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# Modelling the interaction between Calcium and Nickel in the soil – plant system

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# 1 Introduction

Pollution with heavy metals is one of the main problems in biosystems ecology. The most important subject for research in this area is the development of strategies for reducing the transfer of heavy metals into agricultural products and the food chain.

Recently Nickel (Ni) has become a very serious pollutant and its redistribution in environment should be of major concern (Iljin 1991).

Ni belongs to group VIII of the Periodic Table and has an atomic weight of 58.71. It is characterised by five stable isotopes. Nickel normally occurs in biological systems in II oxidation state, but can also appear in the states Ni (I) and Ni (III) (Ivanov 1994; Cammack et al. 1988). Nickel forms stable complexes, for example with cysteine and citrate (Thauer et al. 1980). In nickel-enzymes it is coordinated to various ligands (Marschner 2003).

Ni is essential for mammals as a micronutrient, but at higher concentrations it turns out to become very toxic mainly inducing carcinogen processes (Iljin 1991; Saprikin 1999). Among other known negative effects on health Ni can cause skin allergies, lung fibroses, variable degrees of kidney and cardiovascular system poisoning (Denkhaus & Salnikow 2002).

The essentiality of Ni for plants is still under dispute, although it is included in the list of micronutrients (Marschner 2003) and many scientists report its beneficial effect on plants (Mengel & Kirkby 1978; Andreeva et. al 2001). Dixon et al. (1975) discovered that Ni is a component of the enzyme urease. Urease so far is the only known Ni-containing enzyme in higher plants. It has a molecular weight of 590 kDa[1] and consists of six subunits (i.e. it is hexametric), where each subunit contains two Nickel atoms. In the subunits Ni is coordinated to N-and O-ligands (Alagna et al. 1984) and water molecules can possibly displace one of the Ni-O bonds during hydrolytic reactions (Fig. 1.1).

[1] kDa - kilodalton

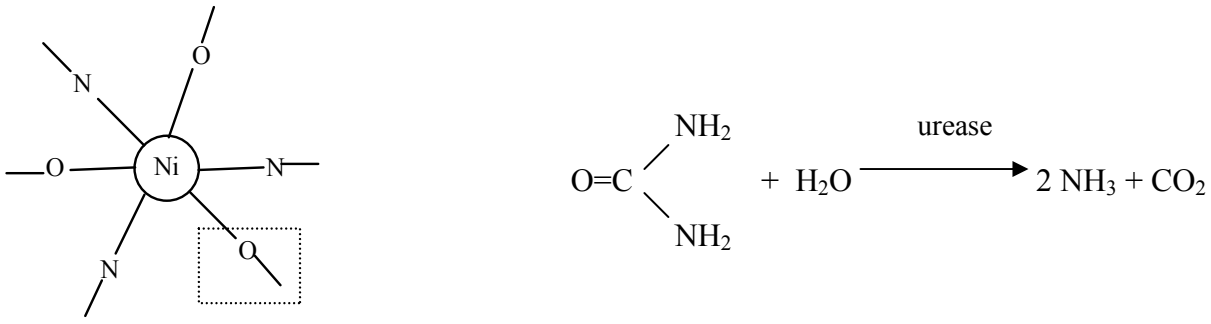


Figure 1.1: Schematic structure of enzyme urease (left) and reaction of urea hydrolysis (right) (Marschner 2003).

Welch (1979) concluded that Ni might be required by nodulated legumes that transport nitrogen (N) from the roots to the top in form of ureide compounds. Winkler et al. (1988) showed that there is no particularly high requirement for Ni to be expected in nodulated soybean and other ureide-type legumes, compared to soybean supplied with mineral nitrogen. Regardless of the type of nitrogen nutrition in soybean and cowpea, without Ni supply large amounts of urea accumulate in the leaves and symptoms of leaf tip necrosis are severe (Eskew et al. 1984). Effects of Ni on growth, N metabolism and leaf urease activity of six crop species (rye, wheat, soybean, rape, zucchini and sunflower) were studied by Gerendas & Sattelmacher (1997). All tested species showed shoot growth reductions in Ni-free nutrient solutions compared to Ni containing solutions. The plants appeared chlorotic as a result of metabolic N deficiency. So far there is no clear evidence of Ni deficiency in soil-grown plants (Dalton et al. 1985), although in a pot experiment in wheat performed by Singh et al. (1990) on a calcareous soil fertilised with urea, simultaneous supply of Ni enhanced growth.

The average total Ni concentration in soil on a global basis is estimated to be 20 mg $kg^{-1}$ Ni (Quipilg et al. 1984) with an overall range from 10 to 1000 mg $kg^{-1}$ Ni (Yagodin et al. 1991). Considerable variations are due to the parent material quality as well as anthropogenic sources. Nickel concentrations in anthropogenic-polluted soils can reach up to 200-26000 mg $kg^{-1}$ Ni. The primary sources of Ni pollutions are the burning of coal and oil, emissions of smelters and metal-works, municipal wastes, sewage, phosphate fertilisers and pesticides.

The current ecological situation in Russia is critical, even in some regions there is an ecological disaster. Due to economical difficulties industrial enterprises do not invest in the protection of the environment. As a result a complex of anthropogenic factors influences all

compartments of the ecosystem negatively. Totally 2.8 % of the topsoil in Russia is polluted by Ni. This is the second largest pool of heavy metal contamination in soils (following 3.8% of soils polluted with Cu) (Aristarhov & Kharitonova 2002). The most severe polluted area with Ni is the Kola Peninsula due to vast numbers of smelters and metal-works in this region. Only 5 km away from the smelting company "Northnickel" close to the town Monchegorsk, the Ni concentrations in the soil are 40 times higher compared to natural conditions. In a distance of 15 km the concentration is 15-20 times and 25 km away still 4-5 times higher (Evdokimova 1990).

Manifold environmental pollution with different risk potential was produced by unfavourable waste management and intensive mining activities. Detailed investigation of heavy metal mobility behaviour from waste dump material of typical smelting products (e.g. Mansfelder Land county, mining area of Eastern Thuringia) has been taken place in Germany. From these investigations conclusions for long-term behaviour of components and an estimation of the endangerment had to be discussed. Based on different German studies the transfer behaviour of heavy metals, inter alia Ni, from soil to well-chosen food and forage plants was analysed. On this basis a concept for hazard assessment concerning adverse effects of soil contaminations to plants was developed (Knoche et al. 1999; Schoenbuchner 2005).

Ni occurs in several chemical forms in soils, including exchange sites, specific adsorption sites, fixed within the clay lattice, absorbed on oxides and finally, fixed in soil organic matter. Ni occurs in the ionic form and is complexed with either organic or inorganic ligands. No well-defined distribution pattern of Ni within the soil profile has been observed in natural soils, however in some cases a higher concentration has been observed in the soil layer rich in organic matter or high in clay content. General in soils Ni (II) is stable over a wide range of pH and redox conditions (Cotton & Wilkinson 1980). Ni halides and salts of oxo-acids are generally soluble in water, while Ni carbonate is almost insoluble (Yaron et al. 1996).

The risks of a heavy metal transfer into the food chain are dependent on the mobility of the heavy metal species and their availability in the soil (Richards et al. 2000). For the extraction of the mobile forms of heavy metal different kinds of extractants are used. 1.0 M mineral acids extract most heavy metals and the species extracted are considered to represent a pool closely related to the total concentration, which can be mobilised potentially. Heavy metals extracted by an acetate-ammonium buffer solution characterise these mobile pool. Even more mobile is the exchangeable form of the elements extracted by neutral salts, which is also considered as the

most available fraction for plants (Gorbatov & Zyrin 1987). The other forms of elements are more or less immobile. Mobilizations of metals from these forms or transformation from mobile fractions into immobile are very slow processes, which are controlled mainly by kinetic factors.

Haq et al. (1980) evaluated the effectiveness of strong and weak acids, as well as chelates to extract Ni and revealed the following order of effectiveness:

DTPA (Diethylenetriaminepentaacetic acid) > EDTA (Ethylenediaminetetraacetic acid) > NTA (Nitrilotriacetic acid) > $CH_3COOH$ (acetic acid) > $H_2O$.

Obviously chemical forms do not show the real metal distribution in agrocoenosis and let the contribution of one certain compartment to be educed. They only reflect the combined contribution of several compartments in forming one or another metals fraction in soil. For measuring the metal availability for plants it is necessary to take into account a wider range of soil properties such as clay, organic matter and hydrous oxides content, pH and cation exchange capacity (CEC).

Ni is readily and rapidly taken up by plants from soils. Until certain Ni concentrations in plants tissues are reached, the absorption is positively correlated with soil Ni concentrations (Morrison et al. 1980). The Ni content in field-grown material is extremely variable. Besides Ni availability in the soil, the actual Ni content in plants depends on the plant species, plant part and vegetative stage (Gerendas et al. 1999). Nickel is extremely mobile inside the plants. It easily moves in xylem as well as in phloem. Therefore a high danger of Ni accumulation in different agricultural products grown on contaminated soils exists (Andreeva et al. 2001).

There is lot of evidence that genotypic peculiarities of plants have considerable influence on the heavy metal uptake (Kabata-Pendias 2001; Schnug & Strampe 1988). Moreover heavy metal accumulation varies in different plant organs and depends on plant age (Ovcharenko 1997). For instance oat grain accumulates more Ni than the straw, while all other metals are usually accumulated more in the cereal straw (Kabata-Pendias & Wiacek 1985).

The mechanism of Ni toxicity to plants is not well understood so far, although the limited growth of plants and contaminations caused by an excess of this metal have been observed.

As an example the Ni toxicity on water spinach is illustrated in Photo 1.1.

Photo 1.1: A) Necrosis along the vein on water spinach leaves after treatment with 5 mg $l^{-1}$ Ni in water culture; B) Stem necrosis on water spinach as affected by 5 mg $l^{-1}$ Ni in water culture (Sun & Wu 1998).

The most common symptom of Ni phytotoxicity is chlorosis, which seems to be a Fe-induced chlorosis. The absorption of nutrients, root development and metabolism of plants under Ni stress is strongly retarded. Before acute Ni toxicity symptoms are evident, enriched concentrations of this metal are known to inhibit the biosynthesis of chlorophyll, photosynthesis, transpiration and to induce peroxidation of lipid membranes in the plant tissues. It also has been reported that low $N_2$ fixation by soybean plants is caused by Ni excesses (Vesper & Weidensaul 1978; Sheoran et al. 1990; Slivinskaya 1991; Kabata-Pendias 2001). Increased rates of free radical reactions contribute to the toxicity of $Ni^{2+}$ ions, by affecting the functionality of the membrane system due to sylphydryl reactions (Sinha & Pandey 2003).

Individual species differ in their capacity to modify their metabolism to tolerate or accumulate Ni. The modifications may involve sequestration of the metal in vacuoles, biosynthesis of organic compounds that detoxify Ni, or synthesis of modified tissues to exclude the contaminant (Boyd & Davis 2001).

Liming is considered to be an economically acceptable measure that generally helps to reduce the transport of heavy metals into the food chain. Liming has two effects. First it induces an increase in soil pH and supplies $Ca^{2+}$. The solubility and availability/toxicity to organisms of heavy metal cations ($Cd^{2+}$, $Cr^{3+}$, $Fe^{n+}$, $Pb^{2+}$, $Mn^{n+}$, $Hg^{2+}$, $Ni^{2+}$, and $Zn^{2+}$ ) decrease as soil pH increases (McLaughlin 2002). This is due to the increase in the negative charge on variable charge surfaces in soil (Bolan et al. 2003). Nebolsin & Sychev (2000) and Cho & Han (1996) reported a general decrease of Ni uptake with increasing lime doses from experiments with vicia, barley and radish plants.

Many findings confirm that the solubility of heavy metals in soil is directly correlated with the redox potential (Patrick et al. 1990; Masscheleyn et al. 1991; Chuan et al. 1996). Yaron et al. (1996) showed that under same pH values metal solubility increases as redox potential decreases.

Increasing pH, induced by lime activates microbiological processes in the soil. Recently Weyman-Kaczmarkowa & Pedzivilk (2000) reported that alkalinisation showed a very strong stimulation effect on bacterial growth, especially in loose sandy and sandy loam soils. The microbial biomass increases and can accumulate considerably high amounts of certain heavy metals. On the other hand microbiological increases of the heavy metal availability are caused by microorganisms capable of reducing certain compounds (generally Mn and Fe) and also by their variable bioaccumulation of heavy metals (Kovalskiy & Letunova 1974).

Calcium release affected by liming, considerably changes the composition of cations absorbed in the soil solid phase: Most of the $H^+$ ions are replaced with $Ca^{2+}$. This leads to a neutralisation of soil pH and the formation of hydroxide colloids of most of the heavy metals, which are scarcely soluble. For example the water solubility of $Zn(OH)_2$, $Cu(OH)_2$, $Cd(OH)_2$ and $Ni(OH)_2$ is only 0.0005, 0.003, 0.0016 and 0.013 g $l^{-1}$ respectively.

Soil enrichment with Ca contributes to coagulation of soil colloidal particles, starts the development of soil aggregates and improves the soil structure. This also indirectly affects the redox potential and activates oxidation processes. All these combined effects have an influence on heavy metal availability in soil (Alekseev 1987).

In the pH range of 7.1-8.5 carbonate acts as pH buffer. The surfaces of calcite are reactive and various ions may adsorb or interact at the crystal's surface. For example $Mg^{2+}$, $Zn^{2+}$, $Cu^{2+}$, $Fe^{2+}$ and $Al^{3+}$ may replace $Ca^{2+}$ on exposed surface lattice sites. The reactive surfaces of carbonates may adsorb soil contaminants such as $Ba^{2+}$, $Cd^{2+}$ and $Pb^{2+}$ (Ming 2002).

Yudintseva et al. (1980) observed an antagonism between $Ca^{2+}$ and $Mg^{2+}$ in lime and pollutant cations in soil solution. Thus the application of lime decreased the plant uptake of radionuclides belonging to the Periodic Table groups I and II although the solubility of their hydroxides is very high.

Since liming is widely applied all over the world, it looks like everything is already known about this remediation practice. Obviously there is by far no clear understanding of all the processes of lime influencing soils and plants. There are only a limited number of studies about plant response to liming during the vegetation period. Basically no evidences or the evaluation of specific growth rates of plants influenced by different levels of liming are available. The knowledge of the properties of liming concerning control mechanisms of pH, influence of the supply and availability of essential plant nutrients as well as toxic elements, how it affects higher plants and human beings and how liming can be improved is essential for a sustainable management of soils throughout the world.

*Nutrient interactions in the soil-plant system*

The soil-plant system is one of the most important components in agricultural and natural ecosystems. The nutrient dynamics in the soil-plant systems not only reflect the pattern of nutrient flow but also influence food production and the quality as well as the contaminant pathways in agricultural and natural ecosystems. Interactions between nutrients in the soil-plant system occur when the supply of one nutrient affects the movement, absorption or utilization of another nutrient within the soil, soil root interface or plant (Zhang & Shen 2002) (Fig. 1.2).

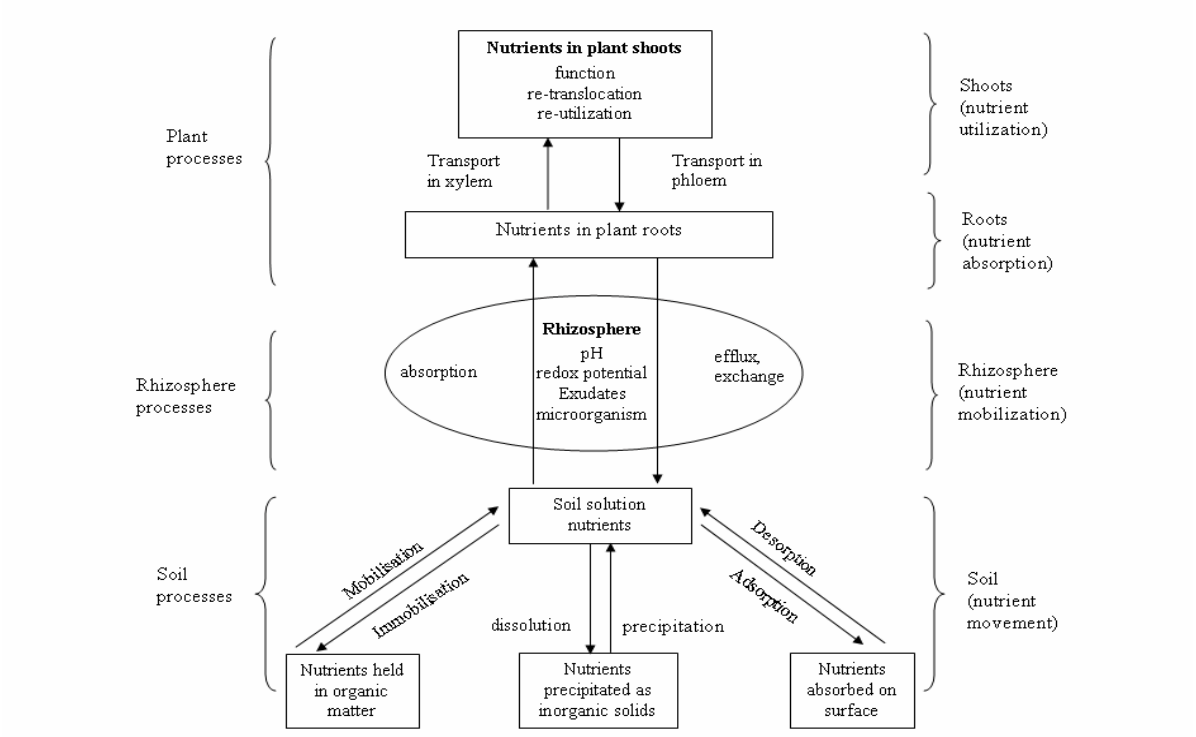


Figure 1.2: Nutrient interactions in the soil-plant system (adapted from Robson & Pitman 1983).

Although it is well known that all the compartments in the soil-plant system are in a dynamic equilibrium and reactions of ion exchange play an important role in all processes of their interactions, further investigations are needed for a better understanding of agrocoenosis.

*Models describing the dynamic of elements in the soil-plant system*

For the description of element dynamics in the soil-plant system various models have been applied. *Transfer Factors* are an example for elementary models, which assume that the system consists only of two compartments – soil, and plant, which are in equilibrium. The constant characteristic of this equilibrium is the *Transfer Factor*. For a long time scientists have effectively used this model, but because the system is very simplified it does not explain many experimental results, for example the high variability of *Transfer Factors* in different systems. Moreover *Transfer Factors* are usually calculated as a ratio of element concentration in plants in respect to the total element concentration in the soil. It does not take into consideration the mobile pool of elements in soil.

For improvement many other models describing the element transfer from soil into plants were elaborated. Bakunov (1989) proposed a non-linear correlation model in which the accumulation of radiocaesium in plants is considered as uptake of $^{137}$Cs mobile forms from soil, which depends on mobile K content. A significant disadvantage of these kinds of models is that the sorption capacity of plant roots has not been taken into account. Another improvement is provided by the work of Konopleva (1999). The author described the migration of radiocaesium in the chain soil-plant on the basis of soil properties and took into account the plant participation on the level of root cells. It assumes that $^{137}$Cs in the soil solution is in dynamic equilibrium with two ion exchangers, the soil and the root surface. The $^{137}$Cs transfer from soil into plants is a result of two main processes:

- soil-geochemical process, dependent on sorption and fixation capacity of the soil for the radionuclides and the concentrations of the main competitive ions
- biological (physiological) process, connected with the element transfer from soil to plants, which also depends significantly on the concentration of other ions in the soil solution.

The hypothesis of this research work is that in the soil-plant system Ca and Ni, added to soil in form of lime and soluble salt, interact competitively on the basis of ion exchange mechanisms.

The main objectives of the research work presented here were to assess:

I. The applicability of a sorption model for describing the Calcium and Nickel interaction in the soil-plant system.
II. The influence of lime application on the mobile Ca and Ni concentration in soil.
III. The influence of lime application and plants growth development on changes of soil pH.
IV. The influence of increasing lime supply on the dynamic of biomass development, specific growth rate and Ca and Ni uptake.
V. The effect of liming on the soil/plant transfer of Ni and its translocation in plants during the vegetation period.

# 2 Material and methods

In order to investigate the interaction of Calcium and Nickel in the soil-plant system and to evaluate the influence of lime on the Ni transfer from soil into plants a two years pot experiment was carried out.

## *2.1 Description of the test soil*

The experiment was conducted during 2000-2001 at the Agricultural Physical Research Institute in St.-Petersburg-Pushkin, Russia. An acid sod-podzolic sandy-loam (Russian soil classification system) or alternatively a dystric cambisol (FAO-Unesco soil classification) was used in this study. It is a typical arable soil in the territories of ancient glacier transition. The soil is characterised by low organic matter content, acid soil reaction and low contents of plant available phosphorus and potassium (Tab. 2.1).

Table 2.1: Description of the test soil (For analytical methods see Tab. 2.3).

| **Organic matter** [%] | **pH(KCl)** | **Exchangeable bases** | | | **P** | **K** |
|---|---|---|---|---|---|---|
| | | **Total** | **$Ca^{2+}$** | **$Mg^{2+}$** | | |
| | | [meq $kg^{-1}$] | | | [mg $kg^{-1}$] | |
| 1.66 | 4.1 | 10.3 | 7.6 | 1.2 | 42.0 | 83.2 |

## *2.2 Experimental design*

### *2.2.1 Crop Selection Experiment (CSE)*

In the year 1999 an additional pot experiment was carried out in order to select crops for further investigations. The main aim was to find a crop, which has an enhanced ability to take up Ni, and can grow in the climatic conditions of Saint-Petersburg. The design of the experiment included different plant species and soil with and without Nickel contamination (Tab. 2.2):

Table 2.2: Design of the Crop Selection Experiment (CSE).

| **Treatment** | **Crop** | **Ni contamination 20 mg kg$^{-1}$** | **Number of plants per pot** |
|---|---|---|---|
| 1 | *Amaranthus florebuntus* | - | 5 |
| 2 | *Amaranthus florebuntus* | + | 5 |
| 3 | *Brassica juncea* | - | 7 |
| 4 | *Brassica juncea* | + | 7 |
| 5 | *Brassica chinensis* | - | 7 |
| 6 | *Brassica chinensis* | + | 7 |
| 7 | *Brassica napus* | - | 10 |
| 8 | *Brassica napus* | + | 10 |

All treatments received the complex mineral fertilizer "Ecofoska" in doses of $N_{0.19}$ $P_{0.10}$ $K_{0.10}$ g kg$^{-1}$. Nine days before sowing the soil was passed through a 5-mm sieve and mixed thoroughly with fertilizer and water solution of $Ni(NO_3)_2 \cdot 6H_2O$. The soil was transferred to plastic pots containing 5 kg of soil dry matter afterwards. All treatments were carried out in three replicates. The crops were harvested in the flowering phase.

### *2.2.2 Basic Modelling Experiment (BME)*

The objective of the Basic Modelling Experiment (BME) was to generate basic data for the modelling of Calcium and Nickel interaction in the soil-plant system. Therefore the soil was contaminated with Ni and treated with increasing amounts of lime.

The experimental design included 5 treatments and one control:

Control
20 mg kg$^{-1}$ Ni + lime 0.41 [g kg$^{-1}$]
20 mg kg$^{-1}$ Ni + lime 0.83 [g kg$^{-1}$]
20 mg kg$^{-1}$ Ni + lime 1.25 [g kg$^{-1}$]
20 mg kg$^{-1}$ Ni + lime 1.66 [g kg$^{-1}$]
20 mg kg$^{-1}$ Ni + lime 2.10 [g kg$^{-1}$]
All treatments were carried out in three replicates.

The control has received neither Ni nor lime. All the treatments received the complex mineral fertilizer "Ecofoska" in doses of $N_{0.15}$ $P_{0.08}$ $K_{0.14}$ g kg$^{-1}$. Seven days before sowing the soil was

passed through a 5-mm sieve before mixing thoroughly with fertiliser, lime and water solution of $Ni(NO_3)_2 \cdot 6H_2O$ and transferred to the plastic pots, containing 5 kg dry soil.

Year 2000 – *Brassica napus*

Photo 2.1: *Brassica napus* L. (copyright by Shöpke Thomas).

Taking into account the high ability of *Brassica napus* (oilseed rape) to accumulate Ni this plant was chosen as experimental crop in the BME. The variety used for the experiment was Oredezh3. Weight of 1000 seeds is 2.6 – 5.0 g (Goltsov et al. 1983).

The plants were sown in May. In each pot 14 plants were cultivated. The pots were located outdoors under a plastic shelter. Water was applied sufficiently for optimum growth. The treatment with the lowest lime dose has been excluded since the pots were inundated with rainwater.

Soil and plants were sampled after 14, 21, 29, 36 and 43 days of growth. At sampling date "day 43" plants were in the flowering phase.

Year 2001 – *Avena sativa*

Photo 2.2: *Avena sativa* L. (copyright by Reynolds Samuel ).

Eight days before sowing, the soil from all pots was removed, watered, mixed and returned to the pots. The investigated variety of the used crop was "Astor" which belongs to early-maturing varieties. Oats (*Avena sativa*) are known to tolerate acid, neutral and basic (alkaline) soils and can even grow in very acid soil. This was the main criterion why it was chosen as crop in the year 2001. The plants were sown in early June. In each pot 12 plants were cultivated. Soils and plants were sampled at the 14, 21, 29, 36 and 43 day of growth. At sampling date "day 43" the plants were at the beginning of milky-wax ripeness phase.

## *2.3 Chemical analysis*

All the chemical analyses were carried out in the Agricultural Physical Research Institute, Saint-Petersburg, Russia.

### *2.3.1 Soil samples*

All analytical methods were carried out on air-dried and sieved soil samples (<2 mm), standard methods were employed (Tab. 2.3).

Table 2.3: Analytical methods of soil samples.

| **Parameter** | **Method** |
|---|---|
| pH | Potentiometrically in 1n KCl suspension (soil:solution = 1:2.5) (Arinushkina 1980) |
| $C_{org}$<br>Soil organic matter | Oxidation with a mixture of $K_2Cr_2O_7$ and $H_2SO_4$ (1:1, vv) Turin method. Calculated assuming that organic matter contains 58% carbon (Arinushkina 1980). |
| Available P and K | Extraction by 0.2n HCl (soil:solution = 1:5). P analysed calorimetrically, K-by flame-photometry. Kirsanov method (Mineev 1989). |
| Exchangeable bases | Extraction by 0.1n HCl (soil:solution = 1:5), titration by 0.1n Na(OH) (Yagodin et al. 1987). |
| Mobile Ni | Extraction by ammonium-acetate buffer (pH 4.8) (soil:solution = 1:5), determined by AAS (Anonym 1993). |
| Mobile Ca | Extraction with 1n KCl, (soil:solution = 1:2.5), determined by AAS (Anonym 1994). |

*Plant available phosphorus and potassium*

Plant available phosphorus and potassium were extracted in 0.2n HCl. The following reagents have been used:

a) Extracting solution: 16.4 ml HCl (d=1.19) was dissolved in 1 litre of distilled water.
b) Reagent A: 6 g of ammonium molybdate $(NH_4)_2MoO_4$ was dissolved in 200 ml distilled water. 0.145 g of antimony potassium tartate $K(SbO)C_4H_4O_6$ was dissolved in 100 ml distilled water. Both solutions were prepared under slight heating. Cooled solutions were added to 500 ml 5n sulphuric acid $H_2SO_4$ , mixed thoroughly and made to 1 litre. The reagent was stored in a pyrex glass bottle in dark cool place.
c) Reagent B: 0.887 g ascorbic acid ($C_6H_8O_6$) was dissolved in 168 ml reagent A and mixed.

Ten grams of soil were placed in 100 ml retort and filled up with 50 ml of 0.2n HCl. The suspension was shaken manually for exactly 1 minute, sedimented and was filtered. The filtrate was analysed for potassium (K) by flame-photometry. For the phosphorus (P) analysis, 5 ml of filtrate was transferred to a 100-ml beaker and 95 ml of reagent B was added. Ten minutes after the solution became coloured phosphorus was analysed calorimetrically.

*Organic matter*

Organic matter was oxidized with a mixture of 0.4n $K_2Cr_2O_7$ and $H_2SO_4$ (1:1, vv). Unused $K_2Cr_2O_7$ was back titrated with Mora salt ($FeSO_4$). The dilution heat of concentrated $K_2Cr_2O_7$ and $H_2SO_4$ is the only source of heat. Because no external heat source was applied, the method provides only an estimate of readily oxidizable organic carbon and was used as a measure of total organic C. Organic matter is estimated assuming that organic matter contains 58% carbon (Arinushkina 1980).

*Mobile Nickel*

The mobile Ni fraction was extracted by an ammonium-acetate buffer (pH 4.8) (soil:solution = 1:5). The suspension was shaken for 1 hour and filtered. The filtrate was analysed directly for Ni by AAS at a wavelength of 232.0 nm in propane-butane flame air.

*Mobile Calcium*

Mobile Ca was extracted by 1n KCl (soil:solution = 1:2.5). The suspension sedimented for 24h and was then filtered. Two ml of filtrate were transferred to a tube (100 ml size) and 50 ml of 20% $SrCl_2 \cdot 6H_2O$ were added. The solution was analysed for Ca by AAC at a wavelength of 422.6 nm in propane-butane flame air.

### *2.3.2 Plant analysis*

All analytical methods were carried out on oven dried plant samples. The plant material was placed in forced-air oven and dried at 80°C for 24 hours. After drying the samples were fine ground by means of an electrical mill.

Table 2.4: Analytical methods of plant material.

| Parameter | Method |
|---|---|
| Ni concentration | Nitric-perchloric acid wet digestion followed by AAS determination of Ni concentration (Anonym 1992a). |
| Ca concentration | Nitric-perchloric acid wet digestion followed by titration with Disodium EDTA (Anonym 1992). |

The analytical method employed for determination of Ni concentration is the same as reported by Miller (1998).

Reagents:

Deionised water

Nitric acid ($HNO_3$) concentrated, reagent grade

Perchloric acid ($HClO_4$), 70% reagent grade

Five standard calibration solutions ranging from 0.001 to 0.008 mg $ml^{-1}$ diluted with 5% $HNO_3$ and 1% $HClO_4$ by a volume of a 100ml tube.

One g of plant dry matter was filled into a 50-ml volumetric digestion tube. Using a pipette, 10 ml of the mixture $HNO_3$ and $HClO_4$ (2:1, vv) was added and swirled to thoroughly wet the sample. 25-mm reflux funnels were placed over samples and allowed to predigest over night. The digestion tubes were placed into a digestion block port for 3 hours at 200°C after the $HNO_3$ fumes have evolved. The funnels were removed 10 minutes before the end of the digestion. The tubes were removed from the digestion block, cooled 20 minutes in a hood and 10 ml deionised water were added on a hot plate (90°C). The contents of the digestion tubes were mixed, cooled and quantitatively transferred into 25-ml volumetric flask and diluted to the final volume. Ni analysis of plant digest were made using AAS with the wavelength 232.0 nm in propane-butane flame air.

For the determination of the Ca concentration 1 g of plant dry matter was filled in 50-ml volumetric digestion tubes and the procedure of digestion according to Miller (1998) was carried out. The contents of the digestion tube were transferred quantitatively into a 25-ml volumetric flask and diluted to the volume. Two ml of the solution were transferred to an Erlenmeyer tube (250 ml size) and dissolved with 100 ml of distilled water. Then the following reagents were added: 3 drops of 2.5% $Na_2S{\cdot}9H_2O$ , 8 drops 5 %$NH_2OH{\cdot}HCl$, 3 ml 10% KOH and 0.02 g mixture of $C_6H_8N_6O_6{\cdot}H_2O$ and NaCl (1:10). The solution was titrated with 0.05n Disodium EDTA until the colour turned violet under permanent shaking.

In the presented study all yields are given in dry matter and all tissue concentrations are estimated on the base of dry matter.

## *2.4 Statistical analysis*

For the statistical analyses the SPSS software package version 10 was employed (SPSS, 1999). The differences between means were tested using the *Tukey test* and *t-test* (LSD) at 5% significance level. The analysis of relationships between factors was performed using the software package ORIGIN 6.0.

The calculated standard deviation is illustrated by bars in all figures.

## *2.5 Sorption model*

For the description of the experimental results the sorption model of elements transfer from soil to plants elaborated by Drichko et al. (1996) was employed. This model is based on the mechanism of ion exchange. In the framework of the model the plant root system and the soil are considered to be sorbents, which simultaneously compete for ions in the soil solution.

It is also assumed that between the soil solution and the soil solid phase and between the soil solution and the plant roots a dynamic equilibrium exists at each time scale. The system is simplified by ignoring the precipitation of ions from the soil solution (Figure 2.1).

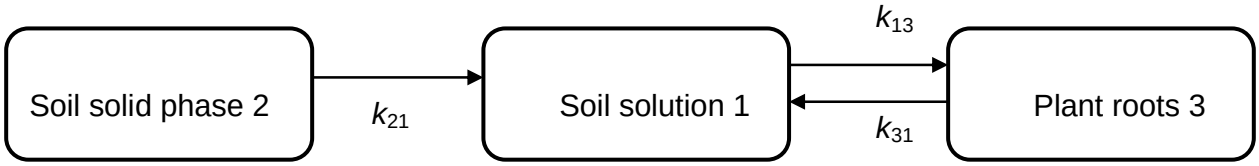


Figure 2.1: Three-chamber scheme of agrocoenosis.

For a mathematical description of the model it is necessary to define the used parameters:

$S$ – total number of exchange places per 1 square unit of root surface [mg cm$^{-2}$]

$\delta$ – fraction of exchange places occupied by element (ion)

$1-\delta$ – fraction of free exchange places

$C_1$ – volumetric concentration of element in soil solution [mg cm$^{-3}$]

$C_2$ – surface concentration of element on the root [mg cm$^{-2}$]

From this it follows that $C_2 = S\delta$.

Assuming that the specific flow of the element from the soil solution to the plant roots ($k_{13}$ [mg $s^{-1}cm^{-2}$]) is proportional to the number of free exchange places on the root surface and the element concentration in soil solution follows:

$$k_{13}=\omega(1-\delta)SC_1 \qquad \text{(Equ. 1.1)}$$

Where:

ω – coefficient of proportionality [$cm^3$ $mg^{-1}$ $s^{-1}$] which characterises the rate of element sorption on the root surface from soil solution.

The specific flow of element through root surface to soil solution ($k_{31}$ [mg $s^{-1}$ $sm^{-2}$]) is:

$$k_{31}=\varphi\delta S=\varphi\ C_2 \qquad \text{(Equ. 1.2)}$$

Where:

φ – coefficient of proportionality [$s^{-1}$] which characterises the rate of element desorption from the root surface.

In the state of equilibrium these flows are equal. Equating equation 1.1 with equation 1.2 it turns out that:

$$C_2 = \frac{\omega S C_1}{\varphi + \omega C_1} \qquad \text{(Equ. 1.3)}$$

Assuming that the element concentration in soil solution is a linear function of its total concentration in soil:

$$C_1 = pC_{soil} \qquad \text{(Equ. 1.4)}$$

Assuming that the element concentration in plant ($C_{plant}$ [mg $g^{-1}$]) is a linear function of its concentration on the root surface:

$$C_{plant} = kC_2 \qquad \text{(Equ. 1.5)}$$

Where $p$ [g cm$^{-3}$] and $k$ [cm$^2$ g$^{-1}$] are constants for the certain kind of plant and soil, it turns out that:

$$C_{plant} = \frac{k\omega SpC_{soil}}{\varphi + \omega pC_{soil}} = \frac{k\alpha SpC_{soil}}{1 + \alpha pC_{soil}} \qquad \text{(Equ. 1.6)}$$

Where:

$\alpha = \frac{\omega}{\varphi}$ – corresponds to the volume of soil solution [cm$^3$ mg$^{-1}$]

$p$ – corresponds to the distribution coefficient ($k_d$) between solid phase and soil solution [g cm$^{-3}$]

$C_{soil}$ – element concentration in soil [mg g$^{-1}$]

The product of coefficients $k$ and $S$ [mg g$^{-1}$] is the specific capacity of plant for an element.

If two elements with equal valence, one is microelement (1) and the other one is macro-element (2), compete for the sorption places, the Equ. 1.6 becomes as follows:

$$C_{plant_1} = \frac{k_1\alpha_1 Sp_1 C_{soil_1}}{1 + \alpha_1 p_1 C_{soil_1} + \alpha_2 p_2 C_{soil_2}} \qquad \text{(Equ. 1.7)}$$

Since $C_{soil1}$ is always much lower than $C_{soil2}$ the Equ. 1.7 can be simplified:

$$C_{plant_1} = \frac{k_1\alpha_1 Sp_1 C_{soil_1}}{1 + \alpha_2 p_2 C_{soil_2}} \qquad \text{(Equ. 1.8)}$$

Hence the *Transfer Factor (TF)* for a microelement can be presented as a value dependent on all parameters described above, which characterise properties of soil, plants, micro-and macro-elements:

$$TF = \frac{C_{plant\ 1}}{C_{soil\ 1}} = \frac{k_1 \alpha_1 Sp_1}{1 + \alpha_2 p_2 C_{soil\ 2}} \qquad \text{(Equ. 1.9)}$$

It is evident from the last equation that the inverse value of the *Transfer Factor* is directly proportional to the concentration of the macroelement in soil:

$$TF^{-1} = a + bC_{soil\ 2} \qquad \text{(Equ. 1.10)}$$

Where:

$$a = \frac{1}{k_1 \alpha_1 Sp_1} \; ; \; b = \frac{\alpha_2 p_2}{k_1 \alpha_1 Sp_1}$$

The coefficient *a* corresponds to the maximum possible *TF* ($TF_0$) which could be observed if there were no mobile forms of the macroelement in the soil ($C_{soil2}$ = 0). It depends on the properties of the microelement, plant and soil. Coefficient *b* depends on properties of the macro-element, plant and soil.

Therefore on the basis of the adsorption isotherm it is possible to evaluate the influence of macro-element concentration in soil on *Transfer Factors* for microelement. If a microelement interacts with a macro-element according to the ion exchange mechanism the direct proportion of the parameter $TF^{-1}$ for the microelement with the concentration of macroelement in soil will be observed (Equ. 1.10).

*Dynamics of element accumulation by plants during vegetation*

The concentration of any element in plants during the vegetation period goes through a maximum, which is usually observed in juvenile phases of plant development. But the concentration as a characteristic is not primary; it depends on plant dry matter growth and element uptake of plants that are functions of time.

The dry matter development is described with a S-shaped curve, which is well approximated by the logistic equation (Walter & Lampreht 1976; Kletschenko 1986; Warpholomeev & Kalyuzhny 1990):

$$M_{(t)} = \frac{M_{max}}{1 + \frac{M_{max}}{M_0} e^{-\mu t}} \qquad \text{(Equ. 1.11)}$$

Where:

| | | |
|---|---|---|
| $M_{(t)}$ | – | accumulated dry matter [g pot$^{-1}$] |
| $M_{max}$ | – | maximum dry matter [g pot$^{-1}$] |
| $M_0$ | – | mass of seeds [g pot$^{-1}$] |
| $\mu$ | – | specific growth rate [d$^{-1}$] |
| $t$ | – | time [d] |

When $M_{max} >> M_0 e^{\mu t}$ the exponential phase of plant growth is observed:

$$M_{(t)} = M_0 e^{\mu t} \qquad \text{(Equ. 1.12)}$$

It might be assumed that the element uptake by plants is approximated with similar functions:

$$A_{(t)} = \frac{A_{max}}{1 + \frac{A_{max}}{A_0} e^{-\varepsilon t}} \qquad \text{(Equ. 1.13)}$$

Where:

| | | |
|---|---|---|
| $A_{(t)}$ | – | accumulated uptake [g pot$^{-1}$] |
| $A_{max}$ | – | maximum macro-element/micro-element uptake by plants [mg pot$^{-1}$] |
| $A_0$ | – | element content in seedling roots [mg pot$^{-1}$] |
| $t$ | – | time after planting [d] |
| $\varepsilon$ | – | specific rate of element uptake [d$^{-1}$] |

When $A_{max} >> A_0 e^{\varepsilon t}$

$$A(t) = A_0 e^{\varepsilon t} \qquad \text{(Equ. 1.14)}$$

Thus the development of element concentration in plants on the exponential phase of growth is expressed as:

$$C(t) = \frac{A(t)}{M(t)} = C_0 e^{-(\mu - \varepsilon)t} \qquad \text{(Equ. 1.15)}$$

Where:

| | | |
|---|---|---|
| $C(t)$ | – | element concentration in plant at a time (t) [mg $kg^{-1}$] |
| $C_0$ | – | element concentration in plants at the beginning of the exponential phase |
| $\mu$ | – | specific growth rate [$d^{-1}$] |
| ε | – | specific rate of element uptake [$d^{-1}$] |

In the case that the specific growth rate ($\mu$) and the specific rate of element uptake ($\varepsilon$) are equal, the element concentration in plants does not change during the vegetation period. If $\mu > \varepsilon$ or $\mu < \varepsilon$ the element concentration in the plant decreases or increases respectively over time proportionally to $\mu - \varepsilon$.

The addition of a macroelement to the soil can decrease the concentration of a microelement in plants due to biological dilution (parameter *M(t)* (Equ. 1.15) increases) or due to competitive exchange between soil solution and root surface (parameter *A(t)* (Equ. 1.15) decreases).

# 3 Results

## *3.1 Accumulation of Ni by different species of plants*

All examined crops are characterised by the high ability to accumulate Ni in their tissues. Depending on the genetically caused peculiarities of plants in the control treatments the Ni concentration in plant shoots differed in a high degree. On the not polluted soil *Amaranthus florebuntus* accumulated 9-12 times less amount of Ni than other examined crops (Tab. 3.1).

Table 3.1: Ni concentration and Ni uptake of different plant species.

| **Treatment** | **Ni concentration in plants** [mg $kg^{-1}$] | | **Ni uptake by plants** [mg $pot^{-1}$] | |
|---|---|---|---|---|
| | **Control** | **Ni 20 mg $kg^{-1}$** | **Control** | **Ni 20 mg $kg^{-1}$** |
| *Amaranthus florebuntus* | 1.33 | 158.0 | 0.03 | 3.06 |
| *Brassica juncea* | 12.60 | 95.0 | 0.33 | 2.70 |
| *Brassica chinensis* | 16.40 | 198.0 | 0.26 | 3.00 |
| *Brassica napus* | 11.40 | 148.3 | 0.28 | 3.80 |
| *LSD(5%)* | *3.50* | *54.9* | *0.11* | *1.10* |

The data testified a high availability of Ni in plants. Thus the Ni concentration in plants increased in relation to the control, in the treatments with Ni contamination in 119, 7.5, 12 and 13 times respectively.

In the polluted soil significant differences in plant Ni concentrations were observed between *Amaranthus florebuntus* and *Brassica juncea* as well as between *Brassica juncea* and *Brassica chinensis.* The highest Ni concentrations were found in *Amaranthus florebuntus* and *Brassica chinensis:* 158 and 198 mg $kg^{-1}$, respectively. The ranking order of investigated species due to their ability to accumulate Ni is the following:

*Brassica chinensis > Amaranthus florebuntus > Brassica napus > Brassica juncea.*

The highest Ni uptake was received in the treatment with *Brassica napus*. The ranking order according to their ability to take up Ni of the investigated species is the following:

*Brassica napus > Brassica chinensis > Amaranthus florebuntus > Brassica juncea.*

## *3.2 Mobile Calcium (Ca) and Nickel (Ni) concentration in soil influenced by lime application*

As expected the application of lime influenced the concentration of mobile Ca in soil significantly. With increasing lime dose the mobile Ca concentration increased in both experimental years (Tab. 3.2).

Table 3.2: Effect of liming on the concentration of mobile Ca in soil [mg $kg^{-1}$].

| **Lime dose** [g $kg^{-1}$] | **Concentration of mobile Ca** [mg $kg^{-1}$] | | | | |
|---|---|---|---|---|---|
| | **Sampling time** [d] | | | | |
| | **14** | **21** | **29** | **36** | **43** |
| **2000** | | | | | |
| 0 | 168 | 177 | 181 | 109 | 117 |
| 0.41 | 477 | 326 | 305 | 349 | 295 |
| 0.83 | 478 | 445 | 482 | 420 | 412 |
| 1.25 | 573 | 509 | 540 | 566 | 555 |
| 1.66 | 712 | 692 | 766 | 708 | 837 |
| 2.10 | 774 | 720 | 787 | 766 | 793 |
| *LSD(5%)* | *43* | *25* | *33* | *21* | *45* |
| **2001** | | | | | |
| 0 | 140 | 146 | 150 | 150 | 142 |
| 0.41 | 341 | 323 | 365 | 375 | 351 |
| 0.83 | 502 | 480 | 582 | 522 | 548 |
| 1.25 | 642 | 631 | 653 | 674 | 658 |
| 1.66 | 900 | 921 | 929 | 899 | 877 |
| 2.10 | 970 | 932 | 930 | 924 | 921 |
| *LSD(5%)* | *37* | *43* | *41* | *47* | *45* |

In general in the year 2001 the mobile Ca concentration in the soil was higher almost at all sampling times. This might be caused by a complete reaction between lime and soil in the second year after lime application. But in the year 2000 the observations in the control and the treatment with the lime dose of 0.41 g $kg^{-1}$, the mobile Ca concentration was higher up to day 29. This might be a prevailing effect of Ca uptake over Ca release from lime at the beginning of the experiment.

A linear relationship between mobile Ca *($Ca_{mob}$)* in soil and the lime doses *(D)*, applied in the experiment was observed at all sampling times, in both experimental years (Fig. 3.1).

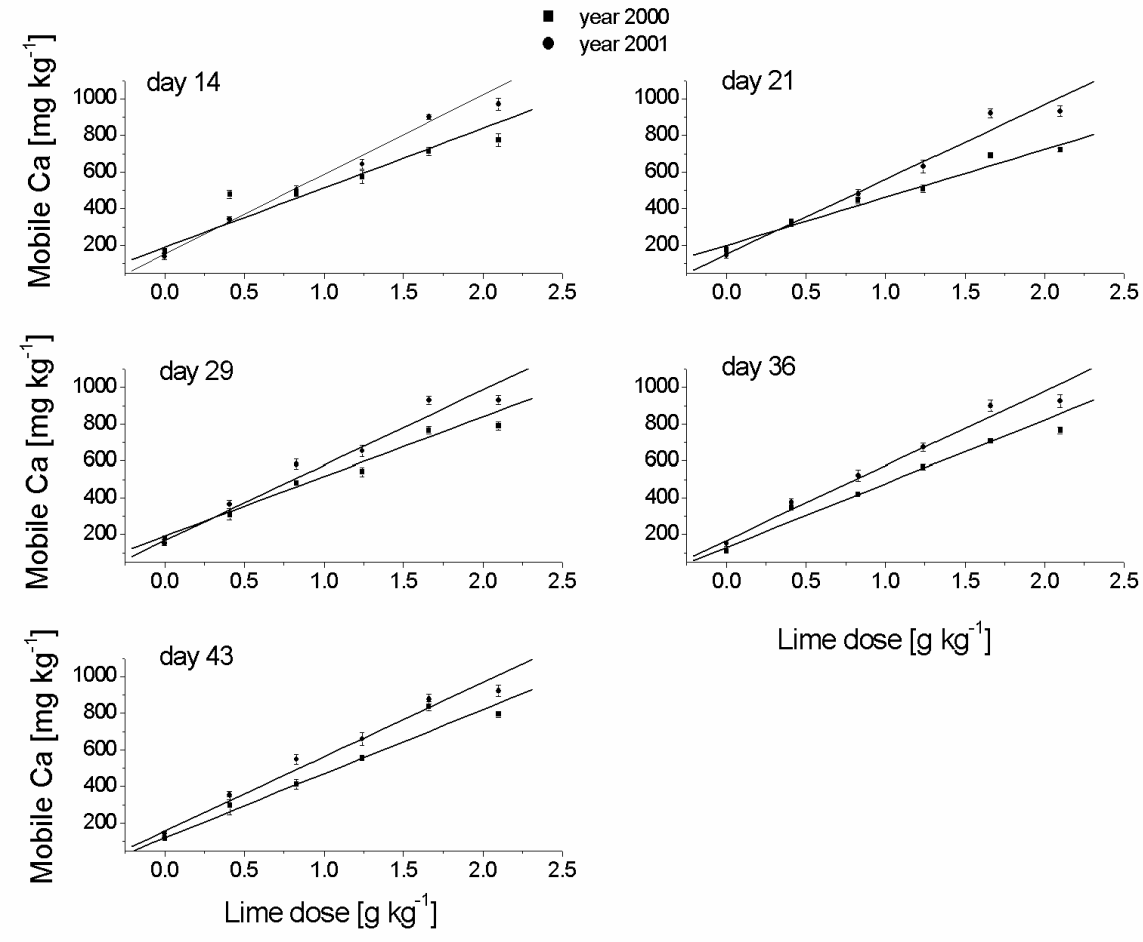


Figure 3.1: Concentration of mobile Ca in soil [mg $kg^{-1}$] depending on the lime dose for the years 2000, 2001 (corresponding to Equ. 3.1, model parameters see Tab. 3.3).

To quantify the relationship between lime dose and mobile Ca concentration in soil the following function was employed:

$$Ca_{mob} = Ca_0 + bD \qquad \text{(Equ. 3.1)}$$

Where:

| | | |
|---|---|---|
| $Ca_0$ | – | initial concentration of mobile Ca in soil (if $D = 0$) [mg $kg^{-1}$] |
| $b$ | – | mobile Ca concentration per unit lime [mg $kg^{-1}$] / [g $kg^{-1}$] |
| $D$ | – | lime dose [g $kg^{-1}$] |

The correlation coefficients between lime dose and mobile Ca concentration, explained by a linear function, were very high in both experimental years. The values of the parameter $Ca_0$ (experimentally determined and calculated by linear function) are close to each other (Tab. 3.3).

Hence there is no difference in use lime dose [g $pot^{-1}$] or [mg $kg^{-1}$] or concentration of mobile Ca [mg $kg^{-1}$] in further calculations.

Table 3.3: Parameters for the linear description of mobile Ca concentration in soil dependent on lime doses.

| **Sampling time** [d] | **Year 2000** | | | | **Year 2001** | | | |
|---|---|---|---|---|---|---|---|---|
| | $R^2$ | $Ca_{0calc}$ | $Ca_{0exper}$ | $b$ | $R^2$ | $Ca_{0calc}$ | $Ca_{0exper}$ | $b$ |
| | | [mg $kg^{-1}$] | | [mg $kg^{-1}$ / g $kg^{-1}$] | | [mg $kg^{-1}$] | | [mg $kg^{-1}$ / g $kg^{-1}$] |
| 14 | 0.86 | 189±31 | 168±8 | 324±41 | 0.98 | 150±25 | 141±16 | 436±22 |
| 21 | 0.98 | 200±23 | 177±9 | 262±18 | 0.98 | 151±29 | 147±15 | 409±28 |
| 29 | 0.90 | 192±19 | 181±8 | 323±23 | 0.98 | 167±32 | 151±11 | 409±33 |
| 36 | 0.98 | 131±21 | 109±7 | 345±18 | 0.98 | 169±23 | 150±13 | 404±27 |
| 43 | 0.98 | 119±16 | 117±5 | 350±22 | 0.98 | 151±19 | 143±11 | 403±25 |

Remarks: ± - error of estimating function; $R^2$ – coefficient of determination between mobile Ca concentration in soil and lime dose (explained by a linear function), figures apply to Equ. 3.1.

The concentration of mobile Ni ($Ni_{mob}$) in the soil during the vegetation period did not change significantly (Tab. 3.4).

Table 3.4: Effect of liming on the mobile Ni concentration in soil [mg $kg^{-1}$].

| **Lime dose** [g $kg^{-1}$] | **Concentration of mobile Ni in soil** [mg $kg^{-1}$] | | | | | | |
|---|---|---|---|---|---|---|---|
| | **Sampling time** [d] | | | | | **Arithmetic means** | **V** [%] |
| | **14** | **21** | **29** | **36** | **43** | | |
| **2000** | | | | | | | |
| 0 | Below detection limit | | | | | | |
| 0.41 | 6.30 | 6.75 | 5.68 | 6.87 | 7.02 | 6.49 | 7.7 |
| 0.83 | 6.80 | 6.07 | 5.78 | 5.93 | 6.08 | 6.13 | 6.6 |
| 1.25 | 5.65 | 5.05 | 5.58 | 5.93 | 6.52 | 5.75 | 8.6 |
| 1.66 | 4.75 | 5.00 | 4.91 | 5.41 | 4.55 | 4.99 | 8.2 |
| 2.10 | 4.95 | 5.25 | 4.83 | 5.15 | 5.10 | 5.06 | 3.9 |
| *LSD(5%)* | *1.30* | *1.50* | *0.90* | *0.80* | *1.00* | | |
| **2001** | | | | | | | |
| 0 | Below detection limit | | | | | | |
| 0.41 | 5.45 | 5.43 | 5.27 | 5.36 | 5.54 | 5.41 | 1.8 |
| 0.83 | 5.21 | 5.22 | 5.25 | 5.21 | 5.23 | 5.22 | 0.2 |
| 1.25 | 4.95 | 4.92 | 4.96 | 4.91 | 4.90 | 4.93 | 0.6 |
| 1.66 | 4.84 | 4.79 | 4.82 | 4.80 | 4.81 | 4.81 | 0.4 |
| 2.10 | 4.76 | 4.74 | 4.75 | 4.75 | 4.77 | 4.75 | 0.2 |
| *LSD(5%)* | *0.20* | *0.20* | *0.20* | *0.10* | *0.20* | | |

Remarks: V- coefficient of variability, $V = \sigma / \bar{x}$ – ratio of standard deviation to arithmetic mean.

The coefficient of variability of the mobile Ni concentration in soil was much less in the second year experiment, compared to the first. This may be caused by a more even distribution of elements in the soil volume in the second year of the experiment.

The concentration of mobile Ni ($C(Ni)_{mob}$) in the soil decreased with increasing lime doses *(D)* in both years of experimentation (Tab. 3.4, Fig. 3.2 and 3.3).

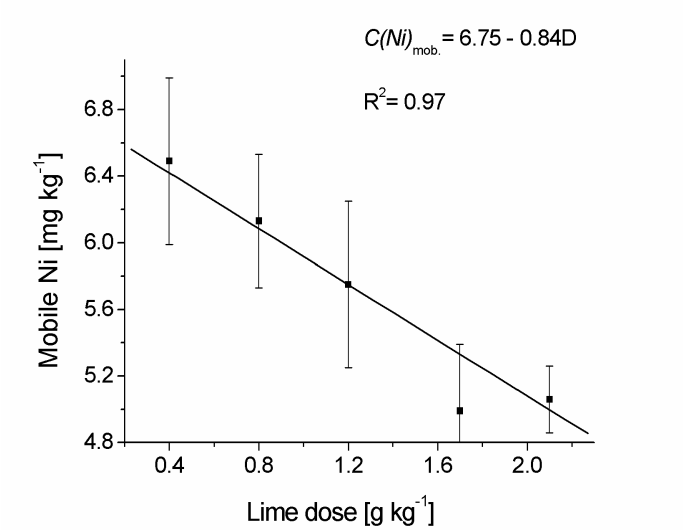


Figure 3.2: Concentration of mobile Ni [mg $kg^{-1}$] in soil influenced by lime application (year 2000, corresponding to Equ. 3.2).

The relationship between liming and mobile Ni concentration ($C(Ni)_{mob}$) in soil can be described well by a linear function similar to equation 3.1:

$$C(Ni)_{mob} = C(Ni)_0 - bD \qquad \text{(Equ. 3.2)}$$

Where:

| | | |
|---|---|---|
| $C(Ni)_0$ | – | initial concentration of mobile Ni in soil (if $D = 0$) [mg $kg^{-1}$] |
| $b$ | – | mobile Ni concentration in soil per unit lime [mg $kg^{-1}$/g $kg^{-1}$] |
| $D$ | – | lime dose [g $kg^{-1}$] |

In 2001 the influence of liming on the mobile Ni concentration in soil could be approximated well with an exponential function (Equ. 3.3) (Fig. 3.3):

$$C(Ni)_{mob} = C(Ni)_0 + C(Ni)_1 \cdot e^{-D/D_1} \qquad \text{(Equ. 3.3)}$$

Where:

| | | |
|---|---|---|
| $C(Ni)_0$ | – | initial concentration of mobile Ni (if $D = 0$) [mg $kg^{-1}$] |
| $C(Ni)_1$ | – | mobile Ni concentration in soil which can be changed by influence of addition of lime [mg $kg^{-1}$] |
| $D_1$ | – | lime dose where the concentration of Ni in soil is double decreased [g $kg^{-1}$] |
| $D$ | – | lime dose [g $kg^{-1}$] |

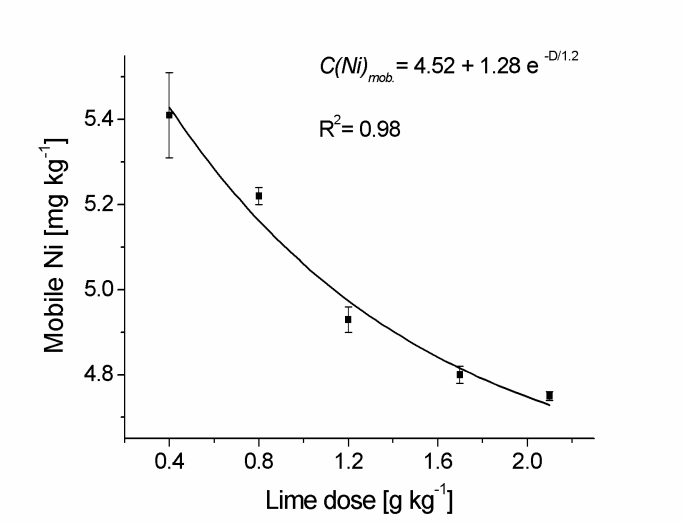


Figure 3.3: Concentration of mobile Ni [mg $kg^{-1}$] in soil influenced by lime application (year 2001, corresponding to Equ. 3.3).

The coefficient of determination between lime dose and mobile Ni concentration in soil in year 2001 was high (Fig. 3.3). More than 90% of the variation in mobile soil Ni concentration could be explained by changes in the lime supply. It should be marked here that the exponential decrease in mobile Ni concentration in soil is applicable only within the range of lime doses used in the experiment. The calculated value of initial Ni concentration ($C(Ni)_0$ , if $D = 0$) is lower than it might be expected in the control treatment and close to the Ni concentration obtained in the treatments with lime doses of 1.66 and 2.10 g $kg^{-1}$ (Fig. 3.3, Tab. 3.4). Under the conditions of presented experiment the most effective lime dose for double decrease in Ni mobility in soil was 1.2 mg $kg^{-1}$ lime.

## *3.3 Changes of soil pH as influenced by lime application and plant growth*

### *3.3.1 Changes of soil pH as influenced by lime application*

The addition of lime considerably influenced the soil pH. It increased with increasing lime doses in 2000 as well as in 2001. But during the vegetation period soil pH decreased in both years of the experiment.

Changes of soil pH as influenced by lime application in the first and second year of the pot experiments are summarized in Tab. 3.5. In general the pH values are very low, which is representative for acid podzolic soils.

Table 3.5: Effect of liming on the soil pH(KCl) (potentiometrically determined).

| **Lime dose** [g $kg^{-1}$] | **Soil pH(KCl)** | | | | |
|---|---|---|---|---|---|
| | **14** | **21** | **29** | **36** | **43** |
| | **Sampling time** [d] | | | | |
| **2000** | | | | | |
| 0 | 4.11 | 4.04 | 3.97 | 3.83 | 3.80 |
| 0.41 | 4.54 | 4.42 | 4.23 | 4.42 | 4.03 |
| 0.83 | 4.84 | 4.69 | 4.52 | 4.23 | 4.22 |
| 1.25 | 5.16 | 5.14 | 4.61 | 4.41 | 4.40 |
| 1.66 | 5.54 | 5.60 | 4.97 | 5.09 | 5.13 |
| 2.10 | 5.73 | 5.42 | 5.17 | 5.17 | 5.25 |
| *LSD(5%)* | *0.07* | *0.07* | *0.22* | *0.10* | *0.05* |
| **2001** | | | | | |
| 0 | 3.98 | 3.94 | 3.53 | 3.46 | 3.35 |
| 0.41 | 4.15 | 4.22 | 4.20 | 4.17 | 4.00 |
| 0.83 | 4.56 | 4.50 | 4.33 | 4.21 | 4.13 |
| 1.25 | 5.23 | 5.34 | 5.12 | 4.99 | 4.52 |
| 1.66 | 5.74 | 5.78 | 5.32 | 5.14 | 4.86 |
| 2.10 | 5.89 | 5.86 | 5.72 | 5.00 | 4.73 |
| *LSD(5%)* | *0.05* | *0.04* | *0.04* | *0.04* | *0.05* |

The relationship between soil pH and lime doses is shown in the Fig. 3.4 and 3.5 reflecting a strong dependency between investigated parameters.

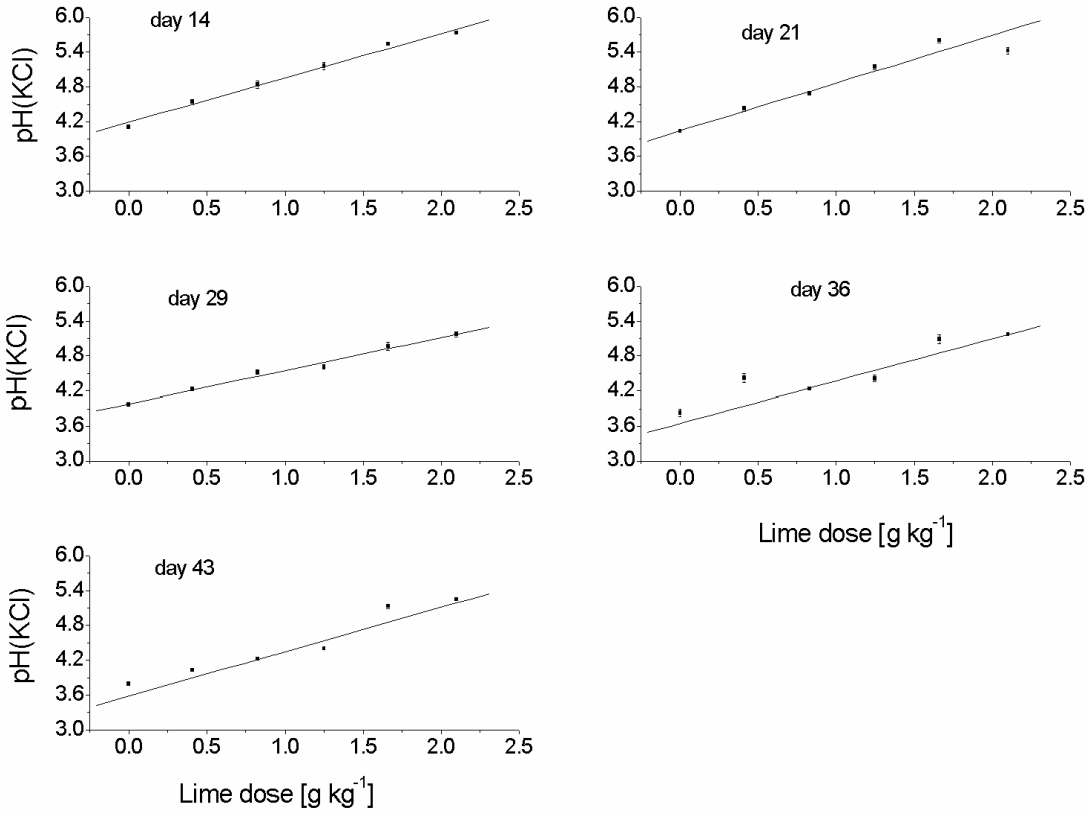


Figure 3.4: Changes of soil pH(KCl) as influenced by lime application (year 2000, corresponding to Equ. 3.4, model parameters see Tab. 3.6).

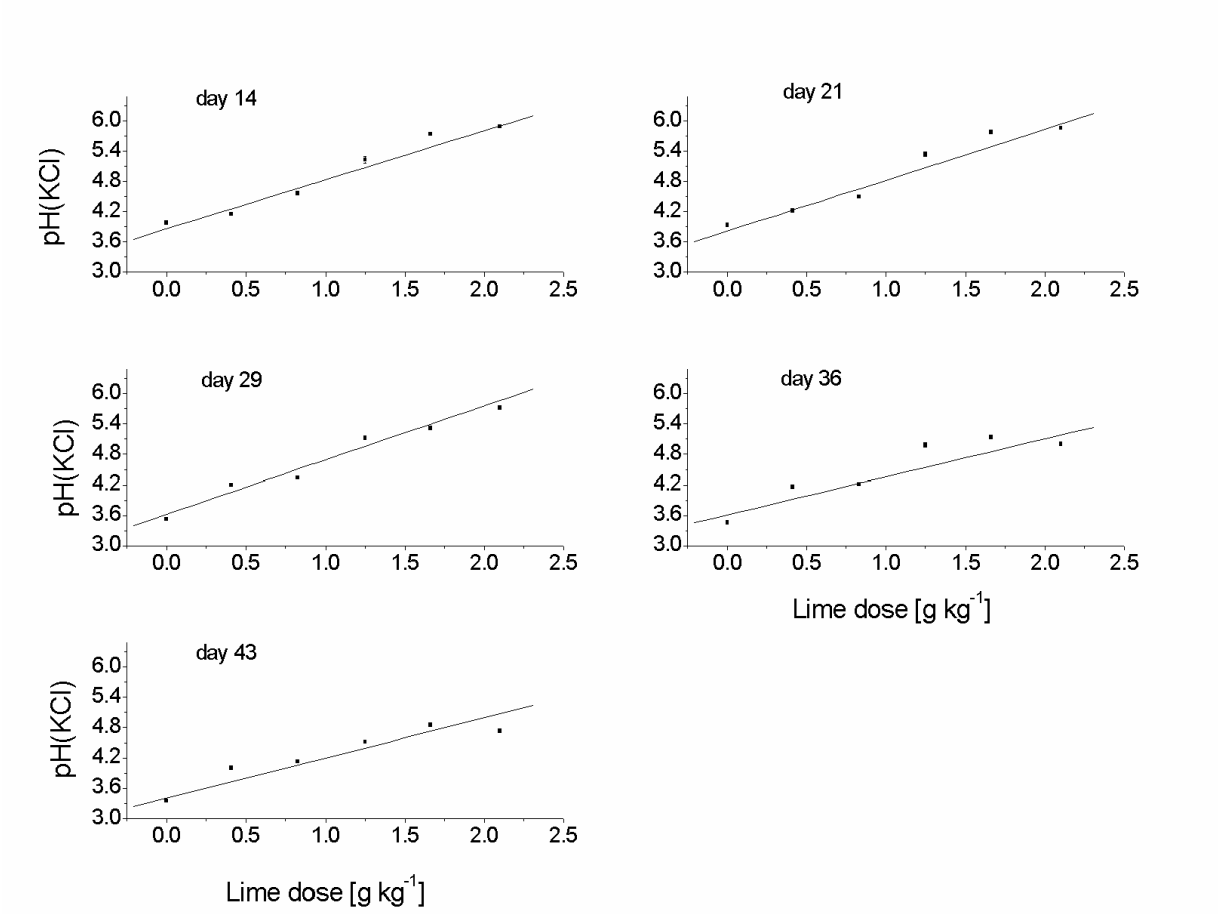


Figure 3.5: Changes of soil pH(KCl) as influenced by lime application (year 2001, corresponding to Equ. 3.4, model parameters see Tab. 3.6).

For the mathematical description of the changes of soil pH influenced by lime application the linear function was employed, for the first and second year of the pot experiments:

$$pH = pH_{D=0} + b_D \cdot D \qquad \text{(Equ. 3.4)}$$

Where:

| | | |
|---|---|---|
| $pH_{D=0}$ | – | pH if $D = 0$ |
| $b_D = \frac{\Delta pH}{\Delta D}$ | – | pH change per unit lime |
| $D$ | – | lime dose [g kg$^{-1}$] |

In the first year of the experiment a reliable decreasing of the parameter $pH_{D=0}$ during the vegetation period was observed (Tab. 3.6). The calculated values agreed closely with the pH of the control treatment, determined analytically (Tab. 3.5).

The parameters $b_D$ are almost equal at all sampling times (except the 29-th day), they can be averaged. The deviations can be explained by effects of unaccounted factors (Tab. 3.6). The average value of $b_D$ is equivalent to 0.72. Hence in the first year of the experiment increasing of lime dose by 1 g $kg^{-1}$ increased soil pH(KCl) by 0.72 units at every time of the observations.

Table 3.6: Parameters for the linear function describing changes of soil pH(KCl) influenced by lime application.

| **Sampling time** [d] | **Year 2000** | | | **Year 2001** | | |
|---|---|---|---|---|---|---|
| | $R^2$ | $pH_{D=0}$ | $b_D$ | $R^2$ | $pH_{D=0}$ | $b_D$ |
| 14 | 0.98 | 4.18±0.09 | 0.77±0.06 | 0.97 | 3.86±0.09 | 1.022±0.09 |
| 21 | 0.98 | 4.04±0.03 | 0.81±0.06 | 0.95 | 3.81±0.08 | 1.030±0.12 |
| 29 | 0.98 | 3.98±0.02 | 0.56±0.03 | 0.97 | 3.62±0.08 | 1.029±0.09 |
| 36 | 0.98 | 3.64±0.06 | 0.72±0.04 | 0.84 | 3.61±0.16 | 0.774±0.67 |
| 43 | 0.94 | 3.58±0.14 | 0.76±0.09 | 0.89 | 3.39±0.08 | 0.670±0.12 |

Remark: ± - error of estimating function; $R^2$- coefficient of determination between soil pH(KCl) and lime dose (explained by a linear function), figures apply to Equ. 3.4.

In the second year of the experiment the decrease of the parameter $pH_{D=0}$ during the vegetation period was obviously lower. This parameter agreed closely with soil pH values in the control treatment (Tab. 3.5). In the contrary with the first year results the parameter $b_D$ ($\Delta pH/\Delta D$) decreased during the vegetation period 2001. That means that one unit of lime changes soil pH in lower extent during the time, the effectiveness of lime decreases (Fig. 3.6).

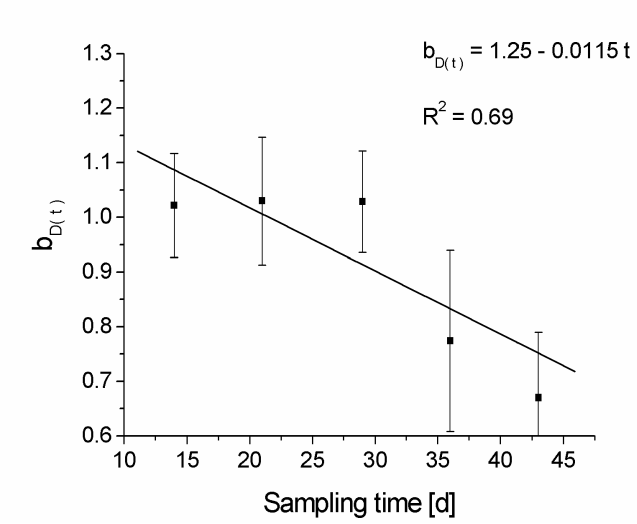


Figure 3.6: Trend of the parameter $b_{D(t)}$ (pH change per unit lime) during the vegetation period (year 2001).

It can be assumed that the parameter $b_D$ is a characteristic value for changes of sod-podzolic soil pH influenced by lime application.

### *3.3.2 Changes of soil pH(KCl) during the vegetation period*

Soil acidification during the vegetation period was observed (Tab. 3.5, Fig. 3.7) in the first and second year of the experiments.

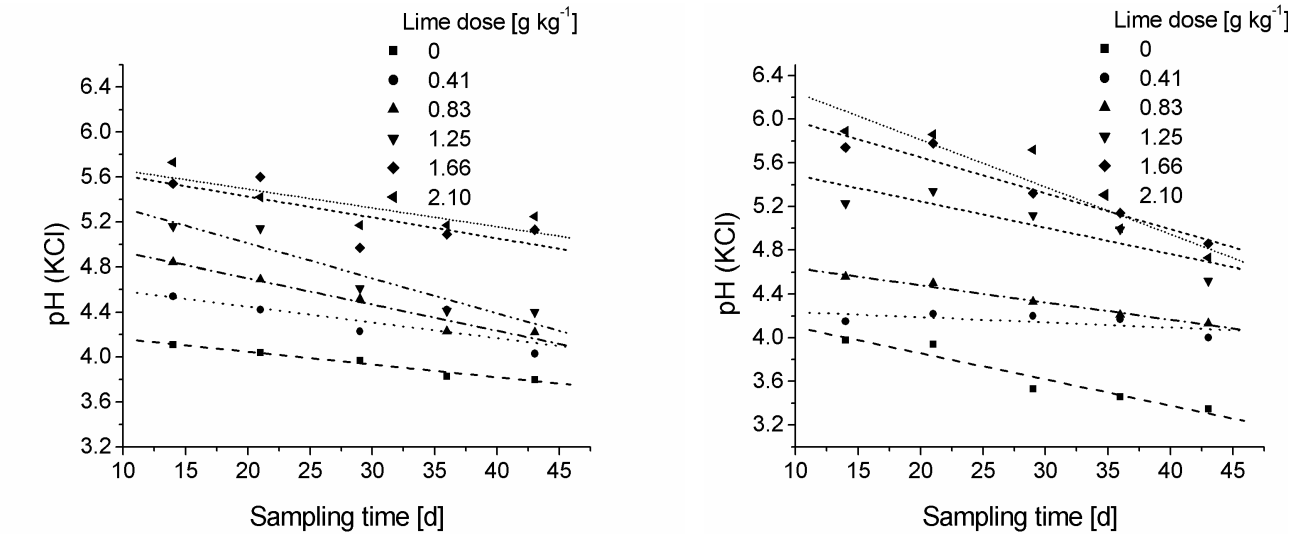


Figure 3.7: Changes of soil pH(KCl) during the vegetation period in the first and second year experiment (2000 left and 2001 right), corresponding to Equ. 3.5, model parameters see Tab. 3.7.

To quantify the temporal changes in soil pH(KCl) a linear function was employed:

$$pH = pH_{t=14} - b_t \cdot t \qquad \text{(Equ. 3.5)}$$

Where:

| | | |
|---|---|---|
| $pH_{t=14}$ | – | pH, for $t = 14$ |
| $b_t = \frac{\Delta pH}{\Delta t}$ | – | rate of pH changes |
| $t$ | – | time [d] |

The parameter $b_t$ is a complex one, it depends on lime dose, plant species and stage of development. In the year 2000 the parameter $b_t$ reliably increased in the treatments with lime doses of 0.41, 0.83 and 1.25 g $kg^{-1}$, respectively (Tab. 3.7). On the contrary $b_t$ decreased in

treatments with lime doses of 1.66 and 2.10 g $kg^{-1}$. In this context it can be assumed that at least two or three mechanisms, which act differently, simultaneously effect on changes of soil pH during the vegetation period. One of them (increasing pH) is related to the lime influence and another one (decreasing pH) to roots exudates and turnover processes. When the lime dose is low pH decreases because of rape root exudates (see chapter 3.3.3) and when the lime dose is high pH slightly increases due to the main effect of lime.

Table 3.7: Parameters of the linear function describing changes of soil pH(KCl) during the vegetation period.

| **Lime dose** [g $kg^{-1}$] | **Year 2000** | | | **Year 2001** | | |
|---|---|---|---|---|---|---|
| | $R^2$ | $pH_{t=14}$ | $b_t$ | $R^2$ | $pH_{t=14}$ | $b_t$ |
| 0 | 0.98 | 4.28±0.035 | -0.011±0.001 | 0.96 | 4.34±0.12 | -0.024±0.004 |
| 0.41 | 0.81 | 4.73±0.180 | -0.014±0.006 | 0.63 | 4.28±0.10 | -0.005±0.003 |
| 0.83 | 0.98 | 5.17±0.009 | -0.023±0.003 | 0.99 | 4.80±0.03 | -0.016±0.001 |
| 1.25 | 0.94 | 5.63±0.190 | -0.031±0.006 | 0.88 | 5.73±0.23 | -0.024±0.008 |
| 1.66 | 0.75 | 5.80±0.280 | -0.019±0.009 | 0.97 | 6.31±0.15 | -0.033±0.005 |
| 2.10 | 0.82 | 5.83±0.210 | -0.017±0.007 | 0.93 | 6.68±0.30 | -0.043±0.010 |

Remarks: ± - error of estimating function; $R^2$ – coefficient of determination between soil pH(KCl) and time (explained by a linear function), figures apply to Equ. 3.5.

In 2001 the rate of pH changes influenced by the lime dose increased in all treatments, except the control (Tab. 3.7). This fact indicates that in the second year the soil pH changed mainly due to the effect of root exudates.

The values of the rate of pH changes are similar in the first and second year of the experiment. Hence it can be assumed that under lime application the main reduction processes of sod-podzolic sandy loam soils are realized within the first year of lime application.

### *3.3.3 Acidification effect of plants*

In the first year of the lime application the influence on plant dry matter production was rather distinct due to the changes of soil pH (Fig. 3.8). Comparing the single lime treatments it can be assumed that the higher the dry matter production is, the lower the soil pH.

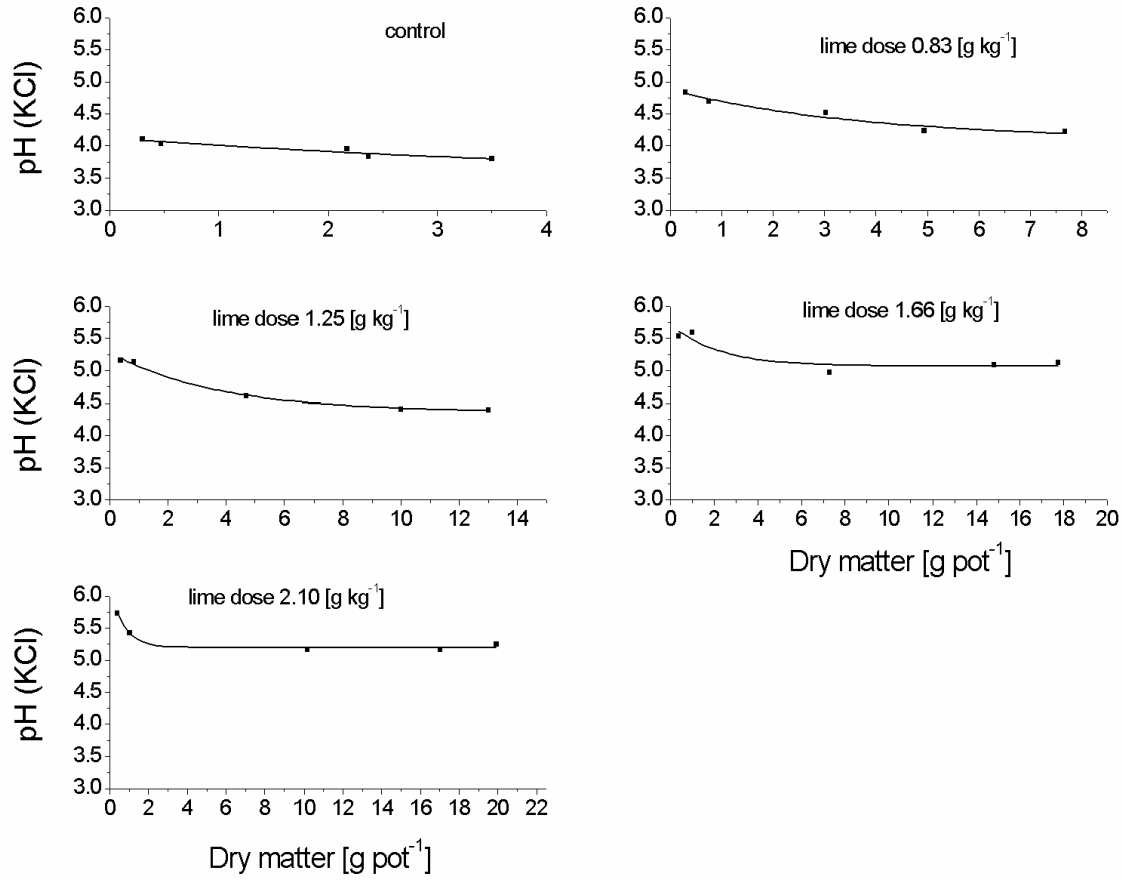


Figure 3.8: Changes of soil pH(KCl) influenced by the growth of *Brassica napus* plants (year 2000, corresponding to Equ. 3.6, model parameters see Tab. 3.8).

For a first approximation the curves presented in Fig. 3.8 can be described by an exponential function:

$$pH = pH_{t=14} + pH_1 \cdot e^{-M / M_1} \qquad \text{(Equ. 3.6)}$$

Where:

$pH_{t=14}$ – initial pH, which responded to the lime addition dependent only on soil properties

$pH_1$ – pH change coefficient, characterising plant species and the intensity of physiological processes of $H^+$ release

$M_1$ – plant dry matter [g $pot^{-1}$]. Changing the value results in a two times higher intensity of $H^+$ release

$M$ – plant dry matter [g $pot^{-1}$]

It should be marked here that the equation 3.6 is only correct under the conditions of the experiment presented here. Taking into account the error of the estimating function lime addition did not affect the parameter $pH_1$, it almost did not change (Tab. 3.8).

A decreasing trend of the parameter $M_1$ could be observed. In this regard it can be assumed that at increasing lime doses less amount of plant dry matter is needed for doubling the increase of $H^+$ release.

Table 3.8: Parameters for the exponential description of the influence of *Brassica napus* on soil pH changes (year 2000).

| **Lime dose** [g kg$^{-1}$] | $pH_{t=14}$ | $pH_1$ | $M_1$ [g pot$^{-1}$] | $R^2$ |
|---|---|---|---|---|
| 0 | 3.46±1.44 | 0.67±1.40 | 5.19±15.61 | 0.91 |
| 0.83 | 4.08±0.25 | 0.79±0.22 | 3.90±2.92 | 0.95 |
| 1.25 | 4.36±0.05 | 0.92±0.05 | 3.72±0.79 | 0.99 |
| 1.66 | 5.06±0.09 | 0.64±0.24 | 2.29±3.03 | 0.88 |
| 2.10 | 5.20±0.03 | 0.93±0.18 | 0.72±0.20 | 0.98 |

Remarks: ± - error of estimating function; $R^2$ - coefficient of determination between soil pH(KCl) and dry matter production of *Brassica napus* plants (explained by an exponential function), figures apply to Equ. 3.6.

The calculations reveal that soil pH changes induced by root exudates of *Brassica napus* cannot be more than 0.3-0.5 units (Fig. 3.8). In the second year of the experiment the plants of *Avena sativa* affected the soil pH in the same way like *Brassica napus* did (Fig. 3.9).

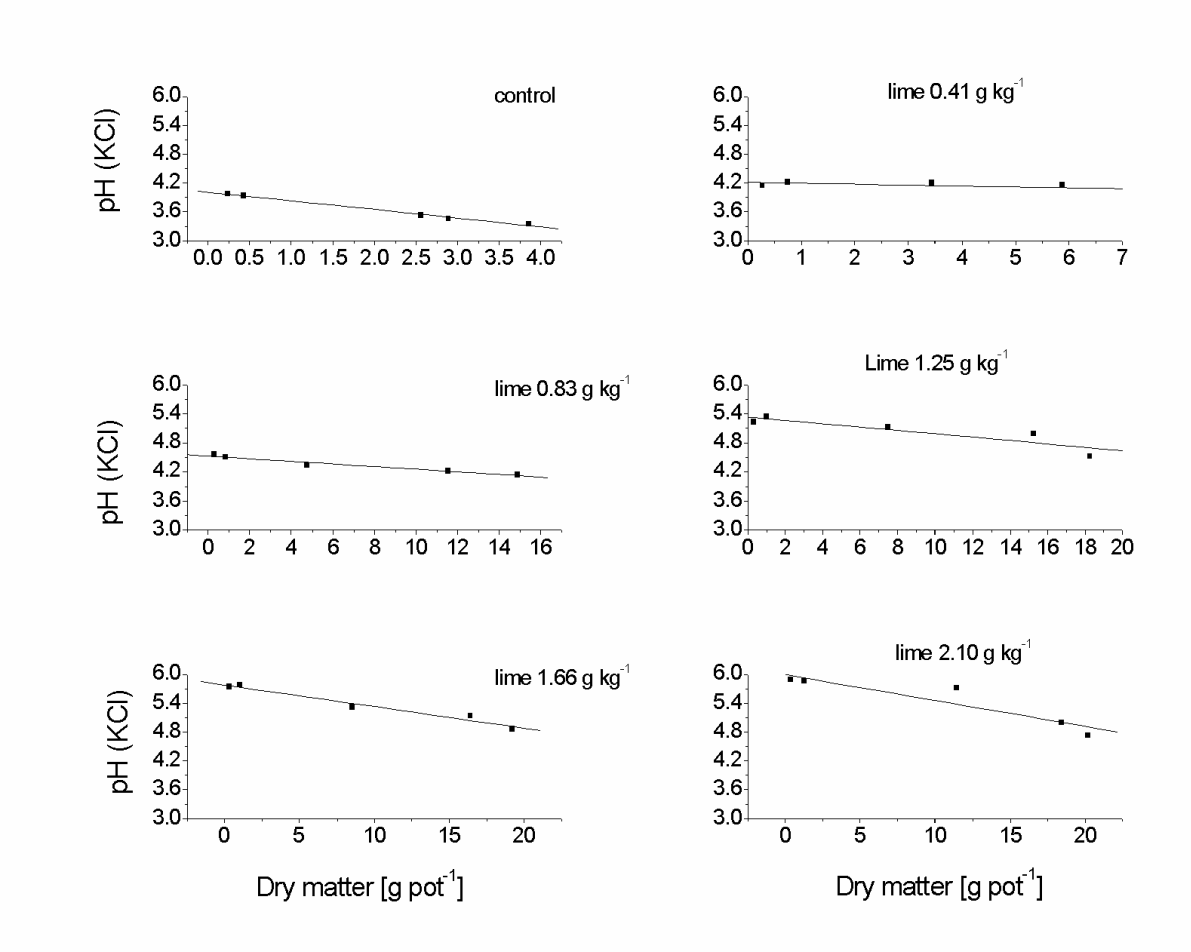


Figure 3.9: Changes of soil pH(KCl) influenced by the growth of *Avena sativa* plants (year 2001, corresponding to Equ. 3.7, model parameters see Tab. 3.9).

The changes of soil pH by *Avena sativa* plants are well described by a linear function:

$$pH = pH_{t=14} - \frac{\Delta pH}{\Delta M} M \qquad \text{(Equ. 3.7)}$$

Where:

| | | |
|---|---|---|
| $pH_{t=14}$ | – | initial pH, which responded to the lime addition, dependent only on soil properties |
| $M$ | – | dry matter of *Avena sativa* plants [g pot$^{-1}$] |
| $\frac{\Delta pH}{\Delta M}$ | – | change of pH per g dry matter |

As it was expected the parameters $pH_{t=14}$ and $\frac{\Delta pH}{\Delta M}$ reliably increased with rising lime doses (Tab. 3.9). This result reveals that one unit of plant dry matter changes the pH in a greater extent with increasing lime doses.

Table 3.9: Influence of *Avena sativa* plants on soil pH changes (parameters for a linear model description) (year 2001).

| **Lime dose** [g $kg^{-1}$] | $pH_{t=14}$ | $\frac{\Delta pH}{\Delta M}$ [pH per g d.m.] | $R^2$ |
|---|---|---|---|
| 0 | 4.01±0.02 | -0.181±0.009 | 0.98 |
| 0.41 | 4.20±0.05 | -0.019±0.012 | 0.44 |
| 0.83 | 4.52±0.03 | -0.028±0.003 | 0.95 |
| 1.25 | 5.33±0.11 | -0.350±0.009 | 0.67 |
| 1.66 | 5.78±0.06 | -0.045±0.005 | 0.95 |
| 2.10 | 6.00±0.16 | -0.054±0.012 | 0.85 |

Remarks: ± - error of estimating function; $R^2$- coefficient of determination between soil pH(KCl) and dry matter production of *Avena sativa* plants (explained by a linear function), figures apply to Equ. 3.7.

## *3.4 Ca and Ni interaction in plant-soil system*

### *3.4.1 Dry matter development of Brassica napus and Avena sativa plants*

The addition of 20 mg $kg^{-1}$ Ni to the soil had no negative effect on growth and development of the plants. Also no visual symptoms of Ni toxicity on any parts of the plant were detected. Lime addition considerably influenced the dry matter production of both investigated crops beginning from the lowest dose. The effect of lime addition on the dry matter development of *Brassica napus* and *Avena sativa* plants is summarised in Tab. 3.10 and Fig. 3.10. Generally the dry matter yield of the investigated plants increased with rising of lime doses during all time of observation. At the day 43 the dry matter yield of *Brassica napus* and *Avena sativa* plants was 5.7 and 5.2 times higher in the treatment with the highest lime dose than in the control treatment respectively (Tab. 3.10).

Table 3.10: Dynamic of dry matter development of *Brassica napus* and *Avena sativa* influenced by lime application.

| **Lime dose** [g $kg^{-1}$] | **Dry matter** [g $pot^{-1}$] | | | | |
|---|---|---|---|---|---|
| | **14** | **21** | **29** | **36** | **43** |
| | **Sampling time** [d] | | | | |
| ***Brassica napus*** | | | | | |
| 0 | 0.30 | 0.47 | 2.17 | 2.37 | 3.50 |
| 0.83 | 0.29 | 0.75 | 3.02 | 4.93 | 7.68 |
| 1.25 | 0.38 | 0.83 | 4.70 | 10.00 | 13.01 |
| 1.66 | 0.37 | 1.00 | 7.29 | 14.80 | 17.75 |
| 2.10 | 0.40 | 1.03 | 10.18 | 17.01 | 19.92 |
| *LSD(5%)* | *0.11* | *0.30* | *2.80* | *2.70* | *2.90* |
| ***Avena sativa*** | | | | | |
| 0 | 0.24 | 0.43 | 2.56 | 2.89 | 3.86 |
| 0.41 | 0.27 | 0.74 | 3.45 | 5.87 | 7.25 |
| 0.83 | 0.32 | 0.85 | 4.78 | 11.54 | 14.89 |
| 1.25 | 0.31 | 1.00 | 7.50 | 15.25 | 18.26 |
| 1.66 | 0.33 | 1.02 | 8.50 | 16.40 | 19.23 |
| 2.10 | 0.34 | 1.25 | 11.40 | 18.43 | 20.19 |
| *LSD (5%)* | *0.16* | *0.40* | *2.70* | *2.60* | *3.11* |

The dry matter development of *Brassica napus* and *Avena sativa* during the vegetation period of all experimental treatments corresponded with a S-shaped curve, which is well approximated by a logistic equation (Fig. 3.10).

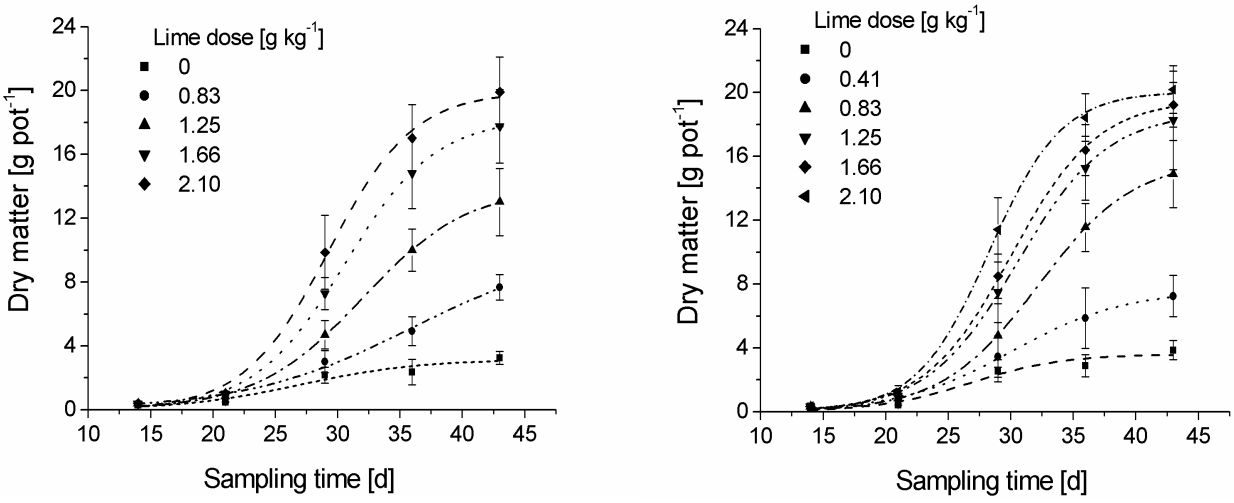


Figure 3.10: Dry matter production of *Brassica napus* (left) and *Avena sativa* (right) influenced by lime application during the vegetation period (corresponding to Equ. 1.11-1.12, model parameters see Tab. 3.11).

It is obvious that the effect of different lime doses does not show up when the plants were young (Fig. 3.10). Beginning from day 25 of the growth a difference in the lime treatments started to become visible. At the end of the observation the most distinct difference occurred between the dry matter yields obtained in the treatments with the highest and lowest lime doses. Fig. 3.10 shows that the exponential phase of plant growth continued until day 35.

The computations according to Equation 1.11 revealed that the parameters describing the dry matter development of both of the investigated plants are dependent on the lime dose (Tab. 3.11). The parameters $M_{max}$ (maximum yield) and $\mu$ (specific growth rate) increased with rising lime doses. Thus, the maximum yield ($M_{max}$) in the treatment with the lime dose of 2.10 g $kg^{-1}$ exceeded the maximum yield in the control treatment without liming by 6 times in the experiment with *Brassica napus* and by 5 times in the experiment with *Avena sativa*. The specific growth rate increased with rising lime doses in both experiments, but in greater extent in the experiment with *Avena sativa* plants. Consequently the parameter $T$ (period of time in which dry matter is doubled) decreased in the treatments with lime application in comparison to the control. These results showed that increasing lime doses promote increasing dry matter yield as well as increasing rates of growth development.

Table 3.11: Parameters for the logistic description of dry matter development of *Brassica napus* and *Avena sativa* grown on a sod-podzolic soil during the vegetation period.

| ***Brassica napus*** | | | | | | ***Avena sativa*** | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Lime dose** [g $kg^{-1}$] | $R^2$ | $M_{max}$, [g $pot^{-1}$] | $M_0$ [g $pot^{-1}$] | $\mu$ [$d^{-1}$] | $T$ [d] | $R^2$ | $M_{max}$ [g $pot^{-1}$] | $M_0$ [g $pot^{-1}$] | $\mu$ [$d^{-1}$] | $T$ [d] |
| 0 | 0.95 | 3.2 ±0.5 | 0.011 | 0.21±0.10 | 3.3 | 0.96 | 3.61±0.4 | 0.0026 | 0.27±0.12 | 2.57 |
| 0.41 | - | - | - | - | - | 0.99 | 7.61±0.3 | 0.0094 | 0.22±0.02 | 3.15 |
| 0.83 | 0.99 | 10.3±2.1 | 0.048 | 0.15±0.03 | 4.6 | 0.99 | 15.82±0.2 | 0.0039 | 0.26±0.01 | 2.66 |
| 1.25 | 0.99 | 14.0±0.3 | 0.008 | 0.23±0.01 | 3.0 | 0.99 | 18.77±0.3 | 0.0039 | 0.28±0.01 | 2.47 |
| 1.66 | 0.99 | 18.3±0.3 | 0.004 | 0.27±0.02 | 2.6 | 0.99 | 19.56±0.4 | 0.0032 | 0.29±0.02 | 2.39 |
| 2.10 | 0.99 | 19.9±0.8 | 0.004 | 0.29±0.04 | 2.4 | 0.99 | 20.07±0.4 | 0.0012 | 0.34±0.03 | 2.04 |

Remarks: ± - error of estimating function; $R^2$-coefficient of determination between dry matter production and lime dose (explained by a logistic function), figures apply to Equ. 1.11 in the text (chapter Material and Methods); $T$ – period of time in which dry matter is doubled; $T$=0.693 $\mu^{-1}$

In order to describe the changes of maximum yield dry matter influenced by the lime doses ($M_{max(D)}$) a hyperbolic function was employed (Mono equation, Warfolomeev & Kalyuzhny 1990):

$$M_{max(D)} = \frac{M_{max1} \cdot D}{D_{1/2} + D} \qquad \text{(Equ. 3.8)}$$

Where:

$M_{max1}$ – absolute maximum yield [g pot$^{-1}$]

$D_{1/2}$ – lime dose where $M_{max(D)} = \frac{M_{max1}}{2}$ [g kg$^{-1}$]

$D$ – lime dose [g kg$^{-1}$]

The calculated values $M_{max1}$ and $D_{1/2}$ are hypothetical. The parameter $M_{max1}$ shows the absolute maximum dry matter which plants can develop in the conditions of presented experiment (Tab. 3.12).

Table 3.12: Parameters for the hyperbolic description of maximum yield of plants ($M_{max}(D)$) depending on lime dose.

| ***Brassica napus*** | | | ***Avena sativa*** | | |
|---|---|---|---|---|---|
| $M_{max1}$ [g pot$^{-1}$] | $D_{1/2}$ [g kg$^{-1}$] | $R^2$ | $M_{max1}$ [g pot$^{-1}$] | $D_{1/2}$ [g kg$^{-1}$] | $R^2$ |
| 52.0±16.3 | 3.2±1.5 | 0.97 | 30.2±5.0 | 0.9±0.4 | 0.93 |

Remarks: ± - error of estimating function; $R^2$- coefficient of determination between maximum yield of plants and lime dose (explained by a hyperbolic function), figures apply to Equ. 3.8.

However this function allows to evaluate the changes of $M_{max(D)}$ per unit lime with rather high accuracy (Fig. 3.11). The calculated values of absolute maximum dry matter which plants could develop are 2.6 (*Brassica napus*) and 1.5 (*Avena sativa*) times higher than obtained in the experiment. This result shows that besides Ca concentration in soil other factors limited the plants growth.

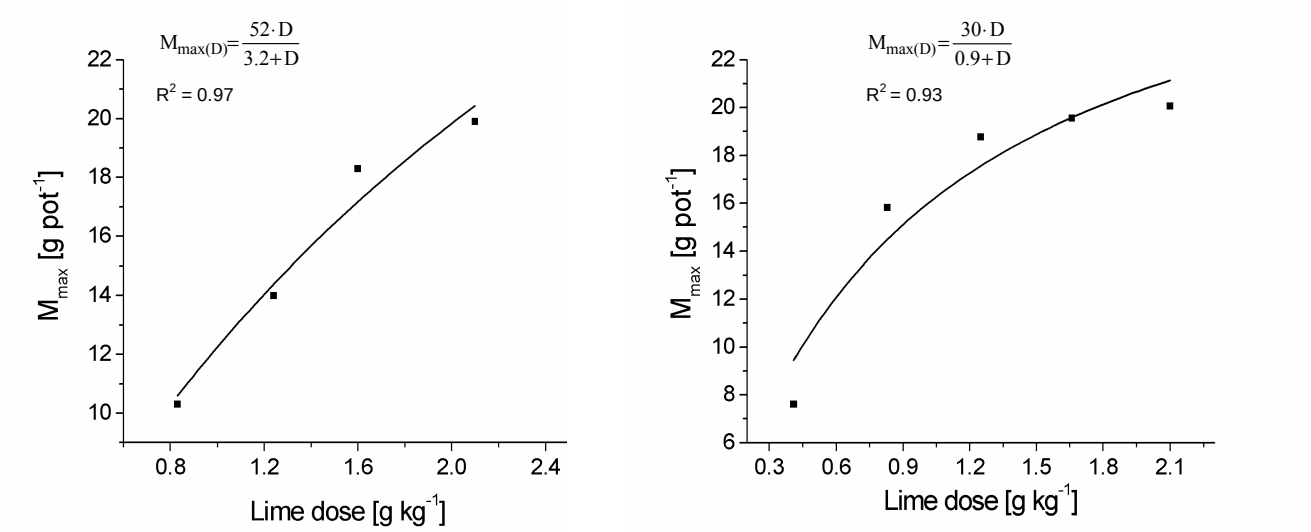


Figure 3.11: Changes of maximum yield ($M_{max(D)}$) of *Brassica napus* (left) and *Avena sativa* (right) depending on the lime dose.

The parameter $M_0$ (Tab. 3.11) is a calculated value, in the experiment with *Brassica napus* the averaged $M_0$ was 0.015±0.017 g pot$^{-1}$. Taking into consideration a determination error of this value it coincides virtually with the mass of *Brassica napus* seeds sown in each pot ($M_0$ = 0.04 g pot$^{-1}$). But in the experiment with *Avena sativa* $M_0$ = 0.004±0.003 g pot$^{-1}$ was much less than the mass of the oat seeds sown in each pot ($M_0$ = 0.4 g pot$^{-1}$).

The logistic function allows to calculate such an important parameter as the specific rate of plant growth ($\mu$ [d$^{-1}$]). The specific rate of plant growth is a function of the cell fission and reflects the growth conditions and genetic potential of the plants.

In the first year of the experiment the specific rate of plant growth was enhanced with each lime level. The same tendency was observed in the second year of the experiment, but the change was not as smooth as in the first year. The growth rate of *Avena sativa* increased in the treatments with lime doses of 0.41-1.25 g kg$^{-1}$. In the treatment with 1.66 g kg$^{-1}$ it was close to the value received in the treatment with 1.25 g kg$^{-1}$ and then started to increase again in the treatments with highest lime doses (Tab. 3.11).

The changes of specific rate of plant growth are also described well by the Mono equation (Equ. 3.9, Fig. 3.12) (Warfolomeev & Kalyuzhny 1990):

$$\mu_t = \frac{\mu_{max} \cdot D}{D_{1/2} + D} \qquad \text{(Equ. 3.9)}$$

Where:

$\mu_{max}$ – maximum specific growth rate of dry matter [$d^{-1}$]

$D_{1/2}$ – lime dose where the specific growth rate of plants is equal the half of maximum specific growth rate of plants [g $kg^{-1}$]

$D$ – lime dose [g $kg^{-1}$]

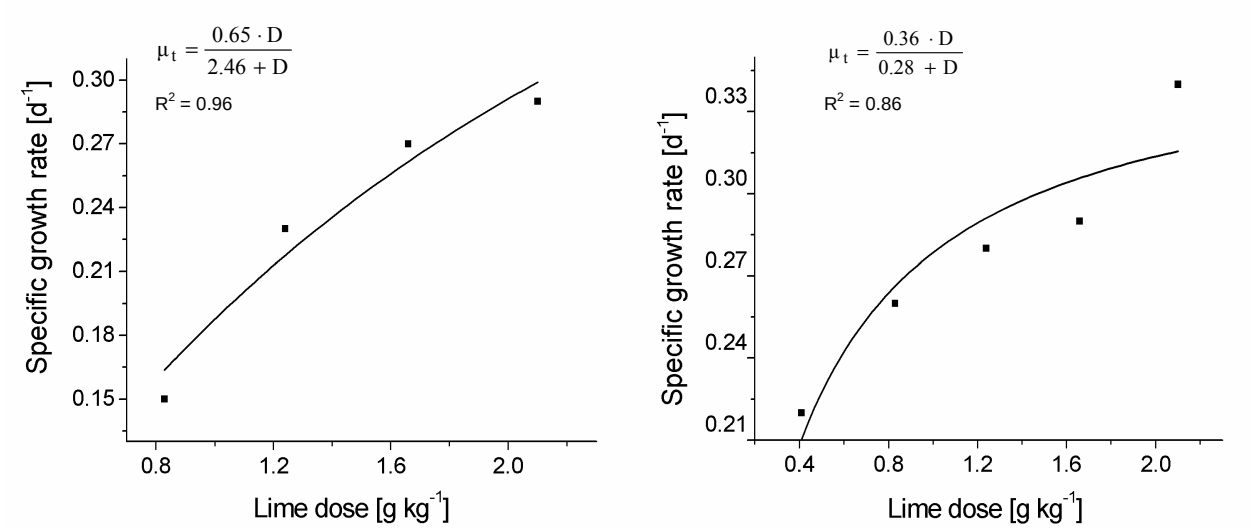


Figure 3.12: Changes of specific rate of *Brassica napus* (left) and *Avena sativa* (right) growth depending on lime dose.

The parameters for the hyperbolic description of the specific growth rate affected by lime application are summarized in the Tab. 3.13.

Table 3.13: Parameters for hyperbolic description of specific rate of plants growth as affected by lime application.

| ***Brassica napus*** | | | ***Avena sativa*** | | |
|---|---|---|---|---|---|
| $\mu_{max}$ [$d^{-1}$] | $D_{1/2}$ [g $kg^{-1}$] | $R^2$ | $\mu_{max}$ [$d^{-1}$] | $D_{1/2}$ [g $kg^{-1}$] | $R^2$ |
| 0.65±0.18 | 2.46±1.2 | 0.96 | 0.36±0.03 | 0.28±0.09 | 0.86 |

Remarks: ± - error of estimating function; $R^2$- coefficient of determination between specific growth rate and lime dose (explained by a hyperbolic function), figures apply to Equ. 3.9.

The parameter $\mu_{max}$ is the maximum rate of plant growth (Tab. 3.13) at ideal (absolute optimum) nutrition, light, temperature and moisture conditions. In other words it depends only on the genetic configuration of the plant development. Under real conditions, with an increasing lime dose it can not be observed, but it shows the absolute maximum of the growth rate, which plants can develop. For *Brassica napus* the maximum growth rate was estimated as 0.65 $d^{-1}$, which is 2.5 times higher than obtained in the experiment. That means every 24 hours the dry matter of plants can be doubled ($T=\frac{0.693}{0.65}=1.07$ ). The hypothetical maximum specific growth rate of *Avena sativa* is very close to the experimentally obtained and equal 0.36 $d^{-1}$ (Tab. 3.13). The period of time in which the dry matter of *Avena sativa* can be doubled (*T*) is 1.9 d. This is almost two times slower than that of *Brassica napus.* The parameter $D_{1/2}$ is a function of plant properties and is considered as a value which shows plants response on the addition of lime. The lower the parameter $D_{1/2}$, the greater the response of plants to changes in soil status caused by liming. Hence $D_{1/2}$ is a quantitative measure of plant response on the lime supply. It is supposed that changes in soil nutrition concentrations lead to changes in the specific rate of plant growth. In this context the parameter $D_{1/2}$ will be a measure of plant response on this change. In the experiment with *Avena sativa* the parameter $D_{1/2}$ is much lower than that in the experiment with *Brassica napus*. *Avena sativa* plants were nearly 9 times more efficient to the addition of lime (Tab. 3.13).

### *3.4.2 Dry matter development of Brassica napus and Avena sativa influenced by lime application*

A distinct influence of lime addition on the dry matter development of *Brassica napus* and *Avena sativa* plants was observed at nearly every sampling time, excluding 14 and 21 day when the plants were very small (Fig. 3.13).

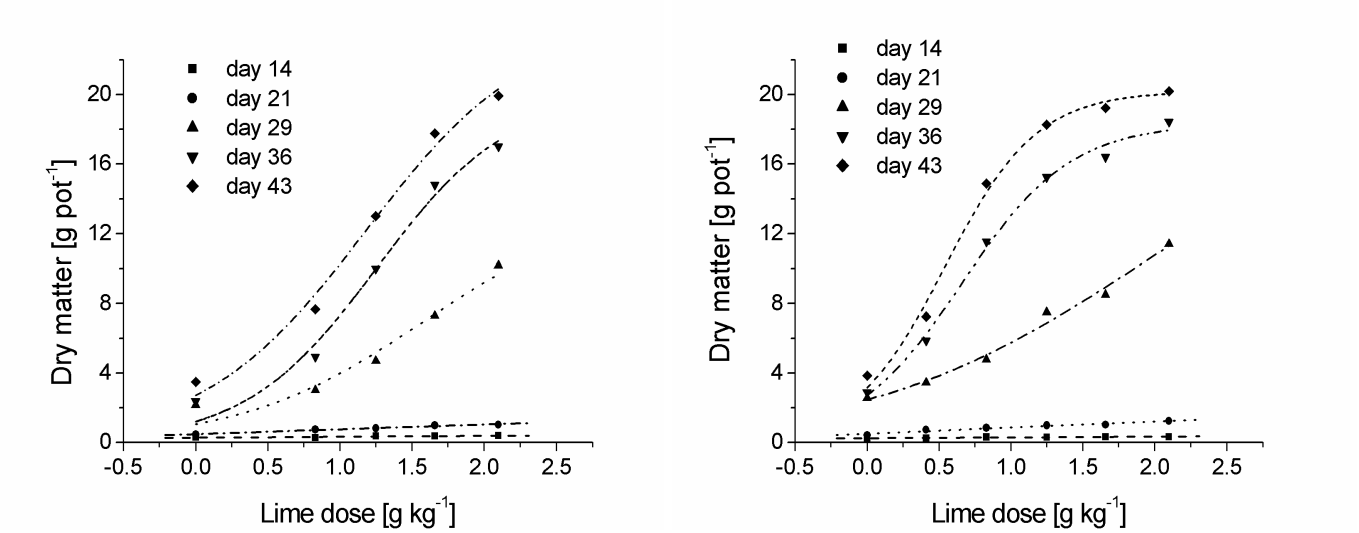


Figure 3.13: Influence of lime addition on dry matter development of *Brassica napus* (left) and *Avena sativa* (right) (corresponding to Equ. 3.10 and 3.11, model parameters see Tab. 3.14).

A linear function was employed in order to describe the experimental results of the plant development at sampling time 14 and 21 mathematically:

$$M(D) = M_{0D} + (\Delta M / \Delta D) \cdot D \qquad \text{(Equ. 3.10)}$$

Where:

| | | |
|---|---|---|
| $M$ | – | yield of dry matter [g pot$^{-1}$] |
| $M_{0D}$ | – | yield of dry matter if $D$ = 0 [g pot$^{-1}$] |
| $\Delta M/\Delta D$ | – | change of dry matter per unit of lime |
| $D$ | – | lime dose [g kg$^{-1}$] |

Starting from day 29 the development of dry matter influenced by lime dose can be described by the logistic function with high accuracy:

$$M(D) = \frac{M_{\max D}}{1 + \frac{M_{\max D}}{M_{0D}} e^{-\mu_D D}} \qquad \text{(Equ. 3.11)}$$

Where:

$M_{maxD}$ – maximum dry matter [g pot$^{-1}$]

$M_{0D}$ – dry matter if $D = 0$ [g pot$^{-1}$]

$\mu_D$ – constant increase of dry matter; $\mu_D = \frac{1}{D_{0D}}$

$D_{0D}$ – characteristic lime dose which double decrease the second item of Equ. 3.12 [g kg$^{-1}$] (valid for the conditions of the experiment)

$D$ – lime dose [g kg$^{-1}$]

The calculated values $M_{0D}$ (dry matter which is not dependent on lime dose, Tab. 3.14) are very close to the dry matter yield of both investigated crops obtained at sampling days 14 and 21 day on the control treatments (Tab. 3.10). In both experiments at day 21 the dimension of the parameter $M_{0D}$ (dry matter change per lime unit) considerably exceeded those at day 14. Starting from day 29 of observation the parameter $\mu_D$, which is physically equivalent to $\Delta M/\Delta D$ did not change in the experiment with *Brassica napus* until the end of observation. In the experiment with *Avena sativa* it continued to increase during the vegetation period (Tab. 3.14). The presented result showed that young plants of *Brassica napus* responded on the addition of lime significantly more than mature plants. The plants of *Avena sativa* kept a high response on lime addition during all periods of observation.

Table 3.14: Parameters for the linear and logistic description of dry matter development of *Brassica napus* and *Avena sativa* influenced by lime addition.

| ***Brassica napus*** | | | | ***Avena sativa*** | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Linear function** | | | | | | | | | |
| **Sampling time** [d] | $R^2$ | $M_0$ [g pot$^{-1}$] | $\Delta M/\Delta D$ [g d.m. per g kg$^{-1}$ lime] | $R^2$ | $M_0$ [g pot$^{-1}$] | $\Delta M/\Delta D$ [g d.m. per g kg$^{-1}$ lime] | | | |
| 14 | 0.74 | 0.29±0.03 | 0.05±0.018 | 0.85 | 0.25±0.01 | 0.04±0.002 | | | |
| 21 | 0.98 | 0.49±0.03 | 0.28±0.030 | 0.92 | 0.52±0.05 | 0.35±0.040 | | | |
| **Logistic function** | | | | | | | | | |
| | $R^2$ | $M_{max}$ [g pot$^{-1}$] | $M_{0D}$ [g pot$^{-1}$] | $\mu_{(D)}$ | $D_{1/2}$ [g kg$^{-1}$] | $R^2$ | $M_{max}$ [g pot$^{-1}$] | $M_{0D}$ [g pot$^{-1}$] | $\mu_{(D)}$ | $D_{1/2}$ [g kg$^{-1}$] |
| 29 | 0.96 | 14.0±1.4 | 1.1 | 1.57±0.25 | 0.44 | 0.99 | 20.4±9.05 | 2.8 | 1.04±0.3 | 0.66 |
| 36 | 0.99 | 20.1±3.3 | 1.3 | 2.18±0.63 | 0.32 | 0.99 | 18.3±0.70 | 3.2 | 2.60±0.3 | 0.26 |
| 43 | 0.99 | 24.4±3.7 | 3.1 | 1.76±0.40 | 0.39 | 0.99 | 20.2±0.60 | 3.7 | 3.10±0.4 | 0.22 |

Remarks: ± - error of estimating functions; $R^2$ – coefficient of determination, explained by linear and logistic functions, figures apply to Equ. 3.10 and 3.11; $D_{1/2}$- lime dose which increases dry matter double; $D_{1/2}$=0.693 $\mu_D^{-1}$ [g kg$^{-1}$]

*3.4.3 Dynamics of Ni concentration in plants depending on the lime dose*

For the description of the dynamics of changes in Ni concentrations in plants during the vegetation period the following equation for the sigmoidal Boltzman function was employed:

$$C_{(D)} = \frac{C_{(Ni)\max} - C_{(Ni)\min}}{1 + e^{(D-D_0)/\Delta D}} + C_{(Ni)\min} \qquad \text{(Equ. 3.12)}$$

Where:

| | | |
|---|---|---|
| $C_{(Ni)\ min}$ | – | Ni concentration in plants grown on soil with a high lime dose [mg kg$^{-1}$] |
| $C_{(Ni)max}$ | – | Ni concentration in plants grown on soil with a low lime dose [mg kg$^{-1}$] |
| $D_0$ | – | lime dose where the change of Ni concentration in plants per unit of lime is maximum |
| $\Delta D$ | – | constant, characteristic lime dose which describes the changes in Ni concentrations from the maximum to the minimum [g kg$^{-1}$] (valid for the conditions of the experiment) |

During the first phase of the development of *Brassica napus* the Ni concentration smoothly decreased with increasing lime doses. This tendency continues during the more mature phases of the plant development, but in the flowering phase there was an extremely sharp change of the Ni concentration (Fig. 3.14).

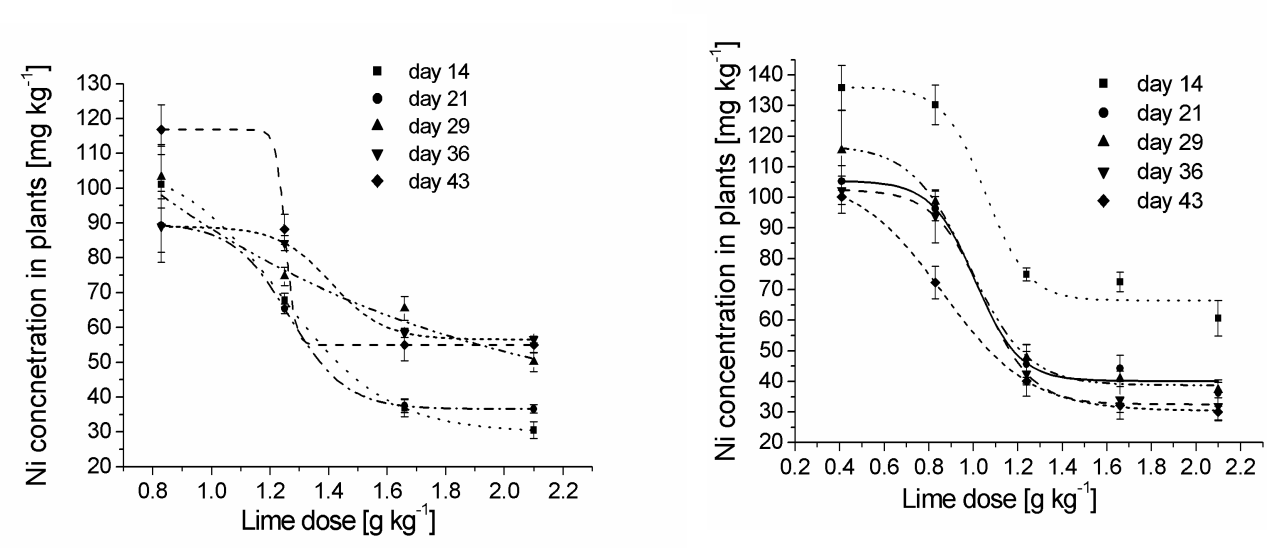


Figure 3.14: Influence of liming on Ni concentration in *Brassica napus* (left) and *Avena sativa* (right) grown on a sod-podzolic soil (corresponding Equ. 3.12, model parameters see Tab. 3.15).

Due to the negative $D_0$ value at day 29 (Tab. 3.15) the calculated Ni concentrations of the employed function ($C_{(Ni)max}$, $\Delta D$) are unreliable concerning *Brassica napus*. Applying a linear function might be more reasonable for the description of the Ni behaviour at this plant development phase. In all periods of observation the parameter $D_0$ was almost constant and equivalent to 1.24 g $kg^{-1}$.

In the experiment with *Avena sativa* the Ni concentration in plants smoothly decreased with increasing lime doses during all time of observation (Fig. 3.14). The maximum and minimum values of the Ni concentration are statistically indistinguishable at all sampling times, except day 14 (Tab. 3.15). The parameter $D_0$ , similar to the experiment with *Brassica napus*, was almost constant and equivalent to 1 g $kg^{-1}$.

Table 3.15: Parameters of the sigmoidal Boltzman function for the description of changes in Ni concentrations in *Brassica napus* and *Avena sativa* depending on lime applications.

| **Sampling time** [d] | ***Brassica napus*** | | | | | ***Avena sativa*** | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $R^2$ | $C_{(Ni)max}$ [mg kg$^{-1}$] | $C_{(Ni)min}$ [mg kg$^{-1}$] | $D_0$ [g kg$^{-1}$] | $\Delta D$ [g kg$^{-1}$] | $R^2$ | $C_{(Ni)max}$ [mg kg$^{-1}$] | $C_{(Ni)min}$ [mg kg$^{-1}$] | $D_0$ [g kg$^{-1}$] | $\Delta D$ [g kg$^{-1}$] |
| 14 | 1.00 | 108.6 | 29.8 | 1.22 | 0.19 | 0.98 | 136.0±7.4 | 69.7±5.9 | 1.03±0.10 | 0.09±0.05 |
| 21 | 1.00 | 89.9 | 36.6 | 1.26 | 0.09 | 0.99 | 105.5±5.4 | 40.2±4.0 | 1.00±0.07 | 0.09±0.03 |
| 29 | 0.98 | 575.0 | 39.9 | -0.60 | 0.38 | 0.99 | 117.1±14 | 38.8±1.8 | 1.00±0.08 | 0.13±0.03 |
| 36 | 1.00 | 88.9 | 56.6 | 1.24 | 0.09 | 0.99 | 102.6±4.9 | 32.5±3.8 | 1.00±0.08 | 0.11±0.01 |
| 43 | 1.00 | 116.8 | 55.0 | 1.24 | 0.01 | 0.99 | 107.0±10.0 | 30.3±2.1 | 0.90±0.08 | 0.19±0.04 |

Remarks: ± - error of estimating function; $R^2$- coefficient of determination between Ni concentration in plants and lime dose (explained by the sigmoidal Boltzman function), figures apply to Equ. 3.12.

*3.4.4 Development of Ca and Ni uptake by Brassica napus and Avena sativa during the vegetation period*

To describe the plant nutrient accumulation during the vegetation period it is convenient to use the parameter "uptake", because this parameter as well as plant growth is integral characteristics of the plant status.

The development of Ca and Ni uptake during the vegetation period influenced by increasing lime doses is summarised in Tab. 3.16.

Table 3.16: Development of Ca and Ni uptake by *Brassica napus* and *Avena sativa* plants during the vegetation period influenced by lime application.

| **Lime dose** [g kg$^{-1}$] | **Ca uptake** [mg pot$^{-1}$] | | | | | **Ni uptake** [mg pot$^{-1}$] | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | **Sampling time** [d] | | | | | | | | | |
| | **14** | **21** | **29** | **36** | **43** | **14** | **21** | **29** | **36** | **43** |
| ***Brassica napus*** | | | | | | | | | | |
| 0 | 3.9 | 6.1 | 18.0 | 17.3 | 33.6 | - | - | - | - | - |
| 0.41 | - | - | - | - | - | - | - | - | - | - |
| 0.83 | 6.2 | 21.0 | 68.2 | 37.9 | 109.1 | 0.029 | 0.067 | 0.312 | 0.438 | 0.897 |
| 1.25 | 7.0 | 23.1 | 89.3 | 97.0 | 197.7 | 0.026 | 0.054 | 0.351 | 0.842 | 1.147 |
| 1.66 | 10.1 | 23.5 | 164.7 | 214.6 | 282.2 | 0.014 | 0.038 | 0.477 | 0.866 | 0.976 |
| 2.10 | 11.2 | 27.4 | 262.6 | 246.6 | 344.6 | 0.012 | 0.038 | 0.510 | 0.963 | 1.096 |
| *LSD(5%)* | *2.8* | *3.2* | *25.8* | *15.7* | *67.4* | *0.001* | *0.001* | *0.130* | *0.170* | *0.205* |
| ***Avena sativa*** | | | | | | | | | | |
| 0 | 0.7 | 1.2 | 3.3 | 3.5 | 4.6 | - | - | - | - | - |
| 0.41 | 3.1 | 8.1 | 37.6 | 63.4 | 72.5 | 0.032 | 0.045 | 0.397 | 0.600 | 0.726 |
| 0.83 | 6.0 | 11.0 | 47.8 | 109.6 | 110.2 | 0.035 | 0.071 | 0.471 | 1.083 | 1.077 |
| 1.25 | 6.1 | 16.0 | 105.0 | 167.7 | 153.4 | 0.024 | 0.038 | 0.357 | 0.648 | 0.732 |
| 1.66 | 8.1 | 23.7 | 181.9 | 328.0 | 371.1 | 0.022 | 0.044 | 0.347 | 0.559 | 0.618 |
| 2.10 | 9.7 | 25.5 | 225.7 | 339.1 | 294.7 | 0.021 | 0.045 | 0.424 | 0.587 | 0.606 |
| *LSD(5%)* | *3.9* | *8.5* | *46.5* | *39.7* | *45.1* | *0.020* | *0.020* | *0.230* | *0.270* | *0.280* |

Tab. 3.16 shows that the Ca uptake of the investigated plants increased over time and with rising lime doses. This is caused by a promoting effect of lime application on plant growth and increasing dry matter development. The Ni uptake by *Brassica napus* and *Avena sativa* plants increased during the vegetation period as well. But with rising lime doses a decreasing

tendency of this parameter was observed. This is caused by the fact that the concentration in plant material considerably decreased.

According to the theory (see Material and Methods) the dynamics of Ca and Ni uptake by plants during the vegetation period are approximated with similar functions as dry matter growth (Equ. 1.13 and 1.14). The results of the presented experiment revealed that the Ca uptake corresponds well with the logistic form of the curve (Fig. 3.15).

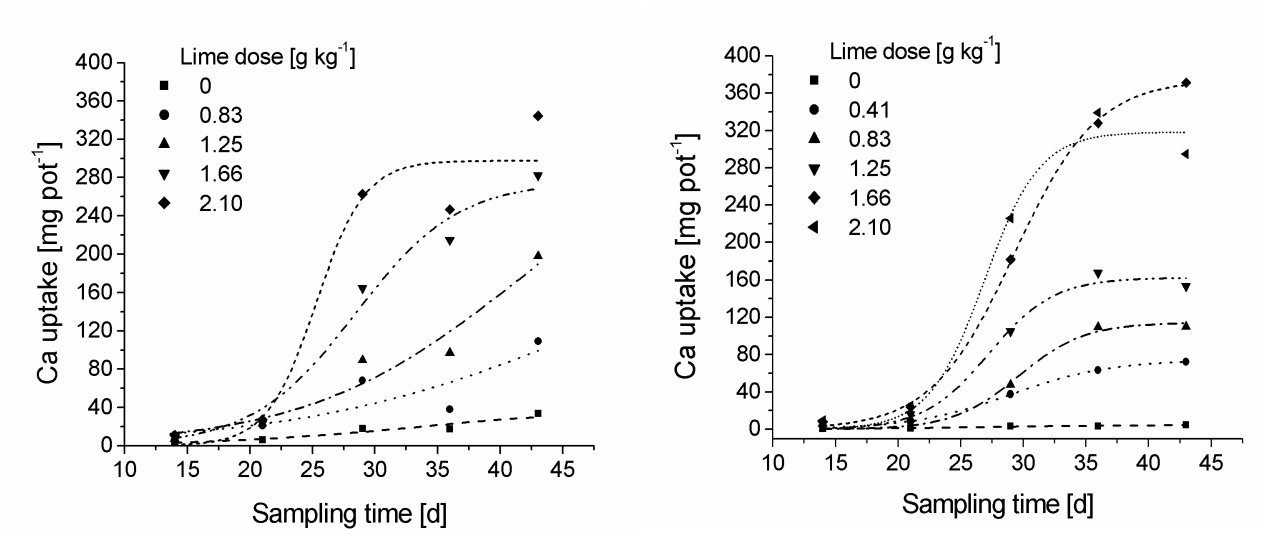


Figure 3.15: Development of Ca uptake by *Brassica napus* (left) and *Avena sativa* (right) during the vegetation period (corresponding to Equ. 1.13, model parameters see Tab. 3.17).

The parameters for the description of the lime application influence on Ca uptake by *Brassica napus* and *Avena sativa* are summarised in Tab. 3.17. In both experiments the tendency of increasing maximum Ca uptake ($A_{max(Ca)}$) with rising lime doses was observed. The parameter $A_0$ (element content in seeds or in seedling roots at the beginning of germination) was significantly higher in the experiment with *Brassica napus* plants. The specific rate of Ca uptake ($\varepsilon_{(Ca)}$) by rape plants increased with increasing lime doses. Thus the period of time in which Ca uptake is doubled changed from 6 days in the treatment with a lime does of 0.83 g kg $^{-1}$ up to 3 days in the treatment with the maximum lime dose. The same tendency of increasing the specific rate of the Ca uptake with increasing lime doses was observed in the experiment with *Avena sativa*. But taking into consideration the determination error of $\varepsilon_{(Ca)}$ in the treatments with lime doses 0.83-2.10 g kg $^{-1}$ the values of this parameter can be averaged and equivalent to 0.38±0.06 d $^{-1}$.

It is remarkable that in all treatments the parameter $T$ was higher in the experiment with *Avena sativa* than in the experiment with *Brassica napus*. This means that *Avena sativa* plants accumulated Ca 1.3-3.2 times faster than plants of *Brassica napus* (Tab. 3.17).

Table 3.17: Parameters for the logistic description of changes in Ca uptake $A_{Ca}(t)$ by *Brassica napus* and *Avena sativa* during vegetation period.

| ***Brassica napus*** | | | | | | ***Avena sativa*** | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Lime dose** [g kg$^{-1}$] | $R^2$ | $A_{max}$ [mg pot$^{-1}$] | $A_0$ [mg pot$^{-1}$] | $\varepsilon_{(Ca)}$ [d$^{-1}$] | $T$ [d] | $R^2$ | $A_{max}$ [mg pot$^{-1}$] | $A_0$ [mg pot$^{-1}$] | $\varepsilon_{(Ca)}$ [d$^{-1}$] | $T$ [d] |
| 0 | 0.92 | 60 | 1.13 | 0.10±0.02 | 6.9 | 0.95 | 4.7±0.8 | 0.074 | 0.16±0.07 | 4.3 |
| 0.41 | - | - | - | - | - | 0.99 | 74.6±1.5 | 0.052 | 0.25±0.02 | 2.7 |
| 0.83 | 0.74 | 120 | 3.40 | 0.12±0.06 | 5.8 | 0.99 | 114.0±8.0 | 0.014 | 0.38±0.15 | 1.8 |
| 1.25 | 0.92 | 220 | 1.12 | 0.16±0.04 | 4.6 | 0.99 | 163.0±9.0 | 0.004 | 0.39±0.11 | 1.7 |
| 1.66 | 0.98 | 276±32 | 0.28 | 0.24±0.09 | 2.9 | 0.99 | 375.0±7.0 | 0.050 | 0.30±0.02 | 2.3 |
| 2.10 | 0.91 | 350 | 0.42 | 0.25±0.11 | 2.7 | 0.99 | 318.0±20.0 | 0.017 | 0.45±0.17 | 1.5 |

Remarks: ± - error of estimating function; $R^2$ – coefficient of determination between Ca uptake and time (explained by a logistic function), figures apply to Equ. 1.13; $T$-period of time in which Ca uptake is doubled; $T$=0.693 $\varepsilon_{(Ca)}^{-1}$; Values of *Brassica napus* $A_{max}$ were chosen based on the maximum uptake values obtained experimentally (at every sampling time).

The development of the Ni uptake by *Brassica napus* and *Avena sativa* over time is shown in Fig. 3.16.

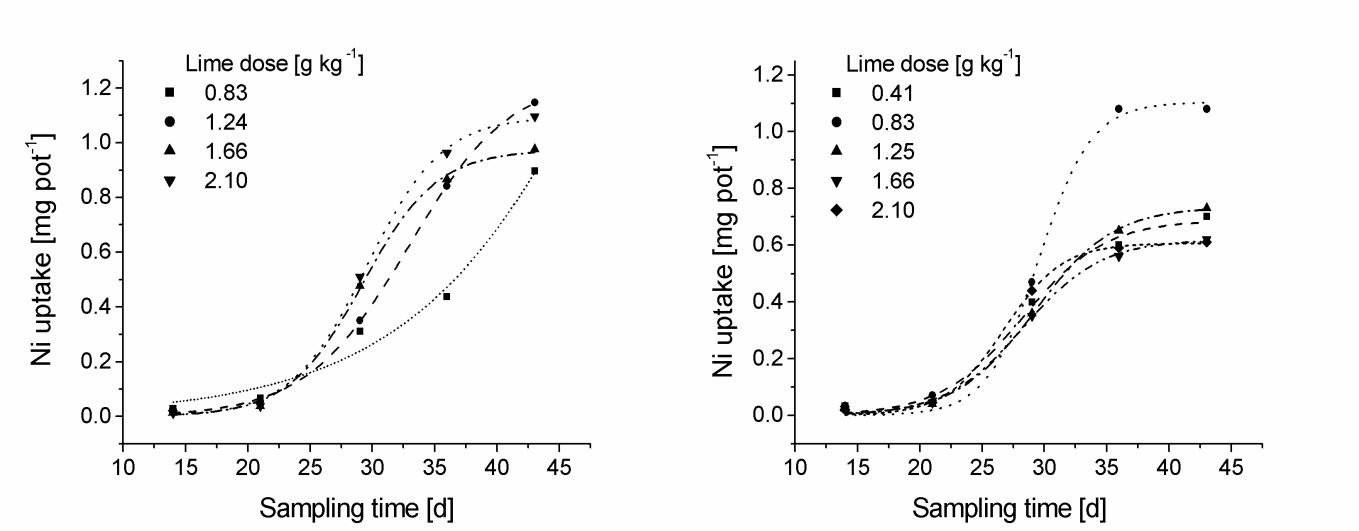


Figure 3.16: Ni uptake by *Brassica napus* (left) and *Avena sativa* (right) during vegetation period (corresponding to Equ. 1.13, model parameters see Tab. 3.18).

The parameters for the logistic function describing the Ni uptake by *Brassica napus* and *Avena sativa* are summarized in the Tab. 3.18. In the treatment with a lime dose of 0.83 g kg $^{-1}$ the calculated value of the maximum Ni uptake by *Brassica napus* has a low accuracy. In the treatments with lime doses of 1.66 and 2.10 g kg $^{-1}$ the value of $A_{max(Ni)}$ is statistically indistinguishable, while in the treatment with 1.25 g kg $^{-1}$ it differs significantly. Hence it is possible to assume that Ni uptake depended on lime dose, i.e. the higher the lime dose, the lower the Ni uptake by *Brassica napus*. The dependence of the specific rate of Ni uptake ($\varepsilon_{(Ni)}$) by *Brassica napus* plants on lime dose was more distinct. With raising lime doses the specific rate of Ni uptake increased. Consequently the period of time in which Ni uptake is doubled ($T$) decreased from 7 days in the treatment with the lowest lime dose up to 2 days in the treatment with the highest one.

Table 3.18: Parameters for the logistic function describing Ni uptake $A_{Ni}(t)$ by *Brassica napus* and *Avena sativa* during the vegetation period.

| **Lime dose** [g kg$^{-1}$] | ***Brassica napus*** | | | | | ***Avena sativa*** | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $R^2$ | $A_{max}$ [mg pot$^{-1}$] | $A_0$ [mg pot$^{-1}$] | $\varepsilon_{(Ni)}$ [d$^{-1}$] | $T$ [d] | $R^2$ | $A_{max}$ [mg pot$^{-1}$] | $A_0$ [mg pot$^{-1}$] | $\varepsilon_{(Ni)}$ [d$^{-1}$] | $T$ [d] |
| 0.41 | - | - | - | - | - | 0.99 | 0.69±0.04 | 0.00004 | 0.21±0.03 | 3.3 |
| 0.83 | 0.99 | 4.90±21.0 | 0.012 | 0.10±0.05 | 6.9 | 0.99 | 1.10±0.05 | 0.000008 | 0.27±0.09 | 2.6 |
| 1.25 | 0.99 | 1.25±0.03 | 0.0004 | 0.24±0.01 | 2.9 | 0.99 | 0.73±0.02 | 0.00007 | 0.25±0.02 | 2.7 |
| 1.66 | 0.99 | 0.97±0.02 | 0.00005 | 0.34±0.04 | 2.0 | 0.99 | 0.62±0.02 | 0.00007 | 0.24±0.04 | 2.9 |
| 2.10 | 0.99 | 1.10±0.03 | 0.00006 | 0.33±0.04 | 2.1 | 0.99 | 0.61±0.01 | 0.000006 | 0.26±0.04 | 2.7 |

Remarks: ± - error of estimating function; $R^2$ – coefficient of determination between Ni uptake and time (explained by logistic function, figures apply to Equ. 1.13 (see chapter Material and Methods); $T$- period of time in which Ni uptake is doubled; $T$=0.693 $\varepsilon_{(Ni)}^{-1}$

The tendency of decreasing $A_{max(Ni)}$ values (Tab. 3.18) depending on increasing lime doses was observed in the experiment with *Avena sativa,* except from the treatment with a lime dose of 0.83 g $kg^{-1}$. In this treatment the parameter $A_{max(Ni)}$ was about 34-45% higher compared to the other treatments.

Taking into consideration the standard error of the estimating function the specific rate of Ni uptake ($\varepsilon_{(Ni)}$) by *Avena sativa* plants was almost equal in all the treatments with the average value of 0.25 $d^{-1}$.

Following the theory described in chapter Material and Methods the specific rate of plants growth ($\mu_{(t)}$) and specific rate of *Ni* and *Ca* uptake by plants ($\varepsilon_{(Ni)}$ and $\varepsilon_{(Ca)}$) on the exponential section of the Growth Curve were compared (Tab. 3.19).

Table 3.19: Specific rate of plant growth ($\mu(t)$) and specific rate of Ni and Ca uptake by plants ($\varepsilon_{(Ni)}$ and $\varepsilon_{(Ca)}$) depending on lime dose.

| **Lime dose** [g $kg^{-1}$] | ***Brassica napus*** | | | ***Avena sativa*** | | |
|---|---|---|---|---|---|---|
| | $\mu_{(t)}$ | $\varepsilon_{(Ca)}$ | $\varepsilon_{(Ni)}$ | $\mu_{(t)}$ | $\varepsilon_{(Ca)}$ | $\varepsilon_{(Ni)}$ |
| | [$d^{-1}$] | | | | | |
| 0 | 0.21±0.10 | 0.10±0.02 | - | 0.27±0.12 | 0.16±0.07 | - |
| 0.41 | - | - | - | 0.22±0.02 | 0.25±0.02 | 0.21±0.03 |
| 0.83 | 0.15±0.03 | 0.12±0.06 | 0.10±0.05 | 0.26±0.01 | 0.38±0.15 | 0.27±0.09 |
| 1.25 | 0.23±0.01 | 0.16±0.04 | 0.24±0.01 | 0.28±0.02 | 0.39±0.11 | 0.25±0.02 |
| 1.66 | 0.27±0.02 | 0.24±0.09 | 0.34±0.04 | 0.29±0.02 | 0.30±0.02 | 0.24±0.04 |
| 2.10 | 0.29±0.04 | 0.25±0.11 | 0.33±0.04 | 0.34±0.03 | 0.45±0.17 | 0.26±0.04 |

As shown in Tab. 3.19 in the experiment with *Brassica napus* the specific growth rate of plants is higher than the specific rate of Ca uptake and lower than the specific rate of Ni uptake. According to Equation 1.15 it has to be expected that the concentration of Ca would decrease and concentration of Ni would increase in *Brassica napus* plants over the time. In the experiment with *Avena sativa* the specific rate of the Ni uptake was lower than the specific growth rate of plants while the specific rate of the Ca uptake was higher. Hence the expected pattern of the dynamic of Ca and Ni concentrations in plants is different. Ca concentration is expected to decrease and Ni concentration to increase in *Avena sativa* plants over time.

To show the vector of changes in the Ca and Ni plant concentration in plants during the vegetation period, a linear function was employed (Fig. 3.17 and 3.18). As it was expected the

Ca concentration decreased and the Ni concentration increased in *Brassica napus* plants during the vegetation period (Fig. 3.17)

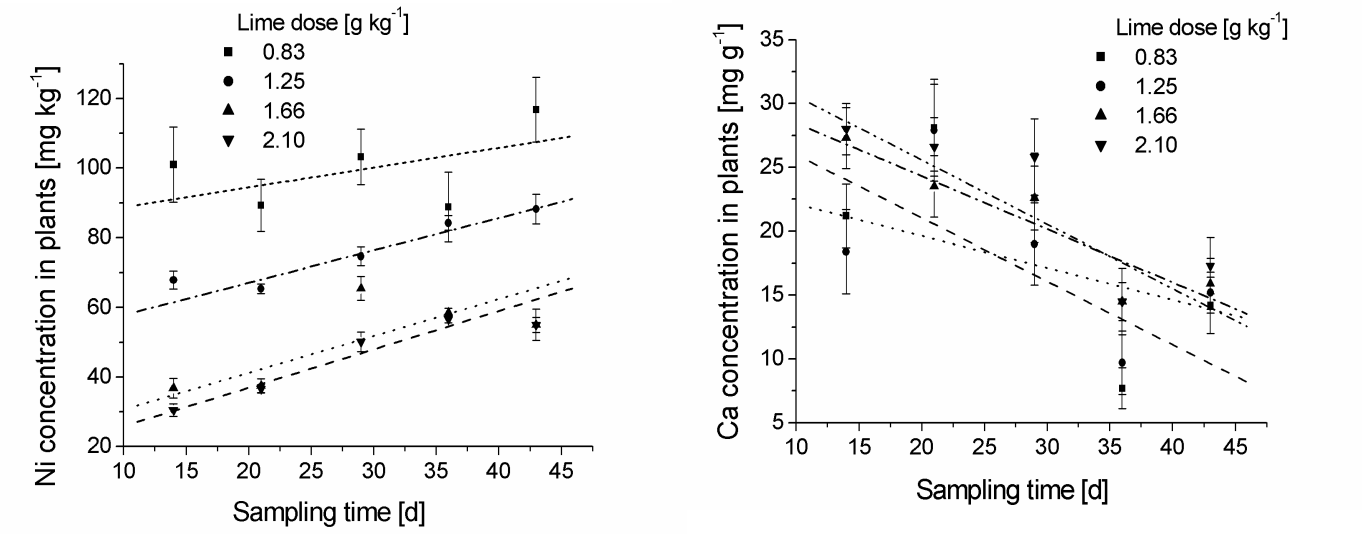


Figure 3.17: Dynamics of Ni (left) and Ca (right) concentrations in *Brassica napus* plants during the vegetation period depending on different lime application rates.

In the experiment with *Avena sativa* the expected effect of decreasing Ni concentration over time was observed. But in contrary with theoretical expectations the Ca concentration in plants also decreased (Fig. 3.18).

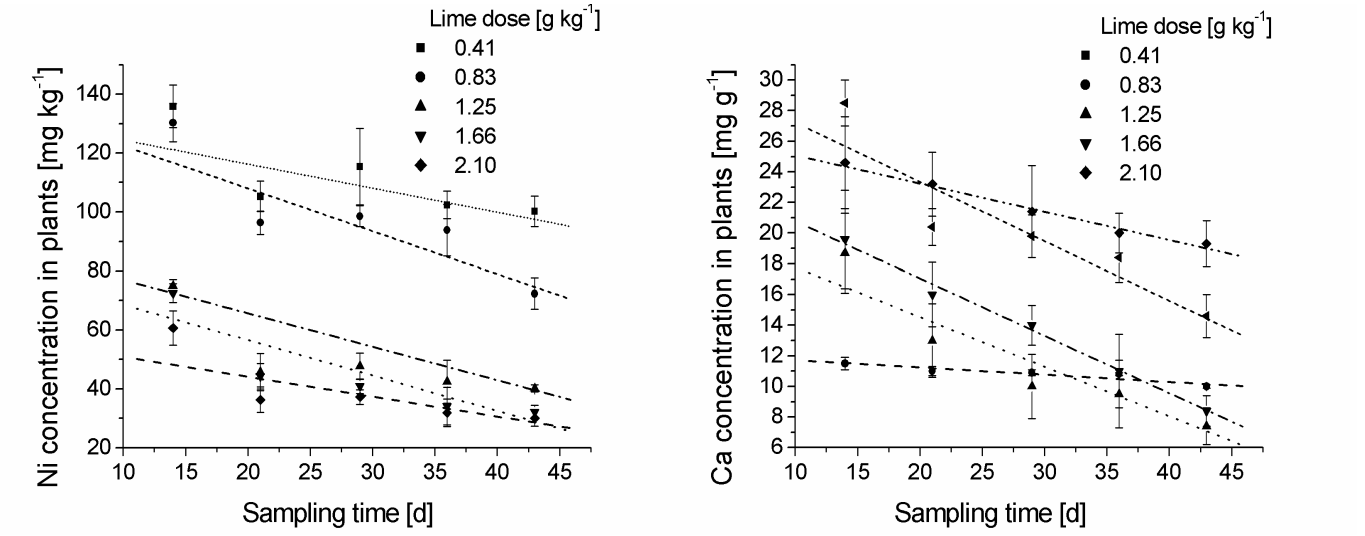


Figure 3.18: Dynamics of Ni (left) and Ca (right) concentrations in *Avena sativa* during vegetation period depending on different lime application rates.

Despite of this fact it can be assumed that interaction between Ca and Ni in the soil-plant system is realised competitively, on the basis of ion exchange mechanism.

### *3.4.5 Development of Ca and Ni uptake by plants as influenced by lime application*

The development of Ca uptake by *Brassica napus* and *Avena sativa* plants is presented in Fig. 3.19. A low effect of lime application during the sampling days 14 and 21 was observed. It might be due to the low dry matter content at this phase of plant development.

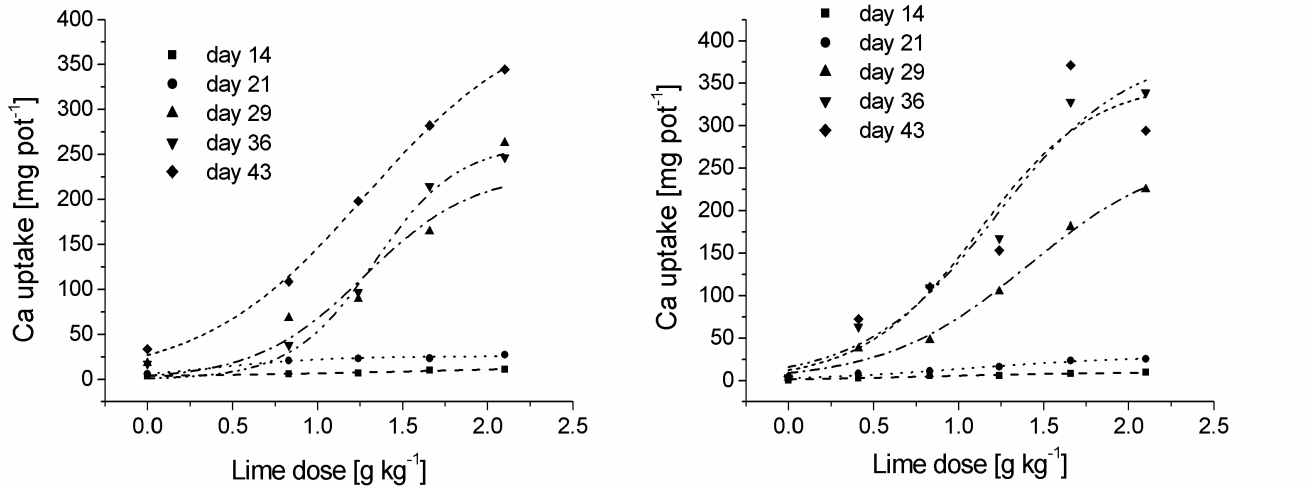


Figure 3.19: Development of Ca uptake by *Brassica napus* (left) and *Avena sativa* (right) as influenced by lime application (corresponding to Equ. 3.13, model parameters see Tab. 3.20).

The relationship between lime application and Ca uptake by plants was well described by the logistic function:

$$A(D) = \frac{A_{\max\ D}}{1 + \frac{A_{\max\ D}}{A_{0\,D}} e^{-\varepsilon_D D}} \qquad \text{(Equ. 3.13)}$$

Where:

$A_{maxD}$ – maximum Ca uptake by plants [mg pot$^{-1}$]

$A_{0D}$ – Ca uptake by seedlings if $D = 0$ [mg pot$^{-1}$]

$D$ – lime dose [g kg$^{-1}$]

$\varepsilon_D$ – Ca uptake constant. $\varepsilon_{(D)} = \frac{1}{D_{0D}}$

$D_{0D}$ – characteristic lime dose which double decrease the second item of Equ. 3.13 [g kg$^{-1}$] (valid for the conditions of the experiment)

The maximum Ca uptake by *Brassica napus* has a very high variability at day 14 of the observations, because the plants were too small (Tab. 3.20). Starting from the day 21 a reliable increase in the Ca uptake was observed. In the experiment with *Avena sativa* the maximum Ca uptake ($A_{Camax}$) increased during all times of observation, but a slight decrease of this parameter was observed at day 43.

Table 3.20: Parameters for the logistic function describing Ca uptake ($A_{Ca}(D)$) by *Brassica napus* and *Avena sativa* effected by lime application.

| **Sampling time** [d] | ***Brassica napus*** | | | | | ***Avena sativa*** | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $R^2$ | $A_{max}$ [mg pot$^{-1}$] | $A_{0D}$ [mg pot$^{-1}$] | $\varepsilon_{(D)}$ | $D_{1/2}$ [g kg$^{-1}$] | $R^2$ | $A_{max}$ [mg pot$^{-1}$] | $A_{0D}$ [mg pot$^{-1}$] | $\varepsilon_{(D)}$ | $D_{1/2}$ [g kg$^{-1}$] |
| 14 | 0.97 | 37±85.0 | 4.25 | 0.13±0.08 | 5.3 | 0.96 | 10±1.7 | 1.74 | 2.05±0.7 | 0.3 |
| 21 | 0.97 | 26±1.6 | 8.34 | 0.59±0.16 | 1.2 | 0.98 | 29±4.2 | 3.36 | 2.05±0.5 | 0.3 |
| 29 | 0.94 | 230±10.0 | 3.95 | 0.64±0.27 | 1.1 | 0.99 | 270±34.9 | 7.74 | 2.39±0.4 | 0.2 |
| 36 | 0.98 | 264±25.7 | 1.19 | 0.80±0.21 | 0.9 | 0.97 | 390±66.7 | 16.60 | 2.57±0.8 | 0.2 |
| 43 | 0.99 | 419±24.8 | 29.40 | 0.40±0.03 | 1.7 | 0.87 | 353±95.9 | 12.80 | 2.92±1.9 | 0.2 |

Remarks: ± - error of estimating function; $R^2$ – coefficient of determination between Ca uptake and lime dose (explained by a logistic function), figures apply to Equ. 3.13; $D_{1/2} = 0.693\ \varepsilon_{(D)}^{-1}$

Using the parameter $A_0$ it is possible to calculate the content of an element in the seed or in that part of the seed which is responsible for plant development. Parameters $A_0$, calculated by Equ. 3.13 and Equ. 1.13 should be close to each other. But these values are very low and the calculation errors are too high.

The description of Ni uptake by *Brassica napus* plants depending on lime dose was not possible with acceptable accuracy by any available function. It might be explained by the lack of sampling points or by uncompleted reaction between lime and soil, especially on the treatments with high lime doses. However it is obvious from the Fig. 3.20 that starting from day 29 the Ni uptake by *Brassica plants* slightly increased with increasing lime doses.

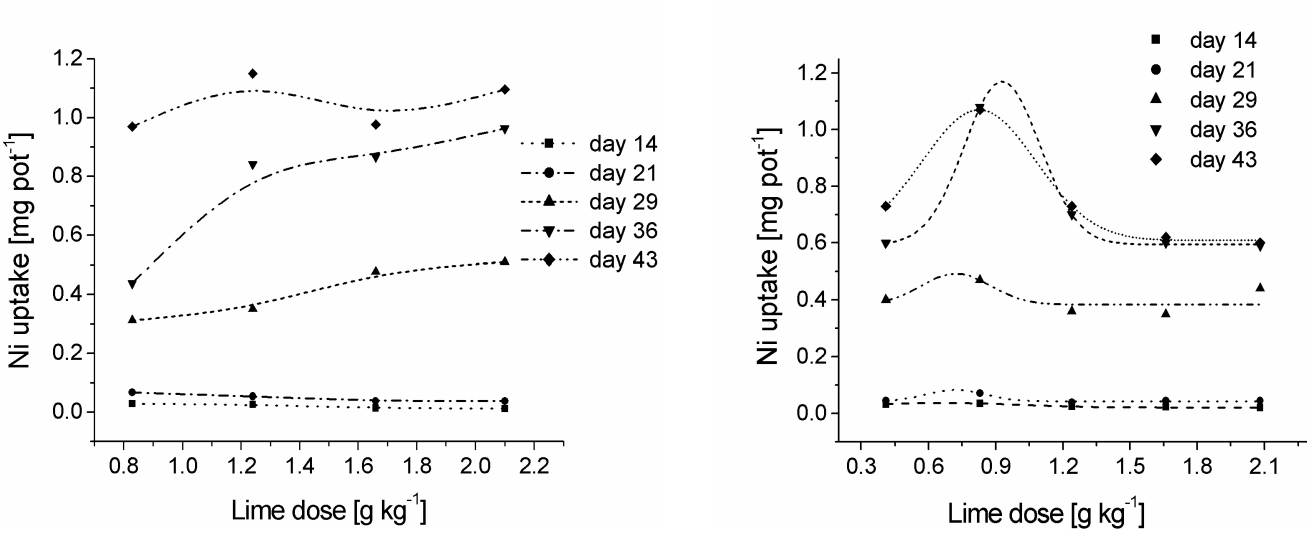


Figure 3.20: Ni uptake by *Brassica napus* (left) and *Avena sativa* (right) plants depending on lime dose.

The Ni uptake depending on lime dose by *Avena sativa* plants can be described well by the Gauss function:

$$A = A_0 + \frac{A_1}{\omega\sqrt{\pi/2}} e^{-2\frac{(D-D_1)}{\omega^2}} \qquad \text{(Equ. 3.14)}$$

Where:

| | | |
|---|---|---|
| $A$ | – | Ni uptake by *Avena sativa* [mg pot$^{-1}$] |
| $A_0$ | – | Ni uptake by *Avena sativa* not dependent on lime dose [mg pot$^{-1}$] |
| $\frac{A_1}{\omega\sqrt{\pi/2}} = A_{\max(Ni)}$ | – | maximum Ni uptake [mg pot$^{-1}$] |
| $\omega$ | – | width of peak at the half height |

$D$ – lime dose [mg pot$^{-1}$]

$D_1$ – lime dose under which Ni uptake is maximum [mg pot$^{-1}$]

An interesting effect of maximum Ni ($A_{max(Ni)}$) uptake in the treatments with a lime dose of 0.83 g kg$^{-1}$ was observed over all times of observations (Fig. 3.20, right). Mostly probably it is caused by enhanced high dry matter production in these treatments.

The parameters for the Gauss function describing the Ni uptake by *Avena sativa* plants are summarized in Tab. 3.21.

Table 3.21: Parameters for the Gauss function describing the Ni uptake by *Avena sativa* plants depending on lime dose.

| **Sampling time** [d] | $A_{max}$ [mg pot$^{-1}$] | $A_0$ [mg pot$^{-1}$] | $D_1$ [g kg$^{-1}$] | $\omega$ | $A_1$ | $R^2$ |
|---|---|---|---|---|---|---|
| 14 | 0.02 | 0.02±0.001 | 0.7±0.02 | 0.63±0.05 | 0.06±0.01 | 0.99 |
| 21 | 0.04 | 0.04±0.004 | 0.7±0.10 | 0.26±25 | 0.60±1.00 | 0.96 |
| 29 | 0.10 | 0.38±0.050 | 0.7±0.80 | 0.31±22 | 0.20±0.90 | 0.54 |
| 36 | 0.60 | 0.59±0.005 | 0.9±0.10 | 0.34±0.2 | 1.20±0.03 | 0.99 |
| 43 | 0.50 | 0.61±0.009 | 0.8±0.06 | 0.51±0.1 | 1.50±0.08 | 0.99 |

Remarks: ± - error of estimating function; $R^2$ – coefficient of determination between Ni uptake and lime dose (explained by the Gauss function), figures apply to Equ. 3.14.

A tendency of increasing the maximum Ni uptake by *Avena sativa* plants over the time of the observations till day 36 was observed. A slight decline of this parameter at the day 43 may be explained by decreasing of dry matter. The parameter $A_0$ increased during the vegetation period (Ni uptake by oat plants is not dependent on lime dose). Taking into consideration the determination error the important parameter $D_1$ (lime dose under which Ni uptake is maximum) was almost the same at every sampling time and was equivalent to 0.6-0.7 g kg$^{-1}$.

### *3.4.6 Development of the soil-plant Transfer Factors for Ni during the vegetation period of Brassica napus and Avena sativa plants.*

For a quantitative estimation of the heavy metal availability for plants commonly a coefficient is used, which takes plant and soil properties into account. The so called *Transfer Factor* (*TF*) is defined as the ratio of element concentration in plants to total element concentration in soil [mg kg$^{-1}$]. In this work the Ni *Transfer Factors (TF)* were calculated as the ratio of Ni

concentration in plants to mobile Ni concentration in soil. The development of the Ni concentration in plants, the mobile Ni concentration in soil and the *Transfer Factors (Ni)* for *Brassica napus* and *Avena sativa* plants are summarised in Tab. 3.22.

The addition of lime significantly influenced the Ni transfer (*TF(Ni)*) from the soil into plants. *Transfer Factors (Ni)* for *Brassica napus* and *Avena sativa* decreased with rising lime dose (Tab. 3.22). In the experiment with *Brassica napus* the *Transfer Factors* obtained in the treatments with the lowest lime dose were 1.8 - 2.4 times higher then those in the treatments with the highest lime dose. In the experiment with *Avena sativa* the difference between *Transfer Factors (Ni)* in the treatments with the lowest and highest lime doses was 2.0 - 2.9 times. *Avena sativa* plants showed a higher ability to accumulate Ni in their tissues in the treatments with low lime application and in the junior stage of development (up to 21 days). But in the treatments with lime doses of 1.25-2.10 g $kg^{-1}$ and starting from day 29 the *Transfer Factors (Ni)* for *Avena sativa* plants are lower then those for *Brassica napus* plants.

Table 3.22: Effect of liming on the concentration of Ni in plants [mg kg$^{-1}$], the mobile Ni concentration in soil [mg kg$^{-1}$] and *Transfer Factors (Ni)* for *Brassica napus* and *Avena sativa* plants.

| **Lime dose** [g kg$^{-1}$] | **Concentration of Ni in plants** [mg kg$^{-1}$] | | | | | **Concentration of mobile Ni in soil** [mg kg$^{-1}$] | | | | | **Transfer Factors (Ni)** | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Sampling time** [d] | | | | | | | | | | | | | | |
| | **14** | **21** | **29** | **36** | **43** | **14** | **21** | **29** | **36** | **43** | **14** | **21** | **29** | **36** | **43** |
| ***Brassica napus*** | | | | | | | | | | | | | | | |
| 0.41 | No plant material | | | | | 6.30 | 6.7 | 5.7 | 6.8 | 7.0 | No plant material | | | | |
| 0.83 | 101.0 | 89.3 | 103.2 | 88.8 | 116.8 | 6.80 | 6.1 | 5.8 | 5.9 | 6.1 | 14.8 | 14.6 | 17.8 | 15.0 | 19.1 |
| 1.24 | 67.9 | 65.4 | 74.6 | 84.2 | 88.2 | 5.60 | 5.1 | 5.6 | 5.9 | 6.5 | 12.1 | 12.8 | 13.3 | 14.2 | 13.5 |
| 1.66 | 36.8 | 37.5 | 65.5 | 58.5 | 55.0 | 4.70 | 5.3 | 4.9 | 5.4 | 4.5 | 7.8 | 7.0 | 13.4 | 10.8 | 12.1 |
| 2.10 | 30.5 | 36.6 | 50.1 | 56.6 | 55.0 | 4.90 | 5.2 | 4.8 | 5.2 | 5.1 | 6.2 | 7.0 | 10.4 | 10.9 | 10.8 |
| *LSD(5%)* | *3.9* | *4.1* | *4.8* | *3.0* | *24.3* | *1.30* | *1.5* | *0.9* | *0.8* | *1.0* | *1.9* | *1.7* | *3.0* | *2.5* | *2.9* |
| ***Avena sativa*** | | | | | | | | | | | | | | | |
| 0.41 | 135.9 | 105.3 | 115.3 | 102.4 | 100.2 | 5.4 | 5.4 | 5.3 | 5.4 | 5.5 | 25.2 | 19.5 | 21.7 | 19.0 | 18.2 |
| 0.83 | 130.3 | 96.3 | 98.6 | 93.9 | 72.3 | 5.2 | 5.2 | 5.3 | 5.2 | 5.2 | 25.0 | 18.5 | 18.6 | 18.1 | 13.9 |
| 1.24 | 75.0 | 45.7 | 47.7 | 42.5 | 40.1 | 4.9 | 4.9 | 5.0 | 5.0 | 4.9 | 15.3 | 9.3 | 9.5 | 8.5 | 8.2 |
| 1.66 | 72.5 | 44.3 | 40.9 | 34.1 | 32.1 | 4.8 | 4.8 | 5.0 | 5.0 | 4.8 | 15.1 | 9.2 | 8.2 | 6.8 | 6.7 |
| 2.10 | 60.7 | 36.3 | 37.2 | 31.9 | 30.0 | 4.8 | 4.7 | 4.7 | 4.7 | 4.8 | 12.6 | 7.7 | 7.9 | 6.8 | 6.2 |
| *LSD(5%)* | *12.2* | *17.5* | *6.8* | *10.8* | *6.2* | *0.2* | *0.2* | *0.2* | *0.1* | *0.2* | *2.8* | *3.0* | *1.6* | *3.6* | *1.8* |

For a mathematical description of *TF(Ni)* changes for *Brassica napus* and *Avena sativa* during the vegetation period a hyperbolic function was employed:

$$TF(t) = \frac{TF_{\max} \cdot t}{t + t_1} \qquad \text{(Equ. 3.15)}$$

Where:

$TF_{max}$ – maximum *Transfer Factor*

$t_1$ – time when *TF* amounts the half of the maximum *TF* ( $TF = \frac{TF_{\max}}{2}$ ) [d]

$t$ – time [d]

Due to low coefficients of determination in all treatments except one with the highest lime dose, the hyperbolic function is not optimal for describing results of the experiment with *Brassica napus* (Tab. 3.21). However this function allows to make some estimations of the development of *TF(Ni)* for *Brassica napus* during the vegetation period.

Table 3.23: Parameters for the hyperbolic function describing changes of *Transfer Factors (Ni)* for *Brassica napus* and *Avena sativa* plants during the vegetation period.

| **Lime dose** [g kg$^{-1}$] | ***Brassica napus*** | | | ***Avena sativa*** | | |
|---|---|---|---|---|---|---|
| | $TF_{max}$ | $t_1$ [d] | $R^2$ | $TF_{max}$ | $t_1$ [d] | $R^2$ |
| 0.41 | - | - | - | 18.2±1.2 | 4.6±1.0 | 0.80 |
| 0.83 | 17.3±2.8 | 1.5±3.9 | 0.50 | 14.4±1.2 | 6.4±1.0 | 0.84 |
| 1.24 | 17.7±2.1 | 9.0±4.2 | 0.74 | 6.5±0.4 | 7.9±0.6 | 0.94 |
| 1.66 | 17.8±7.0 | 19.8±19.0 | 0.60 | 5.3±0.2 | 8.9±0.3 | 0.99 |
| 2.10 | 20.4±4.1 | 34.1±13.1 | 0.94 | 4.9±0.3 | 8.4±0.5 | 0.96 |

Remarks: ± - error of estimating function; $R^2$ – coefficient of determination between *TF(Ni)* and time (explained by a hyperbolic function), figures apply to Equ. 3.15.

The increasing tendency of *TF(Ni)* during the vegetation period was observed (Fig. 3.21, left). The calculated values of $TF_{max}$ were almost the same in all treatments, with an average value of 18.3. But the time of amounting half of the maximum *TF* changed from 1.5 days in the treatment with low lime dose up to 34 days in the treatment with high lime dose.

The hyperbolic function describes the changes of *TF(Ni)* for *Avena sativa* plants with a much better accuracy. (Tab. 3.23, Fig. 3.21, right).

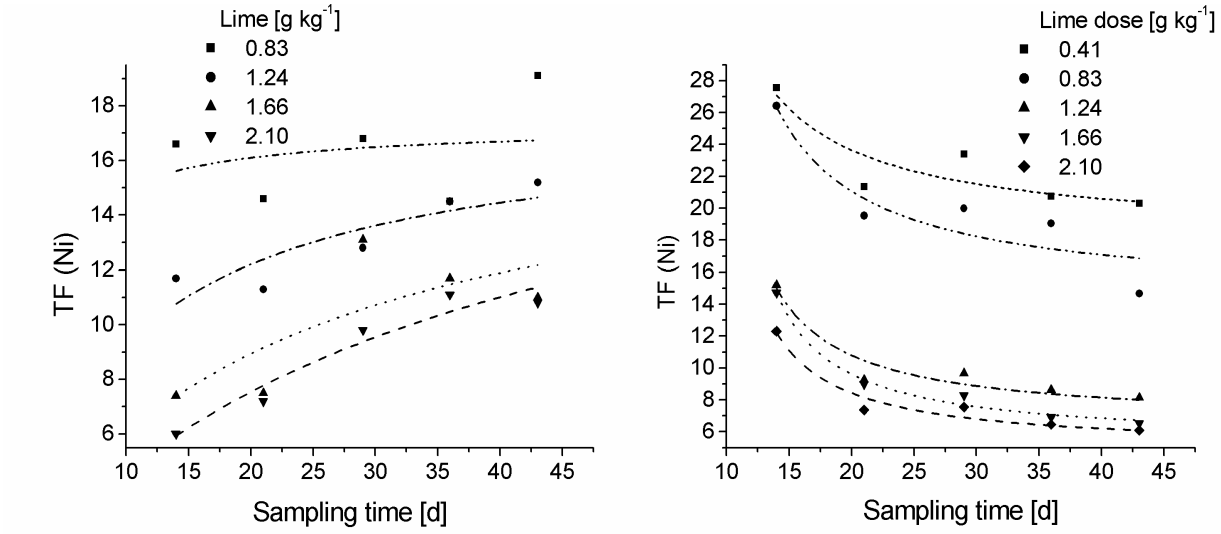


Figure 3.21: Changes of *TF(Ni)* for *Brassica napus* (left) and *Avena sativa* (right) plants during vegetation period.

The effect of reducing the heavy metal mobility in soil might be possible due to the mechanism of direct (competitive) interactions between Ca and Ni. The processing of the data of the experiment with *Avena sativa* shows that there was a distinct dependence of maximum *TF(Ni)* on lime doses. It decreased with increasing lime doses. The time of amounting the half of the maximum *TF* increased in all treatments except the treatment with the highest lime dose.

The results reveal that the higher the lime dose the more time *Brassica napus* and *Avena sativa* plants need to achieve the maximum *TF(Ni)*.

### *3.4.7 Development of TF(Ni) as influenced by lime application*

In order to demonstrate *TF(Ni)* changes for *Brassica napus* plants the linear function was employed. This function fitted only low to the experimental results, but a tendency of decrease of *TF* with increasing lime doses was observed (Tab. 3.22, Fig. 3.22, left).

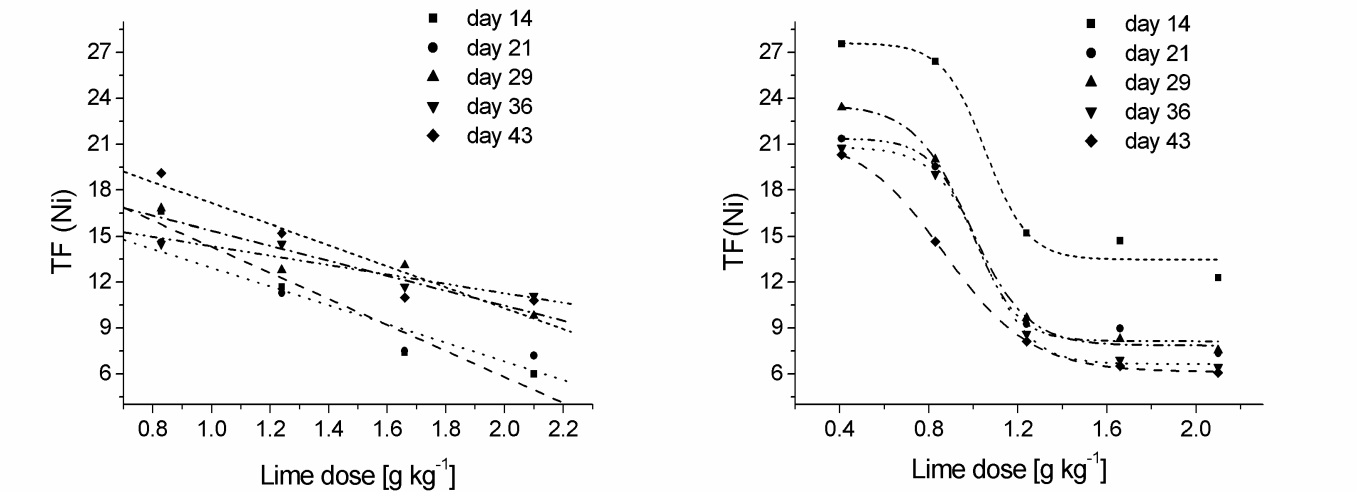


Figure 3.22: The influence of lime doses on changes of the Ni *Transfer Factors* into *Brassica napus* (left) and *Avena sativa* (right) plants grown on a sod-podzolic soil.

The lime application reduced the Ni transfer into the plants significantly. The highest decrease in the *Transfer Factors* was observed in the treatments with lime doses of 1.25-1.66 g $kg^{-1}$. The minimum *TF's* were observed on the first phases of the plant development. A tendency of increasing *TF* simultaneously with increasing plant age (maturation) was observed (comparing *TF* obtained at the sampling days of the same treatment).

The changes of *TF(Ni)* for *Avena sativa* were described employing the sigmoidal Boltzman function:

$$TF(D) = \frac{TF_{\max} - TF_{\min}}{1 + e^{(D - D_0)/\Delta D}} + TF_{\min} \qquad \text{(Equ. 3.16)}$$

Where:

$TF_{max}$ – Ni *Transfer Factors* for *Avena sativa* grown on soil with a low lime dose

$TF_{min}$ – Ni *Transfer Factors* for *Avena sativa* grown on soil with a high lime dose

$D_0$ – lime dose, where $TF = \frac{TF_{\max} + TF_{\min}}{2}$ [g $kg^{-1}$]

$\Delta D$ – constant, characteristic lime dose; describes the changes in *TF(Ni)* from the maximum towards the minimum [g $kg^{-1}$] (valid for the conditions of the experiment)

$D$ – lime dose [g $kg^{-1}$]

In contrast to increasing *TF(Ni)* for *Brassica napus* plants, the decreasing *TF(Ni)* for *Avena sativa* plants during the vegetation period was observed (Tab. 3.24).

Table 3.24: Parameters of the sigmoidal Boltzman function for the description of changes in *TF(Ni)* for *Avena sativa* plants depending on lime applications.

| **Sampling time** [d] | $TF_{max}$ | $TF_{min}$ | $D_0$ [g kg$^{-1}$] | $\Delta D$ [g kg$^{-1}$] | $R^2$ |
|---|---|---|---|---|---|
| 14 | 27.6±1.7 | 13.5±1.2 | 5.3±0.6 | 0.5±0.3 | 0.99 |
| 21 | 21.4±1.2 | 8.1±0.8 | 5.0±0.4 | 0.5±0.2 | 0.99 |
| 29 | 23.6±0.5 | 7.9±0.4 | 4.9±0.1 | 0.6±0.1 | 0.99 |
| 36 | 20.8±0.3 | 6.6±0.2 | 5.2±0.1 | 0.5±0.1 | 0.99 |
| 43 | 21.8±0.3 | 6.1±0.1 | 4.3±0.1 | 1.0±0.1 | 0.99 |

Remarks: $TF_{max}$ - the maximum *Transfer Factor* for plants grown on soil with a low lime dose; $TF_{min}$ - the minimum *Transfer Factor* for plants grown on soil with a high lime dose; ± - error of estimating function, $R^2$ – coefficient of determination between *TF(Ni)* and lime dose (explained by the sigmoidal Boltzman function), figures apply to Equ. 3.16.

In the experiment with *Avena sativa* plants a significant lime effect on reducing of *TF(Ni)* was implicated. The parameters $D_0$ and $\Delta D$ almost did not change in all periods of the observation. Negligible decreasing of $D_0$ and increasing of $\Delta D$ on the day 43 were observed. That means that independently of the *Avena sativa* ontogenesis phase there is a distinct optimum of lime dose equivalent to 1 g kg$^{-1}$ for the change of *TF(Ni)* for plants from the maximum towards minimum (Fig. 3.22, right).

### *3.4.8 Relationship between Ca concentration in soil and the inverse value of Nickel Transfer Factor (TF(Ni)$^{-1}$)*

As shown in chapter 3.2 the lime doses and Ca concentrations in soils are significant correlated. That means that it is possible to use lime doses instead of Ca concentrations in soil ($C_{Casoil}$) to quantify the relationship between Calcium in soil and the inverse value of the Nickel *Transfer Factor (TF(Ni)$^{-1}$)*. In both experimental years a linear relationship between lime dose and *TF(Ni)$^{-1}$* according to Equ. 1.10. was observed (Fig. 3.23).

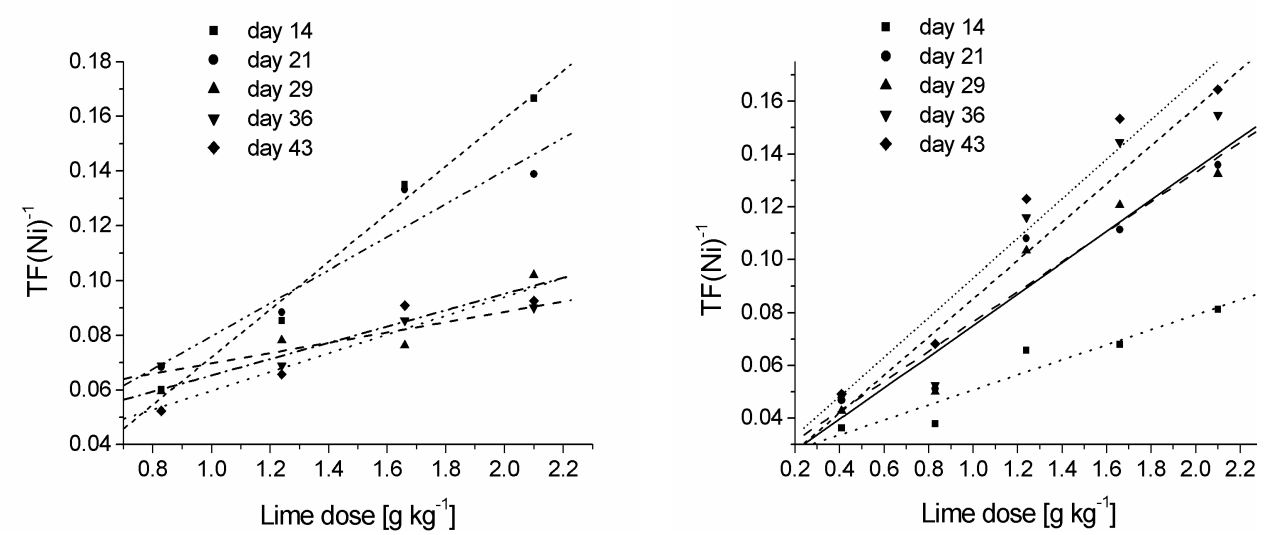


Figure 3.23: Parameter $TF(Ni)^{-1}$- lime dose relationship for *Brassica napus* (left) and *Avena sativa* (right), corresponding Equ. 1.10 (see Material and Methods), model parameters see Tab. 3.25.

Parameters of the linear function for the description of relationship between $TF(Ni)^{-1}$ and lime dose for *Brassica napus* and *Avena sativa* plants are shown in the Tab. 3.25.

Table 3.25: Parameters of the linear function for the description of parameter $TF(Ni)^{-1}$ – lime dose relationship for *Brassica napus* and *Avena sativa* .

| **Sampling time** [d] | ***Brassica napus*** | | | ***Avena sativa*** | | |
|---|---|---|---|---|---|---|
| | $1/a_1$ | $\frac{b_2}{a_1}$ | $R^2$ | $1/a_1$ | $\frac{b_2}{a_1}$ | $R^2$ |
| 14 | 0.02±0.01 | 0.020±0.002 | 0.98 | 0.02±0.01 | 0.006±0.001 | 0.90 |
| 21 | 0.02±0.02 | 0.010±0.002 | 0.92 | 0.02±0.01 | 0.011±0.002 | 0.90 |
| 29 | 0.03±0.01 | 0.006±0.002 | 0.86 | 0.02±0.01 | 0.012±0.002 | 0.92 |
| 36 | 0.05±0.01 | 0.004±0.001 | 0.88 | 0.01±0.02 | 0.015±0.002 | 0.92 |
| 43 | 0.02±0.01 | 0.007±0.001 | 0.92 | 0.02±0.01 | 0.015±0.002 | 0.97 |

Remarks: The explanation of the coefficients see chapter Material and Methods, Equ. 1.10; ± - error of estimating function; $R^2$ – coefficient of determination between inverse value of *Ni Transfer Factor* and lime dose (explained by a linear function), figures apply to Equ. 1.10.

The inverse value of the Nickel *Transfer Factor* ($TF(Ni)^{-1}$ and lime dose (Ca concentration) are in strong correlation (high coefficient of determination at all sampling days (Tab. 3.25)).

Taking into consideration the determination error the parameter $a_1$ was almost constant over the time of observation, the average value calculated from the column $1/a_1$ (Tab. 3.25) was 37 and 51 for *Brassica napus* and *Avena sativa* respectively. In other words these are the maximum *TF(Ni)* of *Brassica napus* and *Avena sativa* which could be observed in case of total absence of

mobile Ca in soil. The coefficient $b_2$, which characterizes the behaviour of macroelement (i.e. Ca in the investigated system) only, decreased during the vegetation period in the experiment with *Brassica napus* and increased over the time in the experiment with *Avena sativa*. The increasing of the coefficient $b_2$ in the experiment with *Avena sativa* can be explained by decreasing of Ca ion flow from plant roots to soil solution if:

a) The distribution coefficient ($k_d$) of Ca ions between soil and soil solution does not change at all or changes slightly
b) The specific rate of Ca sorption by plant roots from soil solution changes insignificantly.

In the experiment with *Brassica napus* the interpretation of the decreasing of the coefficient $b_2$ is uncertain. It can be due to a surplus of Ca in soil (Ca content of lime, which had not reacted with soil).

Due to a linear dependence of the parameter $TF^{-1}$ on the Ca concentration in soil it is possible to assume that Ca and Ni interact competitively by the mechanism of ion exchange.

# 4 Discussion

The main objective of this research work was to investigate the mechanism of Calcium and Nickel interaction in the soil-plant system by accessing the applicability of the sorption model. To achieve this goal two pot experiments were conducted. The first experiment was carried out to study different plant species regarding their ability to accumulate Ni and to find a crop for the further experimentation. The second experiment was conducted to generate the basic data for modelling of Ca and Ni interaction in the soil-plant system. Therefore the soil was contaminated with Ni and treated with increasing amounts of lime. Investigated crops were *Brassica napus* and *Avena sativa*, which were grown for up to 43 days. Samples of soil and plant material were taken 5 times during the vegetation period and analysed.

## *4.1 Assessment of sorption model applicability*

The uptake of chemical elements by plants depends mainly on physical and chemical properties of the elements, agrochemical properties of the soil and physiological properties of the plants. There is much evidence that the plant uptake of radionuclides and microelements is inversely proportional to the concentration of plant available macroelements - analogous (ions which demonstrate general physiological equivalence with microelements) in soil (Arkhipov et al. 1969; Polyakov 1970; Arkhipov et al. 1975).

Proposed by Arkhipov et al. (1969) a complex parameter for the prediction of $^{90}Sr$ uptake accounts the concentration of exchangeable Ca in soil. Moreover it was also determined that $^{90}Sr$ and $^{137}Cs$ uptake are in direct relationship with plants requirements in $Ca^{2+}$ and $K^{+}$ (Rassel 1971). The higher the concentration of the “analogoues” in the plants the higher the concentration of $^{90}Sr$ and $^{137}Cs$.

So it is considered that the common rules for radionuclide and microelement transfer from soil into plants are:

1) The inversely proportional dependence of radionuclide/microelement uptake by plants on the concentration of macroelement-analogue in soil.
2) The direct proportional dependence of radionuclide/microelement uptake on the plants requirements in this macroelement-analogue.

In order to explain the results obtained in the experiments the consequences of the mass flow law and adsorption isotherms are used (Tikhomirov 1980; Barber 1995). But at the same time the interpretation of the results can not be absolutely strict due to at least two facts: The soil-plant

system is extremely complicated and there are no experimental values of necessary parameters which characterize this complex system.

Proceeding from the assumption of the exchange way in ion sorption by soil solid phase and plant roots, in the frame of two-chamber model of the soil-plant system the exchange of macroelement and radionuclide/microelement can be expressed as follows:

$$TF = A \cdot C_{soil2}^{-z_1/z_2} \qquad \text{(Equ. 4.1)}$$

Where:

| | | |
|---|---|---|
| $TF$ | – | *Transfer Factor* of microelement |
| $z_1$ and $z_2$ | – | valency of exchanging ions |
| $A$ | – | constant dependent on the ratio of constants for ion exchange between soil solid phase and plant roots |
| $C_{soil2}$ | – | concentration of macroelement in soil |

The Equation 4.1 is the Freundlich isotherm. In the case of homovalent exchange (exchange of ions with equal charge) the exponent of this equation is equal to 1. Results of an experiment with several pairs of elements (Cs-K, Ba-Ca, Sb-P) in soil and barley plants responded well to the Equation 4.1 (Drichko & Tsvetkova 1990). But the deviations in the *Transfer Factors* for alkaline earth cations were very high. It was shown that under low concentrations of macroelements in soil the Freundlich isotherm describes the interactions between elements in the soil-plant system with insufficient accuracy.

The Equation used in the presented study (according to the sorption model, Equ. 1.8) is analogue to the Langmuir adsorption isotherm:

$$q = \frac{aBC_1}{1 + aC_1} \qquad \text{(Equ. 4.2)}$$

Where:

| | | |
|---|---|---|
| $q$ | – | the moles of a substance, absorbed per unit mass of solid |
| $C_1$ | – | the concentration of substance in solution |
| $a$ | – | an affinity parameter related to bonding energy |
| $B$ | – | the adsorption maximum (Holford & Mattingley 1976) |

The analysis of the experimental results showed the strict dependency to the Langmuir equation (Equ. 1.8-1.10, Tab. 3.25, and Fig. 3.23). This situation itself does not prove a mechanism of Ni or Ca uptake, i.e. it does not allow to decide between adsorption mechanism and mechanism of ion exchange. In other words the Equation in the presented form is not mechanism-sensitive. However it describes not only the absorption of one element by plants, but also the interaction between two elements (Ca and Ni in the given system). The same effect of competition between Ca and Ni could be expected if instead of lime another source of calcium (e.g. $CaSO_4$) would be applied. $CaSO_4$ is a neutral salt and has no substantial neutralizing or acidifying ability, but it is more soluble than limestone, supplies higher levels of soluble Ca and increases exchangeable Ca.

Theoretically sorption (adsorption of neutral particles by surface of soil solid phase due to disperse forces or adsorption of charged particles due to charge of surface) as well as ion exchange (exchange of one cation on another without changes in surface charge) are based on the idea of the existence of so called active centres. This idea is widely used in recently developed models for describing interactions between pairs of elements (Konoplev 1998; Konoplev & Bulgakov 1999). In the theory of ion exchange the active centres have a certain structure (for example -COOH groups) whereas disperse forces characterize the general heterogeneity of the surface energy. If it would be possible to carry out special experiments for the determination of coefficients of the sorption model Equation and if they would coincident with the parameters determined by independent methods it would have been possible to indicate the mechanism of ion exchange.

Meanwhile this form of the Equation is not in contrary with the experimental data and may be interpreted as operation of an ion exchange mechanism.

### *4.2 Assessment of lime influence on mobile Ca and Ni concentration in soil*

In the experiments an increase of the mobile Ca concentration in soil was observed with increasing lime supply (Fig. 3.1, Tab. 3.2). This is in line with results of numerous researchers (Mengel & Kirkby 1982; Alekseev 1985; Nebolsin & Sychev 2000). Drichko et al. (2002) reported from an experiment with an acid sod-podzolic soil and increasing chalk supply (0.3 - 3.2 g $kg^{-1}$) the general increase of mobile Ca concentration in soil with increasing chalk doses. The character of the dependence was linear and coefficients of correlation were high (0.93-0.99).

The present investigations proved that the concentration of mobile Ni in soil decreased with increasing lime supply, in both years of experiment (Fig. 3.2 and 3.3, Tab 3.4). There are many

findings confirming this fact. Chaudhuri et al. (2003) reported about a sequential extraction procedure that has been used to study the changes in the distribution and mobility of Cd, Cr, Cu, Ni, Pb and Zn in an acid lateritic soil amended with 2 Mg $ha^{-1}$ lime. It was shown that the metal mobility in their labile forms was restricted, positive responses of peanut yield were observed.

The lime addition reduced the transfer and accumulation of metals from the soil to the plant. In an experiment with Ni contaminated soil (5.7 mg $g^{-1}$) the amount of Ni extracted by ammonium acetate was reduced by 36% in the limed soil (10 t $ha^{-1}$ lime) in comparison to the untreated soil (Bissesar 1989).

The experimental results confirm that liming of acid sod-podzolic soil leads to a decrease of the mobility of heavy metals. Linear and exponential functions applied in the presented study for the description of this phenomenon showed very high accuracy and might be recommended as estimation functions.

### *4.3 Assessment of changes of soil pH as influenced by lime application and plant growth*

It is well known that soil pH is in direct relationship with lime fertilization. The higher the lime dose the higher the soil pH (Zyrin & Orlov 1980; Nebolsin & Nebolsina 1998; Nebolsin & Sychev 2000). Increasing the lime supply significantly influenced soil pH in the presented experiments (Fig. 3.4 and 3.5, Tab. 3.5) as it was expected. The parameter $b_D$ (Tab. 3.6), which shows the soil pH change per unit of lime is quantified for accessing the effectiveness of lime supply on soil pH changes. In the first experimental year 1 unit of lime (1 g $kg^{-1}$) changed the soil pH by 0.72 units during the observation period. In the second year the parameter $b_D$ (Fig. 3.7) decreased during the vegetation period and showed that the effectiveness of lime application reliably decreased over time. The difference in the behaviour of the parameter $b_D$ is most likely related to the incomplete reaction between lime and soil (especially in the treatments with high lime dose) in the year 2000. Furthermore, the plant specific differences (root length density, $H^+$ release, specific growth rates, etc.) influenced the process as well.

The influence of increasing lime supply on the pH of sod-podzolic acid soil was studied in the experiment reported by Nebolsin & Sychev (2000). The treatments included increasing organic matter content in soil. The mathematical description of the reported results showed that soil pH changed according to Equ. 3.4. The parameter $b_D$ (pH change per unit lime) was about 2 up to 1.5 times less than obtained in the first year of the experiment presented in this thesis. However with increasing soil organic matter contents values of parameter $b_D$ coincided with those obtained in the described experiment during the second year of the investigation.

It is obvious that $b_D$ depends on soil and plant properties and represents the specific value for the characterisation of pH changes under liming of sod-podzolic acid soils.

In both evaluated experiments a decrease of soil pH during the vegetation period was observed (Fig 3.7). There are insufficient available data in scientific literature concerning changes of soil pH within vegetation periods. Seasonable pH variations are mostly attributed to changes in soil moisture, soil temperature, and crop development (Obenauf 1987). However there are evidences of soil acidification during long term observations caused by different factors such as acid deposition, application of nitrogen fertilisers in ammonium form, nutrient uptake by plants (Goulding & Blake 1997; Goulding & Blake 1998; Vietiene 2002; Porter 2004).

The present work shows that there is a direct relationship between lime dose and rate of pH changes (Tab. 3.7, parameter $b_t$). In the first year of experimentation $b_t$ increased in the treatments with lime doses of 0-1.25 g $kg^{-1}$ and afterwards decreased. On the other hand the $b_t$ values in 2001 (Cultivated crop: *Avena sativa*) were correlated with increasing lime amounts. So the seasonable pH decrease increased with high lime doses. A possible reason can be the high Ca uptake by *Avena sativa* in case of high lime doses. This result is in line with one reported by Tsadilas et al. (2005). In a four years plot experiment soil pH declined during the growing seasons and decreased by an average of 0.2 units per year up to 0.7 units in the last season. Despite the pH reduction during the growing season, pH increased in the fall and winter periods. The authors attributed decreasing pH to lime uptake by plants (tobacco) and the nitrification of ammonium fertilizer. Tsadilas et al. (2005) assumed that the increasing pH values in fall and winter were caused by the reduction of microbial activity during these times.

A very important influence on the pH values around roots is growth itself (Raven 1986; Raven & Wollenweber 1992). A century ago Deherain (1902) reported in his "Treatise of Agricultural Chemistry" on an experiment by Sachs, which demonstrated that by growing roots of beans over the surface of a polished marble plate, that roots secreted an acid strong enough to dissolve calcium carbonate, thereby leaving clearly visible imprints in the rock. In the first half of the 20th century, such acidic root secretions were attributed to carbonic and organic acids produced by rhizosphere microflora and roots through respiration and exudation. Since the late 1960s evidence has accumulated that roots can substantially change their rhizosphere pH by releasing $H^+$ or $OH^-$ to compensate for an unbalanced cation-anion uptake at the soil-root interface (Riley & Barber 1969; Riley & Barber 1971). At present time such pH changes are attributed to following origins:

- cation-anion exchange balance
- organic anions release

- root exudation
- respiration and redox-coupled processes (Hinsinger et al. 2003).

The effect of bulk soil on root-induced changes in the rhizosphere pH has rarely been reported in the literature. However it can be rather dramatic, as shown by Youssef & Chino (1989). Chaignon et al. (2002) reported about acidification of calcareous soil up to 2 pH units by the rhizosphere of oilseed rape and tomato. In other experiments with different lime dose application the plants of oilseed rape consistently produced significant acidification at a pH above 4.8 (Guivarch et al. 1999).

The quantity of root exudates significantly dependent on plant species and varieties as well as soil conditions (Uren 2000). The most intensive production of root exudates is observed on early phases of plants development and gradually decreases with plant maturation (Brady & Weil 1999; Brimecombe et al 2001).

Taking into account the fact that the experiment presented here was conducted in rather small pots the main cause of decreasing pH during the vegetation period may be acid exudates of the cultivated crops (Fig. 3.8 and 3.9).

### *4.4 Assessment of increasing lime supply on the plant dry matter dynamic and specific growth rate*

Generally the development of biomass can be described by a S-shaped curve which is called *Saks Curve* or *Big Growth Curve*. Using this curve it is possible to describe any time related process (for example chemical reaction) in general (Batygin 1986).

Based on the law of the "Big Period of Growth" by Saks, Goryachkin (1924) supposed that every phenomenon can be considered as the change of quantity and every change can be considered as a motion. Hence in analogues with motion the quantity part of a phenomenon should be characterised by three indices at every time scale: Uptake, rate of uptake and acceleration of change of the analysed value.

The process of growth can be non-uniform; slower at the beginning or in the finishing period. The form of the describing curves changes respectively (Shmidt & Dibirov 1979). In the presented study the dynamic of plant dry matter development was described by a classical S-shaped curve which is well approximated by the logistic equation (Equ. 1.11, Fig. 3.10).

It was clearly shown that there are dependences between calculated parameters of the Equ. 1.11 (Tab. 3.11) and lime doses. The maximum yield ($M_{max}$) increased with increasing lime

supply. This result is in line with numerous other investigations. Arshad et al. (1999) reported about increasing barley grain yield (17%) and stover yield (13%) on limed soil (7.5 Mg $ha^{-1}$ lime) in comparison to untreated soil and attributed it to a soil pH (6.2 after liming compared to 5.0 without liming). In an experiment with *Bromus inermis* liming significantly increased the yield of hay in the third year after lime application (Malhi 1998). The same effect of lime on different plant species was demonstrated by Bezdicek et al. (2003), Lukin & Epplin (2003) and Hartley et al. (2004).

Taking into consideration a determination error of the parameter $M_0$ (mass of the seeds sown in each pot, Tab. 3.11) it coincides virtually with the mass of rape seeds sown in each pot in the experiment with *Brassica napus*. But in the experiment with *Avena sativa* this parameter was much less than the mass of the oat seeds sown in each pot. Other experiments with timothy and potato plants (data are not published) showed that the lower the seed mass the closer the calculated $M_0$ to the mass of seeds taken for the experiment. The more the seed mass, the worse the coincidence of calculated and experimentally estimated $M_0$ values. It appears that the calculated $M_0$ is correlated with some active parts of a seed, which is directly responsible for the plant growth.

As it was expected theoretically the specific growth rate ($\mu_t$) of the investigated crops increased and parameter $T$ (period of time in which the dry matter is doubled) consequently decreased with increasing lime doses (Tab 3.11). The specific growth rate of *Brassica napus* and *Avena sativa* ($\mu_t$) increased by 51 and 76 % respectively with three times increasing of lime dose (Tab. 3.11). A comparable effect on the specific growth rate was shown in a K fertilisation experiment with timothy conducted by Drichko et al. (1994). In the first year of that experiment doubling K doses did not influence the parameter $\mu$, but in the second year an increase of 40% was observed. The parameters $T$ for rape and oat (2-5 and 2-3 days respectively) are less than for timothy (5-8 days). It should be stressed out that values of $\mu_{max}$ (the maximum specific rate of dry matter growth) calculated by hyperbolic function (Equ. 3.9, Tab. 3.13) are hypothetical. The high values of parameter $T$ (periods of time in which plant dry matter is doubled), 1.07 days and 1.9 days for *Brassica napus* and *Avena sativa* respectively, can not be expected in real conditions of pot or field experiment. But these values show the absolute maximum of plant development rates.

The specific growth rate is in relation with the rate of plant cell fission and, consequently reflects the growth conditions as well as the genetic potential of the plants. The applied functions allowed to estimate this important parameter and to show the response of the investigated crops on lime addition during the vegetation period. But this question is not enough understood,

therefore there are no data available in the scientific literature and it is impossible to compare the obtained values. Further investigations in this field are needed.

### *4.5 Assessment the consequences of liming on the concentration of Ni in Brassica napus and Avena sativa plants*

Plants grown on limed soils usually contained less heavy metals than those grown on soils without lime additions (Alekseev 1987; Bolan et al. 2003; Chaudhur 2003; Lee et al. 2004). In the presented experiment lime supply influenced the Ni concentration in plants the same way as the most heavy metals, it decreased with increasing lime doses.

The lime dose under which the change in the plant Ni concentration per unit of lime reaches the maximum ($D_0$) was different for *Brassica napus* and *Avena sativa*, but almost equal over time of observation in both experiments (Fig. 3.14, Tab. 3.15). It can be assumed that the parameter $D_0$ is a characteristic value for proving Ca-Ni interactions. Under the conditions of the presented experiment lime doses of 1.24 and 1.00 g $kg^{-1}$ are distinct optimum amounts for reducing the Ni concentration in *Brassica napus* and *Avena sativa* plants, respectively. The application of lower or higher doses seems to be non-effective. If the experimental conditions are changed (another type of soil, plant, etc), it is very likely that the parameter $D_0$ will be different as well. The decrease in the Ni concentration in plants due to interaction with Ca is possible not more than 4 times also taking into account the variability in acidity in agricultural soils. This conclusion is in line with findings of Drichko et al. (1990) and Wang (2002) who investigated other pairs of elements, such as K-Cs, Sr-Ca, Sb-P, S-Se an P-As.

### *4.6 Assessment of the consequences of lime influence on Ca and Ni uptake*

The Ni and Ca uptake by *Brassica napus* and *Avena sativa* plants during the vegetation period followed a S-shaped curve. To quantify the rate characteristics of the element uptake the curve was approximated by a logistic equation. It was shown that the maximum uptake of Ca by both plant species increased with increasing lime doses (Tab. 3.17). This is in agreement with results of Chang & Sung (2004) who showed enhanced uptake of Ca and other macroelements by rice crops caused by increasing lime supply.

The maximum Ni uptake by *Brassica napus* decreased in the juvenile phases and slightly increased starting from the day 29 of the vegetation period depending on lime dose (Fig. 3.20). This might be due to the fact that at day 29 the decrease in the Ni concentration in *Brassica napus* dry matter was fully compensated by the increase in dry matter production which was

caused by liming. The maximum Ni uptake by *Avena sativa* plants decreased with increasing of lime dose (Tab. 3.18, Fig. 3.20). A lot of scientists reported the same effect of lime on the uptake of Ni and other heavy metals. The following relations were observed: Zhao et al. (2002) showed a decrease in the Cd uptake of intact seedlings of Prayon (ecotype of *Thlaspi caerulescens*) with increasing Ca concentration in the nutrient solution. The Cd uptake of the low Cd-accumulating ecotype took place partly via Ca channels. Szomolanyi & Lehoczky (2002) studied the Cd uptake in experiments with slightly acidic Eutric Fluvisol and strongly acidic Mollic Fluvisol and increasing lime supply. On the slightly acid soil the addition of lime in doses of 4.5 g $kg^{-1}$ decreased the Cd uptake of lettuce plants by 32% compared to the control. On the strongly acidic soil under lime treatments a 70% decrease in the Cd uptake by plants was observed. Szomolanyi & Lehoczky (2002) explained this fact by changes of soil pH and hydrolytic acidity because these properties are determinants regarding the solubility of Cd in soil and its availability to plants (Han & Lee 1996). In experiments with different soil types (ranging from poor sandy to fertile black chernozem) and increased doses of calcium carbonate, a significant decrease in the Ni uptake of ryegrass with increasing $CaCO_3$ doses was observed. Mostly this effect was pronounced on poor sandy soils whereas on chernozem the decrease in the Ni uptake of plants was less (Vago et al. 1996). Robinson et al. (1999) used pot trials to investigate the influence of $MgCO_3$ and $CaCO_3$ on Ni and cobalt uptake of the South African Ni hyperaccumulator *Berkheya coddii*. The fertilizer components $MgCO_3$ and $CaCO_3$ caused significant decreases in the Ni and Co uptake, as well as a decreasing solubility in soil. After the addition of $MgCO_3$ there was a significant increase in soil pH. The reduction in metal uptake by plants could not be solely attributed to the action of magnesium. Since $CaCO_3$ had no significant effect on soil pH, the authors supposed that calcium directly inhibits the uptake of cobalt and nickel.

It should be marked here that in the presented experiment liming significantly influenced the specific rate of Ca and Ni uptake by plants. It increased with increasing lime doses (Tab. 3.17 and 3.18). The comparison of specific growth rate and specific rate of Ca and Ni uptake showed that in most cases the experimental results followed the theoretical expectations (Tab. 3.19). Only in case of *Avena sativa* the Ca concentration in plants decreased during the time of observation and disagreed with theoretical expectations. This fact is difficult to explain. There might be some other mechanisms, which lead to a fast dilution of the Ca concentration in *Avena sativa* plants. Further investigations are needed to clarify this point.

## *4.7 Assessment of lime influence on the Ni Transfer Factors(TF(Ni)) for Brassica napus and Avena sativa*

The values of *Transfer Factors* are inherently variable, typically spanning three to five orders of magnitude (Sheppard & Evenden 1988).

A compilation of the *Ni Transfer Factors* from literature and obtained in described experiments is presented in Tab. 4.1.

As shown in Tab. 4.1 the sources of the variability include all the physical chemical and biological complexities of the soil-plant system as well as features of the *TF* model itself. Sheppard & Evenden (1988) completed an extensive review of properties that influence *TF* model. A strict translation of the model implies a linear relationship between plant and soil concentrations. In the field as well as in the pot this rarely exists, perhaps because soil concentration is only one of the many factors that influence plant uptake or because of saturation type mechanisms in either the soil chemistry or the plant uptake processes. Whatever deviation from the simple ratio model is another source of variability. The lack of correlation between plant and soil concentrations leads to a generalisation about the frequency distributions for *TF* values. This generalisation is based on the central limit theorem (Durand 1971), which states that the sums of independent variables tend to be normally distributed. The antilog of such a summation equation becomes a multiplicative equation. It follows that ratios of independent variables tend to be log-normally distributed. Furthermore *TF* values can approach but cannot be less than zero and this also tends to skew the distributions. Reflecting these arguments *TF* values tend to be log-normally distributed and the most appropriate measures of central tendency and dispersion for *TF* therefore are the geometric mean and geometric standard deviation (Gilbert & Simpson 1985).

Table 4.1: Compilation of the *Ni Transfer Factors* from literature and obtained in described experiments.

| **Mean *TF(Ni)*** | **Ni fraction in soil** | **Crop** | **Comments** | **Reference** |
|---|---|---|---|---|
| 6-19 | mobile | rape | dependent on lime dose and plant age | Presented theses |
| 6-25 | mobile | oat | dependent on lime dose and plant age | Presented theses |
| 6-11 | mobile | grass | tip soil | Schoenbuchner 2005 |
| 7-18 | mobile | clever | tip soil | Schoenbuchner 2005 |
| 8-12 | mobile | spinach | tip soil | Schoenbuchner 2005 |
| 16 | mobile | yarrow | average of soils and regions | Knoche et al. 1999 |
| <0.06 | total | rape (leaves) | with lime | Hein et al. 1995 |
| <0.1 | total | rape (leaves) | without lime | Hein et al. 1995 |
| <0.1 | total | oat (grain) | with lime | Hein et al. 1995 |
| <0.2 | total | oat (grain) | without lime | Hein et al. 1995 |
| <0.02 | total | oat (straw) | with lime | Hein et al. 1995 |
| <0.06 | total | oat (straw) | without lime | Hein et al. 1995 |
| 0.40 | total | beans | Luvisol, Ni 29.7 mg $kg^{-1}$ | Guo et al. 1995 |
| 0.65 | total | ryegrass | Luvisol, Ni 29.7 mg $kg^{-1}$ | Guo et al. 1995 |
| 0.50 | total | curly kale | Luvisol, Ni 29.7 mg $kg^{-1}$ | Guo et al. 1995 |
| 2.98 | total | ryegrass | Podzolic sandy soil, Ni 50 mg $kg^{-1}$ | Vago et al. 1997 |
| 0.53 | total | ryegrass | non-contaminated podzolic sandy soil | Vago et al. 1997 |
| 0.66 | total | ryegrass | chernozem, Ni 50 mg $kg^{-1}$ | Vago et al. 1997 |

Another source of variability relates to experimental methodologies. Hydroponic studies, pot culture and controlled environment studies do not provide data relevant for field conditions. To provide valid data, pot culture studies must use large outdoor containers with natural soil, temperature and moisture conditions (Sheppard & Evenden 1988).

Moreover values of *TF* are not always expressed in the same way. Most commonly the ratio of concentrations is expressed on a dry plant and dry soil basis. Food-chain models often use *TF* values expressed on a fresh plant weight basis (Zach 1982) and in bio-, geo-prospecting they are usually expressed on an ash weight basis (Kovalevsky 1987). The variability of *TF* values on a dry weight basis is significantly less than that on a fresh weight basis because it excludes the variability in plant water content (Sheppard & Evenden 1988).

In spite of many disadvantages of *Transfer Factors* for estimating the soil-plant system it remains a model which has been universally recommended by regulatory agencies and most assessments rely on it.

In the presented study *TF(Ni)* for *Brassica napus* and *Avena sativa* plants were expressed on the base of dry plant and dry soil. Instead of the total the mobile concentration of Ni in soil was used for calculations. The absolute values of *TF* had a very high variability during the vegetation period and dependent on lime doses, fluctuations between 6 and 25 were observed (Tab. 3.22). High values of *TF* are most likely due to low organic matter content in tested soil and high Ni mobility. The fluctuations of *TF* reflect differences between plant species, changes caused by addition of lime as well as stages of plants development.

The changes of *TF(Ni)* for *Brassica napus* and *Avena sativa* plants during the vegetation period were described employing the hyperbolic function (Equ. 3.15). The tendency of decreasing of *TF(Ni)* for *Brassica napus* plants was observed (Tab. 3.23). The low coefficients of determination received in the first year of experimentation are most likely due to uncompleted reactions between lime and soil. It is well known that the rate of reaction (rate at which lime will change soil pH) is mainly a function of surface area of the lime particles and their contact with the soil. The finer the grind of lime and the more the surface area, the faster the reaction (Alekseev 1986). Moreover the lime interacts with soil gradually and the system comes to its equilibrium only in the second-third year after lime application (Yagodin 1989). This was confirmed by the results received in the second year of the presented experiment. The hyperbolic equation described the changes of *TF(Ni)* for *Avena sativa* with high accuracy (Tab. 3.23). It was clearly shown that $TF_{max}$ decreased with increasing lime doses. This result is in line with many reports in scientific literature (Kabata-Pendias 2001).

The differences in the behaviour of *Transfer Factors (Ni)* over time of the observation were shown. In case of *Brassica napus* the *Transfer Factors (Ni)* increased during the vegetation period (Fig. 3.21, left). In case of *Avena sativa* plants the *Transfer factors (Ni)* decreased over time of observation (Fig. 3.21, right). This might be attributed to genetic peculiarities of plants.

This is confirmed by investigations of Andreeva (2003). In an experiment with *Avena sativa* and *Vicia faba* grown on Ni contaminated (25 mg $kg^{-1}$ Ni) sod-podzolic soil, the *Transfer Factor (Ni) for* oat plants was 1.4 in the phase of tillering and decreased up to 0.5 in the phase of milk-wax ripeness, whereas *Transfer Factors (Ni)* for *Vicia faba* plants increased during the vegetation period and amounted maximum value in the phase of complete ripeness.

Summarising the results of presented work it may be concluded that the future research needs to find criteria for identifying Ni transfer from soil into plants that could be comparable in different studies. The mechanisms involved in heavy metals solubility and mobility in soil, their transfer and uptake into plants should be studied considering rate characteristics.

However the modelling of interactions between Ca and Ni in the soil - plant system and the derivation of Ni transfer are of high importance for elaborating environmental concepts.

# 5 Summary

The main objective of the present research work was to investigate the interactions between Calcium and Nickel in the soil-plant system considering the influence of lime on the Ni transfer from soil into plants. Apart from increasing the knowledge of Ni and Ca behaviour in the soil-plant system and possible mechanism of these elements interaction, the important rate characteristics of processes involved in soil acidification and neutralization, plants growth and elements uptake were obtained.

Investigations were carried out in the Agricultural Physical Research Institute situated in Saint-Petersburg, Russia. In a two years pot experiment oilseed rape (*Brassica napus*) and oat (*Avena sativa*) were grown for up to 43 days without and with Ni contamination (20 mg $kg^{-1}$ Ni) and increasing lime supply (0 - 2.1 g $kg^{-1}$) on an acid sandy-loam soil (pH(KCl) 4.1). During the vegetation period soil and plant samples were taken (5 times) and analysed. The sorption model elaborated by Drichko (1990) was employed for describing the experimental data.

The main results of the presented research work were:

- The sorption model describes interactions between Calcium and Nickel with high accuracy. The experimental data follows to the Langmuir equation. The linear correlation between inverse values of *Transfer Factors (Ni)* for *Brassica napus* and *Avena sativa* plants and Ca concentration in soil was observed. This fact can be attributed to competitive interactions between Calcium and Nickel based on ion-exchange mechanism.

- Lime addition significantly affected the concentration of mobile Ca and Ni in soil. The concentration of mobile Ca increased and concentration of mobile Ni decreased with increasing lime supply.

- Lime addition considerably influenced changes of soil pH. With increasing lime dose the soil pH increased. This change is described by linear function with very high accuracy. The pH changes were less per unit of lime over time of observation. The soil pH change per lime unit (parameter $b_D$) depends on soil and plant properties and represents the specific criterion for the characterisation of pH changes under liming sod-podzolic acid soils. During the vegetation period soil pH decreased. This fact is attributed to acid

exudates of investigated plants (*Brassica napus* and *Avena sativa*). The acidification effect of plants was well described by exponential function in the experiment with *Brassica napus* and by linear function in the experiment with *Avena sativa* plants. It was shown that the higher the lime dose the less plant biomass is needed for double increasing of the intensity of $H^+$ release.

- Dry matter development of both investigated crops corresponded to the classical S-shaped curve which was well approximated by a logistic function. Lime addition considerably influenced the dry matter production of *Brassica napus* and *Avena sativa* plants. Besides increasing yield, the specific rate of plant growth was enhanced with each lime level. The lime dose under which the specific rate of plant growth is equivalent to the half of the maximum specific growth rate (parameter $D_{1/2}$) is proposed as a quantitative criterion for estimating plant response on lime supply. It was shown that *Avena sativa* plants are much more responsive on lime addition.

- Ni and Ca uptake by plants during the vegetation period followed a S-shaped curve which is well described by a logistic equation. The Ca uptake by plants increased with increasing lime doses. The Ni uptake decreased with increasing lime supply. In the experiment with *Brassica napus* lime doses influenced the specific rate of Ca uptake to a lower extent than the specific rate of plant growth. This caused the decrease of Ca concentration in *Brassica napus* plants over time. The specific rate of Ni uptake by *Brassica napus* was enhanced by lime dose greater than the specific rate of plant growth. This led to increasing Ni concentrations in the plant over time. In the experiment with *Avena sativa* the specific rate of Ni uptake was lower than the specific rate of plant growth whereas the specific rate of Ca uptake was higher. In spite of theoretical expectations the Ca concentration in *Avena sativa* plants decreased. Other mechanisms accounts for the fast decrease of the plant Ca concentration.

- Lime addition considerably influenced the transfer of Ni into plants (*TF*). TF decreased with increasing lime doses. Differences in *Transfer Factors* during the vegetation period (in case of rape *TF(Ni)* slightly increased and in case of oat *TF(Ni)* decreased) are attributed to the genetic peculiarities of the plants species.

- The dynamic of the Ni concentrations in plants was well described by the Sigmoidal function. Under conditions of the presented experiment lime doses of 1.24 g $kg^{-1}$ and 1.0 g $kg^{-1}$ were the distinct optimum for reducing Ni concentration in *Brassica napus* and *Avena sativa* plants respectively. The lime dose under which the change in plant Ni concentrations per unit of lime is maximum (parameter $D_0$) is supposed to be a characteristic criterion for assessing Ca-Ni interactions. Calculations revealed that decrease in Ni concentration due to the interaction with Ca is limited and depends on plant and soil conditions.

The results of the work revealed that Ni and Ca possibly interact directly and competitively following the ion-exchange mechanism. Further investigations are needed to determine empirical coefficients of the key equation of the sorption model and to prove this type of Ca and Ni interaction in the soil-plant system. Lime addition to acid sod-podzolic sandy-loam soil considerably changes the system. It significantly affects not only crop yield but also growth rate and element uptake. Every specific condition (other types of soil, plants, etc.) demands for estimating specific Ni transfer from soil into plants.

**Zusammenfassung: Modellierung der Wechselwirkung zwischen Calcium und Nickel im System Boden-Pflanze**

Hauptziel der vorliegenden Arbeit war es, die Beziehungen zwischen Calcium (Ca) und Nickel (Ni) im System Boden-Pflanze unter Berücksichtigung des Einflusses von Kalk auf den Ni-Transfer vom Boden in die Pflanze zu untersuchen. Neben der Erweiterung des Kenntnisstandes über das Verhalten von Ni und Ca im System Boden-Pflanze und ihrer Interaktionen wurden wichtige Eigenschaften der Umsetzungsprozesse untersucht, die Bodenversauerung bzw. –neutralisation charakterisieren.

Die Untersuchungen wurden am Agrophysikalischen Forschungsinstitut in Sankt-Petersburg durchgeführt. In einem Gefäßversuch über 2 Jahre wurden Raps (*Brassica napus*) und Hafer (*Avena sativa*) mit und ohne Ni-Kontamination (20 mg $kg^{-1}$ Ni) sowie ansteigenden Kalkgaben (0 - 2.1g $kg^{-1}$) für eine Zeitdauer von jeweils 43 Tagen auf einem sauren, sandigen Lehmboden (pH(KCl) 4.1) angebaut. Während der Vegetationsperiode wurden an 5 Terminen Boden- und Pflanzenproben entnommen und analysiert. Zur Beschreibung der experimentellen Daten wurde das Sorptionsmodell von Drichko (1990) genutzt.

Folgende Ergebnisse wurden erzielt:

- Die Interaktionen zwischen Calcium und Nickel konnten durch das verwendete Sorptionsmodell mit hoher Genauigkeit beschrieben werden. Die experimentellen Daten folgten der Langmuir Gleichung. Zwischen den inversen Werten der Ni-Transferfaktoren für *Brassica napus* und *Avena sativa* und der Ca-Konzentration im Boden wurde eine lineare Korrelation nachgewiesen. Dieser Fakt wird auf die antagonistischen Beziehungen zwischen Calcium und Nickel in den Ionen-Austausch-Mechanismen zurückgeführt.

- Kalkung beeinflusste signifikant die mobilen Ca- und Ni-Konzentrationen im Boden. Mit steigenden Kalkgaben stieg die mobile Ca-Konzentration an und die mobile Ni-Konzentration nahm ab.

- Kalkung bewirkte deutliche Änderungen des Boden-pH. Der pH-Wert stieg mit zunehmenden Kalkgaben. Diese Beziehung wurde durch eine lineare Funktion mit hoher

Genauigkeit beschrieben. Die pH-Änderungen verringerten sich mit zunehmender Untersuchungsdauer. Die pH-Änderung je Einheit verabreichter Kalkmenge (Parameter $b_D$) ist abhängig von den Boden- und Pflanzeneigenschaften und repräsentiert ein spezifisches Kriterium zur Charakterisierung von pH-Änderungen gekalkter saurer Podsolböden. Während der Vegetationsperiode nahm der pH-Wert infolge saurer Exsudate der untersuchten Pflanzen (*Brassica napus* und *Avena sativa*) ab. Die versauernde Wirkung von *Brassica napus* wurde durch eine Exponentialfunktion, die von *Avena sativa* durch eine lineare Funktion im Experiment gut beschrieben. Es wurde aufgezeigt, dass mit zunehmender Kalkgabe weniger Pflanzenbiomasse für die Verdopplung der $H^+$-Freisetzung notwendig ist.

- Die Trockenmasseentwicklung der untersuchten Fruchtarten entsprach der klassischen S-Kurve, die mittels logistischer Funktion gut beschrieben wurde. Kalkung beeinflusste die Trockenmasseproduktion von *Brassica napus* und *Avena sativa* signifikant. Neben dem Ertragsanstieg erhöhte sich auch die spezifische Wachstumsrate mit jeder Kalkgabe. Die Kalkmenge, bei der die spezifische Wachstumsrate der Hälfte der maximalen Wachstumsrate entspricht (Parameter $D_{1/2}$) wird als quantitatives Kriterium zur Beurteilung der Pflanzenreaktion auf die Kalkzufuhr vorgeschlagen. Es wurde aufgezeigt, dass *Avena sativa* deutlicher auf Kalkzufuhr reagiert.

- Die Ni- und Ca-Aufnahme der Pflanzen während der Vegetationsperiode folgten einer S-Kurve, die mittels logistischer Funktion in vorliegender Arbeit gut beschrieben wurde. Die Ca-Aufnahme der Pflanzen stieg mit steigenden Kalkgaben an, die Ni-Aufnahme verminderte sich mit ansteigender Kalkzufuhr. Im Experiment mit *Brassica napus* beeinflussten Kalkgaben die spezifische Rate der Ca-Aufnahme in geringerem Maße als die spezifische Wachstumsrate der Pflanzen. Dies resultierte in einer Abnahme der Ca-Konzentration bei *Brassica napus* im Vegetationsverlauf. Die spezifische Ni-Aufnahme bei *Brassica napus* wurde durch Kalkung stärker gefördert als die spezifische Wachstumsrate. Dies führte zu einer ansteigenden Ni-Konzentration in der Pflanzensubstanz im Vegetationsverlauf. Im Experiment mit *Avena sativa* war die spezifische Ni-Aufnahmerate niedriger als die spezifische Wachstumsrate, während die spezifische Ca-Aufnahmerate höher war. Trotz der theoretischen Erwartungen nahm die Ca-Konzentration bei *Avena sativa* ab. Für den starken Abfall der Ca-Konzentration im Pflanzenmaterial sind andere Mechanismen verantwortlich.

- Kalkzufuhr beeinflusste den Transfer von Ni in die Pflanzen (*TF*) beträchtlich. TF wurde mit steigenden Kalkgaben vermindert. Unterschiede in den *Transfer-Faktoren* während der Vegetationsperiode (Raps: *TF(Ni)* leichte Erhöhung; Hafer: *TF(Ni)* Abnahme) sind auf genetische Besonderheiten der Pflanzenarten zurückzuführen.

- Die Dynamik der Ni-Konzentration in den Pflanzen konnte durch die Sigmoidal Funktion gut beschrieben werden. Unter den Bedingungen der durchgeführten Experimente waren Kalkgaben von 1.24 g $kg^{-1}$ bzw. 1.0 $g.kg^{-1}$ optimal für die Reduktion der Ni-Konzentration bei *Brassica napus* und *Avena sativa*. Die Kalkmenge, bei der die Änderung der Ni-Konzentration in der Pflanze je Einheit Kalk das Maximum erreicht (Parameter $D_0$) wird als charakteristisches Kriterium zur Beurteilung der Ca-Ni Interaktionen betrachtet. Die Ergebnisse zeigten, dass die Absenkung der Ni-Konzentration in den Pflanzen durch die Interaktion mit Ca aufgrund der hohen Variabilität der Bodenazidität nur begrenzt möglich ist.

Mit den Ergebnissen der Untersuchungen konnte dargelegt werden, dass die Elemente Ni und Ca, dem Ionen-Austausch-Mechanismus folgend, sich direkt aber auch antagonistisch gegenseitig beeinflussen. Weitere Experimente sind notwendig, um die empirischen Koeffizienten für die Hauptgleichung des Sorptionsmodells zu evaluieren und die Ca-Ni-Interaktionen im System Boden-Pflanze zu überprüfen. Die Kalkung saurer, podsoliger, sandiger Lehmböden verändert das System erheblich. Ertrag, Wachstumsrate und Elementaufnahme werden signifikant beeinflusst. Spezifische Bedingungen (andere Boden- oder Pflanzenarten, etc.) erfordern die Ableitung spezifischer Ni-Transfer-Faktoren.

# 6 References

**Alagna L, Hasnain S, Pigott B, Williams D** (1984) The nickel ion environment in jack bean urease. Biochem. J. 220: 591-595

**Alekseev Y** (1987) Heavy metals in soil and plants. Leningrad branch of Publishing House Agropromizdat, Leningrad, 142 p /in Russian/

**Andreeva I** (2003) The peculiarities of Ni accumulation and distribution in some agricultural crops. PhD thesis abstract. ANO, Publishing House of Moscow Agricultural Academy, Moscow, 22 p /in Russian/

**Andreeva I, Govorina V, Vinogradov S, Yagodin B** (2001) Nickel in plants. Agricultural chemistry 3: 82-94 /in Russian/

**Anonym** (1992) Determination of Ca in forages, mixed fodder, raw fodder. State Standard 26570-85. Publishing House TSINAO, 35 p /in Russian/

**Anonym** (1992a) Methodical instructions on determination of heavy metals and their mibile forms in soils and agricultural products. Publishing House TSINAO, 24 p /in Russian/

**Anonym** (1993) Methodical instructions on determination of mobile Ni forms in soils by atomic-absorbic method. Russian Ministry of agriculture, Printing house of Russian Academy of agricultural Sciences, Moscow, 13 p /in Russian/

**Anonym** (1994) Determination of exchangeable Ca and Mg by TSINAO method. Collected State Standards. State Standard 26487-85. Publishing House "Standard", pp 20-33 /in Russian/

**Arinushkina E** (1980) Guidance on chemical analyses. Moscow State University, Moscow, 400 p /in Russian/

**Aristarhov A, Kharitonova A** (2002) The status and forecast methodology of soils pollution with heavy metals. Soil Fertlity 3: 22-25 /in Russian/

**Arkhipov N, Egorov A, Klechkovskij V** (1969) For the assessment of the $^{90}$Sr transfer from soil into plants and its accumulation in the yield. Reports of VASHNIL, Vol. 1, pp 2-10 /in Russian/

**Arkhipov N, Federov E, Aleksahin R** (1975) Soil chemistry and root uptake of artificial radionuclide in crops yield. Eurasian Soil Science 11: 40-52 /in Russian/

**Arshad M, Franzluebbers A, Gill K** (1999) Improving barley yield on an acidic Boralf with crop rotation, lime and zero tillage. Soil and Tillage Research 50: 47-53

**Bakunov N** (1989) About $^{137}$Cs accumulation in plants and specificity of its behaviour in soils. Agricultural chemistry 5: 94-99 /in Russian/

**Barber S** (1995) Soil Nutrition Bioavailability. A mechanistic approach. 2nd ed. John Wiley & Sons, Inc., 414 p

**Batygin N** (1986) Ontogenesis of higher plants. Publishing House Agropromizdat, Moscow, 100 p /in Russian/

**Bezdicek D, Beaver T, Granastein D** (2003) Subsoil ridge tillage and lime effects on soil microbial activity, soil pH, erosion, and wheat and pea yield in the Pacific Northwest, USA. Soil and Tillage Research 74: 55-63

**Bissesar S** (1989) Effects of lime on nickel uptake and toxicity in celery grown on muck soil contaminated by a nickel refinery. The Science of the Total Environment, Vol. 84: 83-90

**Bolan N, Adriano D, Curtin D** (2003) Soil acidification and liming interactions with nutrient and heavy metal transformation and bioavailability. Advances in Agronomy, Vol. 78: 215-272

**Bolan N, Adriano D, Mani P, Duraisamy A** (2003) Immobilisation and phytoavailability of cadmium in variable charged soils. II. Effect of lime addition. Plant and Soil 251: 187-198

**Boyd R, Davis M** (2001) Metals tolerance and accumulation ability of the hyperaccumulator *Streptanthus polygaloides* Gray (*Brassicaceae*). Int. J. Phytorem. 3: 353-367

**Brady N, Weil R** (1999) The Nature and Property of Soils. 12th ed. Prentice Hall. Upper Saddle Hall. NJ

**Brimecombe M, De Leij Frans A, Lynch J** (2001) Nematode community structure as a sensitive indicator of microbial perturbations induced by a genetically modified *Pseudomonas fluorescens* strain. Biology and fertility of soils, Vol. 34 (4): 270-275

**Cammack R, Fernandez V, Schneider K** (1998) Nickel in hydrogenases from sulphate-reducing, photosynthetic, and hydrogen-oxidizing bacteria. In: The Bioorganic Chemistry of Nickel, Lancaster J. jr (ed.), Verlag Chemie, Weinheim, pp 167-190

**Chaignon V, Bedin F, Hinsinger Ph** (2002) Copper bioavailability and rhizosphere pH changes as effected by nitrogen supply for tomato and oilseed rape cropped on an acidic and calcareous soil. Plant Soil 243: 219-228

**Chang C, Sung J** (2004) Nutrient uptake and yield responses of peanuts and rice to lime and fused magnesium phosphate in an acid soil. Field Crops Research, Vol. 89, Issues 2-3: 319-325

**Chaudhuri D, Tripathy S, Veeresh H, Powell M, Hart B** (2003) Mobility and bioavailability of selected heavy metals in coal ash- and sewage sludge-amended acid soil. Environmental Geology 44 (4): 419–432

**Cho J, Han K** (1996) Comparison of growth and physiological responses in radish for assay of nickel toxicity. I. Growth of radish and adsorption and translocation of nickel. Agricultural Chemistry and Biotechnology, Vol. 39, Issue 4: 287-292

**Chuan M, Shu Y and Liu J** (1996) Solubility of heavy metals in a contaminated soil: effects of redox potential and pH. Water, Air Soil Pollut. 90: 543–556

**Cotton F, Wilkinson G** (1980) Advanced inorganic chemistry. Wiley, New York, 314 p

**Dalton D, Evans H, Hanus F** (1985) Stimulation by nickel of soil microbial urease activity and urease and hydrogenase activity in soybeans grown in a low-nickel soil. Plant Soil 88: 245-258

**Deherain P** (1902) Traite de Chimie Agricole. Masson. Paris, 969 p

**Denkhaus E, Salnikow K** (2002) Nickel essentiality, toxicity, and carcinogenicity. Crit. Rev. Oncol. Hematol. 42: 35-56

**Dixon N, Gazzorola C, Blakeley R, Zarer B** (1975) Jack bean urease. A metalloenzyme. A simple biological role for nickel? J. Am. Chem. Soc.: 4131-4133

**Drichko V, Tsvetkova V** (1990) Sorption model of radionuclides transfer from soil to plants. USSR Academy of Science, Soil Science, Issue 10: 35-40 /in Russian/

**Drichko V, Efremova M, Ponikarova T** (1994) Uptake of $^{134}$Cs from peatsoil by timothy in vegetation. Radiobiology. Radioecology, Vol. 34, Issues 4-5: 723-728 /in Russian/

**Drichko V, Ponikarova T, Efremova M** (1996) Uptake of $^{137}$Cs by grasses from peatsoil under increasing K- and N-fertilization rates. Radiobiology. Radioecology, Vol. 36, Issue 4: 524-530 /in Russian/

**Drichko V, Litvinovich A, Pavlova O** (2002) Strontium and Calcium uptake by plants under increasing chalk supply. Agricultural chemistry 4: 81-87 /in Russian/

**Durand D** (1971) Stable Chaos, an Introduction to statistical control. General Learning Press, Morristown, NJ, ch.13, 582 p

**Eskew D, Welch R, Norwell W** (1984) Nickel in higher plants. Further evidence for an essential role. Plant Physiol 76: 691-693

**Evdokimova G** (1990) Ecological-microbiological bases of soil preservation in conditions of industrial effect on Far North. ANO, Publishing house of Moscow Agricultural Academy, Moscow, 36 p /in Russian/

**Gerendas J, Sattelmacher B** (1997) Significance of Ni supply for growth, urease activity and the concentrations of the amino acids, mineral nutrients of urea-grown plants. Plant and Soil 190: 153-162

**Gerendas J, Polacco J, Freyermuth S, Sattelmacher B** (1999) Significance of nickel for plant growth and metabolism. J. Plant Nutr. Soil Sci. 162: 241-256

**Gilbert R, Simpson J** (1985) Comparing computing formulas for estimating concentration ratios. Environ. Antl. 11: 25-47

**Goltsov A, Kovalchuk A, Abramov V, Milaschenko N** (1983) Rape and Cole-seed. Printing House Kolos, Moscow, 190 p /in Russian/

**Gorbatov V, Zyrin N** (1987) About choosing of substance for extraction of exchangeable heavy metals kations from soils. Bulletin of Moscow State University, Issue Soil Science 2, pp 22-26 /in Russian/

**Goryachkin V** (1924) The general schema of phenomena. Scientific-Agronomy Journal 1: 12-34 /in Russian/

**Goulding K, Blake L** (1997) Soil acidification and mobilization of toxic metals caused by acid deposition and fertilizer application. Natural and anthropogenic causes and effects of soil acidification. Lublin., pp 15-20

**Goulding K, Blake L** (1998) Land use, liming and the mobilization of potentially toxic metals. Agriculture. Ecosystems and Environment 67: 135-144

**Guivarch A, Hinsinger P, Staunton S** (1999) Root uptake and distribution of radiocaesium from contaminated soils and the enhancement of Cs adsorption in the rhizosphere. Plant Soil 211: 131-138

**Guo Y, Schulz R, Marschner H** (1995) Genotypic differences in uptake and distribution of cadmium and nickel in plants. Angewandte Botanik 69: 42-48

**Han D, Lee H** (1996) Effects of Liming on uptake of lead and cadmium by *Raphanus sativa*. Archives of Environmental Contamination and Toxicology, Vol. 31 (4): 488-493

**Haq A, Bates T, Soon Y** (1980) Comparison of extractants for plant-available zinc, cadmium, nickel and copper in contaminated soils. Soil Sci. Soc. Amer. J. 44: 772-777

**Hartley E, Gemell G, Herridge D** (2004) Lime pelleting inoculated serradella (Ornithopus spp.) increases nodulation and yield. Soil Biology and Biochemistry 36: 1289-1294

**Hein A, Sauerbeck D, Horst H, Bruene H** (1995) Die Nickelaufnahme von Pflanzen aus verschiedenen Boeden und Bindungsformen und ihre Prognose durch chemische Eztraktionsverfahren. Texte 33, Umwelt Bundes Amt, Berlin, 197 p

**Hinsinger Ph, Passard C, Tang C, Jaillard B** (2003) Origins of root-mediated pH changes in the rhizosphere and their responses to environmental constraints: A review. Plant and Soil 248: 43-59

**Holford I, Mattingley G** (1976) Phosphorus adsorption and plant availability of P. Plant Soil 44: 377-389

**Iljin V** (1991) Heavy metals in the plant-soil system. Publishing House Nauka, Novosibirsk, Russia, 151 p /in Russian/

**Ivanov V** (1994) Guidance. Ecological geochemistry of elements, Printing House Nedra, Moscow, 457 p /in Russian/

**Kabata-Pendias A** (2001) Trace elements in Soils and Plants. 3d ed. CRC Press LLC, USA, 331 p

**Kabata-Pendias A, Wiacek K** (1985) Excessive uptake of heavy metals by plants from contaminated soil, Soil Sci. Ann. 36 (4): 332-345

**Kletschenko A** (1986) Assessment of grain crops condition by distant means. Printing House Gidrometeoizdat, Leningrad, 190 p /in Russian/

**Knoche H, Brand P, Goette-Viereck, Boeken H** (1999) Schwermetalltransfer Boden-Pflanze. Ergebnisse der Auswertungen hinsitlich der Koenigswasser- und Ammoniumnitrat-Extraction anhand der Datebank TRANSFER. Texte 11, Umwelt Bundes Amt, Berlin, ISSN: 0722-186X, 213 p

**Konoplev A** (1998) Mobility and bioavailability of radiocaesium and radiostrontium of accidental origin in soil-water system. Doctor of Science Thesis. RIA RAE, Obninsk, 200 p /in Russian/

**Konoplev A, Bulgakov A** (1999) Kinetics of 90 Sr leaching from fuel particles in soils in the nearest zone of the Chernobyl NPP. Atomnaya Energiya (Atomic Energy) 86 (2): 129-134 /in Russian/

**Konopleva I** (1999) Investigation of mechanisms of $^{137}$Cs bioavailability in soils of forest ecosystem. PhD theses, Obninsk. VNIISKHRAE, 119 p /in Russian/

**Kovalskiy V, Letunova S** (1974) Geochemical ecology of microorganisms. Tr. Biogeochim. Lab, 13 (3): 15-25 /in Russian/

**Kovalevski A** (1987) Biogeochemical Exploration for mineral deposits. Coronet Books Inc., Pennsilvaniya, USA, 238 p

**Lee Tse-Ming, Lai Hung-Yu, Chen Zueng-Sang** (2004) Effect of chemical amendments on the concentration of cadmium and lead in long-term contaminated soils. Chemosphere 57: 1459-1471

**Lukin V, Epplin F** (2003) Optimal frequency and quantity of agricultural lime applications. Agricultural systems, Vol. 76, Issue 3: 949-967

**Malhi S, Nyborg M, Harapiak J** (1998). Effects of long-term N fertilizer-induced acidification and liming on micronutrients in soil and in bromegrass hay. Soil and Tillage Research 48: 91-101

**Marschner H** (2003) Mineral Nutrition of Higher plants (second ed.) Academic press, London, 889 p

**McLaughlin M** (2002) Heavy metals. In: Encyclopedia of Soil Science, Lal R (eds), pp 650-653

**Masscheleyn P, Pardue J, Delaune, R, Patrick J** (1991) Effect of redox potential and pH on As speciation and solubility in a contaminated soil. Environ. Sci. Tech. 25: 1414–1419

**Mengel K, Kirkby E** (1978) Principles of plant nutrition, International Potash Institute, Worblaufen-Bern, 593 p

**Miller R** (1998) Nitric-Perchloric Acid Wet Digestion in an Open Vessel. In Handbook of Reference Methods for Plant Analysis, Kalra Ya. (eds), CRC Press LLC, USA, pp 57-63

**Mineev V** (eds.) (1989) Guidance on Agricultural Chemistry. Moscow State University, Moscow , 303 p /in Russian/

**Ming D** (2002) Carbonates. In: Encyclopedia of Soil Science, Lal R (eds), pp 139-142

**Morrison R, Brooks R, Reeves R** (1980) Nickel uptake by Allysum species, Plant Sci. Lett. 17: 451

**Nebolsin A, Nebolsina Z** (1998) Role of organic substance in soil acidity and changes of humus status of sod-podzolic soils under lime application. Agricultural chemistry 8: 14-20 /in Russian/

**Nebolsin A, Sychev V** (eds.) (2000) Ecological-economical recommendations on liming adapted to the certain soil conditions. Publishing House of the Central Institute of Agrochemical Service (TSINAO), Moscow, 80 p /in Russian/

**Obenauf S** (1987) Variabilität von Bodenfruchtbarkeitskennziffernwährend der Vegetationszeit im Ap sandiger Ackerböden. Archiv für Acker-und Pflanzenbau und bodenkunde, Berlin, 3: 137-145

**Ovcharenko M** (eds.) (1997) Heavy metals in the soil-plant-fertilizer system, Printing House Proletarskij Svetoch, Moscow, 290 p /in Russian/

**Patrick H, Ronald D, Patrick J** (1990) Transformations of Se, As affected by sediment oxidation–reduction potential and pH. Environ. Sci. Tech. 24 : 91–96

**Polyakov Yu** (1970) Radioecology and soil deactivation. Publishing House Atomizdat, Moscow. 303 p /in Russian/

**Porter W** (2004) Soil Acidification – the Cause. Publication on-line: http://regional.org.au/au/roc/1981/roc198131.htm

**Posypanov G** (eds.) (1997) Plant Breeding. Printing House Kolos, Moscow, 423 p /in Russian/

**Quipilg Z, Chuliang Y, Lihua T, Sunxiang X** (1984) Content and distribution of trace elements in limestone soils of China. Acta Pedologica Sinica 21: 58-67

**Rassel R** (eds.) (1971) Radioactivity and food. Publishing House Atomizdat, Moscow, 303 p

**Raven J** (1986) Biochemical disposal of excess $H^+$ in growing plants? New Phytol. 104: 175-206

**Raven J, Wollenweber B** (1992) Temporal and spatial aspects of acid-based regulation. Curr Top Plant Biochem Physiol. 11: 270-294

**Richards B, Steenhus T, Peverly J, McBride M** (2000) Effect of sludge-processing mode, soil texture and soil pH on metal mobility in undisturbed soil columns under accelerated loading. Environmental Pollution 109: 327-346

**Riley D, Barber S** (1969) Bicarbonate accumulation and pH changes at the soybean (Glycine max(L.) Merr.) root-soil interface. Soil Sci. Soc. Am. Proc. 33: 905-908

**Riley D, Barber S** (1971) Effect of ammonium and nitrate fertilization on phosphorus uptake as related to root-induced pH changes at the root –soil interface. Soil Sci. Soc. Am. Proc. 35: 301-306

**Robinson B, Brooks R, Clothier B** (1999) Soil Amendments Affecting Nickel and Cobalt Uptake by Berkheya coddii: Potential Use for Phytomining and Phytoremediation. Annals of Botany, Vol. 84, Issue 6: 689-694

**Robson A, Pitman M** (1983) Interactions Between Nutrients in Higher plants. In Inorganic Plant Nutrition; Lauchli A, Bielski R, (eds.). Springer –Verlag: New York, pp 147-180

**Saprikin F** (1999) Ecological conditions of St.-Petersburg - City Museum of Europe architecture. City transformation to the zone of tourism and rest. Publishing House Nedra, St.-Petersburg, Russia, 45 p /in Russian/

**Schnug E, Strampe U** (1988) Sortentypische Unterschiede der Nährelementkonzentrationen von Winterweizen. J. Agr. & Crop Sci. 160: 163-172

**Schoenbuchner H** (2005) Untersuchungen zu Mobilitaet und Boden-Pflanze-Transfer von Schvermetallen auf/in uranhaltigen Haldenboeden. Dissertation Dr. Ere. Nat., Gemisch-Geowissenschaftlichen Fakultaet der Friedrich-Schiller-Universitaet Jena. Publikation on-line: http://www.db-thueringen.de/servlets/DerivateServlet/Derivate-1304/Dissertation.pdf

**Sheoran I, Singal H, Singh R** (1990) Effect of cadmium and nickel on photosynthesis and enzymes of the photosynthetic carbon reduction cycle in the pigeon pea (Cajanus cajan). Photosynth. Res. 23: 345-352

**Sheppard S, Evenden W** (1988) Critical compilation and review of plant/soil concentration ratios for Uranium, Thorium and Lead, J. Environ. Radioactivity 8: 255-285

**Shmidt V, Dibirov M** (1979) Some morphogenetic aspects of investigation of variability of Higher plants populations. Publishing House Nauka, Leningrad, 202 p /in Russian/

**Sinha S, Pandey K** (2003) Nickel induced toxic effects and bioaccumulation in the submerged plant, *Hydrilla verticillata* (L.F.) Royle under repeated metal exposure. Bull. Environ. Contam. Toxicol. 71: 1175-1183

**Singh B, Dang Y, Mehta S** (1990) Influence of nitrogen on the behaviour of nickel in wheat. Plant Soil 127: 213-218

**Slivinskaya S** (1991) Nickel effect on sunflower leaf cell membranes. Acta Bot. 40: 133-138

**Sun E, Wu F** (1998) Along-vein necrosis as indicator symptom on water spinach caused by nickel in water culture. Bot. Bull. Acad. Sin. 39: 255-259

**Szomolanyi A, Lehoczky E** (2002) Study on the Cd uptake by lettuce plants in liming experiment. Proceedings of the 7th Hungarian Congress on Plant Physiology, S2-P23, Vol. 46 (3-4), pp 123-124

**Thauer R, Diekert G, Schönheit P** (1980) Biological role of nickel. Trends Biochem. Sci. 5: 304-306

**Tikhomirov F** (1980) Theoretical and applied questions of preservation the soil-vegetative surface from radioactive pollution. Reports of The Higher School., Biological Sciences, Moscow, Vol. 4, pp 18-25 /in Russian/

**Tsadilas C, Karaivazoglou N, Tsotsolis N, Stamatiadis S, Samaras V** (2005) Cadmium uptake by tobacco as affected by liming, N form, and year of cultivation. Environmental Pollution 134 : 239-246

**Uren N** (2000) Types, amounts and possible functions of compounds released into the rhizosphere by soil-grown plants. In The Rhizosphere: Biochemistry and Organic Substances at the Soil- Plant Interface. Eds. R Pinton. Z Varanini and P Nannipieri. Marcel Dekker. Inc. New York. pp 19–40

**Vago I, Loch J, Gyori Z** (1997) The nickel uptake by ryegrass. Proceedings of the Second International Seminar on Soil Plant Environment Relationship, Debrecen, Hungary, Vol. 1-2, pp 228-239

**Vago I, Zoltan G, Jakab L** (1996) Comparison of chromium and nickel uptake of plants grown in different soils. Fresenius Journal of Analytical Chemistry, Vol. 354 (5-6): 714-724

**Veitene R** (2002) Acidification of soil – the indicator of chemical soil degradation process. Proceedings of the 17-th WCSS, 14-21 August 2002, Thailand, pp 10-1 – 10-7

**Vesper S, Weidensaul T** (1978) Effects of cadmium, nickel, copper and zinc on nitrogen fixation by soybeans. Water, Air Soil Pollut. 9: 413-423

**Walter R, Lampreht I** (1976) Thermodynamics of biological processes. Publishing House Nauka, Moscow, pp 98-112 /in Russian/

**Wang J, Yhao F, Meharg A, Raab A, Feldmann J, McGraph S** (2002) Mechanisms of Arsenic Hyperaccumulation in Pteris vittata. Uptake kinetics, Interactions with Phosphate, and Arsenic Speciation. Plant Physiology 130: 1552-1561

**Warpholomeev S, Kalyuzhny S** (1990) Biotechnology: Kinetic bases of microbiological processes. Printing House Vysshaya Shkola, Moscow, 296 p /in Russian/

**Welch R** (1979) The biological significance of Ni. 36th International Symposium on Trace Elements Stress in plants. Los-Angeles, USA, 345 p

**Weyman-Kaczmarkowa W, Pedziwilk Z** (2000) The development of fungi as affected by pH and type of soil, in relation to the occurrence of bacteria and soil fungi static activity. Microbiological Research 155 (2): 107-112

**Winkler R, Blevins D, Polacco J, Randall D** (1987) Ureide catabolism in nitrogen-fixing legumes. Trends Biochem. Sci. 11: 97-100

**Yagodin B, Deryugin Yu, Zharkov P** (1987) Practicum on Agricultural chemistry, Printing House Agropromizdat, Moscow, Russia, 512 p /in Russian/

**Yagodin B** (eds.) (1989) Agricultural Chemistry. Printing House Agropromizdat, Moscow, Russia, 465 p /in Russian/

**Yagodin B, Govorina V, Vinogradova N** (1991) Nickel in the soil-fertilizer-plants-animals-man system. Agricultural chemistry 1: 128-158 /in Russian/

**Yaron B, Calvet R, Prost R** (1996) Soil Pollution Processes and Dynamics. Springer-Verlag Berlin Heidelberg 313 p

**Youssef R, Chino M** (1989) Root-induced changes in rhizosphere of the plants. I. pH changes in relation to the bulk soil. Soil Sci. Plant Nutr. 35: 461-468

**Yudintseva E, Zhigareva T, Sidorova E** (1980) Influence of lime application on radionuclides availability for plants. Agricultural Chemistry 6: 93-98 /in Russian/

**Zach R** (1982) LIMCAL. A comprehensive food chain model for predicting radiation exposure to man in long-term nuclear waste management. Atomic energy Canada limited, AECL-6827.

**Zhang F, Shen J** (2002) Nutrient interactions in soil-plant system. In Encyclopedia of Soil Science, Lal R (eds), pp 885-890

**Zhao F, Hamon R, Lombi E, McLaughlin M, McGrath S** (2002) Characteristics of cadmium uptake in two contrasting ecotypes of the hyperaccumulator Thlaspi caerulescens. Journal of Experimental Botany, Vol. 53 (368): 535-543

**Zyrin D, Orlov D** (eds.) (1980) Physical and chemical investigation of soil. Publishing House of Moscow State University, Moscow, 382 p /in Russian/

# 7 Appendix

Table A.1: Concentration of mobile Ca in soil, year 2000.

| **Lime dose** [g kg$^{-1}$] | **Concentration of mobile Ca in soil** [mg kg$^{-1}$] | | | | |
|---|---|---|---|---|---|
| | **Sampling time** [d] | | | | |
| | **14** | **21** | **29** | **36** | **43** |
| 0 | 172.3 | 168.7 | 188.3 | 115.3 | 122.7 |
| 0 | 159.0 | 186.1 | 173.4 | 101.2 | 112.5 |
| 0 | 174.2 | 178.9 | 181.9 | 110.5 | 118.2 |
| **mean** | **168.5±8.3** | **177.9±8.7** | **181.2±7.5** | **109.0±7.3** | **117.8±5.0** |
| 0.41 | 464.5 | 335.5 | 327.2 | 362.3 | 351.6 |
| 0.41 | 464.7 | 317.8 | 278.8 | 333.6 | 266.4 |
| 0.41 | 504.5 | 324.7 | 311.7 | 351.1 | 267.6 |
| **mean** | **477.9±23.0** | **326.0±9.0** | **305.9±24.7** | **349.0±14.5** | **295±48.0** |
| 0..83 | 490.3 | 462.9 | 489.3 | 416.9 | 436.8 |
| 0.83 | 466.0 | 424.5 | 475.1 | 424.7 | 384.6 |
| 0.83 | 479.2 | 450.0 | 481.6 | 420.5 | 416.7 |
| **mean** | **478.5±12.2** | **445.8±19.5** | **482.0±7.2** | **420.7±3.9** | **412.7±26.3** |
| 1.24 | 534.4 | 529.1 | 563.9 | 582.3 | 568.3 |
| 1.24 | 605.8 | 485.0 | 513.3 | 551.4 | 542.0 |
| 1.24 | 580.9 | 512.9 | 544.0 | 564.3 | 556.8 |
| **mean** | **573.7±36.0** | **509.0±22.3** | **540.4±25.5** | **566.0±15.5** | **555.7±13.2** |
| 1.66 | 734.8 | 702.3 | 785.4 | 713.4 | 859.6 |
| 1.66 | 691.3 | 678.2 | 743.4 | 703.5 | 811.3 |
| 1.66 | 710.2 | 696.7 | 771.2 | 709.8 | 840.7 |
| **mean** | **712.1±22.0** | **692.4±12.5** | **766.6±21.3** | **708.5±5.0** | **837.2±24.3** |
| 2.10 | 807.6 | 729.3 | 808.6 | 769.6 | 773.4 |
| 2.10 | 735.5 | 710.4 | 763.8 | 783.3 | 808.1 |
| 2.10 | 780.1 | 719.7 | 791.3 | 745.1 | 798.7 |
| **mean** | **774.4±36.3** | **719.8±9.4** | **787.9±22.6** | **766.0±19.1** | **793.4±17.9** |

Table A.2: Concentration of mobile Ca in soil, year 2001.

| **Lime dose** [g kg$^{-1}$] | **Concentration of mobile Ca in soil** [mg kg$^{-1}$] | | | | |
|---|---|---|---|---|---|
| | **Sampling time** [d] | | | | |
| | **14** | **21** | **29** | **36** | **43** |
| 0 | 154.3 | 158.2 | 159.0 | 161.8 | 152.9 |
| 0 | 123.2 | 129.8 | 138.2 | 136.5 | 130.5 |
| 0 | 142.5 | 152.4 | 154.9 | 153.2 | 144.4 |
| **mean** | **140.0±15.7** | **146.8±15.0** | **150.7±11.0** | **150.5±13.0** | **142.6±11.3** |
| 0.41 | 352.8 | 340.5 | 386.0 | 395.5 | 326.4 |
| 0.41 | 325.5 | 302.1 | 339.8 | 357.6 | 373.4 |
| 0.41 | 346.0 | 326.6 | 370.1 | 373.8 | 353.9 |
| **mean** | **341.4±14.2** | **323.1±19.4** | **365.3±23.5** | **375.6±19.0** | **351.2±23.6** |
| 0..83 | 523.3 | 454.8 | 606.0 | 552.7 | 572.7 |
| 0.83 | 475.8 | 500.4 | 555.1 | 489.5 | 521.5 |
| 0.83 | 508.6 | 484.8 | 585.3 | 524.6 | 550.5 |
| **mean** | **502.6±24.0** | **480.0±23.0** | **582.1±25.6** | **522.3±31.6** | **548.2±25.6** |
| 1.24 | 666.8 | 664.0 | 682.8 | 695.3 | 691.3 |
| 1.24 | 614.5 | 594.5 | 619.0 | 649.4 | 622.6 |
| 1.24 | 646.8 | 634.6 | 658.2 | 677.9 | 662.9 |
| **mean** | **642.4±26.4** | **631.0±34.9** | **653.3±32.1** | **674.2±23.2** | **658.9±34.5** |
| 1.66 | 904.5 | 894.6 | 951.9 | 873.4 | 901.3 |
| 1.66 | 886.3 | 945.0 | 905.2 | 925.6 | 849.2 |
| 1.66 | 910.5 | 925.6 | 931.3 | 871.6 | 881.2 |
| **mean** | **900.4±12.6** | **921.7±25.4** | **929.5±23.4** | **890.2±30.6** | **877.2±26.3** |
| 2.10 | 998.5 | 958.5 | 952.6 | 958.7 | 948.5 |
| 2.10 | 936.0 | 902.0 | 904.0 | 888.2 | 887.3 |
| 2.10 | 976.6 | 936.6 | 933.4 | 927.3 | 927.9 |
| **mean** | **970.4±31.7** | **932.0±28.5** | **930.0±24.5** | **924.7±35.3** | **921.2±31.1** |

Table A.3: Concentration of mobile Ni in soil, year 2000.

| **Lime dose** [g kg$^{-1}$] | **Concentration of mobile Ni in soil** [mg kg$^{-1}$] | | | | |
|---|---|---|---|---|---|
| | **Sampling time** [d] | | | | |
| | **14** | **21** | **29** | **36** | **43** |
| 0 | Under detection limit | | | | |
| 0.41 | 7.35 | 8.70 | 5.75 | 6.95 | 6.50 |
| 0.41 | 6.00 | 5.45 | 5.85 | 6.77 | 7.55 |
| 0.41 | 5.55 | 6.10 | 5.45 | 6.90 | 7.02 |
| **mean** | **6.30±0.9** | **6.75±1.7** | **5.68±0.2** | **6.87±0.1** | **7.02±0.5** |
| 0.83 | 5.60 | 5.85 | 5.75 | 5.15 | 6.25 |
| 0.83 | 6.45 | 6.30 | 6.00 | 6.50 | 6.25 |
| 0.83 | 8.35 | 6.07 | 5.60 | 6.15 | 5.75 |
| **mean** | **6.80±1.4** | **6.07±0.2** | **5.78±0.2** | **5.93±0.7** | **6.08±0.3** |
| 1.24 | 5.60 | 5.15 | 5.85 | 5.90 | 6.00 |
| 1.24 | 5.60 | 4.55 | 5.15 | 5.90 | 7.55 |
| 1.24 | 5.75 | 5.45 | 5.75 | 6.00 | 6.01 |
| **mean** | **5.65±0.1** | **5.05±0.4** | **5.58±0.4** | **5.93±0.05** | **6.52±0.9** |
| 1.66 | 4.85 | 4.55 | 4.15 | 5.45 | 4.55 |
| 1.66 | 4.55 | 4.85 | 4.85 | 4.75 | 3.85 |
| 1.66 | 4.85 | 5.60 | 5.75 | 6.05 | 5.25 |
| **mean** | **4.75±0.2** | **5.00±0.5** | **4.91±0.8** | **5.41±0.6** | **4.55±0.7** |
| 2.10 | 5.45 | 5.45 | 4.45 | 5.80 | 4.75 |
| 2.10 | 4.55 | 4.70 | 5.60 | 4.90 | 5.10 |
| 2.10 | 4.85 | 5.60 | 4.45 | 4.75 | 5.45 |
| **mean** | **4.95±0.4** | **5.25±0.5** | **4.83±0.7** | **5.15±0.6** | **5.10±0.4** |

Table A.4: Concentration of mobile Ni in soil, year 2001.

| **Lime dose** [g kg$^{-1}$] | **Concentration of mobile Ni in soil** [mg kg$^{-1}$] | | | | |
|---|---|---|---|---|---|
| | **Sampling time** [d] | | | | |
| | **14** | **21** | **29** | **36** | **43** |
| 0 | Under detection limit | | | | |
| 0.41 | 5.40 | 5.57 | 5.25 | 5.40 | 5.60 |
| 0.41 | 5.50 | 5.53 | 5.27 | 5.33 | 5.53 |
| 0.41 | 5.45 | 5.20 | 5.28 | 5.35 | 5.50 |
| **mean** | **5.45±0.05** | **5.43±0.2** | **5.27±0.01** | **5.36±0.04** | **5.54±0.05** |
| 0.83 | 5.20 | 5.15 | 5.20 | 5.21 | 5.27 |
| 0.83 | 5.22 | 5.31 | 5.29 | 5.22 | 5.22 |
| 0.83 | 5.20 | 5.20 | 5.25 | 5.20 | 5.19 |
| **mean** | **5.21±0.01** | **5.22±0.08** | **5.25±0.04** | **5.21±0.01** | **5.23±0.04** |
| 1.24 | 5.00 | 4.90 | 5.00 | 4.93 | 4.87 |
| 1.24 | 4.90 | 5.10 | 4.90 | 4.89 | 4.94 |
| 1.24 | 4.95 | 4.75 | 4.97 | 4.90 | 4.90 |
| **mean** | **4.95±0.05** | **4.92±0.2** | **4.96±0.05** | **4.91±0.02** | **4.90±0.03** |
| 1.66 | 4.80 | 4.83 | 4.80 | 4.78 | 4.83 |
| 1.66 | 4.90 | 4.87 | 4.79 | 4.83 | 4.80 |
| 1.66 | 4.82 | 4.68 | 4.87 | 4.79 | 4.81 |
| **mean** | **4.84±0.05** | **4.79±0.1** | **4.82±0.04** | **4.80±0.03** | **4.81±0.01** |
| 2.10 | 4.83 | 4.65 | 4.76 | 4.80 | 4.83 |
| 2.10 | 4.55 | 4.75 | 4.75 | 4.71 | 4.75 |
| 2.10 | 4.90 | 4.82 | 4.75 | 4.73 | 4.73 |
| **mean** | **4.76±0.2** | **4.74±0.08** | **4.75±0.01** | **4.75±0.05** | **4.77±0.05** |

Table A.5: Soil pH(KCl), year 2000.

| **Lime dose** [g kg$^{-1}$] | **pH(KCl)** | | | | |
|---|---|---|---|---|---|
| | **Sampling time** [d] | | | | |
| | **14** | **21** | **29** | **36** | **43** |
| 0 | 4.13 | 4.03 | 3.95 | 3.90 | 3.78 |
| 0 | 4.10 | 4.04 | 3.99 | 3.81 | 3.79 |
| 0 | 4.10 | 4.05 | 3.97 | 3.78 | 3.83 |
| **mean** | **4.11±0.02** | **4.04±0.01** | **3.97±0.02** | **3.83±0.06** | **3.80±0.03** |
| 0.41 | 4.55 | 4.42 | 4.20 | 4.34 | 4.01 |
| 0.41 | 4.49 | 4.47 | 4.24 | 4.41 | 4.05 |
| 0.41 | 4.58 | 4.37 | 4.25 | 4.51 | 4.03 |
| **mean** | **4.54±0.04** | **4.42±0.05** | **4.23±0.03** | **4.42±0.08** | **4.03±0.02** |
| 0.83 | 4.91 | 4.72 | 4.49 | 4.24 | 4.20 |
| 0.83 | 4.82 | 4.66 | 4.51 | 4.23 | 4.22 |
| 0.83 | 4.79 | 4.69 | 4.56 | 4.22 | 4.24 |
| **mean** | **4.84±0.06** | **4.69±0.03** | **4.52±0.04** | **4.23±0.01** | **4.22±0.02** |
| 1.24 | 5.19 | 5.19 | 4.60 | 4.40 | 4.39 |
| 1.24 | 5.20 | 5.13 | 4.65 | 4.48 | 4.41 |
| 1.24 | 5.09 | 5.10 | 4.58 | 4.35 | 4.40 |
| **mean** | **5.16±0.06** | **5.14±0.05** | **4.61±0.04** | **4.41±0.06** | **4.40±0.01** |
| 1.66 | - | 5.56 | 4.91 | 5.10 | 5.12 |
| 1.66 | 5.55 | 5.65 | 5.05 | 5.00 | 5.10 |
| 1.66 | 5.54 | 5.59 | 4.95 | 5.17 | 5.17 |
| **mean** | **5.54±0.01** | **5.60±0.04** | **4.97±0.07** | **5.09±0.08** | **5.13±0.04** |
| 2.10 | 5.74 | 5.36 | 5.12 | 5.16 | 5.24 |
| 2.10 | 5.72 | 5.41 | 5.20 | 5.17 | 5.26 |
| 2.10 | 5.73 | 5.49 | 5.19 | 5.18 | 5.25 |
| **mean** | **5.73±0.01** | **5.42±0.06** | **5.17±0.04** | **5.17±0.01** | **5.25±0.01** |

Table A.6: Soil pH(KCl), year 2001.

| **Lime dose** [g kg$^{-1}$] | **pH(KCl)** | | | | |
|---|---|---|---|---|---|
| | **Sampling time** [d] | | | | |
| | **14** | **21** | **29** | **36** | **43** |
| 0 | 3.96 | 3.91 | 3.53 | 3.44 | 3.34 |
| 0 | 3.99 | 3.95 | 3.54 | 3.46 | 3.36 |
| 0 | 3.99 | 3.96 | 3.52 | 3.48 | 3.35 |
| **mean** | **3.98±0.02** | **3.94±0.03** | **3.53±0.01** | **3.46±0.02** | **3.35±0.01** |
| 0.41 | 4.13 | 4.21 | 4.19 | 4.15 | 3.97 |
| 0.41 | 4.15 | 4.22 | 4.20 | 4.16 | 4.02 |
| 0.41 | 4.17 | 4.23 | 4.21 | 4.20 | 4.01 |
| **mean** | **4.15±0.02** | **4.22±0.01** | **4.20±0.01** | **4.17±0.03** | **4.00±0.03** |
| 0.83 | 4.55 | 4.48 | 4.31 | 4.20 | 4.11 |
| 0.83 | 4.55 | 4.50 | 4.33 | 4.20 | 4.13 |
| 0.83 | 4.58 | 4.52 | 4.35 | 4.23 | 4.15 |
| **mean** | **4.56±0.02** | **4.50±0.02** | **4.33±0.02** | **4.21±0.02** | **4.13±0.02** |
| 1.24 | 5.17 | 5.30 | 5.10 | 4.95 | 4.50 |
| 1.24 | 5.21 | 5.35 | 5.11 | 5.00 | 4.52 |
| 1.24 | 5.31 | 5.37 | 5.15 | 5.02 | 4.54 |
| **mean** | **5.23±0.07** | **5.34±0.04** | **5.12±0.03** | **4.99±0.04** | **4.52±0.02** |
| 1.66 | 5.72 | 5.80 | 5.28 | 5.13 | 4.81 |
| 1.66 | 5.73 | 5.79 | 5.33 | 5.12 | 4.88 |
| 1.66 | 5.77 | 5.75 | 5.35 | 5.17 | 4.89 |
| **mean** | **5.74±0.03** | **5.78±0.03** | **5.32±0.04** | **5.14±0.03** | **4.86±0.04** |
| 2.10 | 5.88 | 5.88 | 5.70 | 4.98 | 4.69 |
| 2.10 | 5.89 | 5.86 | 5.71 | 5.00 | 4.75 |
| 2.10 | 5.90 | 5.84 | 5.75 | 5.02 | 4.75 |
| **mean** | **5.89±0.01** | **5.86±0.02** | **5.72±0.03** | **5.00±0.02** | **4.73±0.03** |

Table A.7: Dry matter, year 2000.

| **Lime dose** [g kg$^{-1}$] | **Dry matter** [g pot$^{-1}$] | | | | |
|---|---|---|---|---|---|
| | **Sampling time** [d] | | | | |
| | **14** | **21** | **29** | **36** | **43** |
| 0 | 0.29 | 0.50 | 1.69 | 1.57 | 3.65 |
| 0 | 0.35 | 0.42 | 2.67 | 3.15 | 2.87 |
| 0 | 0.26 | 0.49 | 2.15 | 2.39 | 3.23 |
| **mean** | **0.30±0.04** | **0.47±0.04** | **2.17±0.5** | **2.37±0.8** | **3.25±0.4** |
| 0.83 | 0.34 | 0.73 | 2.34 | 4.03 | 7.70 |
| 0.83 | 0.22 | 0.81 | 3.72 | 4.95 | 6.88 |
| 0.83 | 0.31 | 0.71 | 3.00 | 5.81 | 8.46 |
| **mean** | **0.29±0.06** | **0.75±0.05** | **3.02±0.7** | **4.93±0.9** | **7.68±0.8** |
| 1.24 | 0.34 | 0.82 | 3.90 | 9.90 | 12.99 |
| 1.24 | 0.37 | 0.91 | 5.59 | 11.30 | 15.11 |
| 1.24 | 0.43 | 0.76 | 4.61 | 8.80 | 10.93 |
| **mean** | **0.38±0.04** | **0.83±0.07** | **4.70±0.8** | **10.00±1.2** | **13.01±2.1** |
| 1.66 | 0.35 | 1.06 | 6.31 | 15.0 | 17.95 |
| 1.66 | 0.47 | 1.03 | 7.27 | 16.8 | 19.85 |
| 1.66 | 0.29 | 0.91 | 8.29 | 12.6 | 15.45 |
| **mean** | **0.37±0.09** | **1.00±0.08** | **7.29±0.9** | **14.8±2.1** | **17.75±2.2** |
| 2.10 | 0.41 | 1.11 | 7.57 | 14.92 | 19.95 |
| 2.10 | 0.36 | 0.96 | 9.89 | 19.11 | 17.72 |
| 2.10 | 0.43 | 1.02 | 12.15 | 17.00 | 22.09 |
| **mean** | **0.40±0.04** | **1.03±0.07** | **9.87±2.3** | **17.01±2.1** | **19.92±2.2** |

Table A.8: Dry matter, year 2001.

| **Lime dose** [g kg$^{-1}$] | **Dry matter** [g pot$^{-1}$] | | | | |
|---|---|---|---|---|---|
| | **Sampling time** [d] | | | | |
| | **14** | **21** | **29** | **36** | **43** |
| 0 | 0.22 | 0.38 | 1.87 | 2.19 | 3.83 |
| 0 | 0.23 | 0.46 | 2.55 | 2.91 | 4.46 |
| 0 | 0.27 | 0.45 | 3.26 | 3.57 | 3.29 |
| **mean** | **0.24±0.03** | **0.43±0.04** | **2.56±0.7** | **2.89±0.7** | **3.86±0.6** |
| 0.41 | 0.30 | 0.75 | 2.18 | 7.75 | 7.21 |
| 0.41 | 0.28 | 0.76 | 4.75 | 5.89 | 8.55 |
| 0.41 | 0.23 | 0.71 | 3.42 | 3.97 | 5.99 |
| **mean** | **0.27±0.04** | **0.74±0.03** | **3.45±1.3** | **5.87±1.9** | **7.25±1.3** |
| 0.83 | 0.33 | 0.88 | 2.78 | 11.55 | 12.83 |
| 0.83 | 0.36 | 0.87 | 6.77 | 10.04 | 16.99 |
| 0.83 | 0.27 | 0.80 | 4.79 | 13.03 | 14.85 |
| **mean** | **0.32±0.04** | **0.85±0.04** | **4.78±2.0** | **11.54±1.5** | **14.89±2.1** |
| 1.24 | 0.32 | 0.99 | 5.60 | 13.30 | 18.30 |
| 1.24 | 0.35 | 1.30 | 9.30 | 15.20 | 21.32 |
| 1.24 | 0.26 | 0.71 | 7.60 | 17.25 | 15.16 |
| **mean** | **0.31±0.04** | **1.00±0.3** | **7.50±1.8** | **15.25±1.9** | **18.26±3.1** |
| 1.66 | 0.51 | 0.72 | 9.90 | 16.30 | 17.83 |
| 1.66 | 0.35 | 1.08 | 8.40 | 14.90 | 19.25 |
| 1.66 | 0.13 | 1.26 | 7.20 | 18.00 | 20.61 |
| **mean** | **0.33±0.2** | **1.02±0.3** | **8.5±1.3** | **16.4±1.5** | **19.23±1.4** |
| 2.10 | 0.33 | 1.23 | 9.4 | 16.95 | 18.69 |
| 2.10 | 0.44 | 1.65 | 11.5 | 18.41 | 20.21 |
| 2.10 | 0.25 | 0.87 | 13.3 | 19.93 | 21.67 |
| **mean** | **0.34±0.09** | **1.25±0.4** | **11.4±1.9** | **18.43±1.5** | **20.19±1.5** |

Table A.9: Ni concentration in plants, year 2000.

| **Lime dose** [g kg$^{-1}$] | **Ni concentration in plants** [mg kg$^{-1}$] | | | | |
|---|---|---|---|---|---|
| | **Sampling time** [d] | | | | |
| | **14** | **21** | **29** | **36** | **43** |
| 0 | Under detection limit | | | | |
| 0.83 | 107.4 | 92.4 | 108.2 | 91.9 | 124.05 |
| 0.83 | 87.9 | 80.5 | 108.5 | 97.3 | 109.80 |
| 0.83 | 108.0 | 95.0 | 92.9 | 77.5 | 116.55 |
| **mean** | **101.1±11.4** | **89.3±7.7** | **103.2±8.9** | **88.90±10.2** | **116.8±7.1** |
| 1.24 | 69.70 | 66.73 | 77.23 | 86.00 | 92.35 |
| 1.24 | 65.78 | 64.02 | 71.75 | 82.05 | 83.77 |
| 1.24 | 68.20 | 65.45 | 74.82 | 84.55 | 88.48 |
| **mean** | **67.9±2.0** | **65.4±1.4** | **74.6±2.7** | **84.2±2.0** | **88.2±4.3** |
| 1.66 | 38.74 | 39.47 | 68.88 | 60.05 | 59.30 |
| 1.66 | 33.70 | 35.58 | 62.00 | 57.60 | 50.90 |
| 1.66 | 37.46 | 37.45 | 65.62 | 58.75 | 54.80 |
| **mean** | **36.8±2.6** | **37.5±2.0** | **65.5±3.4** | **58.8±1.2** | **55.0±4.2** |
| 2.10 | 27.64 | 37.10 | 52.87 | 57.40 | 57.00 |
| 2.10 | 32.36 | 37.45 | 47.40 | 55.63 | 52.85 |
| 2.10 | 31.50 | 35.15 | 50.03 | 56.77 | 55.15 |
| **mean** | **30.5±2.6** | **36.6±1.2** | **50.1±2.7** | **56.6±1.0** | **55.0±2.1** |

Table A.10: Ni concentration in plants, year 2001.

| **Lime dose** [g kg$^{-1}$] | **Ni concentration in plants** [mg kg$^{-1}$] | | | | |
|---|---|---|---|---|---|
| | **Sampling time** [d] | | | | |
| | **14** | **21** | **29** | **36** | **43** |
| 0 | Under detection limit | | | | |
| 0.41 | 136.9 | 99.25 | 127.75 | 107.00 | 105.40 |
| 0.41 | 142.2 | 109.10 | 116.30 | 98.30 | 95.12 |
| 0.41 | 128.8 | 107.43 | 102.17 | 101.78 | 100.08 |
| **mean** | **135.9±6.7** | **105.3±5.3** | **115.4±13.0** | **102.4±4.4** | **100.2±5.1** |
| 0.83 | 123.29 | 100.28 | 99.45 | 101.54 | 77.60 |
| 0.83 | 136.44 | 92.35 | 101.35 | 84.26 | 68.01 |
| 0.83 | 131.11 | 96.39 | 99.88 | 95.81 | 71.41 |
| **mean** | **130.3±6.6** | **96.3±4.0** | **98.6±3.6** | **93.9±8.8** | **72.3±5.0** |
| 1.24 | 73.00 | 38.65 | 52.10 | 48.69 | 41.30 |
| 1.24 | 77.20 | 51.20 | 43.90 | 34.30 | 38.97 |
| 1.24 | 74.80 | 47.16 | 47.04 | 44.51 | 40.09 |
| **mean** | **75.0±2.1** | **45.7±6.4** | **47.7±4.1** | **42.5±7.4** | **40.1±1.2** |
| 1.66 | 75.65 | 48.27 | 43.05 | 40.00 | 33.99 |
| 1.66 | 69.80 | 39.75 | 38.20 | 27.48 | 29.50 |
| 1.66 | 72.05 | 44.79 | 41.42 | 35.12 | 33.00 |
| **mean** | **72.5±3.0** | **44.3±4.3** | **40.9±2.4** | **34.2±6.3** | **32.2±2.3** |
| 2.10 | 65.45 | 39.77 | 39.66 | 35.55 | 32.55 |
| 2.10 | 53.92 | 31.24 | 34.75 | 26.23 | 27.60 |
| 2.10 | 62.67 | 37.80 | 37.22 | 33.83 | 29.89 |
| **mean** | **60.7±6.0** | **36.3±4.4** | **37.2±2.5** | **31.9±4.9** | **30.0±2.5** |

Table A.11: Ca concentration in plants, year 2000.

| **Lime dose** [g kg$^{-1}$] | **Ca concentration in plants** [mg g$^{-1}$] | | | | |
|---|---|---|---|---|---|
| | **Sampling time** [d] | | | | |
| | **14** | **21** | **29** | **36** | **43** |
| 0 | 13.5 | 10.4 | 4.8 | 4.6 | 8.2 |
| 0 | 10.7 | 13.5 | 9.2 | 8.4 | 9.7 |
| 0 | 15.0 | 14.7 | 10.9 | 8.9 | 10.9 |
| **mean** | **13.1±2.1** | **12.9±2.2** | **8.3±3.1** | **7.3±2.1** | **9.6±1.4** |
| 0.83 | 18.4 | 27.4 | 19.9 | 5.9 | 11.8 |
| 0.83 | 21.8 | 28.2 | 23.0 | 8.1 | 16.2 |
| 0.83 | 23.3 | 31.4 | 24.6 | 9.0 | 14.6 |
| **mean** | **21.2±2.5** | **29.0±2.1** | **22.5±2.4** | **7.7±1.5** | **14.2±2.2** |
| 1.24 | 14.8 | 23.6 | 15.4 | 7.1 | 13.3 |
| 1.24 | 19.2 | 28.5 | 19.9 | 10.0 | 16.0 |
| 1.24 | 21.2 | 31.6 | 21.7 | 11.9 | 16.3 |
| **mean** | **18.4±3.2** | **27.9±4.0** | **19.0±3.2** | **9.7±2.4** | **15.2±1.5** |
| 1.66 | 24.6 | 20.9 | 18.8 | 11.6 | 13.8 |
| 1.66 | 28.0 | 24.0 | 23.4 | 15.2 | 16.3 |
| 1.66 | 29.3 | 25.6 | 25.6 | 16.6 | 17.6 |
| **mean** | **27.3±2.4** | **23.5±2.4** | **22.6±3.4** | **14.5±2.5** | **15.9±1.9** |
| 2.10 | 26.0 | 24.1 | 22.7 | 12.8 | 14.8 |
| 2.10 | 28.3 | 27.1 | 26.1 | 15.0 | 18.0 |
| 2.10 | 29.7 | 28.6 | 28.6 | 15.7 | 19.0 |
| **mean** | **28.0±1.8** | **26.6±2.2** | **25.8±2.9** | **14.5±1.5** | **17.3±2.1** |

Table A.12: Ca concentration in plants, year 2001.

| **Lime dose** [g kg$^{-1}$] | **Ca concentration in plants** [mg g$^{-1}$] | | | | |
|---|---|---|---|---|---|
| | **Sampling time** [d] | | | | |
| | **14** | **21** | **29** | **36** | **43** |
| 0 | 3.5 | 3.3 | 1.3 | 1.3 | 1.4 |
| 0 | 3.3 | 2.3 | 1.2 | 1.1 | 1.0 |
| 0 | 2.7 | 2.8 | 1.4 | 1.2 | 1.2 |
| **mean** | **3.0±0.4** | **2.8±0.3** | **1.3±0.2** | **1.2±0.1** | **1.2±0.2** |
| 0.41 | 9.0 | 13.6 | 13.3 | 10.3 | 9.6 |
| 0.41 | 13.8 | 8.9 | 10.4 | 8.6 | 11.4 |
| 0.41 | 11.7 | 10.5 | 9.0 | 13.5 | 9.0 |
| **mean** | **11.5±2.4** | **11.0±2.4** | **10.9±2.2** | **10.8±2.4** | **10.0±1.2** |
| 0.83 | 22.0 | 15.5 | 11.5 | 7.5 | 6.7 |
| 0.83 | 15.8 | 11.2 | 9.0 | 12.3 | 6.8 |
| 0.83 | 18.3 | 12.3 | 10.5 | 8.7 | 8.7 |
| **mean** | **18.7±3.2** | **13.0±2.2** | **10.0±1.3** | **9.5±2.5** | **7.4±1.1** |
| 1.24 | 23.2 | 18.3 | 13.3 | 10.0 | 7.9 |
| 1.24 | 16.8 | 15.5 | 17.5 | 10.4 | 7.1 |
| 1.24 | 18.8 | 14.2 | 11.2 | 12.6 | 10.2 |
| **mean** | **19.6±3.3** | **16.0±2.1** | **14.0±3.2** | **11.0±1.4** | **8.4±1.6** |
| 1.66 | 26.5 | 22.8 | 23.0 | 19.3 | 18.3 |
| 1.66 | 24.3 | 21.8 | 20.5 | 22.0 | 21.0 |
| 1.66 | 23.0 | 25.0 | 20.7 | 18.7 | 18.6 |
| **mean** | **24.3±1.8** | **23.2±1.6** | **21.4±1.4** | **20.0±1.8** | **19.3±1.4** |
| 2.10 | 31.0 | 19.4 | 22.0 | 16.5 | 12.8 |
| 2.10 | 27.7 | 19.0 | 19.1 | 17.7 | 14.0 |
| 2.10 | 26.8 | 22.8 | 18.3 | 21.0 | 17.0 |
| **mean** | **28.5±2.2** | **20.4±2.1** | **19.8±1.9** | **18.4±2.3** | **14.6±2.0** |

Table A.13: *Transfer Factor (Ni)*, year 2000.

| **Lime dose** [g kg$^{-1}$] | ***Ni Transfer Factor*** | | | | |
|---|---|---|---|---|---|
| | **Sampling time** [d] | | | | |
| | **14** | **21** | **29** | **36** | **43** |
| 0 | Under detection limit | | | | |
| 0.83 | 14.6 | 10.6 | 18.8 | 13.2 | 19.1 |
| 0.83 | 14.6 | 14.7 | 18.5 | 14.4 | 14.5 |
| 0.83 | 19.4 | 15.6 | 17.0 | 11.2 | 16.6 |
| 1.24 | 12.4 | 12.9 | 13.2 | 14.6 | 15.4 |
| 1.24 | 11.7 | 14.1 | 13.9 | 13.9 | 11.1 |
| 1.24 | 11.9 | 12.0 | 13.0 | 14.1 | 14.7 |
| 1.66 | 8.0 | 8.7 | 16.6 | 11.0 | 13.0 |
| 1.66 | 7.4 | 7.3 | 12.8 | 12.1 | 13.2 |
| 1.66 | 7.7 | 6.7 | 11.4 | 9.7 | 10.4 |
| 2.10 | 5.1 | 6.8 | 11.9 | 9.9 | 12.0 |
| 2.10 | 7.1 | 7.9 | 8.5 | 11.3 | 10.4 |
| 2.10 | 6.5 | 6.3 | 11.2 | 11.9 | 10.1 |

Table A.14: *Transfer Factor(Ni)*, year 2001.

| **Lime dose** [g kg$^{-1}$] | ***Ni Transfer Factor*** | | | | |
|---|---|---|---|---|---|
| | **Sampling time** [d] | | | | |
| | **14** | **21** | **29** | **36** | **43** |
| 0 | Under detection limit | | | | |
| 0.41 | 25.3 | 17.8 | 24.3 | 19.8 | 18.8 |
| 0.41 | 25.8 | 19.7 | 22.1 | 18.4 | 17.2 |
| 0.41 | 23.6 | 20.6 | 19.4 | 19.0 | 18.2 |
| 0.83 | 23.7 | 19.5 | 18.2 | 19.5 | 14.7 |
| 0.83 | 26.1 | 17.4 | 19.1 | 16.1 | 13.0 |
| 0.83 | 25.2 | 18.5 | 19.0 | 18.4 | 13.7 |
| 1.24 | 14.6 | 7.8 | 10.4 | 9.9 | 8.5 |
| 1.24 | 15.7 | 10.0 | 8.9 | 7.0 | 7.9 |
| 1.24 | 15.1 | 9.9 | 9.5 | 9.1 | 8.2 |
| 1.66 | 15.7 | 9.9 | 9.0 | 8.4 | 7.0 |
| 1.66 | 14.2 | 8.2 | 8.0 | 5.7 | 6.1 |
| 1.66 | 14.9 | 9.5 | 8.5 | 7.3 | 6.8 |
| 2.10 | 13.5 | 8.5 | 8.3 | 7.4 | 6.7 |
| 2.10 | 11.8 | 6.6 | 7.3 | 5.6 | 5.8 |
| 2.10 | 12.8 | 7.8 | 7.8 | 7.1 | 6.3 |

Table A.15: Ni Uptake, year 2000.

| **Lime dose** [g kg$^{-1}$] | **Ni Uptake** [mg pot$^{-1}$] | | | | |
|---|---|---|---|---|---|
| | **Sampling time** [d] | | | | |
| | **14** | **21** | **29** | **36** | **43** |
| 0.83 | 0.036 | 0.067 | 0.253 | 0.370 | 0.955 |
| 0.83 | 0.019 | 0.065 | 0.404 | 0.481 | 0.755 |
| 0.83 | 0.033 | 0.067 | 0.278 | 0.450 | 0.986 |
| 1.24 | 0.024 | 0.054 | 0.301 | 0.815 | 1.199 |
| 1.24 | 0.024 | 0.058 | 0.401 | 0.927 | 1.265 |
| 1.24 | 0.029 | 0.049 | 0.344 | 0.744 | 0.967 |
| 1.66 | 0.013 | 0.041 | 0.434 | 0.900 | 1.064 |
| 1.66 | 0.016 | 0.036 | 0.450 | 0.967 | 1.010 |
| 1.66 | 0.109 | 0.034 | 0.544 | 0.740 | 0.840 |
| 2.10 | 0.011 | 0.041 | 0.400 | 0.856 | 1.137 |
| 2.10 | 0.012 | 0.036 | 0.469 | 1.063 | 0.936 |
| 2.10 | 0.013 | 0.036 | 0.608 | 0.965 | 1.218 |

Table A.16: Ni Uptake, year 2001.

| **Lime dose** [g kg$^{-1}$] | **Ni Uptake** [mg pot$^{-1}$] | | | | |
|---|---|---|---|---|---|
| | **Sampling time** [d] | | | | |
| | **14** | **21** | **29** | **36** | **43** |
| 0.41 | 0.041 | 0.074 | 0.278 | 0.829 | 0.759 |
| 0.41 | 0.039 | 0.083 | 0.552 | 0.579 | 0.813 |
| 0.41 | 0.029 | 0.076 | 0.349 | 0.404 | 0.599 |
| 0.83 | 0.041 | 0.088 | 0.263 | 1.172 | 0.995 |
| 0.83 | 0.049 | 0.080 | 0.686 | 0.845 | 1.555 |
| 0.83 | 0.035 | 0.077 | 0.478 | 1.248 | 1.060 |
| 1.24 | 0.023 | 0.038 | 0.292 | 0.647 | 0.756 |
| 1.24 | 0.027 | 0.067 | 0.408 | 0.521 | 0.831 |
| 1.24 | 0.019 | 0.033 | 0.357 | 0.768 | 0.608 |
| 1.66 | 0.038 | 0.035 | 0.426 | 0.652 | 0.606 |
| 1.66 | 0.024 | 0.043 | 0.321 | 0.409 | 0.568 |
| 1.66 | 0.009 | 0.056 | 0.298 | 0.632 | 0.680 |
| 2.10 | 0.022 | 0.049 | 0.373 | 0.602 | 0.608 |
| 2.10 | 0.024 | 0.051 | 0.399 | 0.482 | 0.558 |
| 2.10 | 0.016 | 0.033 | 0.495 | 0.674 | 0.647 |

Table A.17: Ca uptake, year 2000.

| **Lime dose** [g kg$^{-1}$] | **Ca Uptake** [mg pot$^{-1}$] | | | | |
|---|---|---|---|---|---|
| | **Sampling time** [d] | | | | |
| | **14** | **21** | **29** | **36** | **43** |
| 0 | 3.92 | 5.20 | 8.11 | 7.22 | 29.93 |
| 0 | 3.74 | 5.67 | 24.56 | 26.46 | 27.83 |
| 0 | 3.90 | 7.20 | 23.45 | 21.27 | 35.21 |
| 0.83 | 6.26 | 20.00 | 46.56 | 23.77 | 90.86 |
| 0.83 | 4.79 | 22.84 | 85.56 | 40.09 | 111.46 |
| 0.83 | 7.22 | 22.29 | 73.80 | 52.29 | 123.52 |
| 1.24 | 5.03 | 19.35 | 60.06 | 70.29 | 172.77 |
| 1.24 | 7.10 | 25.90 | 111.24 | 113.00 | 241.76 |
| 1.24 | 9.11 | 24.01 | 100.03 | 104.72 | 178.16 |
| 1.66 | 8.61 | 22.15 | 118.63 | 174.00 | 247.71 |
| 1.66 | 13.16 | 24.72 | 170.12 | 255.36 | 323.55 |
| 1.66 | 8.49 | 23.96 | 212.22 | 209.16 | 271.92 |
| 2.10 | 10.66 | 26.75 | 171.83 | 190.97 | 295.26 |
| 2.10 | 10.18 | 26.01 | 258.13 | 286.65 | 318.96 |
| 2.10 | 12.77 | 29.70 | 347.49 | 266.90 | 419.71 |

Table A.18: Ca uptake, year 2001.

| **Lime dose** [g kg$^{-1}$] | **Ca Uptake** [mg pot$^{-1}$] | | | | |
|---|---|---|---|---|---|
| | **Sampling time** [d] | | | | |
| | **14** | **21** | **29** | **36** | **43** |
| 0 | 0.77 | 1.25 | 2.43 | 2.84 | 5.36 |
| 0 | 0.75 | 1.05 | 3.06 | 3.20 | 4.46 |
| 0 | 0.72 | 1.26 | 4.56 | 4.28 | 3.94 |
| 0.41 | 2.70 | 10.20 | 28.99 | 79.82 | 69.21 |
| 0.41 | 3.86 | 6.76 | 49.40 | 50.65 | 97.47 |
| 0.41 | 2.69 | 7.45 | 30.78 | 53.59 | 53.91 |
| 0.83 | 7.26 | 13.64 | 31.97 | 86.62 | 85.96 |
| 0.83 | 5.68 | 9.74 | 60.93 | 123.49 | 115.53 |
| 0.83 | 4.94 | 9.84 | 50.29 | 113.36 | 129.19 |
| 1.24 | 7.42 | 18.11 | 74.48 | 133.00 | 144.57 |
| 1.24 | 5.88 | 20.15 | 162.75 | 158.08 | 151.37 |
| 1.24 | 4.88 | 10.08 | 85.12 | 217.35 | 154.63 |
| 1.66 | 13.51 | 16.41 | 227.70 | 314.59 | 326.28 |
| 1.66 | 8.50 | 23.54 | 172.20 | 327.80 | 404.25 |
| 1.66 | 2.99 | 31.50 | 149.04 | 336.60 | 383.34 |
| 2.10 | 10.23 | 23.86 | 206.80 | 279.67 | 239.23 |
| 2.10 | 12.19 | 31.35 | 219.65 | 325.85 | 282.94 |
| 2.10 | 6.70 | 19.83 | 243.39 | 418.53 | 368.39 |

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