanatory dependent variables were the silicon concentrations, obtained with the CaCl_2 and NaOH extraction methods applied on the archived soil samples. The continuous independent available variables that we included in the analysis are nine

and they are described in detail in chapter 3.2: 2 are related to climate conditions (precipitation and temperature values), 6 describing soil texture and chemical-physical properties of the soil (pH, lime and organic matter content) and one categorical variable defining the soil use.

We had a total number of 95 observations. We associated to each observation the Si concentrations, soil properties and climate factors of the specific site, from where the analyzed soil was collected. We divided the observations into two groups, separating the calcareous soils from the non-calcareous soils, in order to have a better estimation of the influence of the lime content and the pH values on the Si concentrations. The non-calcareous observations are 40 and the calcareous are 55. The lime content variable was not included in the regression analysis for the non-calcareous soils.

The accuracy of the model depends on how well a series of preliminary assumptions related to the analyzed variables are met.

The redundancy of the independent variables is an important factor to take into consideration as one of the preliminary assumption. We found that the dependent variables were not only directly correlated with the silicon contents, but a significant multicollinearity between them also occurred.

A co-linearity diagnostic was performed by SPSS, which reports values of *tolerance* and *VIF (Variance Inflation Factor)* for each included variable in the model.

Other conditions for obtaining a good multiple regression analysis, once this is performed, is to examine whether the errors between the observed and the fitted values of the response variable have the same variance (homoscedasticity), are normally distributed, if the relation between each dependent and independent variable is linear and if significant outliers are present.

We performed the analysis, including in the regression the variables which showed a normal distribution and passed the Wilk-Shapiro test with significance $p > 0.05$. For the variables which showed a non-normal distribution, we either applied a log or a square transformation and we included the normally distributed transformed variables in the analysis.

For the non-calcareous soils, we applied a square transformation to the dependent variable NaOH-extractable Si concentrations and a log transformation to the CaCl₂-extractable Si concentration. The independent variables included in the regression were clay content, pH and organic matter. The variables precipitation, temperature and sand were not included, because they were not normally distributed, and the variables silt and soil use were excluded because they did not contribute significantly to the model (significance level $p = 0.05$).

The assumptions of linearity, homoscedasticity and normal distribution of the errors were confirmed, after visual inspection of the plot-studentized residuals against

standardized predicted values and the partial regression plots. No evidence of multicollinearity was detected, having tolerance values <0.1 , but one leverage value with >0.2 was found and the corresponding observation deleted (sample n. 48).

The same procedures were followed for the squared NaOH-extractable Si concentrations as dependent variable.

Several variable transformations were performed only for the calcareous soils: the NaOH-extractable Si concentrations were squared and the same transformation was applied to the lime content variable. A log transformation was applied to sand and organic matter content. Precipitation, temperature and pH were excluded because did not show a normal distribution. Clay and soil use did not contribute significantly to the model and we left them out of the model.

The transformed variables lime, sand and organic matter and the variable silt were initially included as independent variables to predict CaCl_2 -extractable Si concentrations. The same variables, except for silt, which was not significantly contributing to the model, were included to predict the transformed NaOH-extractable Si. The assumptions were positively tested. One leverage value was >0.2 and the relative observation was excluded from the analysis (sample n. 50). After the exclusion of this observation, the squared transformed lime variable didn't show any more a significant contribution to the model predicting the CaCl_2 -extractable Si and this is the reason why we didn't include this variable in the analysis.

4. Results and discussion

4.1. Current state and temporal changes of potentially plant-available silicon

The general descriptive statistics of the 0.01M CaCl₂-extractable Si data are summarized in Table 2.

	<i>Archived soils (n=95)</i>	<i>Re- sampled soils (n=95)</i>
	(mg/kg)	(mg/kg)
Min	3.8	5.2
Max	69.7	79.6
Mean	27.5	24.8
Median	29	20.5
SD	16	15.3
Skewness	0.4	1.2
Kurtosis	-0.7	1.2

Table 2: General descriptive statistics (minimum, maximum, mean, median, standard deviation, skewness and kurtosis) of CaCl₂-extractable Si concentrations of archived and re-sampled soils.

Figures 5 and 6 show the frequency distributions for both sampling times, indicating a peak at 20 mg Si/kg in the re-sampled soils which is not present in the archived soils, which show higher abundance in the interval between 30 and 40 mg Si/kg.

Using the entire dataset, a Mann Whitney u-test was run to determine if there were differences in Si concentrations between archived and re-sampled soils. Median score for archived (29 mg Si/kg) and re-sampled soils (20.5 mg Si/kg) was not statistically significantly different, $U=4084.5$, $Z=-1.1$, $p=0.3$.

We also run an independent samples t-test to identify if a significant decrease in plant-available silicon could be detected within the subgroup of the arable soils. The average Si concentration in re-sampled soils (30.6 mg/kg) were lower than in archived soils (33.8 mg/kg), but not statistically significant ($p=0.3$). A Mann-Whitney test run for the subgroup of the grassland soils revealed that the median score was not statistically significant between archived and re-sampled soils ($U=660$, $z=-0.27$, $p=0.8$).

If we consider the individual sampling sites, a decrease in CaCl₂-extractable Si over the past 2-3 decades occurred in 57 sites out of 95 and within this group of samples, CaCl₂-extractable Si concentrations decreased on average by 8.5 mg/kg. A t-test applied to this sub-group showed a significant difference ($p=0.001$) between the

archived and re-sampled soils. A Mann-Whitney test applied to the remaining 38 samples for which there was an increase in Si concentrations, did not indicate a significant difference ($U=540$, $Z=-1.89$, $p=0.059$).

The archived soil samples having plant available Si concentrations below the critical value for plant-available Si (20 mg/kg) were 39% of the total number. This percentage increased in the re-sampled soil samples, reaching a value of 47%.

Our results confirm Hypothesis 2 in terms of our expectation of a substantial proportion of soil displaying plant-available silicon concentrations below the critical value. However, the expected decrease of plant-available silicon during the past 2-3 decades was not statistically significant for the averages of the entire dataset and those of the subgroups arable and grassland soils. If considering only the subset of soils with decreased plant-available silicon concentrations, this decrease becomes significant.

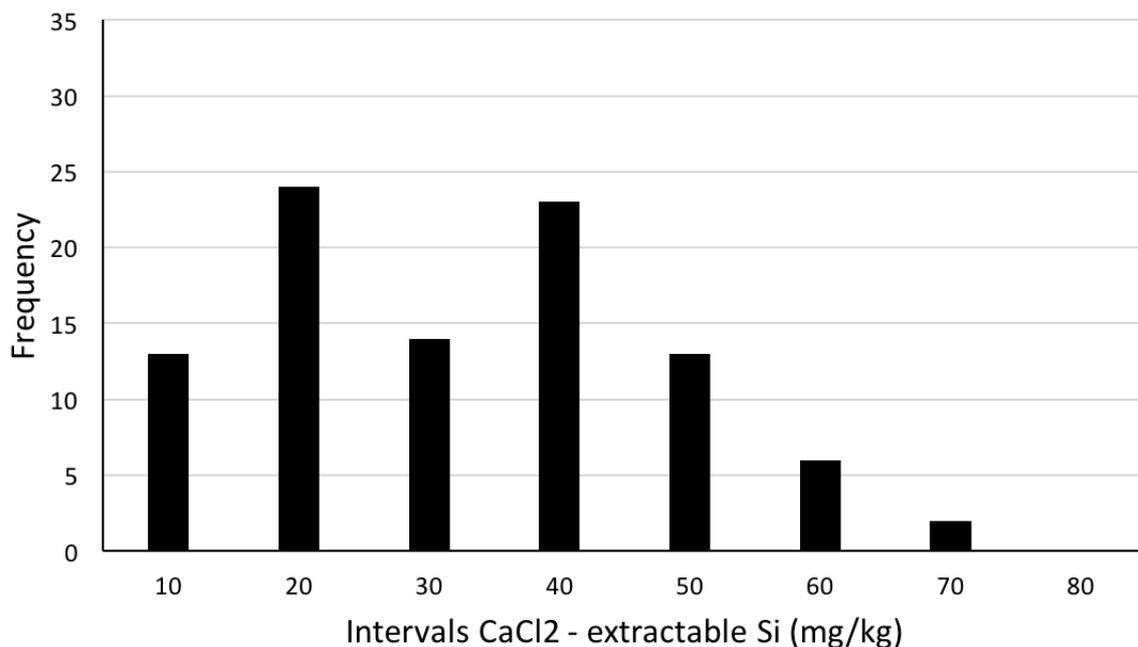


Figure 5: Frequency distribution of CaCl₂-extractable Si concentrations in archived soil samples

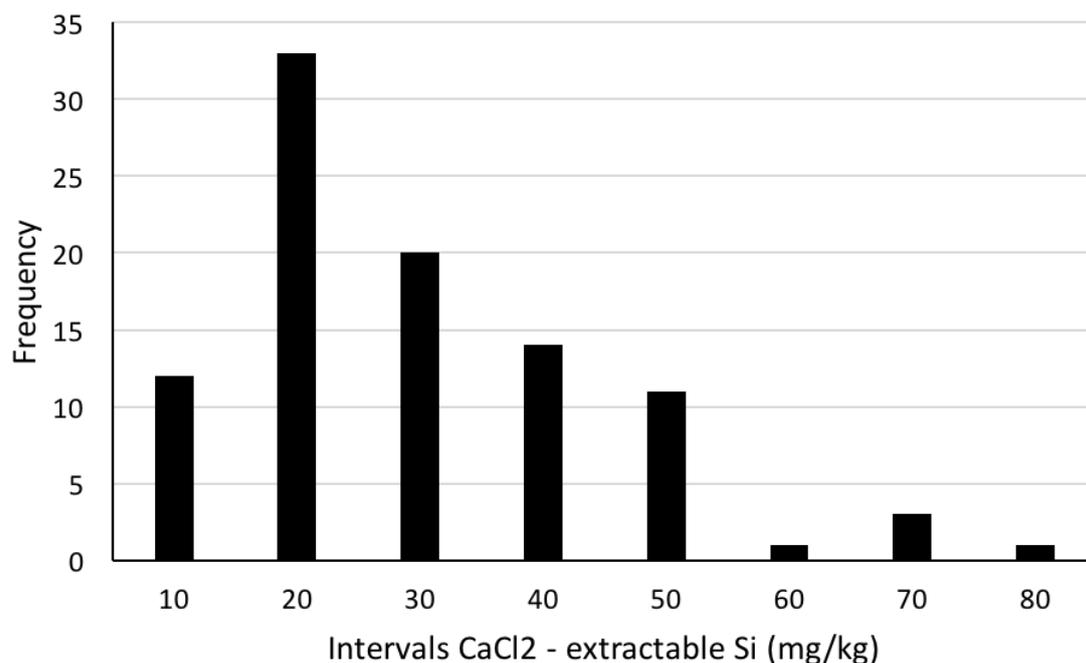


Figure 6: Frequency distribution of CaCl₂-extractable Si concentrations in re-sampled soil samples

4.2. Effect of principal type of land use on plant available Si concentrations

According to Hypothesis 4 we expected smaller concentrations of plant-available silicon in arable as compared to grassland soils. Our results for both archived and re-sampled soils showed the opposite trend. As both distributions of Si concentrations in the archived and re-sampled grassland soils are not normal, we performed Mann-Whitney u-tests on each of the datasets. Within both archived ($U=451$, $z=-4.7$, $p=0$) and re-sampled soils ($U=438$, $z=-4.8$, $p=0$), the median scores were statistically significant between arable and grassland soils. The descriptive statistics for archived and re-sampled soils and further divided between different soil uses is shown in Table 3.

We considered the soil use as a determining effect on the amount of plant-available silicon in soil and in fact we found a significant difference between arable and grassland soils Si concentrations. We must indeed consider that the soil use may not only directly affect plant-available silicon in soil but also through other factors that correlate with the distribution of land use. Most of the grassland soil samples were located in the rainy, hilly southern regions of Lower Austria, had on average lower soil pH but larger organic matter content as compared to the arable soils that are mostly located in the northern, flat and drier areas. Table 3A (Annex) indeed reveals that the mean annual precipitation of the sampling sites under grassland was almost double

(1325 mm) than that of the arable sites (649 mm), the double amount of organic matter (59 g/kg as compared to 28 g/kg) and lower pH (6.96 versus 6.03, archived samples). We conclude that enhanced leaching, dilution with organic matter and immobilization of silicon at lower pH may at least partly explain the smaller concentrations of plant-available silicon in grassland soils.

	<i>Archived soils (n=95)</i>		<i>Re-sampled soils (n=95)</i>	
	<i>Arable soils (n=58)</i>	<i>Grassland soils (n=37)</i>	<i>Arable soils (n=58)</i>	<i>Grassland soils (n=37)</i>
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Min	3.8	3.8	5.2	5.5
Max	69.7	55.2	79.6	35.7
Mean	33.8	17.6	30.6	15.7
Median	34	13.3	29.9	14.2
SD	15	11.9	16.4	6.8
Skewness	-0.1	1.4	0.7	1.3
Kurtosis	-0.2	1.6	0.4	2

Table 3: General descriptive statistics (minimum, maximum, mean, median, standard deviation, skewness and kurtosis) of CaCl₂-extractable Si concentrations in archived and re-sampled soils, with further subdivision in arable and grassland soil use.

4.3. Current state and temporal changes of the amorphous silicon fraction

The descriptive statistics of NaOH-extractable (amorphous) Si concentrations in both archived and re-sampled soils is reported in Table 4. Figures 7 and 8 are showing the frequency distributions which are both characterized by a positive skewness.

The amount of silicon extracted with the 0.2M NaOH solution is approximately 100 times higher than the silicon extracted with the CaCl₂. Georgiadis et al. (2013) reported NaOH-extractable (amorphous) silicon concentrations in a range between 1510 mg/kg and 3720 mg/kg in different topsoils (A horizons). Before performing the NaOH extraction, they removed the mobile Si (extracted by CaCl₂ solution), adsorbed Si (extracted by acetic acid), Si in soil organic matter (released by H₂O₂) and Si in pedogenic oxides (released by NH₄-oxalate under UV radiation). Our results are shown in Table 4 and they vary between 142 mg/kg and 7430 mg/kg. The mean Si concentration is 3036 mg/kg oven-dry soil (105°C). As in contrast to Georgiadis et al.

(2013) we did not remove Si with the first three extraction steps of their procedure, our results are only indicative of the amorphous Si content, but considering the average Si concentrations reported by Georgiadis et al. (2014) for each of the previous fractions, the amorphous Si is 5 to 20 times higher than their sum reported for A horizons, providing evidence that our results are only marginally biased

	<i>Archived soils (n=95)</i>	<i>Re- sampled soils (n=95)</i>
	(mg/kg)	(mg/kg)
Min	142	265
Max	7430	6688
Mean	3160	2912
Median	2734	2624
SD	1587	1516
Skewness	0.58	0.62
Kurtosis	-0.09	-0.14

Table 4: General descriptive statistics (minimum, maximum, mean, median, standard deviation, skewness and kurtosis) of NaOH-extractable Si concentrations in archived and re-sampled soils

A Mann-Whitney u-test was performed on archived and re-sampled soil did not show any significant temporal difference ($p=0.29$).

We isolated the arable and the grassland soils and checked again if a temporal difference in Si concentrations could be detected by Mann-Whitney u-tests. The u-tests showed no significant temporal change in amorphous Si concentrations in arable ($p=0.5$) and grassland soils ($p=0.5$).

We assumed (Hypothesis 1) that in particular arable soils would be subjected to Si depletion, because of the removal of crops with harvest and utilization of crop residues for non-food purposes. The absence of a significant temporal difference seems to exclude a relevant impact of recent agricultural practices on the amorphous silicon fraction in Lower Austrian soils. We must although consider that the fraction that we extracted does not only include the biogenic Si, but primarily consists of minerogenic Si. According to Georgiadis et al. (2014), the minerogenic Si concentration can be up to 25 times higher than the biogenic fraction and this prevalence makes the detection of a possible decrease in biogenic Si difficult without further refinement of the analytical approach.

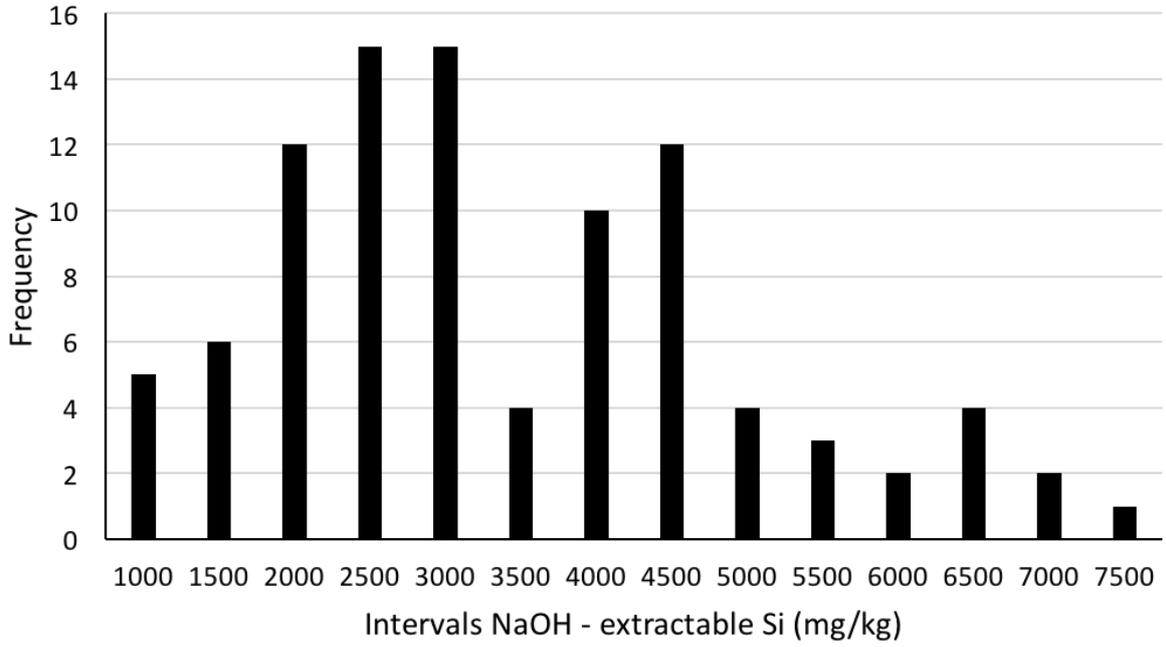


Figure 7: Frequency distribution of NaOH-extractable (amorphous) Si values in archived soils

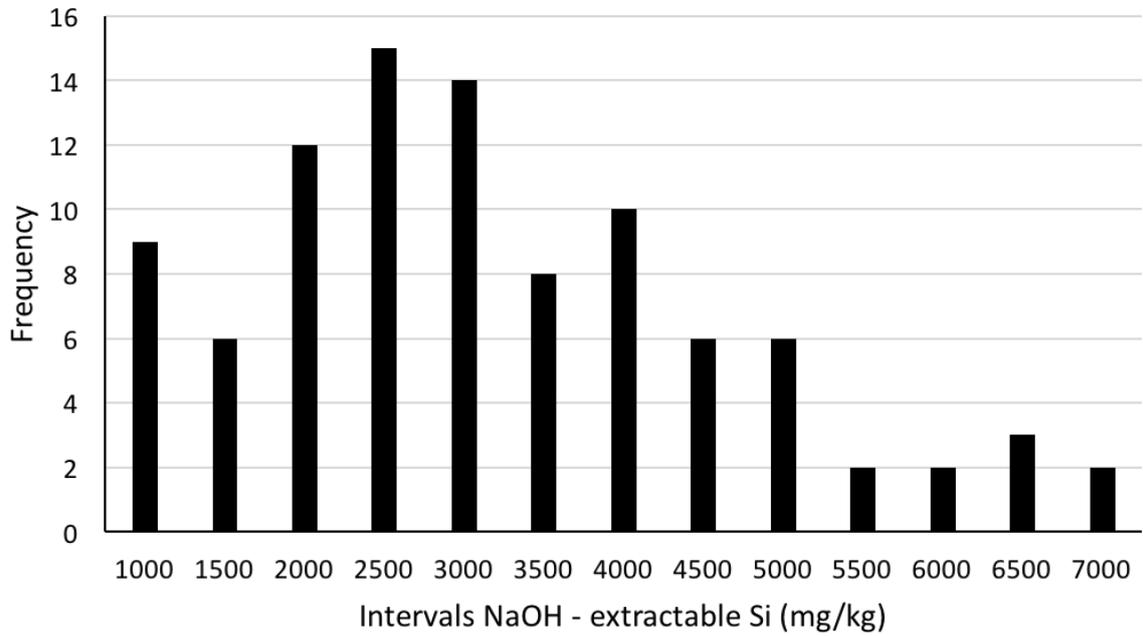


Figure 8: Frequency distribution of NaOH-extractable (amorphous) Si concentrations in re-sampled soils

4.4. Principal type of land use as determining factor for amorphous Si concentrations differences

	<i>Archived soils (n=95)</i>		<i>Re-sampled soils (n=95)</i>	
	<i>Arable soils (n=58)</i>	<i>Grassland soils (n=37)</i>	<i>Arable soils (n=58)</i>	<i>Grassland soils (n=37)</i>
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Min	142	355	265	612
Max	7430	6499	6594	6688
Mean	3231	3049	2983	2803
Median	2803	2666	2773	2562
SD	1614	1560	1429	1657
Skewness	0.6	0.55	0.71	0.6
Kurtosis	0	-0.16	0.27	-0.47

Table 5: General descriptive statistics (minimum, maximum, mean, median, standard deviation, skewness and kurtosis) of NaOH-extractable Si conc. in archived and re-sampled soils, with further subdivision in arable and grassland soil use.

In Table 5 the descriptive statistics of amorphous Si concentrations in archived and re-sampled soils is shown divided by soil use. After confirming the equality of the variances according to Levene's test ($p=0.68$), the t-test used to compare the means of the amorphous Si concentrations in arable and grassland soils showed no significant difference within archived soils ($p=0.59$) and re-sampled soils ($p=0.41$) respectively.

According to hypothesis 4, we expected to find higher concentrations of amorphous Si in grassland than in arable soils, but we observed no significant difference between the two soil uses.

4.5. Soil Si concentrations and soil groups

In Table 4A in the Annex, the average silicon concentrations for each soil group are presented separately for sampling times and soil uses.

The average amorphous Si concentrations in each soil group are increasing following this order: Fluvisol < Leptosol < Regosol < Phaeozem < Cambisol < Umbrisol. The degree of development for each soil group, follows the same increasing order, explaining the reason why soil groups like the more weathered Cambisols and Umbrisols contain more amorphous Si than the recently formed Fluvisols and Leptosols.

The increasing amorphous Si concentrations from little to moderate developed soils is reflected in the plant-available Si concentrations. Leptosols, Fluvisol, Regosols and Phaeozem have a similar trend in terms of plant-available Si concentrations. On the contrary, Cambisols and Umbrisols contain much less, even though their amorphous Si pools are the most abundant.

Umbrisols are soils which have a high accumulation of organic matter in the mineral topsoil, they are non-calcareous soils and pH and clay content are generally low, compared to other soil groups (Table 5A in the Annex). This is reflected in the low average plant-available silicon concentration: 7 mg/kg for the re-sampled samples and 5.4 mg/kg for the archived samples. The Cambisols, which are defined as moderately developed soils have the following CaCl₂- extractable Si concentrations: 17.6 mg/kg for the re-sampled soils and 19.5 mg/kg for the archived samples. Cambisols are also characterized by relatively low pH values but they have a high clay content. The acidic pH values may have played a more important role than the soil development, in Umbrisols and Cambisols, explaining their low plant-available Si concentrations.

It is interesting to note that in Leptosols and Stagnosols the mean value of soil pH decreased consistently with time. This pH change is clearly reflected in the plant-available silicon concentrations in both the Leptosols (from 29.7 mg/kg to 10.1 mg/kg), and the Stagnosols (from 19 mg/kg to 12.4 mg/kg).

The Phaeozem, Regosols and Gleysols have all similar characteristics: pH values ranging between 6 and 7, almost the same texture with a high clay fraction and similar organic matter content. Consequently, both the NaOH and CaCl₂ extractable silicon concentrations are within the same range and have similar medians (Figure 9 and 10). For these soil groups, and the Cambisols, the largest number of observations is available. The main relevant distinction of the latter four soil groups is the significant difference in plant available silicon between different soil uses: for the soil groups for which we have more observations (83 out of 95 soils are included in these 4 groups), the grassland soils consistently have a lower mean value of plant-available silicon than

the arable soils. As discussed in section 4.2.3, this difference is probably not caused directly by the soil use but rather influenced by the different pH values.

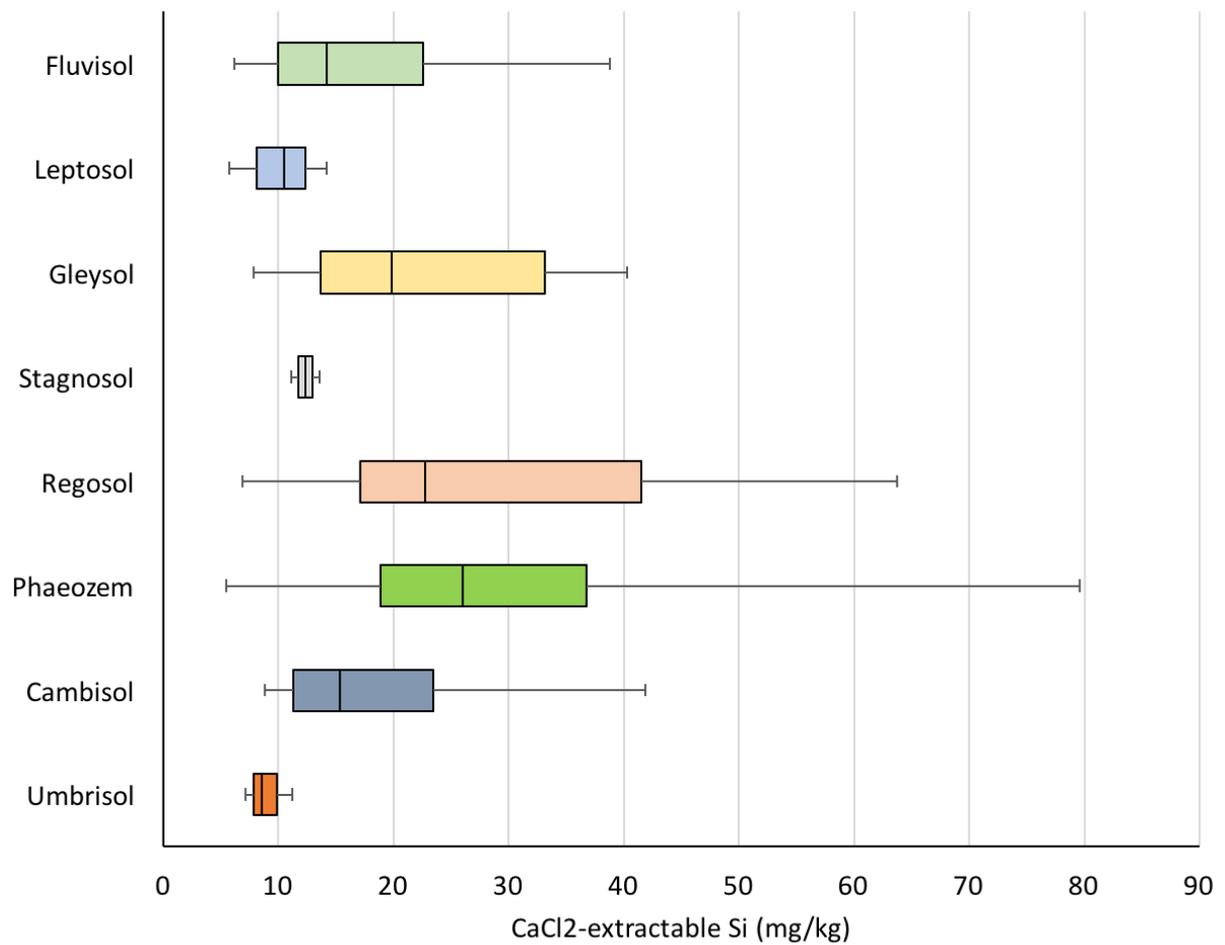


Figure 9: Boxplots of the CaCl₂- extractable Si concentrations in different soil groups

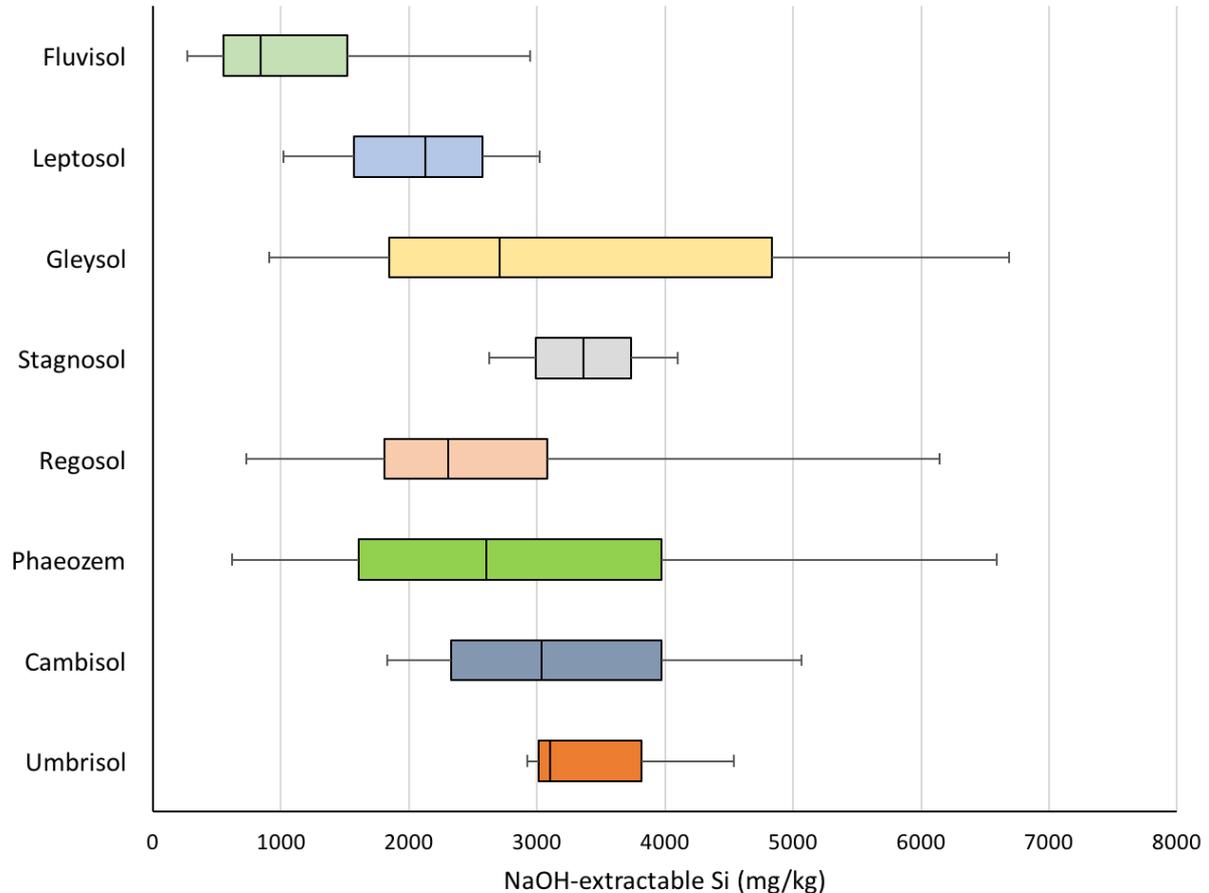


Figure 10: Boxplots of the NaOH- extractable Si concentrations in different soil groups

4.6. Analysis on environmental parameters and soil properties as determining factors for soil silicon fractions

The purpose of this chapter is to assess how selected environmental parameters and soil properties influence the amount of silicon (amorphous and plant available) present in our soil samples. In chapter 3.7.1., we described the statistical approach which will help us defining the existing relationships between the variables and verify our hypothesis. In the following chapters, we will report our considerations.

4.6.1. Multiple regression analysis results – Non-calcareous soils

A multiple regression model was run to predict CaCl_2 - extractable Si and NaOH-extractable Si concentrations from clay (g/kg), pH values and organic matter content (g/kg), when considering only the non-calcareous soil samples.

Starting with the CaCl_2 -extractable Si concentrations as dependent variable, we found that the R^2 for the overall model is 81.8% and the adjusted R^2 is 80.3%. Clay, pH and

organic matter content statistically significantly predict CaCl₂-extractable Si concentrations (F(3,35)=52.54, with p<0.0005), which is below our set significance level p=0.05.

We formulated the following equation, associating the unstandardized B coefficients to each variable:

$$\text{PREDICTED log(CaCl}_2\text{_{Si})} = -0.32 + (0.24) * pH + (0.002) * CLAY + (-0.005) * OM$$

Unstandardized coefficients indicate how much the dependent variables vary with an independent variable, when all other independent variables are held constant.

The overall model produced using as dependent variable the squared NaOH-extractable Si concentrations appeared to be statistically significant, when including pH, clay and organic matter content as independent variables (R(3,35)=3.35, p=0.03). Nevertheless, the individual significance value associated to the B coefficient of the pH variable was p >0.05 and after its removal from the model, it was not possible to correlate all remaining variables significantly. We concluded that it was not possible to obtain a useful linear multiple regression model for predicting NaOH – extractable Si concentrations in non-calcareous soils and we excluded this group of values from our analysis.

4.6.2. Multiple regression analysis results – Calcareous soils

When considering only the calcareous soil samples, the independent variables which statistically significantly predict the dependent CaCl₂-extractable Si concentrations include sand (g/kg), silt (g/kg) and organic matter content (g/kg). Sand and organic matter variables were log-transformed before being included in the model.

The R² for the overall model is 39.6% and the adjusted R² is 35.9% with F(3,50)=10.9, and p<0.0005.

The equation used to calculate the predicted CaCl₂-extractable Si is the following:

$$\begin{aligned} \text{PREDICTED CaCl}_2\text{_{Si}} \\ = 141.51 + (-11.73) * LOG_OM + (-26.25) * LOG_SAND + (-0.056) \\ * SILT \end{aligned}$$

We found that sand, lime content and organic matter statistically significantly predict the NaOH-extractable Si concentrations. All variables were log or squared transformed, producing a statistically significant model with an R² of 45.2% and adjusted R² of 41.9%(F(3,50)=13.76, p<0.0005).

The equation is the following:

PREDICTED SQRT(NaOH_Si)

$$= 143.15 + (-24.26) * LOG_OM + (-20.96) * LOG_SAND + (-0.85) * SQRT_LIME$$

4.6.3. Discussion – Environmental factors determining plant available Si concentrations in soil

The outcome of the multiple regression analysis for predicting the CaCl₂-extractable Si concentrations showed statistically significant linear correlations between the plant available silicon fraction and organic matter, clay, sand, silt and pH values.

In both calcareous and non-calcareous soils, the organic matter content is negatively correlated with the plant available Si. The amorphous Si fraction is also negatively related to the organic matter and we will explain in the following section why this finding contradicts our statement of hypothesis 4, predicting an opposite positive correlation. We correlated pH values and CaCl₂ – extractable Si only when considering the non-calcareous soils and we found a very strong correlation, with a positive B coefficient of 0.24, which is 120 times higher than the one for the clay content and approximately 50 times higher (in absolute terms) than the organic matter coefficient. Our prediction of hypothesis 4 was verified. At low pH values, the solubility of silicates increases, but the silicon is either leached or taken up by the plants (Ma and Takahashi, 2003). An increase of pH, decreases the silicon dissolved from the primary silicates, but it increases the release of the colloid-adsorbed Si (McKeague and Cline, 1963) and the solubility of phytoliths (Frayse et al., 2009), which we know being one of the main sources of plant-available silicon. At neutral pH levels, silicon is present in the soil solution as a monomer of silicic acid, but with increasing pH values and at high concentrations (>28 mg L⁻¹ Si), polymerization reactions occur and silicon precipitates as amorphous silica. Adsorption to Fe and Al hydrous oxides plays also a role in Si solubility, as already discussed in the introduction, and at high pH values, this reaction is favored, because of the formation of silicate ions (H₃SiO₄⁻), limiting the amount of silicon in soil solution. The overall balance of silicon contained in the soil solution at high pH is typically higher than at lower pH values. The positive trend CaCl₂ - extractable Si with pH is clearly visible in Figure 11, for non-calcareous soils (a), but it is not present in calcareous soils (b).

Within the group of calcareous soils, the particle size distribution plays an important role in predicting the CaCl₂ - extractable Si: both sand and silt are negatively correlated with the plant available Si and the B coefficient related to the variable sand has a higher absolute value than the coefficient of silt. Furthermore, the positive relation of clay with Si, within the non-calcareous soils, confirms our fourth hypothesis and the

previous findings (Makabe et al., 2009, Yanai et al., 2006): Si concentrations in soil solution are higher where the clay size fraction of soil is prevalent, because of its higher Si storage capacity compared to sand size soil particles.

High precipitation increases the amount of silicon leaching and at the same time, induces lower redox potentials in soils. A considerable fraction of silicon is adsorbed to Fe and Al ions, which increase their reactive surface once the soil reduction increases and this leads to a higher solubilisation of silicon (Ma and Takahashi, 2002). Tables 6A and 7A in the Annex report the Si concentrations together with climate and soil properties, for each soil mapping region. The yearly average values of precipitation at our sampling sites range between 495 mm and 1937 mm. The highest precipitation values are concentrated in the southern regions, having mean values above 1000 mm (KB n. 163, 178, 191, 192, 196, 200, 205 - see Figure 3), whereas the remaining soil mapping areas in the northern part of Lower Austria and around the city of Vienna are drier, with annual precipitation below 700 mm. The average concentrations of plant-available silicon are significantly higher in the latter regions, according to a Mann-Whitney u-test (U=258, Z=-6.48, p<0.0005)

It was not possible to evaluate the individual impact of precipitation, temperature and soil use on the Si fractions using the multiple regression analysis, as either the assumptions of multiple regression were not verified or the relative coefficients B were insignificantly different from 0, leading to removal of these variables from the models.

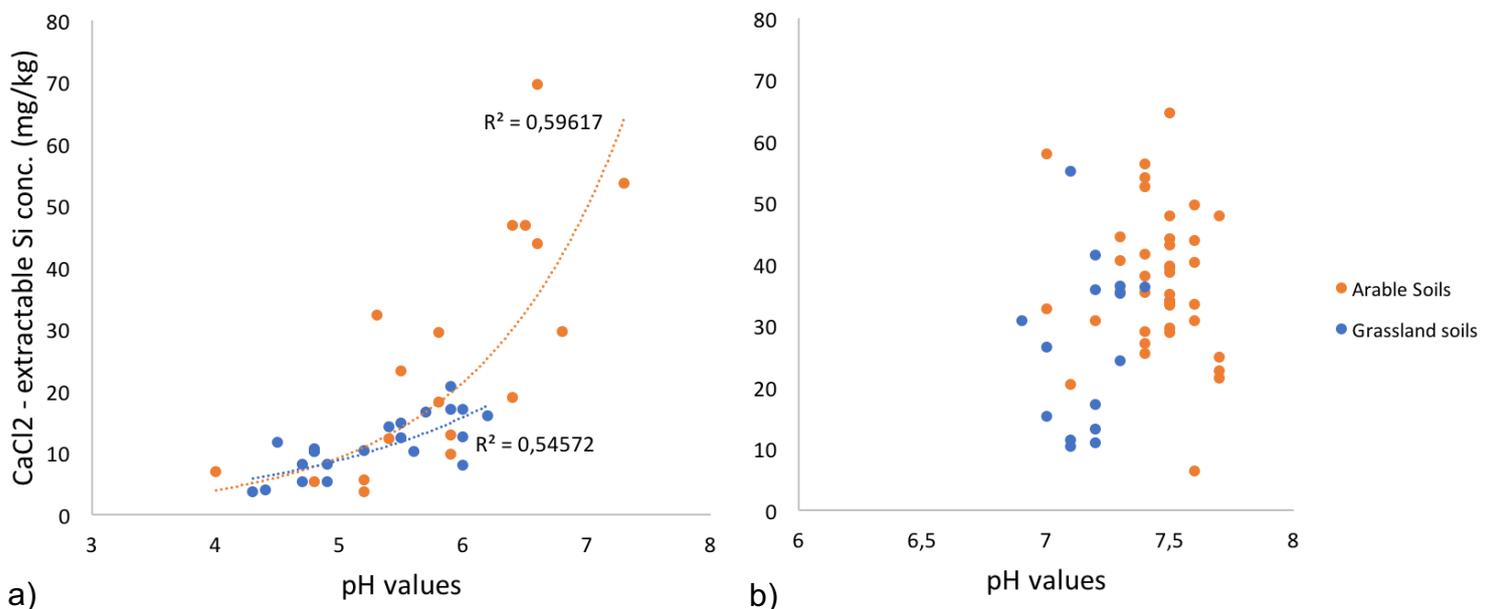


Figure 11: pH values against CaCl₂- extractable Si concentrations in archived soil samples for non-calcareous (a) and calcareous soils (b).

4.6.4. Discussion – Environmental factors determining amorphous silicon concentrations in soil

Using multiple linear regression, we found three significant variables between the concentrations of NaOH–extractable Si and the soil properties in calcareous soils: the organic matter content plays the most important role, after sand and lime content. The organic matter content accounts for decayed plant material and our hypothesis was that its increase would have positively affected the amount of NaOH – extractable Si, as supported by the research conducted by Clymans et al. (2011) and confirmed by Barão et al. (2014) who measured a parallel increase in biogenic amorphous Si, derived mostly from phytoliths, in the topsoil layers. However, our findings rather suggest that the presence of more organic compounds in the topsoil layers could act as a diluting factor for Si, because the silicates or the other possible Si pools would diminish and consequently, the readily and amorphous Si concentrations would decrease. According to our hypothesis 4, a negative correlation with sand was found for the amorphous Si fraction. Bigger soil particle size indicates diminished weathering and formation of amorphous Si. The presence of more sand and less silt and clay will also increase the rate of leaching through the soil and therefore lower concentrations of amorphous Si in the upper soil horizons. Another assumption supported by our multiple regression analysis, was the linear negative correlation between lime content and amorphous Si. The lime content provides important information on the chemical composition of the parent material, suggesting a higher presence of calcareous rocks, rather than siliceous material. This likely explains why an increase in lime content in our samples is combined with a decrease in amorphous Si concentrations.

5. Conclusions

Investigating the Si status in soils is becoming relevant for agriculture, because of the beneficial role of this element for several of the most important cultivated crops. Plant available silicon and amorphous silicon fractions were examined on a series of soil samples collected in the Lower Austrian region. We hypothesized a temporal reduction in amorphous Si concentrations, especially in arable soils because of Si removal followed by crop material's harvest, but we found no significant decrease in the last 2-3 decades. The mean amorphous Si concentration in the recently collected samples is 2912 mg Si/kg and it is in line with the concentrations reported in the literature. The average plant-available Si concentration in the re-sampled soils was found to be 24.8 mg Si/kg. A temporal decreasing tendency of plant-available Si concentrations confirmed our second hypothesis, depicting a general situation of Si deficiency for Lower Austrian crops. Considering the large proportion of potentially Si-deficient soils in Lower Austria, and the tendency of decreased plant-available Si in the past 20-30 years, soil Si fertilization and related soil management should be considered.

Examining the average Si concentrations of each soil group, demonstrated that increasing degree of development and weathering processes entail to higher accumulation of amorphous Si in soil. The plant-available Si increased accordingly, but apart from the larger amorphous fraction, was low in the most acidic soils (Cambisols and Umbrisols) probably due to the lower solubility of the amorphous Si fraction in this range of pH.

The expectation to find multiple relations between the Si fractions and several environmental characteristics and soil properties was met. Within the calcareous soils, both Si fractions were correlated with the soil texture, suggesting that most of the Si is stored in the clay fraction. Organic matter and lime content played a similar role, acting as a diluting factor for Si concentrations. The positive relation of plant-available Si with pH was confirmed only for non-calcareous soils.

The soil use seems to have a direct strong influence on the plant-available Si, but the large difference in climate conditions between the areas where most of the grassland and the arable soils are located, suggests that caution is required in interpretation of those differences.

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Website link to the Austrian soil map, created by the Bundesforschungs- und Ausbildungszentrum für Wald, Naturgefahren und Landschaft (BFW) (Federal Research and educational center for forest, natural hazard and landscape):

http://bfw.ac.at/rz/document_api.download?content=kb_uebersicht_g.jpg

List of Figures

Figure 1: Silicon fractions in soils, taken from Sauer et. al. 2005, modified from Matichencov and Bocharnikova, 2001	4
Figure 2: Lower Austrian soil map defining soil groups according to WRB (2014) for arable and grassland versus forest soils (Wenzel et al. 2012).....	11
Figure 3: Soil mapping areas of Lower Austria. Mapping areas re-sampled in this study are indicated by red circles.	12
Figure 4: Number of collected soil samples for each soil mapping area	14
Figure 5: Frequency distribution of CaCl ₂ -extractable Si concentrations in archived soil samples	24
Figure 6: Frequency distribution of CaCl ₂ -extractable Si concentrations in re-sampled soil samples	25
Figure 7: Frequency distribution of NaOH-extractable (amorphous) Si values in archived soils	28
Figure 8: Frequency distribution of NaOH-extractable (amorphous) Si concentrations in re-sampled soils	28
Figure 9: Boxplots of the CaCl ₂ - extractable Si concentrations in different soil groups	31
Figure 10: Boxplots of the NaOH- extractable Si concentrations in different soil groups	32
Figure 11: pH values against CaCl ₂ - extractable Si concentrations in archived soil samples for non- calcareous (a) and calcareous soils (b).....	35

List of Tables

Table 1: Selected extractants with respective extraction ratio and extraction time, and the suggested critical levels of potentially plant available Si (Haynes, 2014)	7
Table 2: General descriptive statistics (minimum, maximum, mean, median, standard deviation, skewness and kurtosis) of CaCl ₂ -extractable Si concentrations of archived and re-sampled soils.	23
Table 3: General descriptive statistics (minimum, maximum, mean, median, standard deviation, skewness and kurtosis) of CaCl ₂ -extractable Si concentrations in archived and re-sampled soils, with further subdivision in arable and grassland soil use.	26
Table 4: General descriptive statistics (minimum, maximum, mean, median, standard deviation, skewness and kurtosis) of NaOH-extractable Si concentrations in archived and re-sampled soils	27
Table 5: General descriptive statistics (minimum, maximum, mean, median, standard deviation, skewness and kurtosis) of NaOH-extractable Si conc. in archived and re-sampled soils, with further subdivision in arable and grassland soil use.	29

Annex

The following tables show detail information of all data used in this thesis.

Table 1A: Soil classification according to IUSS Working Group WRB (2014) and Austrian soil classification, together with WGS84 collection site's coordinates

Soil use	Sample number	Mapping area	Profile n.	Coordinates WGS84	IUSS Working Group WRB (2014)	Austrian soil classification
Arable	1	192	28	47.539797,16.114294	Cambic Umbrisol	kalkfreie Felsbraunerde
	2	213	20	48.669247,16.456530	Chernic Phaeozem	Tschernosem
	3	1	28	48.100850,16.627088	Chernic Phaeozem	Tschernosem
	4	200	51	47.683585,16.015531	Calcaric Cambic Phaeozem	kalkhaltige Lockersediment - Braunerde
	5	191	3	48.036938,15.442389	Calcaric Fluvic Chernic Phaeozem	kalkhaltiger Grauer Auboden
	6	213	70	48.646267,16.389219	Calcaric Colluvic Regosol	kalkhaltiges Kolluvium
	7	213	71	48.637778,16.351991	Calcaric Colluvic Regosol	verbrauntes, kalkhaltiges Kolluvium
	8	171	40	48.696171,15.750081	Stagnic Phaeozem	Typischer Pseudogley
	9	1	56	48.045545,16.537231	Calcaric Chernic Gleysol (Colluvic)	überlagerte, kalkhaltige Feuchtschwarzerde
	10	192	23	47.531010,16.066339	Dystric Skeletic Leptosol	kalkfreie Felsbraunerde
	11	171	43	48.700559,15.700622	Relictistagnic Phaeozem	Relikt pseudogley
	12	177	43	48.750891,15.910409	Cambic Phaeozem	entkalkte Lockersediment-Braunerde
	13	1	55	48.096638,16.413352	Calcaric Chernic Gleysol (colluvic)	überlagerte, kalkhaltige Feuchtschwarzerde
	14	1	26	48.058357,16.432914	Calcaric Regosol	Tschernosem
	15	200	47	47.680227,15.991998	Calcaric Skeletic Fluvisol	kalkhaltige Lockersediment - Braunerde
	16	26	60	48.055147,16.283407	Calcaric Cambisol	kalkhaltige Lockersediment - Braunerde
	17	212	34	48.761895,16.486775	Calcaric Chernic Phaeozem	Tschernosem
	18	26	18	48.106331,16.361175	Calcaric Chernic Phaeozem	Tschernosem
	19	212	68	48.708777,16.490134	Chernic Phaeozem (oxyaquic)	entkalkte Feuchtschwarzerde
	20	177	22	48.736988,15.944516	Chernic Phaeozem	Tschernosem
	21	1	24	48.008363,16.420074	Calcaric Regosol	Tschernosem
	22	213	61	48.682622,16.520000	Calcaric Regosol	kalkhaltiger Kulturrohboden
	23	213	15	48.654262,16.450661	Calcaric Regosol	Tschernosem
	24	171	44	48.709412,15.74447	Dystric Relictistagnic Regosol	Relikt pseudogley
	25	212	60	48.695824,16.459434	Calcaric Chernic Phaeozem (oxyaquic)	kalkhaltige Feuchtschwarzerde
	26	171	37	48.706144,15.708088	Luvic Phaeozem	Parabraunerde
	27	177	59	48.694466,15.885816	Calcaric Regosol	kalkhaltiger Kulturrohboden
	28	1	54	48.108960,16.384702	Calcaric Oxygleyic Gleysol	überlagerte, kalkhaltige Feuchtschwarzerde
	29	163	9	48.065902,14.769663	Eutric Stagnosol	Typischer Pseudogley
	30	212	71	48.705061,16.414221	Endosalic Chernic Phaeozem (oxyaquic)	versalzte, entkalkte Feuchtschwarzerde

Soil use	Sample number	Mapping area	Profile n.	Coordinates WGS84	IUSS Working Group WRB (2014)	Austrian soil classification
Arable	31	163	7	48.069876,14.774553	Eutric Cambisol (oxyaquic)	schwach vergleyte Lockersediment - Braunerde, Oberboden kalkhaltig, Unterboden kalkfrei
	32	213	65	48.654979,16.455161	Calcaric Regosol	kalkhaltiger Kulturrohboden
	33	26	62	48.074216,16.182930	Eutric Cambisol (oxyaquic)	vergleyte, kalkhaltige Lockersediment - Braunerde
	34	171	41	48.726658,15.727973	Stagnic Phaeozem	Typischer Pseudogley
	35	212	64	48.726275,16.436539	Calcaric Endocalcic Chernic Phaeozem	versalztes, kalkhaltige Feuchtschwarzerde
	36	26	33	48.059075,16.349296	Calcaric Oxygleyic Gleysol	versalztes, kalkhaltige Feuchtschwarzerde
	37	177	60	48.659759,15.972785	Calcaric Phaeozem	kalkhaltiger Kulturrohboden
	38	26	63	48.099844,16.229821	Calcaric Cambic Phaeozem	pseudovergleyte, kalkhaltige Lockersediment - Braunerde
	39	26	16	48.016545,16.401792	Calcaric Chernic Phaeozem	Tschernosem
	40	26	25	48.044144,16.296242	Calcaric Endosalic Chernic Phaeozem	versalztes Tschernosem
	41	212	22	48.773900,16.539096	Haplic Phaeozem (arenic)	Tschernosem
	43	177	16	48.705278,15.912176	Calcaric Chernic Phaeozem	Tschernosem
	44	212	67	48.765631,16.468215	Relictigleyic Chernic Phaeozem	entkalkte Feuchtschwarzerde
	45	171	34	48.721065,15.737621	Haplic Umbrisol	kalkfreie Lockersediment - Braunerde
	46	177	46	48.715292,15.851776	Cambic Phaeozem	entkalkte Lockersediment - Braunerde
	47	192	24	47.538225,16.137877	Leptic Mollic Umbrisol	kalkfreie Felsbraunerde
	48	177	45	48.703092,15.817920	Haplic Phaeozem (clayic)	entkalkte Lockersediment - Braunerde
	49	1	12	48.130843,16.460067	Calcaric Fluvisol	trockengefallener, kalkhaltiger Grauer Auboden
	50	26	29	48.039401,16.413017	Calcaric Fluvisol	kalkhaltige Feuchtschwarzerde
	51	178	101	47.986183,15.25050	Eutric Cambisol (oxyaquic)	vergleyte, kalkfreie Felsbraunerde
	52	177	61	48.682253,15.979410	Calcaric Regosol	kalkhaltiger Kulturrohboden
	53	212	23	48.730409,16.321512	Calcaric Regosol (arenic)	Tschernosem
	54	212	65	48.754671,16.478913	Calcaric Chernic Phaeozem (oxyaquic)	versalztes, kalkhaltige Feuchtschwarzerde
	55	191	23	48.093821,15.515972	Eutric Stagnic Phaeozem (albic)	pseudovergleyte, kalkfreie Felsbraunerde
	56	200	26	47.686895,16.039546	Calcaric Mollic Leptosol	Pararendsina

Soil use	Sample number	Mapping area	Profile n.	Coordinates WGS84	IUSS Working Group WRB (2014)	Austrian soil classification
Arable	57	200	49	47.640606,15.912431	Calcaric Cambic Phaeozem	kalkhaltige Lockersediment - Braunerde
	98	213	72	48.617541,16.279108	Eutric Colluvic Regosol	verbrauntes, kalkhaltiges Kolluvium
	99	26	31	48.095538,16.373857	Calcaric Fluvic Chernic Phaeozem (endosalic, oxyaquic)	Feuchtschwarzerde
Grassland	59	1	8	48.139832,16.548690	Calcaric Fluvisol (oxyaquic)	kalkhaltiger Grauer Auboden
	60	1	10	48.132154,16.559928	Calcaric Fluvic Gleysol	vergleyter, kalkhaltiger Grauer Auboden
	61	163	22	47.986689,14.626894	Cambic Fluvic Phaeozem	kalkfreier Brauner Auboden
	62	178	35	48.120977,15.149055	Cambic Phaeozem	kalkfreie Felsbraunerde
	63	178	85	47.984906,15.250782	Eutric Mollic Gleysol	entkalkter Typischer Gley, kolluvial beeinflusst
	64	178	86	47.956365,15.223616	Eutric Gleysol	kalkfreier Typischer Gley
	65	178	87	47.926859,15.304092	Eutric Oxygleyic Gleysol (drainic)	entwässerter, kalkfreier Gley
	66	178	97	47.969055,15.235915	Dystric Cambisol	kalkfreie Felsbraunerde
	67	196	19	47.748968,14.902333	Dystric Gleyic Cambisol	vergleyte, kalkfreie Lockersediment - Braunerde
	68	196	21	47.832777,14.925129	Cambic Phaeozem	Braunlehm
	69	196	31	47.924931,15.107026	Dolomitic Cambic Phaeozem	kalkhaltige Felsbraunerde
	70	196	33	47.945676,15.119118	Eutric Cambisol	kalkhaltige Felsbraunerde
	71	196	45	47.861532,15.076119	Epieutric Endodystric Cambisol (oxyaquic)	vergleyte, kalkfreie Lockersediment - Braunerde
	72	196	46	47.760070,14.900536	Eutric Gleyic Cambisol	vergleyte, kalkfreie Lockersediment - Braunerde
	73	196	52	47.824350,14.909807	Leptic Cambisol	Braunlehm
	74	196	54	47.783419,14.936126	Cambic Leptic Phaeozem	Braunlehm
	75	191	2	48.033656,15.442118	Calcaric Fluvic Phaeozem	kalkhaltiger Grauer Auboden
	76	191	5	47.988559,15.359335	Calcaric Fluvic Oxygleyic Chernic	vergleyter, kalkhaltiger Grauer Auboden
	77	191	20	48.029825,15.492329	Eutric Stagnic Regosol	pseudovergleyte, kalkfreie Felsbraunerde
	78	191	21	48.027340,15.466906	Eutric Cambisol (oxyaquic)	pseudovergleyte, kalkfreie Felsbraunerde
	79	205	12	47.848713,15.570881	Calcaric Skeletic Regosol	kalkhaltige Lockersediment - Braunerde
80	205	14	47.819167,15.557611	Calcaric Cambic Phaeozem	kalkhaltige Lockersediment - Braunerde	
81	205	31	48.055181,15.571303	Eutric Stagnic Regosol	Typischer Pseudogley	
82	205	32	48.044187,15.590179	Eutric Stagnosol	Typischer Pseudogley	
83	205	41	47.995482,15.549828	Eutric Leptic Cambisol	kalkfreie Felsbraunerde	

Soil use	Sample number	Mapping area	Profile n.	Coordinates WGS84	IUSS Working Group WRB (2014)	Austrian soil classification
Grassland	84	205	46	47.936269,15.471265	Eurtic Stagnic Regosol	pseudovergleyte, kalkfreie Felsbraunerde
	85	205	48	47.837538,15.267075	Calcaric Cambic Phaeozem	kalkhaltige Lockersediment - Braunerde
	87	205	51	47.871722,15.326126	Eutric Stagnic Regosol	Typischer Pseudogley
	88	192	12	47.525553,15.992770	Gleysol	kalkfreier Hanggley
	89	192	10	47.490281,16.136569	Dystric Oxygleyic Umbric Gleysol	kalkfreier Hanggley
	90	192	11	47.509576,16.055234	Oxygleyic Umbric Gleysol	kalkfreier Hanggley
	91	200	20	47.825923,15.687771	Somerirendzic Leptosol	Rendsina
	92	200	21	47.706723,15.823093	Calcaric Skeletic Phaeozem	Rendsina
	93	200	23	47.696115,15.772929	Calcaric Skeletic Phaeozem	Pararendsina
	94	200	25	47.806554,15.749950	Pararendsina	Calcaric Skeletic Regosol
	95	200	28	47.647621,15.868979	Rendsina	Skeletic Rendzic Leptic Phaeozem
	96	196	32	47.974813,15.040807	kalkhaltige Felsbraunerde	Calcaric Skeletic Cambisol

Table 2A: General important information about the sampling sites, including soil characteristics.

Soil use	Location Data						Archived soil samples' data		Re sa. soil samples' data	Soil texture			Lime (g/kg)	OM (g/kg)
	Sample's number	Mapping area (KB)	Profile n.	Coordinates WGS84	Average yearly precipitation (mm)	Average yearly temperature (°C)	pH	Collection year	pH	Sand (g/kg)	Silt (g/kg)	Clay (g/kg)		
Arable	1	192	28	47.539797,16.114294	938	7.6	4.8	1985	4.03	580	340	80	0	35
	2	213	20	48.669247,16.456530	546	9.6	7	1985	6.11	150	420	430	3	25
	3	1	28	48.100850,16.627088	581	9.9	7.5	1997	7.46	300	530	170	62	26
	4	200	51	47.683585,16.015531	778	9.3	7.5	1986	7.22	410	460	130	109	40
	5	191	3	48.036938,15.442389	1102	8.8	7.3	1988	7.29	140	660	200	229	43
	6	213	70	48.646267,16.389219	601	9.6	7.5	1988	7.45	220	450	330	103	18
	7	213	71	48.637778,16.351991	601	9.6	7.6	1987	7.72	440	430	130	103	10
	8	171	40	48.696171,15.750081	575	9.5	5.3	1985	7.38	140	550	310	0	18
	9	1	56	48.045545,16.537231	610	9.9	7.7	1996	7.48	150	630	220	67	105
	10	192	23	47.531010,16.066339	1009	7.6	5.2	1985	4.12	510	400	90	0	36
	11	171	43	48.700559,15.700622	557	9.5	5.5	1985	6.84	250	510	240	0	12
	12	177	43	48.750891,15.910409	544	9.5	6.6	1986	6.45	110	570	320	0	14
	13	1	55	48.096638,16.413352	585	10.4	7.5	1994	7.48	110	450	440	130	34
	14	1	26	48.058357,16.432914	562	10.4	7.5	1995	7.6	250	440	310	300	34
	15	200	47	47.680227,15.991998	768	9.3	7.4	1986	7.34	520	420	60	55	39
	16	26	60	48.055147,16.283407	618	10	7.5	1992	7.3	350	360	290	140	26
	17	212	34	48.761895,16.486775	516	9.6	7.4	2000	7.41	530	280	190	2	27
	18	26	18	48.106331,16.361175	576	10.4	7.5	1988	7.53	130	570	300	134	23
	19	212	68	48.708777,16.490134	523	9.6	6.6	2000	6.6	360	320	320	0	45
	20	177	22	48.736988,15.944516	495	9.5	7.4	1986	7.77	680	210	110	14	11

Soil use	Location Data						Archived soil samples' data		Re sa. soil samples' data	Soil texture			Lime (g/kg)	OM (g/kg)
	Sample's number	Mapping area (KB)	Profile n.	Coordinates WGS84	Average yearly precipitation (mm)	Average yearly temperature (°C)	pH	Collection year	pH	Sand (g/kg)	Silt (g/kg)	Clay (g/kg)		
Arable	21	1	24	48.008363,16.420074	610	10.1	7.7	1995	7.45	290	450	260	270	39
	22	213	61	48.682622,16.520000	549	9.5	7.4	1985	7.87	380	460	160	232	11
	23	213	15	48.654262,16.450661	546	9.6	7.4	1985	7.43	220	520	260	159	17
	24	171	44	48.709412,15.74447	557	9.5	5.9	1985	6.72	450	450	100	0	9
	25	212	60	48.695824,16.459434	546	9.6	7.6	2000	7.36	80	430	490	98	47
	26	171	37	48.706144,15.708088	557	9.5	5.8	1985	4.59	90	770	140	0	12
	27	177	59	48.694466,15.885816	541	9.5	7.6	1985	7.74	140	650	210	157	12
	28	1	54	48.108960,16.384702	576	10.4	7.5	1994	7.38	50	560	390	170	36
	29	163	9	48.065902,14.769663	929	8.5	6.8	1985	5.39	250	530	220	0	16
	30	212	71	48.705061,16.414221	522	9.6	7.3	1993	6.98	310	450	240	0	27
	31	163	7	48.069876,14.774553	929	8.5	7	1985	6.67	220	620	160	19	24
	32	213	65	48.654979,16.455161	546	9.6	7.4	1985	7.58	150	610	240	243	11
	33	26	62	48.074216,16.182930	749	10	7.5	1993	6.79	160	460	380	10	20
	34	171	41	48.726658,15.727973	557	9.5	5.4	1985	5.28	370	520	110	0	10
	35	212	64	48.726275,16.436539	523	9.6	7.6	1993	6.75	690	190	120	33	20
	36	26	33	48.059075,16.349296	585	10.4	7.5	1989	7.19	110	420	470	111	40
	37	177	60	48.659759,15.972785	513	9.2	7.4	1985	7.53	510	280	210	125	12
	38	26	63	48.099844,16.229821	749	10	7.2	1992	6.15	70	600	330	25	38
	39	26	16	48.016545,16.401792	580	10.4	7.7	1989	7.88	390	440	170	404	31
	40	26	25	48.044144,16.296242	633	10	7.7	1991	7.5	140	390	470	130	36
41	212	22	48.773900,16.539096	528	9.5	7.3	1997	7.22	730	150	120	9	11	
43	177	16	48.705278,15.912176	542	9.5	7.5	1986	7.6	240	510	250	137	21	
44	212	67	48.765631,16.468215	516	9.6	5.8	1995	6.58	650	200	150	0	21	
45	171	34	48.721065,15.737621	557	9.5	4	1985	4.71	610	320	70	0	14	
46	177	46	48.715292,15.851776	542	9.5	6.4	1985	6.09	460	370	170	0	13	

Soil use	Location Data						Archived soil samples' data		Re-sa. soil sample s' data	Soil texture			Lime (g/kg)	OM (g/kg)
	Sampl e's numb er	Mapping area (KB)	Profile n.	Coordinates WGS84	Average yearly precipitati on (mm)	Average yearly temperat ure (°C)	pH	Collectio n year	pH	Sand (g/kg)	Silt (g/kg)	Clay (g/kg)		
Arable	47	192	24	47.538225,16.137877	938	7.6	5.2	1985	4.65	540	400	60	0	44
	48	177	45	48.703092,15.817920	548	9.5	6.5	1987	7.31	130	420	450	0	22
	49	1	12	48.130843,16.460067	565	10.4	7.4	1994	7.41	100	630	270	190	33
	50	26	29	48.039401,16.413017	580	10.4	7.6	1989	7.92	230	430	340	820	32
	51	178	101	47.986183,15.25050	1525	8.8	6.4	1985	5.32	90	690	220	0	51
	52	177	61	48.682253,15.979410	513	9.5	7.5	1985	7.41	160	510	330	144	6
	53	212	23	48.730409,16.321512	515	9.6	7.5	1990	7.79	600	280	120	63	11
	54	212	65	48.754671,16.478913	516	9.6	7.4	1997	7.43	150	450	400	29	29
	55	191	23	48.093821,15.515972	895	8.8	5.9	1987	5.08	160	660	180	0	49
	56	200	26	47.686895,16.039546	778	9.3	7.5	1986	4.31	330	470	200	53	45
	57	200	49	47.640606,15.912431	998	5.6	7.1	1986	7.11	210	640	150	22	67
	98	213	72	48.617541,16.279108	593	9.6	7.3	1988	7.33	300	470	230	35	17
99	26	31	48.095538,16.373857	585	10.4	7.6	1988	7.65	100	540	360	8	28	
Grassland	59	1	8	48.139832,16.548690	583	9.9	7.2	1994	8.06	370	610	20	180	12
	60	1	10	48.132154,16.559928	583	9.9	7.1	1994	7.53	30	830	140	220	35
	61	163	22	47.986689,14.626894	1271	8.3	4.9	1985	6.68	440	410	150	0	23
	62	178	35	48.120977,15.149055	824	8.8	6	1990	4.93	430	440	130	0	26
	63	178	85	47.984906,15.250782	1411	8.8	5.2	1985	6.79	60	700	240	0	58
	64	178	86	47.956365,15.223616	1411	8.8	6.2	1985	6.83	50	820	130	0	57
	65	178	87	47.926859,15.304092	1706	6.1	4.5	1985	4.18	80	670	250	0	47
	66	178	97	47.969055,15.235915	1411	8.8	4.7	1985	5.31	200	620	180	0	44
	67	196	19	47.748968,14.902333	1937	8.5	5.4	1986	6.44	50	750	200	0	33
	68	196	21	47.832777,14.925129	1724	8.1	5.9	1986	4.9	90	630	280	0	51
	69	196	31	47.924931,15.107026	1619	8.1	7.3	1992	7	80	720	200	156	51
	70	196	33	47.945676,15.119118	1619	8.1	7	1987	7.04	110	680	210	121	49

Soil use	Location Data						Archived soil samples' data		Re-sa. soil samples' data	Soil texture			Lime (g/kg)	OM (g/kg)
	Sample's number	Mapping area (KB)	Profile n.	Coordinates WGS84	Average yearly precipitation (mm)	Average yearly temperature (°C)	pH	Collection year	pH	Sand (g/kg)	Silt (g/kg)	Clay (g/kg)		
Grassland	71	196	45	47.861532,15.076119	1686	8.1	4.9	1986	4.06	120	660	220	0	51
	72	196	46	47.760070,14.900536	1875	8.5	5.6	1986	4.33	70	810	120	0	34
	73	196	52	47.824350,14.909807	1852	8.5	4.8	1986	4.37	40	740	220	0	42
	74	196	54	47.783419,14.936126	1848	8.1	5.9	1986	4.17	40	570	390	0	50
	75	191	2	48.033656,15.442118	1102	8.8	7.2	1988	7.25	170	670	160	229	44
	76	191	5	47.988559,15.359335	1477	8.8	6.9	1989	7.16	50	770	180	183	66
	77	191	20	48.029825,15.492329	1102	8.8	6	1988	3.92	80	700	220	0	45
	78	191	21	48.027340,15.466906	1102	8.8	4.8	1988	4.66	50	640	310	0	49
	79	205	12	47.848713,15.570881	1445	6.1	7.2	1997	7.13	140	720	140	164	206
	80	205	14	47.819167,15.557611	1445	6.1	7.3	1997	6.85	220	590	190	141	109
	81	205	31	48.055181,15.571303	895	8.8	5.7	1997	4.8	200	600	200	0	72
	82	205	32	48.044187,15.590179	1205	8.8	6	1997	4.6	130	690	180	0	81
	83	205	41	47.995482,15.549828	1249	6.1	5.5	1997	5.29	110	620	270	0	72
	84	205	46	47.936269,15.471265	1417	6.1	5.5	1995	4.5	50	700	250	0	45
	85	205	48	47.837538,15.267075	1378	6.1	7	1997	6.94	130	690	180	124	157
	87	205	51	47.871722,15.326126	1622	6.1	4.8	1997	5.57	50	710	240	0	50
	88	192	12	47.525553,15.992770	1302	6.7	4.4	1985	3.98	620	310	70	0	51
	89	192	10	47.490281,16.136569	920	7.6	4.7	1985	4.37	440	450	110	0	45
	90	192	11	47.509576,16.055234	1009	6.7	4.3	1985	3.98	540	390	70	0	56
	91	200	20	47.825923,15.687771	1343	8.7	7.3	1988	6.86	180	600	220	403	78
92	200	21	47.706723,15.823093	1245	8.7	7.2	1987	7.4	140	720	140	267	56	
93	200	23	47.696115,15.772929	952	8.7	7.1	1987	7.12	240	660	100	424	48	
94	200	25	47.806554,15.749950	1190	8.7	7.2	1988	6.71	130	600	270	112	97	
95	200	28	47.647621,15.868979	998	5.6	7.1	1987	7.4	430	510	60	518	45	
96	196	32	47.974813,15.040807	1251	8.1	7.4	1988	6.1	60	600	340	84	45	

Table 3A: Average values of soil properties and climate conditions, divided by soil use

Soil use	Prec.	Temp.	Clay	Silt	Sand	OM	Lime	pH old	pH new
	n=95 (mm)	n=95 (°C)	n=95 (g/kg)	n=95 (g/kg)	n=95 (g/kg)	n=95 (g/kg)	n=95 (g/kg)	n=95	n=95
Arable	649	9.5	239	464	296	28	88.7	6.96	6.82
Grassland	1325	8	189	637	174	59	89.9	6.03	5.82

Table 4A: Mean CaCl₂ and NaOH - extractable Si conc. (mg/kg) for each soil group with soil use and temporal subdivision

Soil group	CaCl ₂ -ext. Si						NaOH-ext. Si					
	Total (n=190)		Archived (n=95)		Re-sampled (n=95)		Total (n=190)		Archived (n=95)		Re-sampled (n=95)	
	Arch. (mg/kg)	Re-sa. (mg/kg)	Arable (mg/kg)	Grassland (mg/kg)	Arable (mg/kg)	Grassland (mg/kg)	Arch. (mg/kg)	Re-sa. (mg/kg)	Arable (mg/kg)	Grassland (mg/kg)	Arable (mg/kg)	Grassland (mg/kg)
Umbrisol	5.4	7	5.4	-	6.7	-	3778	3520	3778	-	3520	-
Cambisol	19.5	17.6	30	14.9	27.8	13.1	3525	3564	2633	3921	2741	349
Phaeozem	32.5	30.1	37.5	19.2	34.4	18.6	3316	2991	3551	2696	3295	219
Regosol	30	28.3	36.2	17.3	35.2	14.3	2831	2567	2921	2652	2587	252
Stagnosol	19	12.4	29.7	8.1	13.6	11.1	3224	3363	4423	2026	4102	262
Gleysol	22.9	22.5	33.4	17.6	33.1	17.2	2952	3340	2689	3083	2841	359
Leptosol	29.7	10.1	26.8	35.4	8.1	14.2	2834	2054	2923	2659	2573	101
Fluvisol	26.4	18.4	29.5	17.2	20.7	11.3	2266	1223	2149	2618	1416	643

Table 5A: Mean soil properties and climate factors divided by soil groups

Soil group	Prec. (mm)	Temp. (°C)	Clay (g/kg)	Silt (g/kg)	Sand (g/kg)	OM (g/kg)	Lime (g/kg)	pH old	pH new
Umbrisol	811	8.2	70	353	577	31	0	4.7	4.5
Cambisol	1369	8.5	240	635	125	41.5	28.8	6	5.7
Phaeozem	801	9	230	493	277	36	85.8	6.8	6.8
Regosol	800	8.9	222	542	236	39	115.8	6.9	6.8
Stagnosol	1067	8.7	200	610	190	49	0	6.4	5
Gleysol	1015	8.7	226	583	191	53	73.4	6.1	6.2
Leptosol	1043	8.5	170	490	340	53	152	6.7	5.1
Fluvisol	624	10	173	523	305	29	311	7.4	7.7

Table 6A: Average soil properties and climate factors of soils, divided by soil mapping areas

KB	Prec. (mm)	Temp. (°C)	Clay (g/kg)	Silt (g/kg)	Sand (g/kg)	OM (g/kg)	Lime (g/kg)	pH old	pH new
1	584	10.1	247	570	183	39	177	7.46	7.54
26	628	10.2	346	468	187	30	198	7.53	7.32
163	1043	8.4	177	520	303	21	6.3	6.23	6.25
171	560	9.5	162	520	318	12.5	0	5.32	5.92
177	530	9.5	257	440	304	13.9	72	7.11	7.24
178	1381	8.4	192	657	152	47.2	0	5.50	5.56
191	1130	8.8	208	683	108	49	107	6.35	5.89
192	1019	7.3	80	382	538	44.5	0	4.77	4.19
196	1712	8.2	242	684	73	45	40	6.02	5.38
200	1006	8.2	148	564	288	57	218	7.27	6.83
205	1332	6.8	206	665	129	99	53.6	6.13	5.71
212	523	9.6	239	306	456	26	26	7.17	7.12
213	569	9.6	254	480	266	15.6	125	7.37	7.36

Table 7A: Average CaCl₂ and NaOH- extractable Si concentrations for archived and re-sampled soils, divided by soil use and soil mapping area (KB)

KB	CaCl ₂ -ext. Si						NaOH-ext. Si					
	Total (n=190)		Re-sampled (n=95)		Archived (n=95)		Total (n=190)		Re-sampled (n=95)		Archived (n=95)	
	Archived	Re-sampled	Arable	Grassland	Arable	Grassland	Archived	Re-sampled	Arable	Grassland	Arable	Grasslar
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
1	33.9	27.9	29.2	23.2	33.3	36.2	2316	2247	2458	1507	2270	2474
26	34	27.9	27.9	-	34	-	2654	2371	2371	-	2654	-
163	23.6	17.1	18.7	13.9	31.2	8.2	4260	3022	3215	2636	4050	4682
171	17.2	20.3	20.3	-	17.2	-	4881	4322	4322	-	4881	-
177	38	35.7	35.7	-	38	-	3792	2787	2787	-	3792	-
178	12.6	14.3	15.4	14.1	19	11.3	2677	2676	3969	2417	2276	2757
191	24.8	19.8	23.6	17.9	24.3	25.1	2599	2318	2934	2011	2928	2435
192	5.2	8.9	5.8	11.9	5	5.4	3194	4490	3196	5785	2152	4237
196	19.7	15.3	-	15.3	-	19.7	4412	4068	-	4068	-	4412
200	26.7	17.5	15.2	19.3	33.4	21.3	1931	1316	1625	1068	2539	1445
205	14.2	13.7	-	13.7	-	14.2	2504	2328	-	2328	-	2504
212	49.5	48.3	48.3	-	49.5	-	3599	3249	3249	-	3599	-
213	41.8	43	42.9	-	41.8	-	3249	3517	3517	-	3249	-