Clay Characteristics Affecting the P, K and Mn Dynamics in Peat-Clay Substrates

Von der Naturwissenschaftlichen Fakultät
der Gottfried Wilhelm Leibniz Universität Hannover
zur Erlangung des Grades

DOKTORIN DER GARTENBAUWISSENSCHAFTEN

Dr. rer. hort.

genehmigte Dissertation
von
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geboren am 16. Juli 1983 in Oldenburg (Oldb)

2014

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Tag der Promotion: 20.02.2014

Zusammenfassung

Tonminerale sind wichtige Bestandteile von gartenbaulichen Kultursubstraten. Sie beeinflussen sowohl die physikalischen als auch die chemischen Eigenschaften der Substrate positiv. Durch die Zugabe von Ton können z.B. die Benetzbarkeit und die Bindigkeit von Substraten, sowie die Pufferfähigkeit für die essentiellen Pflanzennährstoffe Phosphor (P) und Kalium (K) erhöht werden. Die Pufferung von P und K ist ein wichtiges Qualitätskriterium von Substraten, um eine ausgeglichene und stabile Nährstoffversorgung der Pflanze zu gewährleisten.

Tone können jedoch sehr stark in ihrer mineralogischen Zusammensetzung und dadurch auch in ihrer Fähigkeit, P und K reversibel zu binden, variieren. Bis heute wurden keine einheitlichen Kriterien für die Bewertung von Tonen definiert und die Auswahl und Zugabe der Minerale erfolgt oft auf Grundlage von Erfahrungswerten. Daher war es Ziel dieser Studie, die P- und K-Sorption und Desorption verschiedener Tone mit geeigneten Methoden zu beschreiben und deren unterschiedliche Auswirkungen auf die P- und K-Aufnahme von Pflanzen zu untersuchen. Hierzu wurden mögliche Fehler bei der Nachdüngung der Pflanzen simuliert.

Aufgrund ihrer Genese können Tone aber auch Elemente enthalten, die in zu hohen Konzentrationen für die Pflanze toxisch wirken können. Hierzu gehört auch der Mikronährstoff Mangan (Mn). Um die Gefahr von Mn-Toxizität bei Topfpflanzen zu vermeiden, wurde von einer Gütesicherung für Substratausgangsstoffe ein Grenzwerte für \`aktives Mn´ (Summe aus austauschbarem und leicht reduzierbarem Mn) festgesetzt. Dieser Grenzwert wurde im Rahmen dieser Arbeit in Vegetationsexperimenten mit unterschiedlichen Torf-Ton-Gemischen unter verschieden Wachstumsbedingungen validiert. Außerdem wurde der Einfluss von Silizium (Si), welches ebenfalls in großen Mengen von Tonen abgegeben wird, auf das Auftreten der Mn-Toxizität untersucht. Dies geschah anhand von Nährlösungsexperimenten.

Die zentralen Ergebnisse dieser Arbeit sind:

(I) Die P- bzw. K-Bindungskapazität der Tone korrelierte sehr stark mit den Gesamtgehalten an oxalat-löslichem Eisen und Aluminium bzw. der Kationenaustauschkapazität. Mit Hilfe von Sorptionsisothermen konnte das P- bzw. K-Sorptionsverhalten der Tone detailliert beschrieben werden. Für ein erstes Screening eigneten sich daneben auch Schüttelexperimente mit einer Zugabe einer hohen Konzentration des jeweiligen Nährstoffs.

(II) Eine höhere P- bzw. K-Bindungskapazität der eingesetzten Tone führte zu niedrigeren P- und K-Konzentrationen in der Substratlösung der jeweiligen Torf-Ton-Mischungen und umgekehrt, obwohl die Gehalte an $CaCl_2$-austauschbarem P und K sich nicht unterschieden. Hierdurch könnte insbesondere bei Freilandkulturen die Gefahr von Nährstoffauswaschung reduziert werden.

(III) Es konnte ebenfalls beobachtet werden, dass höhere P- bzw. K-Bindungskapazität der Tone in den Torf-Ton-Mischungen zu einer verbesserten Pflanzenwachstum und erhöhten P- bzw. K-Gehalten in den Pflanzen führte, wenn diese nicht ausreichend mit den jeweiligen Nährstoffen nachgedüngt wurden. Die Nachlieferungsrate von an den Tonen gebundenem P und K reichte jedoch nicht aus, um ein optimales Wachstum der Pflanzen zu erreichen.

(IV) Der Grenzwert für \`aktives Mn´ stellte sich als nicht gerechtfertigt heraus, da keinerlei Mn-Toxizitätssymptome bei Pflanzen beobachtet werden konnten, auch wenn diese in Torf-Ton-Substraten mit stark erhöhten Mn-Konzentrationen kultiviert wurden. Dies änderte sich auch nicht bei niedrigem Substrat pH-Wert (< 4.5) oder bei sinkendem Redoxpotential durch hohe Substratfeuchte – beides Bedingungen, die eine erhöhte Mn-Verfügbarkeit begünstigen.

(V) Das \`aktive Mn´ der Tone und der gemischten Substrate korrelierte nur schwach mit den erzielten Mn Gehalten in der Pflanzensubstanz oder der Mn-Konzentration in der Substratlösung der jeweiligen Torf-Ton-Mischungen.

(VI) Die Pflanzen tolerierten deutlich höhere Mn-Konzentrationen in der Porenlösung der unterschiedlichen Substrate ohne toxische Reaktionen zu zeigen als in Nährlösungsversuchen. Es konnte gezeigt werden, dass die Zugabe von Si zu der Nährlösung die Mn-Toleranz der Pflanzen deutlich erhöhte. Da auch in der Porenlösung der Torf-Ton-Substrate erhöhte Si-Konzentrationen gemessen wurden, konnte so die verbesserte Toleranz der Pflanzen in Ton-haltigen Substraten erklärt werden.

Schlagworte: Substrattone, Nährstoffpufferung, Aktives Mangan

Abstract

Clay minerals are important components of horticultural substrates and positively affect various chemical and physical substrate characteristics. The clay amendments can increase the wettability and the coherence of the substrate and lead to an enhanced nutrient buffering, especially of the essential plant nutrients phosphorus (P) and potassium (K). The buffering of P and K is a very important substrate quality trait in order to guarantee a balanced and stable nutrient supply of the plants.

Clay minerals may vary strongly in their mineralogical composition and their ability to bind P and K. Up to now no proven standards for the evaluation of clay materials for the use in growing media are available and selection and amendment of clays is done mostly empirically. The aim of this study was to characterize the P and K adsorption and desorption behavior of different substrate clays by suitable methods, and to evaluate the significance for plant P and K uptake at varying levels of P and K fertigation.

Due to their genesis clays may also contain elements which may become toxic to plants when occurring in excess, including the micronutrient manganese (Mn). Therefore, a threshold for active Mn (sum of exchangeable and easily reducible Mn) in substrate clays was given in quality protocols for substrate raw material in order to prevent toxic reactions of pot plants. This threshold value was validated in experiments with peat-clay blends under different growing conditions. Furthermore, the effect of silicic acid, which is also dissolved from the clays in high amounts, on the occurrence of Mn toxicity was investigated in a nutrient solution experiment.

Central results of this work are:

(I) The P and K sorption of different clays highly correlated with the oxalate extractable iron and aluminium contents and the cation exchange capacities, respectively, and could be well-characterized by adsorption isotherms. An extraction with a single high dose of the respective nutrient was well suited for a quick and easy comparison of the P- and K- adsorption between several clays.

(II) A higher P and K sorption capacity of the clays resulted in a lower P and K concentration in the pore solution of mixed substrates and vice versa, while the $CaCl_2$-extractable nutrient concentrations were the same, reducing the risk of nutrient leaching especially in open-field cultivation systems

(III) Without fertigation (P or K), a higher sorption capacity of the clays also led to an enhanced plant yield and to higher nutrient concentrations in the shoots, but the release rates of the nutrients from the clay were too low to ensure optimal plant growth.

(IV) The threshold value for active Mn in substrate clays was considered not justified, as plants grown in substrates amended with Mn-rich clays did not develop any Mn toxicity even at a low redox potential due to a high substrate moisture or low pH conditions (< 4.5) which are known to increase the Mn availability.

(V) The extracted amounts of active Mn did not well reflect the Mn concentrations in plant dry matter and substrate solution.

(VI) Plants tolerated higher Mn concentrations in the substrate pore solution compared to nutrient solution without toxicity symptoms. In nutrient solution the application of silicic acid clearly diminished Mn toxicity, explaining the high Mn tolerance of plants in peat-substrates where high concentrations of silicic acid in the substrate solution were observed.

Keywords: substrate clays, nutrient buffering, active manganese

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Abbreviations

AAS	atomic adsorption spectroscopy
AEC	anion exchange capacity
Al	aluminium
b	buffer power
Ca	calcium
CAL	calcium -acetate-lactate
CAT	calcium-chlorite + DTPA (diethylene triamine pentaacetic acid)
CEC	cation exchange capacity
Cu	copper
D_e	effective diffusion coefficient
DGT	Diffusive Gradient in Thin-Films
DL	Doppellaktat
D_L	diffusion coefficient in water
DM	dry matter
DOM	dissolved organic matter
DPS	degree of phosphorus saturation
DüMV	Düngelmittelverordnung (fertilizer regulation in Germany)
f	impedance factor
Fe	iron
$\sum Fe_{ox}+Al_{ox}$	sum of oxalate extractable iron and aluminium
ICP-MS	inductively coupled plasma-mass spectroscopy
K	potassium
K_{acet}	NH_4OAc-extractable K concentration
K_{CAL}	CAL-extractable K concentration
K_{CAT}	CAT-extractable K concentration
ΔK	adsorbed or desorbed K amount
K_e	K concentration in the equilibrium solution
K_{e-0}	K concentration in the equilibrium solution, where $\Delta K = 0$
K_{max}	maximum K sorption capacity
K_{perc}	K concentration in the percolation solution
K_{sol}	K concentration in the substrate solution
L_e	equilibrium constant of adsorption (Langmuir constant)
Mg	magnesium
Mn	manganese
Mn_{act}	active Mn (sum of exchangeable and easily reducible Mn)

Mn_{sol}	Mn concentration in the substrate solution
N	nitrogen
norm. sol	nutrient solution prepared from distilled water
P	phosphorus
PAR	photosynthetic active radiation
P_{CAT}	CAT-extractable P concentration
PCDD	polychlorinated dibenzo-dioxins
ΔP	adsorbed or desorbed P amount
P_{des}	desorbed P
P_{e}	P concentration in the equilibrium solution
P_{e-0}	P concentration in the equilibrium solution, where $\Delta P = 0$
peat sol.	nutrient solution prepared by by mixing white peat with water and filtering
P_{init}	oxalate extractable P initially adsorbed onto Fe- and Al-oxides
P_{max}	maximum P sorption capacity
P_{new}	P adsorbed by the clays in the batch experiments
P_{sol}	P concentration in the substrate solution
P_{tot}	total P sorption capacity calculated from $P_{new} + P_{init}$
RHP	Regeling Handelspotsgrondon (Dutch Foundation for Growing Media)
RLD	root length density
Si	silicon
$Si(OH)_4$	silicic acid
Si_{sol}	Si concentration in the substrate solution
SSA	specific surface area
θ	volumetric water content

Abbreviations of the used clay minerals

B	bentonitic clay
M	clay mixture
S	saprolitic clay
U	relocated clay
W	clay from Sinntal/Vogelsberg

General Introduction

Today, horticultural substrates have to fulfill highest demands with regard to automated handling and fertigation. Clay is an important substrate component (up to 20-30 vol-%) and positively affects various chemical and physical substrate parameters (e.g. buffering of phosphorus and potassium, wettability, coherence of the substrate). Up to now no proven standards for the evaluation of clay materials for the use in growing media are available. The selection and amendment of clay is done mostly empirically, based on data of mineralogical and chemical composition or simply by experience. The definition of suitable methods for the classification of clays would clearly improve the safety of the products and the plant cultivation.

In the presented study the main focus is laid upon the effect of clay amendments on the chemical characteristics of substrates. However, both, physical and chemical properties are of high importance for an optimal plant growth and they very often interact. Therefore, the most important physical characteristics of horticultural substrates and their modification by the amendment of clay are also described in this introduction.

I.1 Horticultural substrates in pot plant production

A horticultural substrate mainly has to meet the following demands: fixation of the plant, supply of the plant with air, water and nutrients, and guarantee of stable growing conditions throughout the duration of plant cultivation (*Verhagen*, 2009). It is essential that the physical, chemical and biological conditions adjusted at the beginning of plant culture remain constant during the cultivation.

White peat is one of the main components of most horticultural substrates for pot plant production and is regarded as a reference medium with almost optimal physical and chemical properties (*Rivière* and *Caron*, 2001). It shows a high stability over long time periods, optimal water and air retention and a high exchange capacity for divalent cations, but it has only a poor buffering capacity of anions and monovalent cations.

Additionally, a diversity of different other materials are also used as substrate constituents, either in pure form or mixed with other components, including compost material, bark mulch, coco fibres, coir and mineral components, such as clay (*Penningsfeld*, 1983).

I.1.1 Usage of clay minerals in horticultural growing media

About 50 years ago peat-clay mixtures were developed by Professor Fruhstorfer in Germany. The mixtures are still known as ‘Fruhstorfer Erde’ or ‘Einheitserde’ and contain up to 300 kg clay m^{-3} substrate (www.einheitserde.de; as at December 2nd; 2013). Nowadays, much lower clay application rates (20-50 kg m^{-3}) are also common with other producers (e.g. Klasmann-Deilmann GmbH, Germany). Additionally, the grade of clay preparation can be varied, including fine dry powdery products, coarse dry granulates and coarse fresh shredded clay.

The optimal grade and amount of clay in a substrate depend mainly on the future application of the mixed substrate, e.g. tray or press-pot substrates, propagation substrates or pot substrates adapted to specific crops.

The clay amendment should improve the physical and chemical substrate properties and compensate for possible differences in growing conditions or the handling of the plants (e.g. location in the greenhouse, irrigation and fertigation).

I.1.2 Improvement of physical substrate properties by clay amendments

In general the effects of clay on the physical behavior of a substrate is mainly influenced by the grade and the amount of the amended products and to a lesser degree by the type of the minerals and the actual clay content (fraction < 2 µm) (*Verhagen*, 2004). For improving the various physical properties of a substrate small amounts (<40 kg m^{-3}) of finely ground clay are already effective (*Schellhorn* et al., 2013).

The amendment of clay can have the following positive effects:

- Increasing the wettability: A fast re-wetting of dried out substrates is of high importance especially with automated irrigation, e.g. ebb and flow irrigation. Pure peat exposes strong hydrophobic properties when getting dry (*Kukkonen* et al., 2011). The addition of clay leads to a coating of the peat surface resulting in hydrophilic properties (Fig. 1) and a refined pore structure and thus increases the velocity of capillary water transport (*Verhagen*, 2004). However, too high amounts of clay additives can negatively affect the water transport in the substrate.
- Decreasing the amount of easily available water: A restriction of the amount of easily available water is sometimes used for the formation of compact plants, as plants have to exert greater effort to take up water. *Verhagen* (2004) could show that the amount of easily available water in the substrate was reduced by the usage of a finely ground clay.
- Improving the supply with oxygen: *Dresbøll* (2011) observed higher levels of oxygen in peat substrates mixed with finely ground clay (40 kg m^{-3} peat-substrate) than in pure peat right after ebb and flow irrigation. In pure peat, the transport of water from the pot bottom to substrate surface can be reduced after ebb and flow irrigation due to the high proportion of large pores in the peat, resulting in anoxic conditions in the respective lower zones.
- Increasing the coherence of the substrates: Today, pot plants are often handled automatically by special robots. Young plantlets are mostly transplanted by pricking

robots and not handled individually. Therefore, a stable root ball is of high importance. The addition of clay could enhance the coherence of the substrate without negatively affecting its water and air capacity (*Schellhorn* et al., 2013).

- Increasing the weight of the root ball: A high stability of the plant container due to a higher weight of the substrate is advantageous, especially when plants are moved automatically in the greenhouse or cultivated outdoor and affected by wind.

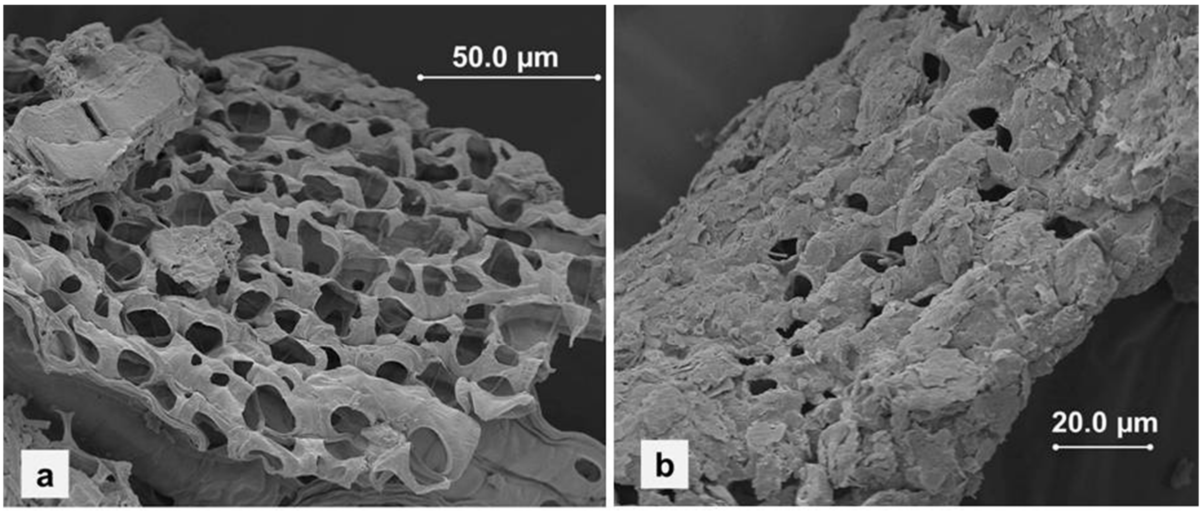

Fig. I.1: Scanning electron microscope (SEM) image of (a) a leaflet of Sphagnum moss from a peat-based growing medium without clay and (b) amended with a saprolitic clay (30 kg m^{-3} peat). The dark holes in the leaflet are sphagnum-typical commissural pores. Single platelets of layer silicates can be clearly seen on the surface of the leaflet.
Source: Stefan Dultz; Institute of Soil Science; Leibniz Universität Hannover, Germany.

I.1.3 Improvement of chemical substrate properties by clay amendments

The buffering of nutrients is a very important quality trait of horticultural substrates in order to guarantee a balanced and stable nutrient supply of the plants. A buffered substrate can absorb nutrients in large amounts by binding and is able to release them again in the substrate solution when plants deplete the nutrient concentration. Pure peat generally shows a higher CEC than most clay minerals but mostly divalent cations, such as Ca^{2+} and Mg^{2+} are bound, whereas the binding capacity for monovalent cations, such as potassium (K), and anions, such as phosphate (P) is often very low. The amendment of clay can increase the buffering capacity of the peat substrate especially for K and P.

A high nutrient buffering capacity may have the following positive effects:

- Leveling of cultivation conditions: Optimal conditions adjusted at the beginning of plant culture remain constant during the cultivation and negative effects of factors such as water quality, fertigation (concentration, composition, and time point), and climatic conditions can be leveled. Furthermore, a good quality of the plants for post-harvest situations (at the supermarket or end-consumer), where no further fertilization takes place, can be ensured.

- Diminishment of nutrient losses due to leaching: Especially, in outdoor cultivation systems leaching can lead to high nutrient losses and a contamination of the ground water. But also in greenhouse production leaching can be problematic and lead to salinity if the irrigation water is recycled. An application of clay to white peat can clearly reduce losses of P and K due to leaching without causing severe nutrient immobilization (*Owen* et al., 2007; *Rosolem* et al., 2010; *Kukkonen* et al., 2011).
- Alleviation of excessive nutrient concentrations: High nutrient concentrations in the substrate solution may also lead to toxic reaction of sensitive plant species. The Christmas rose, *Helleborus niger*, for example, was shown to be very sensitive to high concentrations of P in the substrate solution, indicated by toxic symptoms and leaf shedding (*Dombrowski*, 2008). The application of clay to the growing medium can clearly reduce the nutrient concentration in the substrate solution and thus prevent nutrient toxicity or deficiency of competing ions (*Jakobsen*, 1993).
- Formation of plants: A continuous restricted P supply may hinder extensive growth of plants and may be a possible strategy for the formation of compact plants, decreasing the need for chemical growth regulators (*Verhagen*, 2004).

I.2 Phosphorus and potassium buffering in peat-clay substrates

Phosphorus and potassium are the two major plant nutrients, whose availability to plants is highly affected by the addition of clay minerals to peat-substrates. Therefore, their binding forms and their mobility in soils and clays are explained in more detail in the following section.

I.2.1 Phosphorus and potassium forms in soils and clays minerals

Phosphorus in soils is contained in both organic and inorganic forms. Phosphate ions can form solid phases of low solubility with different metal cations and the type of mineral formed is mainly dependent on the soil pH. In neutral to alkaline soils, P precipitates as calcium (Ca) phosphates and under acidic conditions mainly iron- (Fe) and aluminium (Al) phosphates are formed (*Holford*, 1997; *Hinsinger*, 2001). Thus, the solubility of phosphate is generally highest in the range between pH 5 - 6.

Furthermore, P is adsorbed to the surface of layered clay minerals or to Fe and Al oxides, oxyhydroxides and hydroxides, which are associated with clay minerals. The phosphate anion specifically binds to the oxides by ligand exchange reactions and due to its high specificity the bonding between P and oxides is hardly influenced by the occurrence of other anions such as nitrate, chloride or sulfate (*Weng* et al., 2012). Additionally, P interacts with the charged oxide surface by electrostatic bondings (*Antelo* et al., 2005, 2007). This interaction between the negatively charged phosphate ion and the oxide is higher at low solution pH, because of an increasing protonation of the solid phase resulting in a positive surface charge (*Gao* and *Mucci*, 2001; *Hinsinger*, 2001; *Antelo* et al., 2005).

Due to this high reactivity of phosphate ions with the various soil constituents the P concentration in the soil solution (P_{sol}) is often less than 10 µM, which is one of the major factors limiting plant growth in many ecosystems (*Barber*, 1995; *Raghothama*, 1999).

As for P, K can only be taken up by plants as dissolved K^+ from the soil solution, but the concentration is often low (*Sparks*, 1987). Most of the K in soils is integrated within the crystal structures of clay minerals (“structural K”) and only very slowly released by weathering of the mineral or ion exchange reactions (*Sparks*, 1987). Furthermore, K is associated with 2:1 clay minerals and here it is held between the layers of the clay minerals (“interlayer K”), occurring at the edge of expanding interlayers (“edge K”) or loosely adsorbed to the negatively charged surface of the minerals (“planar K”). The different K binding forms are in equilibrium with each other. “Planar” and “edge K” can be rapidly exchanged by ammonium acetate (NH_4OAc) (“exchangeable”) while the “interlayer K” is regarded as “non-exchangeable”. The K adsorption is generally enhanced with increasing K concentrations in the solution and a high negative layer charge of the clay mineral, but is negatively influenced by competing cations, mainly Ca and Mg (*Huang*, 2005; *Simonsson* et al., 2009).

Traditionally, the fixation of applied K in interlayers of clay minerals was considered to reduce the plant available K amount, resulting in an enhanced K fertilization of agricultural soil beyond immediate needs (*Schneider* et al., 2013). Nowadays, there is a broad consensus, that non-exchangeable K also contributes to plant nutrition (*Meyer* and *Jungk*, 1993; *Moritsuka* et al., 2004) and K adsorption is a favorable factor limiting K leaching (*Jalali* and *Kolahchi*, 2008; *Rosolem* et al., 2010).

I.2.2 Phosphorus and potassium supply to the roots

The plant availability of P and K to plants depends on their dissolved amounts, the replenishment of adsorbed P and K to the soil solution and their mobility in the soil (*Holford*, 1997; *Jungk* and *Claasen*, 1997).

The transport of P and K towards the root occurs mainly by diffusion and only to a small extent by mass-flow (*Nair* et al., 1991; *Claassen* and *Steingrobe*, 1999). The ion diffusion is mainly dependent on the concentration gradient in the soil induced by the nutrient uptake at the root surface and is a function of the diffusion coefficient of the ion in water (D_L), the volumetric water content (θ), the impedance factor (*f*), and the buffer power (*b*) of the soil (equation 1) (*Nye*, 1966; *Rengel*, 1993).

$$D_e = D_L \theta f * \left(\frac{1}{b}\right), \qquad (1)$$

where D_e is the effective diffusion coefficient of the ion. The buffer power describes the relationship between the concentration of ions reversibly adsorbed onto the binding sites of the soil and the ion concentration in the soil solution (*Rengel*, 1993). Due to the high adsorption of P and K onto clay minerals, their concentration in the soil solution is often very low, especially near the root surface, and *b* considerably high, but often *b* of P is 10 to 100 fold higher than of K (*Khandan-Mirkohi*, 2009).

The availability of P and K to plants does not only depend on soil factors but also on plant factors. Plants can adapt to low nutrient levels by an enhanced root length density (*RLD*) and increased root hair length and they have the ability to chemically mobilize bound nutrients by mechanisms such as the release of H^+ or organic anions (*Raghothama*, 1999; *Trehan* and *Sharma*; 2002).

However, there are great differences between the significance of the plant and soil factors affecting the P and K availability between mineral soils and horticultural substrates. The buffer power of P was reported to be much lower in peat-based substrates compared to mineral soils leading to a higher P mobility in substrates (*Khandan-Mirkohi* and *Schenk*, 2008), whereas the buffer power of potassium is not highly different in soils and substrates (*Khandan-Mirkohi,* 2009).

Furthermore, the *RLD* of pot plants is a magnitude higher than for field-grown plants, since the volume available for root growth is strongly restricted in a pot. Thus, the depletion zones around the roots overlap, which leads to a utilization of the whole substrate volume already at early stages of plant growth (*Khandan-Mirkohi* and *Schenk*, 2009). In contrast, space is not restricted under field conditions and plants use only about 20% of the soil volume around roots for nutrient acquisition (*Jungk* and *Claassen*, 1997; *Claassen* and *Steingrobe*, 1999). Thus, the nutrient supply per unit substrate volume has to be much higher for pot plants compared to field conditions, since the substrate volume, and therefore also the absolute amount of nutrients available for plant uptake, is limited. Furthermore, the growth rates of plants are often enhanced under greenhouse conditions leading to an increased nutrient demand per time unit.

I.2.3 Determination of the P- and K adsorption and desorption of clay minerals

The P- and K adsorption capacity of clay minerals is usually determined by sorption isotherms, which relate the nutrient adsorption to the concentration remaining in solution by shaking clay samples with solutions of increasing nutrient concentrations (*Holford*, 1997). The slope of the isotherm is an indicator of the buffering capacity of the sample and additionally information about the P- and K- desorption, respectively, can be obtained from the amount of labile P and K. Because the K adsorption is strongly influenced by the concentration of other cations, often K/Ca exchange isotherms are established which may also be standardized on the *CEC* (*Dultz* and *Pesci*, 2000). The sorption data are commonly fitted to the Langmuir or Freundlich equations for a description of the sorption characteristics of the clay. The Freundlich equation implies that the energy of adsorption decreases exponentially with increasing saturation of the surface, whereas the Langmuir equation is based on the assumption that the energy of adsorption does not vary with the surface coverage and allows a calculation the adsorption maximum (*Bache* and *Williams*, 1971).

A faster and easier comparison of the adsorption capacity of many different samples can also be obtained by an application of a single high dose of the nutrient and the subsequent measurement of the amount adsorbed by the sample (*Bache* and *Williams*, 1971).

Furthermore, it is necessary to quantify the P and K desorption of a clay as it also highly influences the soil solution nutrient concentration. The desorption can be described by a desorption isotherm (*Sato* and *Comerford*, 2006), using different extraction procedures such as increasing dilution or repeated extractions. Furthermore, ion exchange resins or membranes can be used (*Bhatti* and *Comerford*, 2002). Another possibility to determine the releasable P and K amounts is a constant percolation of the clay sample with a P- and K-free solution (*Meyer* and *Jungk*, 1993).

I.2.4 Characterization of the P and K availability in substrates

The estimation or prediction of the P and K availability to plants in a soil or substrate is generally problematic, because the identification and measurement of the quantity of solid phase P and K which possibly buffer the solution concentration is difficult (*Holford*, 1997). However, potentially plant available nutrient amounts in substrates are determined with a large variety of methods differing in the extractants used, the pre-treatments and the sample preparation procedures. Some of the methods are specifically used for the extraction of a certain element while others aim at simultaneously determining many different elements.

The easiest way of determination is the usage of a single-step chemical extraction with water, acids, bases, salts, buffered solutions or ion exchangers. The weakest extraction power is achieved by the usage of a water extract with a certain soil:solution ratio, e.g. the 1:2 volume extract described by *Sonneveld* and *van den Ende* (1971). In Germany, the available P and K amounts of agricultural soils are commonly extracted with Doppellactat (DL) at pH ~3.5 (*Egner* et al., 1960), Ca-acetate-lactate (CAL) at pH ~4.1 (*Schüller*, 1969) or NH_4OAc, which is used worldwide for the characterization of the exchangeable soil K. The isotopically exchangeable P is can considered as available to plants, too (*Frossard* et al., 1994; *Hamon* et al., 2002). In horticultural substrates also CAT ($CaCl_2$ + DTPA) is used, which extracts at the pH of the substrate in the ratio 1:8 (v/v) (*Alt* and *Peters*, 1992). Several other chemical extractions methods are also common, e.g. Bray I (*Bray* and *Kurtz*, 1945), Olsen-P (*Olsen* et al., 1954), Mehlich III extraction (*Mehlich*, 1982), and others. However, the relationships between the determined nutrient concentrations and plant yields are often weak (*Abdu*, 2006).

Furthermore, ion-exchange resins or membranes can be used for the estimation of available amounts of N, P, K, Mg, Ca and several micronutrients (*van Raij* et al., 1986; *Abdu*, 2006). The principle of the method is that the targeted ion is adsorbed at the surface of the resin or membrane while another primary adsorbed ion is released and thus exchanged. By this, naturally occurring exchange reaction in the soil are simulated and a constant sink for the targeted ion is created.

I.3 Silicon release from clays

Clay minerals are also one of the major silicon (Si) pools in soils since Si is contained in crystalline silicates and chemically adsorbed by iron and aluminum oxides and hydroxides (*Sommer* et al., 2006). In the soil solution at pH < 9, Si is present as silicic acid, $Si(OH)_4$, which is also the form taken up by plants, in concentrations from 2.5 and 20 mg L^{-1} (*Epstein*, 1994). Plants contain Si in different amounts ranging from ~0.5 to 100 mg g^{-1} shoot dry weight and can be classified as Si accumulators when they contain more than 10 mg Si g^{-1} shoot dry weight (*Epstein*, 1999). Although Si is not considered essential for most plants, it has a number of beneficial effects, including an enhanced resistance to fungal and bacterial diseases and the diminishment of various abiotic and chemical stresses (*Epstein*, 1999). An alleviative function of Si on manganese (Mn) toxicity has been observed in Si accumulating plant species such as rice, barley and pumpkin, and also in non-accumulators such as common bean (*Ma*, 2004).

I.4 Harmful elements in clays

Due to their genesis clays may also contain elements in high concentrations which may become problematic for plant production, such as different heavy metals. Therefore, thresholds for those elements, including manganese, iron and boron, in substrate clays are given by the Dutch Foundation for Growing Media (*RHP = Regeling Handelspotgrondon; Stichting RHP, 2010*). One of the elements which may become toxic to plants when occurring in excess is the micronutrient Mn.

Under aerobic conditions the Mn concentration in the soil solution is generally very low, since sparingly soluble Mn(III) and Mn(IV) oxides on the surface of clay minerals are dominating

(*Mundus* et al., 2012). At pH <5.5 or under anaerobic conditions Mn oxides can be reduced increasing the concentration of Mn(II) in the soil solution, which is also the form taken up by plants (*Hue*, 1988; *Millaleo* et al., 2010). Therefore, Mn toxicity can occur in soils or substrates with high Mn reserves at low pH values and under reducing conditions.

However, no experimental data exist which describe the direct relationship between extractable Mn contents of clay minerals and the occurrence of Mn toxicity in pot plants, justifying a certain threshold value.

The estimation of plant available Mn is very difficult because of the high redox sensitivity of solution Mn (*Mundus* et al., 2012). It can roughly be differentiated between water-soluble Mn, exchangeable Mn and active Mn (sum of exchangeable and easily reducible Mn; *Baser* and *Saxena*, 1971), while the latter is considered to represent the amount of Mn in a soil which is available to plants even under reducing conditions (*Schachtschabel*, 1957). Furthermore, the technique of Diffusive Gradients in Thin-films (DGT) has been proposed as an alternative to the soil extractions with solutions (*Davison* et al., 2005), but the Mn concentrations measured with the DGT technique and plant-tissue concentrations under aerobic conditions correlated only weakly (*Mundus* et al., 2012).

However, Mn soil tests do often not properly reflect the actual nutrient availability since soil properties, plant species, environmental conditions and temporal fluctuations over a growing season are not considered (*Baser* and *Saxena*, 1971; *Başar,* 2009; *Mundus* et al., 2012).

I.5 Significance and scope of the study

Based on the literature and the presented knowledge, this study aims at characterizing properties of clay minerals, which influence their capacity for the buffering of the nutrients P and K. Methods, which are appropriate for the description of the P and K adsorption and desorption behavior of substrate clays and which are also easily applicable in horticultural practice, are identified, enabling a reliable selection of suitable clays. Furthermore, the significance of the clay mediated nutrient buffering for the nutrient supply of plants in peat-clay substrates is investigated and its contribution to the safety of plant cultivation is evaluated by a simulation of possible errors in the P and K fertigation. The influence of different clay amendments on the P and K buffering of peat-substrates is presented in chapters 1 and 2, respectively.

The potential danger of using Mn-rich clays in horticultural substrates and the method of \`active Mn´ extraction for the determination of plant available Mn are evaluated in the study presented in chapter 3.

Chapter 1

Phosphorus buffering capacity of substrate clays and its significance for plant cultivation

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This is the pre-peer reviewed version of the following article:
Binner, I., Dultz, S. and Schenk, M.K. (2013): Phosphorus buffering capacity of substrate clays and its significance for plant cultivation. *Journal of Plant Nutrition and Soil Science* (submitted December 2013).

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1.1 Abstract

Peat is commonly used as the main component of horticultural substrates, but it has a very low buffering capacity for the anionic macronutrient phosphorus (P), which can be increased by the addition of clays. The aim of this study was to characterize the P sorption capacity of different substrate clays and to evaluate its significance for plant P uptake.

Substrate clays were characterized with a single point batch experiment and adsorption- and desorption-isotherms. The data were fitted to the Langmuir equation for a calculation of the maximum adsorption capacity. Additionally, the contents of oxalate extractable Fe and Al ($\sum Fe_{ox}+Al_{ox}$) were determined. The influence of a varying P sorption capacity of the clays on the P availability to plants in the respective peat-clay substrates and pure peat was investigated in a growth experiment with *Impatiens walleriana* fertigated with 0, 17 and 35 mg P L^{-1} solution, respectively.

The observed and calculated (Langmuir) P sorption capacity of the clays could be well-characterized by both the batch experiment and the adsorption isotherms and was highly correlated with the $\sum Fe_{ox}+Al_{ox}$. A higher P sorption capacity of the clay amendment in mixed substrates resulted in a lower P concentration in the substrate solution, while the CAT extractable P concentration (P_{CAT}) was the same. Plant growth and shoot P concentrations were enhanced in the substrates, showing a higher P sorption capacity, since plants were able to take up the whole amount of P_{CAT}, and also part of the non-CAT extractable P. But the release rate was too low to ensure optimal plant growth, which was in accordance with the result of the desorption experiment. The absolute extent of P release was increased with the increasing P sorption capacity of the clays and higher degree of P saturation (*DPS*).

1.2 Introduction

Phosphorus (P) is an essential plant nutrient and plays a major role as a structural element, and in photosynthesis, respiration and energy transfer. Well-supplied plants contain about 3-5 mg P g^{-1} shoot dry matter (DM) (*Hecht-Buchholz*, 1967). Phosphorus in soils is contained in both organic and inorganic forms, but only a small amount is present in the soil solution (*Holford*, 1997). P is preferentially sorbed to Fe and Al oxides, oxyhydroxides and hydroxides and to the surface of layered clay minerals. The sorption capacity for soils varies widely depending on the content and specific surface area of strongly sorbing phases as well as the solution chemistry (*Nye*, 1979). A good correlation between the P sorption capacity and contents of amorphous Fe and Al oxides is well-known (e.g. *Börling* et al., 2001; *Memon*, 2008). The phosphate anion can bind to the functional groups of the oxides by ligand exchange reactions and interact with the charged oxide surface by electrostatic bonding (*Antelo* et al., 2005, 2007). The electrostatic interaction between phosphate and the oxide surface is highly dependent on the solution pH. Thus, the P adsorption generally decreases with increasing pH values), because of increasing deprotonation of the solid phase and a competition for binding sites with OH^- ions. (*Gao* and *Mucci*, 2001; *Antelo* et al., 2005). Another main chemical factor for the binding of anions to Fe oxides and surfaces of clay minerals are multivalent cations, such as Ca^{2+}, which support sorption by bridging. Furthermore, P can form solid phases of low solubility with Ca^{2+} in alkaline soils and with Fe^{3+} and Al^{3+} in acid soils (*Holford*, 1997). Thus, the P concentration in the soil solution is often very low and ranges between 0.03 and 0.5 mg P L^{-1} in agricultural soils (*Barber*, 1995; *Jungk* and *Claassen*, 1997). It is essential for a continuous P supply to the plants that the solution P concentration at the root surface is replenished quickly when P is taken up by the plant roots. This process of P resupply is dependent on the quantity of labile P, the rate of its dissolution and the speed of ion transport in the solution (*Holford*, 1997; *Jungk* and *Claasen*, 1997). The transport of P towards the root occurs mainly by diffusion, and the diffusion coefficient, D_e, is positively affected by the volumetric water content (θ) and the impedance factor (f), but negatively related to the buffer power (b) (*Nye*, 1966; *Barber*, 1995):

$$D_e = D_L \theta f * \left(\frac{1}{b}\right), \tag{1}$$

where D_L is the diffusion coefficient of the solute in water. The buffer power denotes the ratio between the change in available P from the solid phase and the corresponding change in the P concentration in the soil solution (*Nye*, 1979).

The availability of P is not only dependent on the kind and content of clay minerals and Fe and Al oxides in the soil, but also on plant factors. Plants can adapt to low P levels by changes in root morphology, such as an enhanced root length density (*RLD*) and increased root hair length; additionally, they have the ability to mobilize bound P by mechanisms such as the release of H^+, organic anions or acid phosphatases (*Raghothama*, 1999). The significance of plant and soil factors affecting the P availability is different between mineral soils and horticultural growing media. The P buffer power was reported to be very low in peat-based substrates compared to mineral soils leading to a high P mobility (*Khandan-Mirkohi* and *Schenk*, 2008). Furthermore, the *RLD* is a magnitude higher than under open-field conditions. This leads to an exploitation of the whole substrate volume, since P depletion zones around roots overlap (*Khandan-Mirkohi* and *Schenk*, 2009), which contrasts completely to field conditions, where plants only use about 20% of the soil volume around roots for P acquisition (*Jungk* and *Claassen*, 1997; *Claassen* and *Steingrobe*, 1999). The P utilization per unit substrate volume is increased for pot plants compared to field conditions, since the substrate volume is limited and the growth rates of plants are often enhanced under greenhouse conditions.

Peat is commonly used as the main component of substrates in horticultural practice but it has a very low buffering capacity for nutrients such as anionic phosphate. Its buffering capacity can be increased by the addition of clays. The physical and chemical properties of the clay minerals may vary widely depending on their mineralogical composition and surface properties. Up to now, the selection of suitable clays for the production of growing media has mostly been handled empirically. In order to get a first overview of the P sorption capacity of a clay, *Bache* and *Williams* (1971) proposed the application of a single high dose of P and the subsequent measurement of the amount of P sorbed by the sample. A more detailed characterization of the adsorption behavior can be obtained by adsorption isotherms, allowing the estimation of the maximum adsorption capacity and the buffering capacity of the material analyzed as indicated by the slope of the curve (*Bache* and *Williams*, 1971). The process of P replenishment in the soil solution can be evaluated by desorption isotherms (*Raven* and *Hossner*, 1994; *Sato* and *Comerford*, 2006).

The P pool of a soil or substrate available to plants can be determined by chemical extraction or ion-sink methods using anion exchange resins or membranes (*Abdu*, 2006; *Sato* and *Comerford*, 2006). Several studies have shown that the isotopically exchangeable P is the main source of P available to plants (*Frossard* et al., 1994; *Hamon* et al., 2002), but the method is not applicable for standard use. P which is available to plants in agricultural soils in Germany is commonly extracted with Ca-acetate-lactate (CAL) at pH ~4.1 (*Schüller*, 1969). CAT ($CaCl_2$ + DTPA) is mainly used for horticultural substrates and extracts at the pH of the substrate (*Alt* and *Peters*, 1992). It normally has a lower extraction power than CAL. Generally, substrates are supplied with basic fertilization in order to obtain targeted CAT extractable nutrient concentrations. Thus, a substrate with a higher P buffering capacity needs a higher amount of fertilizer than a substrate with a low buffering capacity in order to reach the same CAT extractable P concentration.

The aims of this study were (i) to characterize clay properties describing the P buffering capacity, (ii) to identify methods for a clay selection regarding the P binding capacity, and (iii) to evaluate the significance of non-CAT soluble P for the P supply of plants in peat-clay substrates and its contribution to the safety of plant cultivation.

1.2 Materials and Methods

1.2.1 Selection and characterization of clays

Fourteen clays were preselected for the characterization of P sorption capacity (Tab. 1). Thirteen clays originated from primary and secondary types of deposits in the Mesozoic-Tertiary weathering mantle of the Rhenish Massif, Westerwald area, and two technical mixtures of different clays were included. The clays were obtained from Stephan Schmidt KG (Langendernbach, Germany). Three different main occurrences of clays in the Westerwald area are distinguished. There are (autochthonic) bentonites and saprolitic clays (primary deposits) formed *in situ* and relocated clays (secondary deposits) formed mainly by saprolitic clays being washed out, transported by water and finally settling down in basins in the Tertiary approx. 30 million years ago. The mineral composition of these clays is based mainly on only four types of minerals, namely illite, kaolinite, quartz, and smectite. Additionally, a clay from Sinntal-Jossa near Fulda (Germany) which is used in the substrate industry was also included for comparison (Tab. 1). The main component of the clay is smectite, indicating that this clay most probably contains weathering products from volcanic rocks in the Vogelsberg area which were relocated. Elevated contents of SO_4^{2-} in this clay point to a formation in a marine environment.

In a first screening, the clays were shaken overhead in a batch experiment at pH ~5.5 in a 0.01 M $CaCL_2$ solution with 500 mg P L^{-1} as KH_2PO_4 at a ratio of 1:10 (w/v) for 24 h in three replicates in order to characterize differences in their P sorption. The adsorbed amounts at equilibrium conditions, P_{new} (mg kg^{-1}) were calculated from the change of the P concentration in the solution. Additionally, the amount of P initially adsorbed onto the Fe and Al oxides (P_{init}) was determined by the extraction with 10 mL 0.2 M ammonium-oxalate and 0.2 M oxalic acid at pH 3.25 in the ratio 1:10 (w/v) (*Schwertmann*, 1964). The total P sorption capacity (P_{tot}) was calculated as the sum of P_{init} and P_{new} (*Freese* et al., 1992), and the degree of P saturation (*DPS*) was calculated as the ratio of P_{init} in P_{tot} (*Börling* et al., 2004).

Afterwards, two clays (clay 04S and clay 01S) with a low P_{tot} and two (clay 06B and clay 39W) with a high P_{tot} were selected for further experiments (Tab. 1). Sorption isotherms were established for these four selected clays. Each 1 g of clay was shaken in centrifugation tubes containing 10 mL of 0.01 M $CaCl_2$ with different P concentrations (0-500 mg P L^{-1} as KH_2PO_4) for 24 h at 20°C. The pH ranged between pH 5.4 and 5.9. The experiment was performed in three replicates. The P amounts adsorbed were calculated from the P depletion in the solution. The data were fitted to the Langmuir equation in order to calculate the maximum adsorption capacity (Equation 2).

$$\Delta P = P_{max}\, L_e\, P_e / \,(1 + \, L_e\, P_e) \qquad (2)$$

where ΔP is the amount adsorbed (mg kg^{-1}), P_e the equilibrium concentration (mg L^{-1}), P_{max} the adsorption capacity (mg kg^{-1}), and L_e the equilibrium constant of adsorption (Langmuir constant).

P release was characterized in a desorption experiment. Each 1 g of the four clays was firstly shaken overhead in a 0.01 M $CaCl_2$ solution containing 75-150 mg P L^{-1} at a ratio of 1:10 (w/v) for 24 h in three replicates in order to reach an equilibrium P concentration of ~65 mg P L^{-1} as it could be observed in fertilized peat substrates. After centrifugation at 1000 rpm for 10 min, the P concentration in the supernatant was measured and half of the supernatant solution was exchanged with fresh $CaCl_2$ solution without P, followed by another shaking period of 24 h. This procedure was repeated 16 times and the equilibrium P concentration was decreased stepwise to <1.5 mg P L^{-1} by this method. The P release (desorbed P = P_{des}) was calculated as follows:

$$P_{des} = (P_{e2} - (P_{e1}/2)) * V/W, \tag{3}$$

where P_{e2} and P_{e1} are the recent and the previous equilibrium concentrations (mg L^{-1}), respectively, and V and W are the liquid volume (L) and the weight of the dried clay sample (kg), respectively.

1.2.2 Preparation of substrates

The four clays were mixed with white peat at a ratio of 200 kg clay per m^3 peat and pure peat was taken as a control. At first, P sorption curves were prepared for each substrate to determine the amount of fertilizer P necessary to achieve the targeted CAT extractable P concentration (P_{CAT}) in each substrate: The substrates were fertilized with 1.5 g L^{-1} of the P free compound fertilizer Ferti® 8 (N : P_2O_5 : K_2O = 20 : 0 : 16 + micronutrients; Planta Düngemittel GmbH, Germany) and the pH was adjusted to pH 6 with $CaCO_3$. Phosphorus was added in increasing concentrations from 0 to 150 mg P L^{-1} substrate as $Ca(H_2PO_4)_2 * H_2O$. The substrates were then equilibrated in an oven at 50°C for 48 h in order to accelerate the P binding, and afterwards, stored at room temperature for another 72 h prior to determining the P_{CAT}. The following P rates were fertilized to reach a P_{CAT} of 25 mg P L^{-1} substrate, which is a usual concentration in horticultural practice (in mg P L^{-1} substrate): peat = 30; peat + clay 04S = 38; peat + clay 01S = 65; peat + clay 06B = 72; peat + clay 39W = 100.

1.2.3 Plant cultivation

Seedlings of *Impatiens walleriana* F1 “Candy® Coral Bee” were planted in plastic pots (∅ 12 cm), each filled with 600 ml of the different peat-clay substrates and only peat as a control. The plants were grown in a greenhouse at day/night heating temperatures of 22°C/18°C, respectively. Natural radiation was supplemented with 80 µmol m^{-2} s^{-1} photosynthetic photon-flux density when the radiation was lower than 100 µmol m^{-2} s^{-1} to extend the photoperiod to 16 h. Fertigation started immediately after planting on top of the substrate surface with a solution containing (in mg L^{-1}): 120 N as KNO_3 and NH_4HO_3, 130 K as KNO_3, K_2SO_4 and KH_2PO_4, 10 Mg as $MgSO_4 * 7\ H_2O$, and 200 Ferty® 10 (micronutrients) (Planta Düngemittel GmbH, Germany). The P concentration in the fertigation solution was varied in three levels (in mg P L^{-1}): 0 (= *no P*), 17 (= *medium P*) and 35 (= *high P*). P was applied as $Ca(H_2PO_4)_2 * H_2O$. Plants were harvested after cultivation for 10 weeks.

1.2.4 Physical and chemical analyses

The texture of clays was determined by sieving and sedimentation after the removal of organic matter by wet oxidation with H_2O_2, according to DIN ISO 11277: 2002-08. The contents of amorphous Fe and Al oxides ($\sum Fe_{ox}+Al_{ox}$) were determined by the extraction of 1 g clay with 10 mL 0.2 M ammonium-oxalate and 0.2 M oxalic acid at pH 3.25 (*Schwertmann*, 1964). The specific surface area (SSA) of the clays was quantified by N_2 adsorption with a Nova 4200 analyzer (Quantachrome).

The pH of the substrates was measured in 0.01 M $CaCl_2$ at a substrate:solution ratio of 1:2.5 (v/v). The determination of the bulk density was conducted by a defined compaction of the samples by repeated tamping, according to *VDLUFA* (1991). Phosphorus which was available to plants was determined according to *Alt* and *Peters* (1992) using the CAT extraction procedure: 20 g fresh substrate was shaken for 1 h in 160 ml CAT solution (0.01 M $CaCl_2$ + 0.002 M DTPA). The separation of the substrate solution took place by centrifugation at 3000 g for 20 min in order to measure the P concentration (P_{sol}). All substrates were watered or dried to the same volumetric water content of 500 ml L^{-1} substrate 48 h before the centrifugation. After filtering (cellulose filter paper; 2-3 µm pore sizes), the P concentration in solutions was determined photometrically (BioTek Instruments, µQuant), according to *Schüller* (1969), with ammonium-vanadate-molybdate, and *Murphy* and *Riley* (1962), with molybdenum blue, respectively. Buffer power (*b*) was calculated as the ratio of P_{CAT} / P_{sol} (*Khandan-Mirkohi* and *Schenk*, 2009).

The plant material was dried at 70°C for 5 d and ground. P in plant tissue was determined after dry-ashing at 480°C for 8 h, dissolving the ash in 1:3 diluted HNO_3 at a ratio of 1:20 (w/v) and then diluting (1:10 v/v) with demineralized water. The measurement of the P concentrations in the digestion solution occurred photometrically with ammonium-vanadate-molybdate at 450 nm wavelength, according to *Gerike* and *Kurmies* (1952).

1.2.5 Statistics

Analyses of the clays and mixed substrates were performed with three replicates. The treatments in the plant experiment were repeated five times, whereby each replicate consisted of five plants in a randomized block design. Statistical analysis was performed with the program R 2.13.2. Means of treatments were compared by analysis of variance and Tukey's test at $P < 5\%$.

1.3 Results

1.3.1 P sorption and desorption of clays

The 14 preselected clays differed clearly in their total P binding capacity ($P_{tot} = \sum P_{new} + P_{init}$) and also oxalate-soluble Fe and Al contents (Fe_{ox} + Al_{ox}) (Tab. 1.1). The relation between Fe_{ox} and Al_{ox} was more or less balanced in all the clays with the exception of 39W, where Fe_{ox} clearly dominated. The degree of P saturation of the clays varied between 0 and 33% (Tab. 1.1).

The P adsorption (P_{new}) of the clays measured was positively correlated with the $\sum Fe_{ox}+Al_{ox}$ (Fig. 1.1-a), but not with the clay content ($R^2 = 0.0$) or the specific surface area (SSA; $R^2 = 0.0$; data not shown).

The adsorption isotherms of three clays 04S, 01S and 06B clearly followed saturation functions, whereas clay 39W showed a more or less continuous increase in P adsorption and was not yet saturated at the highest P level, which was also applied in the batch experiment (Fig. 1.1-b). None of the clays showed considerable P desorption and the equilibrium concentration at which neither desorption nor adsorption occurred, P_{e-0}, was almost the same. The clays 01S and 04S had only gently inclined curves and reached the maximum P adsorption at much lower P concentrations in the solution than the clay 06B.

Tab. 1.1: Texture, specific surface area (SSA), total P adsorption capacity (P_{tot}), initially adsorbed P (P_{init}), and the degree of P saturation (DPS), as well as amorphous Fe (Fe_{ox}) and Al (Al_{ox}) contents of 14 different clays included in the screening. The clays marked were used for further investigations and in the plant experiment.

clay [a]	texture [b]	SSA [c,d]	P_{tot} [d]	P_{init} [d]	DPS [e]	Fe_{ox} [d]	Al_{ox} [d]	Fe_{ox} /Al_{ox}
unit	sand/silt/clay [wt %]	[m^2 g^{-1}]	[mg kg^{-1}]	[mg kg^{-1}]	[%]	[mg kg^{-1}]	[mg kg^{-1}]	
39W	12/18/70	74 ± 1.0	2374 ±34.1	270 ± 9.4	11	5629 ±158.0	529 ± 5.5	10.6
07B	46/41/13	106 ±10.7	2149 ±29.9	616 ±12.2	29	1088 ± 6.4	1314 ±12.8	0.8
06B	41/38/21	110 ± 5.1	2071 ±33.0	674 ± 2.0	33	2061 ± 9.0	1658 ±12.9	1.2
38M	25/40/35	67 ± 6.0	1712 ±13.4	353 ± 9.0	21	771 ± 10.9	992 ±22.0	0.8
14B	15/45/40	60 ± 1.5	728 ±22.9	132 ± 0.6	18	319 ± 4.8	595 ±14.1	0.5
15B	14/51/35	66 ± 2.6	718 ±16.7	138 ± 0.9	19	568 ± 6.6	1194 ± 8.6	0.5
12B	16/45/38	64 ± 0.6	523 ± 4.2	62 ± 0.3	12	110 ± 1.2	316 ± 5.7	0.3
29U	2/28/70	63 ± 1.9	468 ±10.7	1 ± 0.0	0	115 ± 3.5	209 ± 4.0	0.6
01S	42/45/13	14 ± 1.7	316 ± 4.9	81 ± 0.9	25	381 ± 8.7	258 ± 1.0	1.5
03S	26/53/21	18 ± 0.1	313 ± 3.5	29 ± 0.3	9	257 ± 2.0	120 ± 0.3	2.2
28U	2/18/80	52 ± 6.2	282 ± 3.8	2 ± 0.1	1	53 ± 0.8	180 ± 1.5	0.3
33U	8/41/41	16 ± 0.8	253 ± 4.8	20 ± 0.6	8	55 ± 7.4	53 ± 0.5	1.0
36M	2/35/63	27 ± 3.1	162 ± 5.6	22 ± 0.3	14	224 ± 14.5	96 ± 1.8	2.4
04S	26/53/21	8 ± 0.4	47 ± 9.6	2 ± 0.1	5	64 ± 5.1	41 ± 4.9	1.6

[a] Clay denotations: B = bentonitic clay; M = clay mixture; S = saprolitic clay; U = relocated clay; W = clay from Sinntal/Vogelsberg

[b] Particle size distribution according to DIN ISO 11277: 2002-08

[c] Specific surface area determined by N_2-adsorption and multipoint BET

[d] Mean of three replicates ± standard error

[e] The DPS was calculated as the ratio of P_{init} in P_{tot}

The maximum adsorption capacity (P_{max}) could be calculated by fitting the data observed to the Langmuir equation. It was in the same range as the adsorption observed in the batch experiment (P_{new}; Fig. 1.1-a). Only for clay 39W was the calculated adsorption capacity much higher than the P_{new} observed in the batch experiment.

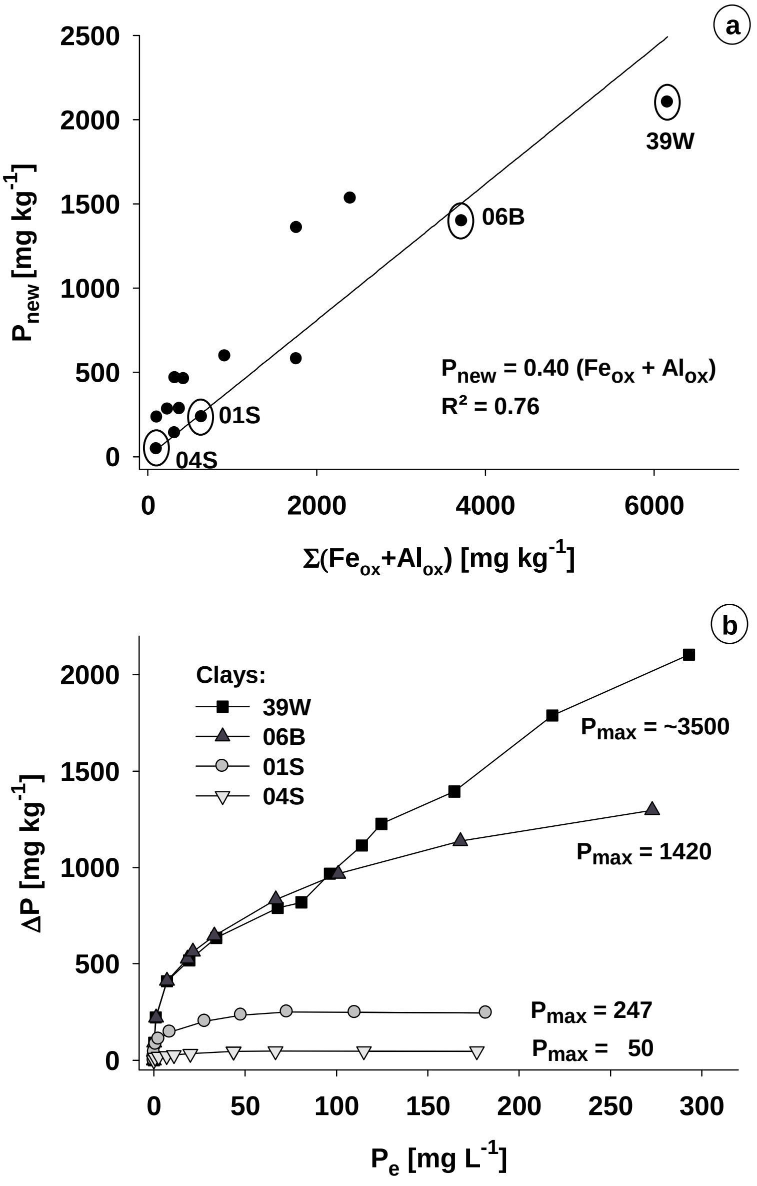

Fig. 1.1: (a) Relationship between the content of oxalate soluble Fe and Al ($\sum Fe_{ox}+Al_{ox}$) and the P adsorption (P_{new}) of 14 clays in a batch experiment. The clays marked were used for detailed analysis of P dynamics and in the plant experiment. (b) Adsorption isotherms of P on the four substrate clays used in the plant experiment (□P = the amount adsorbed, P_e = the equilibrium concentration, P_{max} = the adsorption capacity calculated in mg kg^{-1}).

The P release of the four clays pre-supplied with 750-1500 mg P kg^{-1} clay to adjust a P_e of ~65 mg P L^{-1} solution differed clearly and could be well-described by logarithmic functions (Fig. 1.2-a).

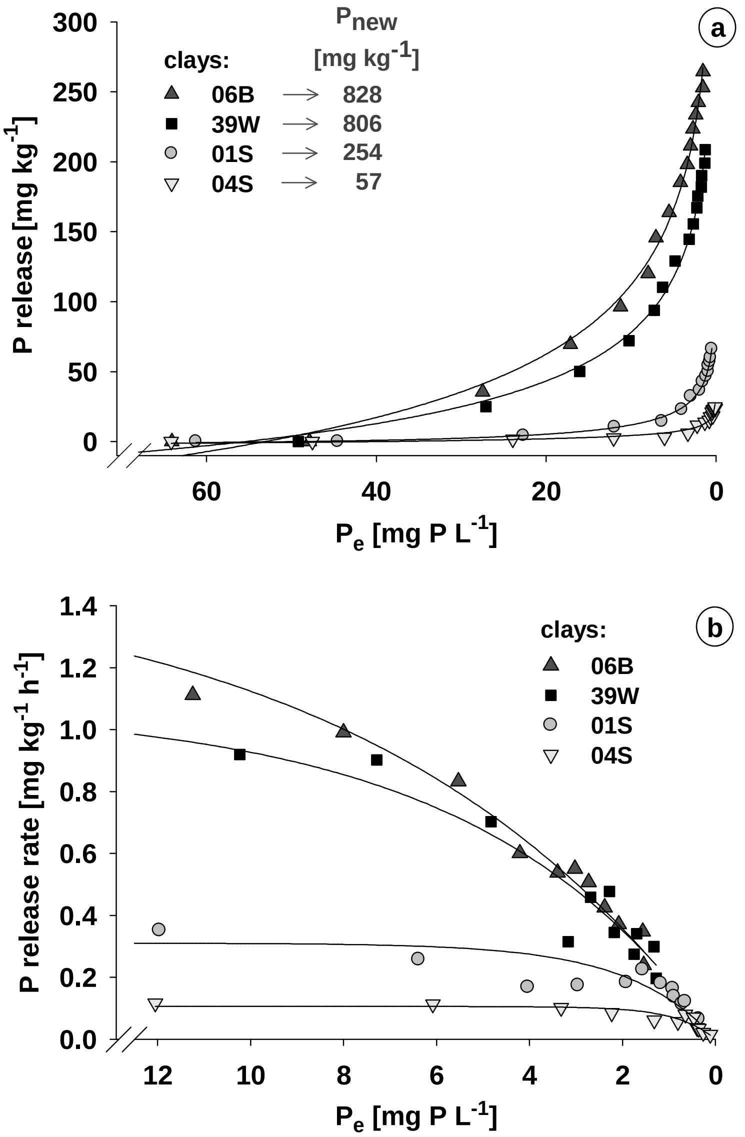

Fig. 1.2: (a) Accumulated P release of the four selected clays with decreasing P concentrations (P_e) in the equilibrium solution. Prior to the desorption experiment, the clays were loaded with P in order to reach an P_e of ~65 mg P L^{-1}. The P amounts adsorbed at the beginning of the desorption experiment (P_{new}) are given. Curves were fitted to the function $y = y_0 + a * \ln(x)$; and (b) P release rates of the four clays with decreasing P_e derived from the desorption experiment. Curves were fitted to the function $y = a * (1 - e^{-b*x})$. Mean values of three replications.

The clay 04S showed a very low absolute P desorption followed by clay 01S. Pronounced P release in both clays did not start until P_e decreased below 5 mg P L^{-1}. The two other clays (06B and 39W) released clearly more P than 01S and 04S, already starting at equilibrium concentrations of about 40-30 mg P L^{-1}. A decrease in P_e from 3 to 2 mg P L^{-1}, for example, caused a P release of 32 mg P kg^{-1} in clay 06B, whereas the desorption from clays 39W, 01S and 04S was only about 70, 20 and 6% of this value, respectively. On average, the clays released between 1/4 and 1/2 of the P_{new} adsorbed at the beginning of the experiment, but the rate of P desorption (P amount released per hour) strongly decreased with decreasing equilibrium concentrations (Fig. 1.2-b).

1.3.2 Plant available P in substrates

At the beginning of the plant experiment, the mixed substrates contained the adjusted CAT extractable P concentration (P_{CAT}) of 20-25 mg L^{-1} substrate. Furthermore, the P concentration in the substrate solution (P_{sol}) was determined and the buffer power (b) was calculated (Fig. 1.3-a). As P_{sol} decreased with the increasing sorption capacity of the substrates, b was increased. Peat-clay blend 39W had a ~4-5 times higher buffer power than peat and peat-clay blend 04S. In the substrates peat, peat + clay 04S and peat + clay 01S, the buffer power calculated was <1 as the solution P concentrations were very high.

At the end of plant culture, the substrate solution of all substrates was strongly depleted of P (Fig. 1.3-b). Considerably high P concentrations were only to be found at 35 mg P L^{-1} fertigation solution, and these were decreased compared to the beginning of cultivation only in peat and peat-clay blend 04S. The same pattern was observed in the CAT extractable P content of the different substrates at the end of plant cultivation (Fig. 1.3-c). The initial P concentration of about 20-25 mg L^{-1} substrate could only be maintained in the highest P fertigation level (35 mg P L^{-1}) in the stronger buffered blends 01S, 06B and 39W compared to peat and peat + clay 04S. At medium (17 mg P L^{-1}) or without P fertigation, P_{CAT} was clearly decreased in all substrates. P_{CAT} after plant cultivation at all fertigation levels was significantly lower in peat and in peat-clay blend 04S than in the blends with other clays, where a clear order was observed: clay 01S < clay 39W < clay 06B.

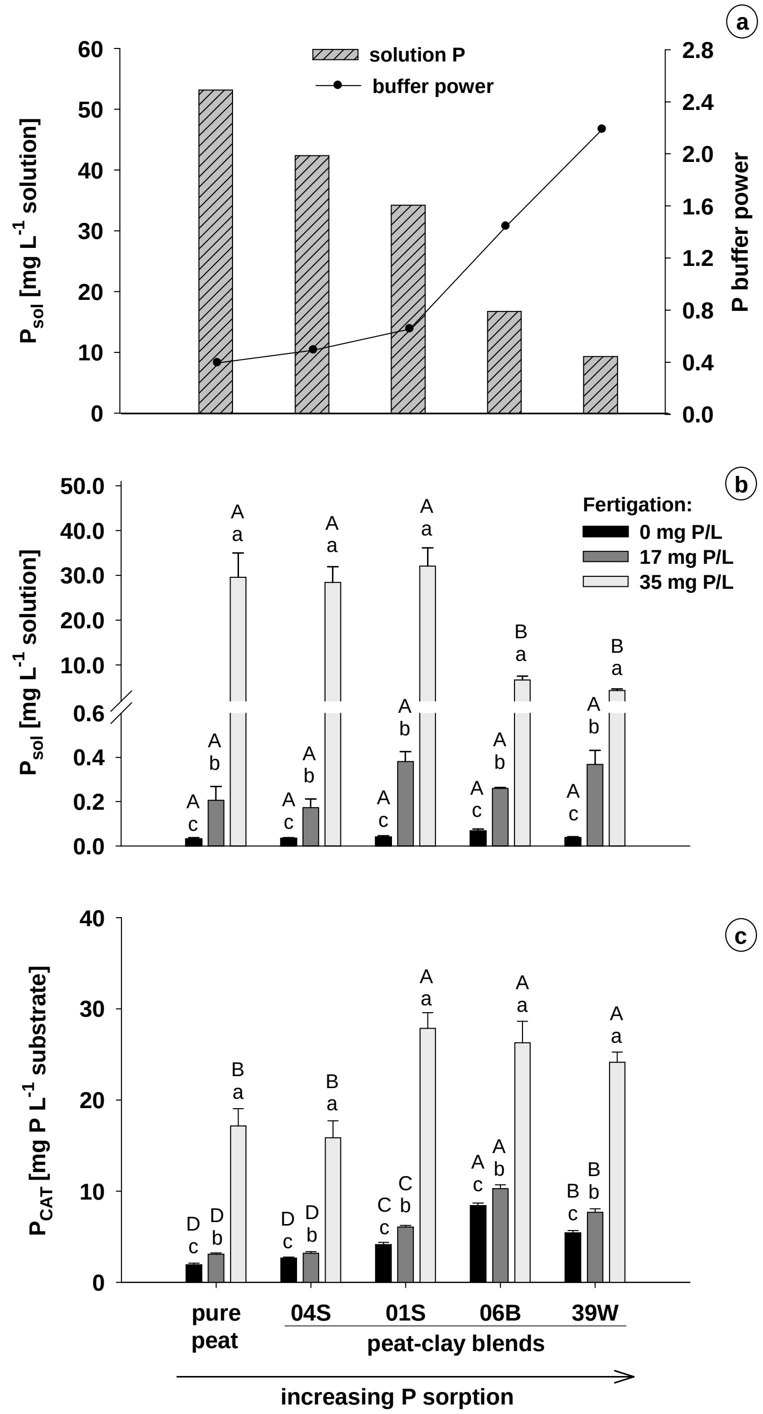

Fig. 1.3: (a) P concentration in the substrate solution (P_{sol}) of peat and peat-clay mixtures and the resulting P buffer power at the beginning of plant culture, (b) P_{sol} and (c) CAT extractable P concentrations (P_{CAT}) of peat and peat-clay mixtures at the end of the experiment at different P concentrations in the fertigation solution. Error bars represent standard errors. Different capital letters indicate significant differences between substrates at the same P fertigation level and different small letters indicate significant differences between fertigation treatments within the same substrate ($p < 0.05$).

1.3.3 Plant growth and availability of non-CAT extractable P

After ten weeks of cultivation, the varied P fertigation resulted in clear differences in plant growth and plant quality among the substrates (Fig. 1.4-a+b). Plants grown without P fertigation in pure peat and in the blend with clay 04S showed clear symptoms of P deficiency as leaf-shedding and stunted habitus. Weak symptoms of P deficiency were also observed in the blend with clay 01S (Fig. S.1, supplementary). The internode length was reduced in these substrates with a lower P-binding capacity compared to peat-clay blends containing clays 06B and 39W, and fertigation of P increased the internode length (Fig. 1.4-a).

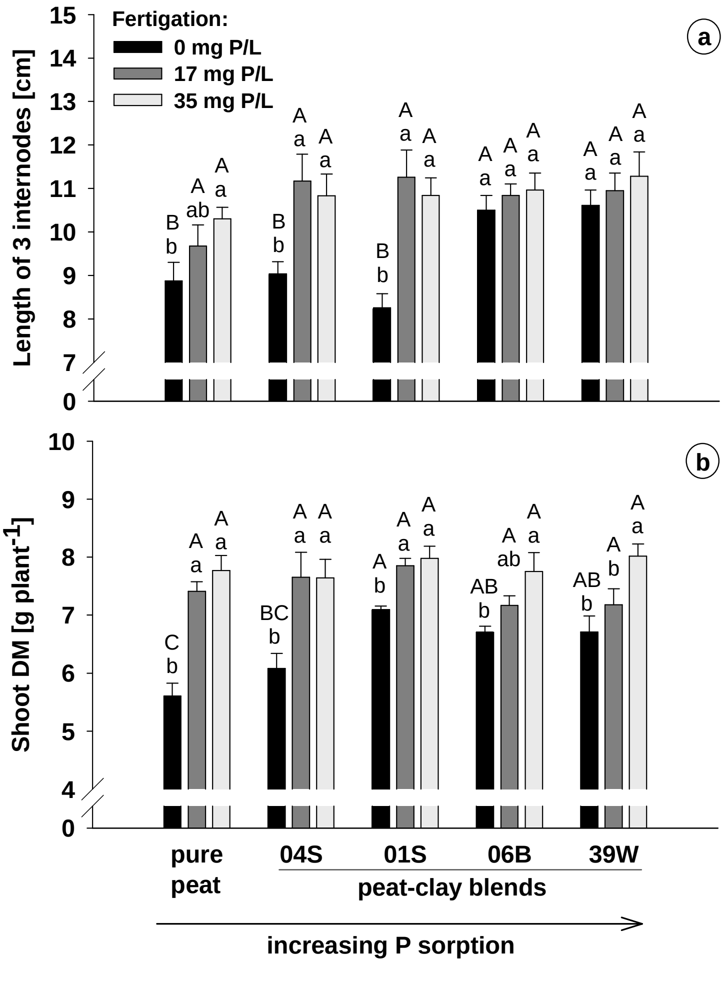

Fig. 1.4: (a) Internode length and (b) shoot dry matter of *Impatiens walleriana* plants grown in peat and different peat-clay mixtures at different P concentrations in the fertigation solution. Error bars represent standard errors. Different capital letters indicate significant differences between substrates at the same P fertigation level and different small letters indicate significant differences between fertigation treatments within the same substrate ($p < 0.05$).

The same trend was observed in the plant diameter and plant height (data not shown). The P fertigation enhanced the dry matter yield of the plants in all five substrates (Fig. 4b). Without P fertigation, the yield of plants grown in peat and in the blend with clay 04S was lower than in the other three peat-clay blends. No differences between the substrates were observed at medium and high P supply.

The increasing P supply via fertigation resulted in increased P concentrations in plants in all substrates (Fig. 1.5-a). Without P fertigation and at 17 mg P L^{-1}, the P concentrations in shoot matter were the lowest in peat and in the peat-clay blend 04S, and the highest in the blend 06B. The differences in shoot P concentrations between substrates were no longer observed at the highest P fertigation level of 35 mg P L^{-1} solution. The P concentrations in plant matter necessary for optimum growth ranged between 5 and 7 mg g^{-1} dry matter at 17 mg P L^{-1} fertigation solution.

The P amount contained in shoot DM was calculated for the treatments without P fertigation to characterize the capacity of different clays to supply P to plants (Fig. 1.5-b). The substrates with amendment of clays 01S, 06B and 39W supplied considerably more P to the plants than pure peat and the blend with clay 04S. In the latter substrates, plants did not contain the P amount determined by CAT extraction before planting, whereas in the other substrates, especially the one with clay 06B, even more P was taken up than quantified as plant-available by the CAT extraction. However, more P was fertilized in all substrates including pure peat than could be extracted by CAT or was taken up by the plants. This was generally more pronounced in the blends with clays having a high binding capacity for P (01S, 06B and 39W).

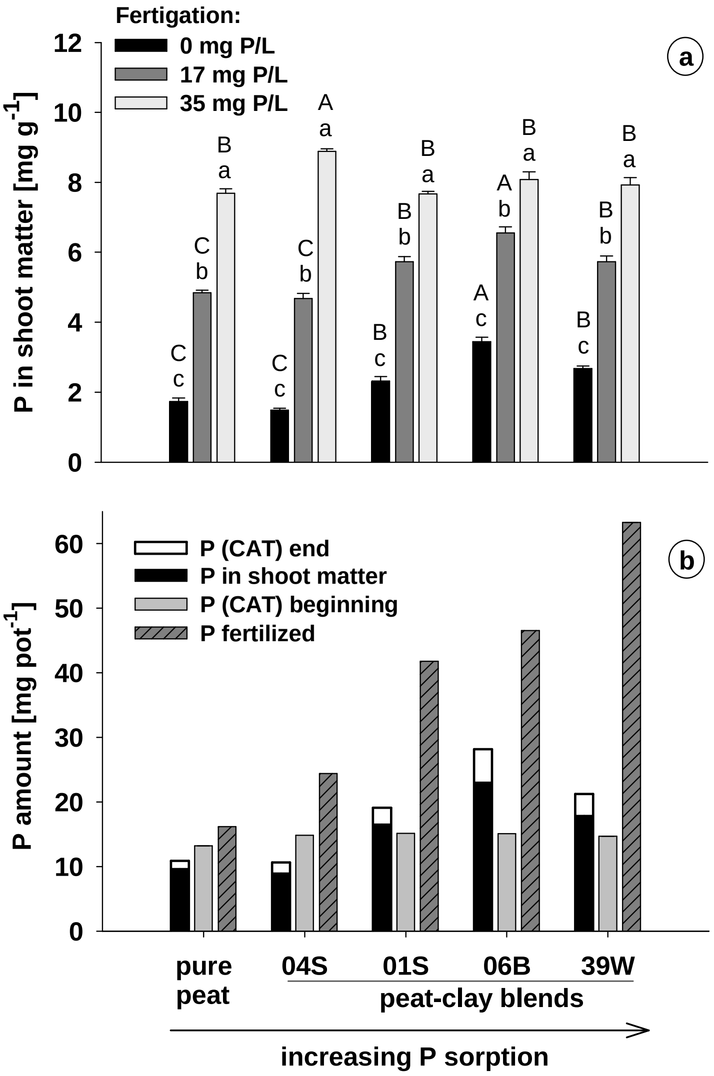

Fig. 1.5: (a) P concentration in shoot dry matter of *Impatiens walleriana* plants grown in peat and different peat-clay mixtures at different P concentrations in the fertigation solution, and (b) comparison between the amounts of fertilized P and CAT extractable P (P_{CAT}) at the beginning of plant culture, and P in shoots of plants grown without P fertigation and P_{CAT} left in the pots at the end of plant culture. Error bars represent standard errors. Different capital letters indicate significant differences between substrates at the same P fertigation level and different small letters indicate significant differences between fertigation treatments within the same substrate ($p < 0.05$).

1.4 Discussion

1.4.1 Growth and P uptake of *I. walleriana*

Without P fertigation, the buffering capacity of the clay amended to the substrate influenced the growth of *I. walleriana* (Fig. 1.4). The higher buffering capacity especially of the substrates with clays 06B and 39W, but also 01S, resulted in an enhanced growth of the plants compared to the more weakly buffered substrates with clay 04S. P deficiency led to chlorosis and leaf-shedding in peat and the blend with clay 04S. *Fredeen* et al. (1989) also described a significant decrease in shoot growth, leaf expansion and leaf surface area with low P supply, which can be explained by an impaired extension of plant cells. The number of leaves can also be decreased under P deficiency mainly through effects on the number of nodes and branching (*Lynch* et al., 1991). *Hansen* and *Nielsen* (2001) recommended a reduced P availability as a method for the non-chemical growth regulation of ornamental plants. When there was P deficiency, we observed a reduction of internode length and compaction of plants in the substrates peat and peat + clay 04S. At the same time, the DM production was decreased and leaf-shedding was induced showing that such a strict shortage of P was not a successful strategy for forming plants.

The P concentrations in plant matter necessary for optimum growth were in the same range as reported by *Khandan-Mirkohi* and *Schenk* (2009) for poinsettia and marigold plants and were achieved with a 17 mg P L^{-1} fertigation solution (Fig. 1.4-b + 1.5-a). However, the P fertilization was high enough only at 35 mg P L^{-1} to approximately maintain the initial P_{Sol} and P_{CAT} during cultivation (Fig. 1.3 - b+c).

1.4.2 P sorption capacity of clays

Our results clearly indicate that P in the clays is mainly bound to Fe and Al oxides because the P adsorption (P_{new}) observed correlated positively with $\sum Fe_{ox}+Al_{ox}$ (Fig. 1.1-a). Many authors described a similar relationship (*Borggaard* et al., 1990; *Börling* et al., 2001; *Wang* et al., 2012), and it is a common practice in the Netherlands and some other countries to determine the P sorption capacity of soils indirectly by the ammonium oxalate extractable amounts of Fe and Al (*Börling* et al., 2004). *Freese* et al. (1992) observed an even closer correlation of $\sum Fe_{ox}+Al_{ox}$ with the total P sorption capacity (P_{tot}), taking the P initially adsorbed onto the Fe- and Al-oxides (P_{init}) into account, for different soils from eastern Germany. This was not the case in our experiment, because the maximum adsorption capacity (P_{max}) was not achieved with clay 39W (Fig. 1.1-b). Information about the adsorption process was obtained by the adsorption isotherms (Fig. 1.1-b). The P_{max} of the clays 04S, 01S and 06B calculated confirmed the results of the batch experiment (Fig. 1.1-a). *Bach*e and *Williams* (1971) and *Wang* et al. (2012) observed a high correlation between the P amounts adsorbed determined in batch experiments and the sorption maxima calculated from sorption isotherms using the Langmuir equation for samples of different acid and alkaline soils. The isotherm of the clay 39W showed a more or less continuous increase and a maximal sorption capacity could only be calculated with uncertainties, but it was about 50% higher than the P_{new} observed in the batch experiment. Thus, the total adsorption capacity of this clay could not be reliably determined in the batch experiment because the P concentration used in the shaking solution was not high enough.

Nevertheless, the order in P sorption of the clays determined, 39W > 06B > 01S > 04S, was also observed in the substrates blended with the clays, where the fertilized P amounts to obtain a P_{CAT} of 25 mg L^{-1} substrate were ranked in this order. However, the differences in the peat-clay substrates were not as pronounced as the differences of P_{max} between the pure clay samples, because the equilibrium concentrations in the substrates were clearly lower (P_{sol} in Fig. 1.3-a). Furthermore, it has to be considered that the clays react with peat and solute compounds in the substrate, thereby changing their surface properties. Hence, their behavior can be different than expected from adsorption isotherms or batch experiments. A change in pH value, high concentrations of dissolved organic matter released from the peat and the presence of other cations and anions in the solution from fertilization and liming may influence the adsorption of P (*Hua* et al., 2008; *Weng* et al., 2012). *Antelo* et al. (2007) could show a reduction of the phosphate adsorption onto goethite with increasing concentrations of a soil humic acid up to 45% under certain pH conditions.

In summary, the batch experiment performed with a single high dose of P is an easy and quick method for the estimation of the P sorption capacity of a clay, even if P_{max} is not achieved, because the equilibrium concentrations in mixed substrates are generally lower than required for P_{max}. An indication of the sorption behavior to be expected can already be obtained by the determination of Fe_{ox}+Al_{ox} contents.

1.4.3 Plant available P in substrates

The five substrates used for the plant experiment had similar CAT extractable P concentrations, but the P_{sol} decreased with the increasing sorption capacity of the clays (Fig. 1.3-a). The amount of P_{CAT} in peat was equivalent to the amount of P found in P_{sol}, whereas the P_{sol} in blend 39W was only 20% of P_{CAT}. P_{sol} in all five substrates was very high and the P sorption and *b* were very low compared to mineral soils (*Barber*, 1995; *Jungk* and *Claassen*, 1997). *Khandan-Mirkohi* and *Schenk* (2008) reported similar P_{sol} values for black peat and peat mixed with mineral components and *b* ranged from 1 to 17. Thus, the P mobility in substrates is high and plants are able to exhaust the whole substrate volume since the RLD is also high (*Khandan-Mirkohi* and *Schenk,* 2008).

In substrates with a higher buffer power P_{sol} is held constantly at a low level, which reduces the risk of P leaching in outdoor cultivation and possible P toxicity, while guaranteeing an adequate P supply of the plants by replenishing the substrate solution (*Marconi* and *Nelson*, 1984; *McDowell* et al., 2001; *Ogutu* et al., 2009). *Owen* et al. (2007) could show a reduction of P loss by leaching of 34% in a pine-park substrate amended with a commercial bentonite compared to a control treatment without mineral amendment. Phosphorus toxicity in

Helleborus niger could be diminished by growing the plants at a P_{sol} of <15 mg P L^{-1} in a peat-clay substrate (*Dombrowski*, 2008 – data unpublished).

Impatiens walleriana plants strongly depleted the P_{sol} in the lower P fertigation levels, 0 and 17 mg P L^{-1} (Fig. 3b) during the cultivation, resulting in a release of previously adsorbed P, as indicated by the reduction of P_{CAT} (Fig. 1.3-c). Fertigation with 17 mg P L^{-1} did not lead to a considerably higher P_{CAT} compared to 0 mg P L^{-1}, but P_{sol} was clearly enhanced in all substrates. Obviously, the rate of P dissolution was not sufficient in the 0-fertigation treatment to replenish the P_{sol}. The same observation was made for the highly buffered blends with clays 06B and 39W, which had P_{CAT} contents twice as high as pure peat and the blend with clay 04S. This is in agreement with the results of the desorption experiment (Fig. 1.2) displaying only low release rates at the respective P_{sol} of <1 mg L^{-1}. The insufficient P supply for compensating the P uptake of the plants resulted in low shoot P concentrations and growth depressions in the 0-fertigation treatment (Fig. 1.4 and 1.5-a). Only at the fertigation with 35 mg P L^{-1} was the P fertilization high enough to match the plant uptake as far as possible, as indicated by a more or less constant P_{sol} and P_{CAT} during the cultivation (Fig. 1.3 - b+c).

The P content of a substrate extracted by CAT is considered as being available to plants (*Alt* and *Peters*, 1992). Thus, substrates with the same P_{CAT} are thought to supply plants with similar amounts of P. Surprisingly, the plants grown in the weakly buffered substrates pure peat and peat + clay 04S did not take up as much P as was determined to be available by CAT (Fig. 1.5-b). This may be due to an underestimation of P uptake, since P was lost by leaf-shedding in these substrates (Fig. S.1, supplementary). Furthermore, P contained in roots was not considered. On the other hand, the plants grown in the highly buffered substrates amended with clays 01S, 06B and 39W were able to take up even more P than was characterized as available to plants by the CAT method at the beginning of the experiment. The proportion of this non-CAT extractable P in P uptake was highest in the substrate with clay 06B, which also showed the highest absolute P release in the desorption experiment (Fig. 1.2-a). Nevertheless, as stated before, the rate of P release from the formerly non-CAT extractable P pool was not high enough to enable optimal plant growth (Fig. 1.4-b). The proportion of P_{CAT} in the fertilized P amount (0.57, 0.35, 0.32, and 0.23 for peat-clay substrates 04S, 01S, 06B, and 39W, respectively; Fig. 1.5-b) agreed well with the proportion of released P in P_{new} of the desorption experiment (0.49, 0.26, 0.32, and 0.26 for peat-clay substrates 04S, 01S, 06B, and 39W, respectively; Fig. 1.2-a). Thus, the amount of easily desorbable P was reliably determined by the CAT extraction. However, the whole amount of fertilized P could not be used by the plants in all peat-clay substrates. The discrepancy between the fertilized and taken up P generally increased with the increasing adsorption capacity of the clays (Fig. 1.5-b). Only in substrate 06B could more than 50% of the P initially fertilized be taken up by the plants.

The high P release of clay 06B could be explained by its high degree of P saturation (*DPS*) and its high P stock, composed of the fertilized P and the high content of P_{init}, compared to the clays 01S and 39W (Tab. 1.1 and Fig. 1.5-b). This is in line with the findings of *Börling* et al. (2004) and *Casson* et al. (2006), who observed a higher risk of P losses by leaching with increasing *DPS.*

1.5 Conclusions

The P-binding capacity of the clays was strongly correlated with their oxalate extractable Fe and Al content and could be quickly determined by a simple single point sorption experiment. A higher P buffer capacity of the substrate resulted in a decreased P_{sol}, although P_{CAT} was the same in all substrates amended with clay, reducing the risk of P leaching and P toxicity. The CAT extraction described the P amount in a substrate which was easily available to plants. Nevertheless, plants were able to take up not only the P amount that was characterized as available to plants by the CAT extraction, but also part of the non-CAT extractable P. Clays with a high P sorption capacity and a high *DPS* generally release more P than those with a low sorption capacity and a low *DPS*. Thus, the non-CAT extractable P contributes to the safety of plant cultivation, but its rate of release may be too low to ensure optimal plant growth.

Chapter 2

Potassium adsorption and release of substrate clays and the impact for plant cultivation

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2.1 Abstract

Clay amendments are widely used in horticultural substrates and they can improve the potassium (K) buffering capacity of peat-based substrates. The aim of this study was to characterize the K adsorption and desorption behavior of different substrate clays and to evaluate the significance for plant K uptake.

The K adsorption of different clays was characterized with a single point batch experiment and adsorption isotherms, fitted to the Langmuir equation for a calculation of the maximum adsorption capacity. The quantification of K desorption took place by a percolation experiment. Additionally, the cation exchange capacity (*CEC*) and the mineralogical composition of the clays were determined. The influence of a varying K sorption capacity of the clays on the K availability to plants was investigated in a growth experiment with *Chrysanthemum indicum*. The K availability in mixed substrates was determined by CAT, CAL and NH_4-acetate. Different cultivation practices were simulated by a varied beginning of K top dressing: `immediate´, `delayed´ and `no´ K top dressing.

The observed and calculated (Langmuir) K sorption capacity of the clays could be well-characterized by both the batch experiment and the adsorption isotherms and was highly correlated with the *CEC*. A higher K adsorption of the amended clay resulted in a lower K concentration in the solution of peat-clay blends, while the CAT extractable K concentration (K_{CAT}) was the same. Without K top dressing, it also led to an enhanced plant growth and higher shoot K concentrations. Plants were able to take up the whole amount of exchangeable K and also part of the non-exchangeable K in some peat-clay blends when no K was additionally fertilized. The K amount released from the clays ranged in the same magnitude as the maximal desorbable K determined in the percolation experiment and was highly dependent on the mineralogical composition of the clays in the order: smectite > illite, kaolinite. However, the released K amounts were far too low to ensure optimal plant growth.

2.2 Introduction

Potassium (K) is an essential plant nutrient and plays a major role in plant growth and metabolism. Plants need about 20-50 mg K g^{-1} shoot dry matter (DM) for optimal growth. Thus, K is quantitatively the second most important plant nutrient, next to nitrogen. Generally soil K can be subdivided into for different fractions which are in equilibrium with each other: structural K, non-exchangeable, exchangeable and solution K, which can directly be taken up by plants (*Sparks*, 1987). Exchangeable K is weakly bound to surfaces of clay minerals and humic substances and can be rapidly exchanged by other cations. The non-exchangeable fractions of K are held between layers of 2:1 clay minerals, e.g. illite, smectite and vermiculite, and are regarded as slowly available while the structural or mineral K is integrated within the crystal structures of minerals and only very slowly released by weathering of the mineral (*Sparks*, 1987). Plants take up nutrients from solution around the roots and thereby create a gradient that drives K diffusion towards the root. By this the equilibrium between adsorbed and dissolved nutrients is disturbed and K is desorbed from the solid phase replenishing the soil solution and the latter is slowly replenished by the non-exchangeable forms. It is known, that plants may promote the expansion of mineral layers which leads to an enhanced K release. *Hinsinger* et al. (1993) could show a vermiculitization of different mica accompanied by a release of interlayer K, possibly due to a root-induced pH decrease in the rhizosphere of rape plants.

Vice versa, soluble or exchangeable K can be bound in the interlayers of clay minerals if the K concentration of the soil solution increases e.g. due to K fertilization, leading to a collapse of silicate layers to 1 nm. This process is called K fixation (*Tice* et al., 1996). In contrast to phosphorus, K fixation and release are considered to be reversible and symmetric at least at a short-term scale (*Schneider* et al., 2013). The K fixation is generally enhanced with increasing K concentrations in the solution and a high negative layer charge of the clay mineral, but is negatively influenced by competing cations, mainly Ca and Mg (*Huang*, 2005; *Simonsson* et al., 2009; *Schneider* et al., 2013). Its small size and the low hydration energy seem to be the major factors for the selectivity and fixation of K. Cations with low hydration energy produce interlayer dehydration and layer collapse and are therefore fixed in interlayer positions (*Sawhney*, 1973).

Easily available soil K is mostly determined by the extraction with NH_4-acetate, Doppellactat (DL; *Egner et al.*, 1960) or Ca-acetate-lactate (CAL) which extract mainly solution- and exchangeable K. In Germany also CAT (0.01 M $CaCl_2$) is widely used for the extraction of plant available nutrients in horticultural substrates, but the extraction power is lower. *Alt* et al. (1993) observed, that the CAT method extracted ~25% less K than CAL. But plants take up not only the solution- and exchangeable K but also part of the non-exchangeable fraction (*Schachtschabel*, 1937; *Meyer* and *Jungk*, 1993; *Hinsinger* and *Jaillard*, 1993; *Jalali* and *Kolahchi*, 2007). The extent of the contribution of non-exchangeable K to plant nutrition is mainly dependent on the type and layer charge of the clay minerals, the initial K status of the soil and on plant factors (*Meyer* and *Jungk*, 1993). Plant roots decrease K to very low concentrations in the solution (*Steingrobe* and *Claassen*, 2000) and release H^+ (*Trehan* and *Sharma*; 2002), enhancing the release of non-exchangeable K. Additionally, K efficient genotypes often show a larger root surface area increasing the area for diffusion.

Peat is commonly used as main component of horticultural substrates but it has a very low buffering capacity for monovalent cations such as potassium (*Jungk*, 1964). This disadvantage can be overcome by the addition of clay minerals, but their chemical properties may vary widely depending on the mineral composition. The aim of this study was (i) to determine the K sorption and desorption characteristics of several substrate clays and (ii) to investigate the contribution of the K supply of clays to plant nutrition and the safety of plant cultivation at missing or delayed K top dressing.

2.3 Material and methods

2.3.1 Characterization of clays

Based on differences in their K adsorption observed in a preliminary batch experiment seven clays were preselected for the characterization of their K sorption capacity. The clays were shaken for 24h in a batch experiment in a 0.01 M $CaCl_2$-solution with 600 mg K L^{-1} as KH_2PO_4 at a ratio of 1:10 (w/v) at pH ~5.5 in three replicates. The adsorbed amounts at equilibrium, ΔK (mg kg^{-1}), were calculated from the change of the K concentration in the solution. Based on the obtained results three clays differing in their sorption capacity were selected for further investigations: clay 04S (low), 01S (medium) and 06B (high K sorption capacity). For these clays K/Ca sorption isotherms were established according to *Fischer* and *Niederbudde* (1978). The Ca concentration of solutions was kept constant (0.01 M $CaCl_2$) while the K concentration was varied from 0 to 400 mg L^{-1}. One gramm of the different clays was dispersed in 10 mL of the solutions with increasing K concentrations and shaken for 24 h in three replicates. From the change of the K concentration in the solution the amount of adsorbed and desorbed K was determined (ΔK) and for the description of the adsorption processes the data were fitted to the Langmuir equation in order to calculate the maximum adsorption capacity (equation 1).

$$\Delta K = K_{max}\, L_e\, K_e / (1 + L_e\, K_e) \qquad (1)$$

where ΔK is the adsorbed amount (mg kg^{-1}), K_e the equilibrium concentration (mg L^{-1}), K_{max} the adsorption capacity (mg kg^{-1}) and L_e the equilibrium constant of adsorption (Langmuir constant).

Additionally, a percolation experiment modified after *Meyer* and *Jungk* (1993) was conducted to characterize desorption behaviour of the untreated clays as influenced by the time and the K concentration in the solution, and to determine the maximal desorbable K amount. One gramm dried clay was placed between two layers of 1.5 g acid washed quartz sand in the cylinder of a 5-mL syringe in three replicates continuously percolated with a 0.01 M $CaCl_2$ solution at a rate of 3 - 5 mL h^{-1} for 7 to 21 days. Samples of the percolate were taken in intervals of 2-4 h (at daytime). The experiment was finished when the infiltration of the clay was reduced clearly.

2.3.2 Preparation of substrates

Peat-clay substrates were prepared by mixing white peat with 200 kg clay per m³ peat. In order to determine the fertilizer amount necessary for reaching the targeted CAT-extractable K concentration (K_{CAT}) K buffering curves were prepared for each substrate. For this, peat and the three peat-clay mixtures were fertilized with 150 mg N and 60 mg P L^{-1} substrate in form of NH_4NO_3 and NaH_2PO_4 * 3 H_2O, respectively. The pH was adjusted to pH 5.5 with $CaCO_3$. Potassium was added in six increasing concentrations from 0 to 300 mg K L^{-1} substrate as K_2SO_4. The fertilized substrates were stored at room temperature for 72 h prior to the determination of K_{CAT}.

For the plant experiment peat-clay mixtures and pure white peat as control were fertilized with (in mg L^{-1} substrate): 150 N as NH_4NO_3, 50 and 100 P as NaH_2PO_4 * 3 H_2O, respectively, depending on the P binding capacity of the clays, and 100 Ferty® 10 (micronutrients; Planta Düngemittel GmbH, Germany). Potassium was supplied according to sorption curves yielding a K_{CAT} of 60 mg K L^{-1} substrate at the following rates (in mg K L^{-1} substrate): peat = 63; peat+04S = 68; peat+01S = 84; peat+06B = 79.

2.3.3 K buffering of clays and safety of plant cultivation

The influence of the K sorption and desorption behaviour of the peat-clay substrates on growth and quality of pot plants was characterized in a plant experiment. Cuttings of *Chrysanthemum indicum hybr. `Mega Time Gold´* were planted in plastic pots (∅ 10 cm, volume ~350 ml) filled with the different peat-clay substrates and peat as control. During the experiment plants were fertilized by top dressing in sum 8 times, once a week on top of the substrate surface with (in mg $plant^{-1}$): 25 N as NH_4HO_3, 4.4 P as NaH_2PO_4* 2 H_2O, 1 Mg as $MgSO_4$ * 7 H_2O, 0.09 B as H_3BO_3, 0.36 Cu as $CuSO_4$* 5 H_2O, 0.09 Mn as $MnSO_4$ * H_2O, 0.15 Mo as $NaMoO_4$ * 2 H_2O, 0.05 Zn as $ZnSO_4$ * 7 H_2O and 0.6 Fe as Fe-EDTA. In order to simulate possible cultivation irregularities the beginning of K liquid top dressing was varied: The fertilization with 25 mg $plant^{-1}$ $week^{-1}$ started 1 week and 4 weeks after planting and the treatments were called *`immediate´* and *`delayed´.* A third treatment did not receive any K top dressing at all (*`none´*). Thus, treatments with immediate and delayed K top dressing received in total 200 and 100 mg K $plant^{-1}$, respectively.

One week after planting plants were pruned in order to inducing branching and by this ~15 mg K $plant^{-1}$ were removed. After 10 weeks of cultivation plant aspect was evaluated and substrate samples were taken. Plant shoots were harvested and divided into four fractions: young, middle and old leaves (including the petioles) and stems. The total K uptake per plant was calculated as the sum of the K amount per plant shoot, roots (5% of the K in shoots) and the pruned plant material. The K content of the cuttings was subtracted.

The K release from the initial K pool of the clays in the mixed substrate was calculated as the difference between the fertilized and taken up K minus the K release from pure peat.

2.3.4 Physical and chemical analyses of clays and substrates

The texture of clays was determined by sieving and sedimentation after removal of organic matter by wet oxidation with H_2O_2 according to DIN ISO 11277: 2002-08. The determination of the cation exchange capacity (*CEC*) occurred using the complex of Cu^{2+} with triethylenetetramine according to *Meier* and *Kahr* (1999). The mineralogical composition of the clay fraction was determined by X-ray diffraction analysis of the oriented samples after removal of Fe-oxides and the chemical composition of the clays took place by x-ray fluorescence (S4 Explorer, Bruker).

The pH of the substrates was measured in 0.01 M $CaCl_2$ at a substrate:solution ratio of 1:2.5 and the determination of the bulk density occurred after a defined compaction of the samples by repeated tamping according to *VDLUFA* (1991). For the determination of CAT extractable K (K_{CAT}) according to *Alt* and *Peters* (1992) 20 g fresh substrate were shaken for 1h in 160 mL CAT-solution (0.01 M $CaCl_2$ + 0.002 M DTPA). CAL soluble K (K_{CAL}) was measured in 0.05 M Ca-acetate with 0.05 M Ca-lactate and 17.9 mL acetic acid (100%) L^{-1} at a ratio of 1:20 (w/v) at pH ~4.0 (*Schüller,* 1969) and the extraction of NH_4-acetate (NH_4OAc) extractable K (K_{acet}) took place with 1 M NH_4OAc, pH 7 at a soil:solution ratio of 1 : 10 with an extraction time of 1h. Furthermore, the substrate solution was separated by centrifugation at 3000 g for 20 min. To ensure comparable conditions all substrates were watered or dried to the same volumetric water content of 45% 48 h before centrifugation and measuring the K concentration in the substrate solution (K_{sol}). All solutions were filtered before analysis (100% cellulose filter paper, 2-3 µm pore sizes). The buffer power (*b*) could be calculated as the ratio of K_{CAT}/K_{sol}. The K concentration in all solutions was measured by AAS (2100 Atomic Absorption Spectrophotometer, Perkin-Elmer, USA).

2.3.5 Chemical analysis of plant material

Plant material was dried at 70℃ for 5 d and ground. Potassium in plant tissue was determined after dry-ashing at 480℃ for 8 h, dissolving the ash in 1:3 diluted HNO_3 at a ratio of 1:20 (w/v) and then diluting (1:10 v/v) with demineralized water. The K concentration in solutions was measured by AAS.

2.3.6 Statistics

Clays and mixed substrates were analysed in three replicates. For the plant experiment treatments were replicated six times (each replicate consisted of 7 plants) in a randomized block design and statistical analysis was performed with the program R 2.13.2. Means were compared between treatments using Tukey-test or Welsh t-test with $P < 5\%$.

2.4 Results

2.4.1 Characterization of clays and mixed substrates

The seven preselected clays had different physical, mineralogical and chemical characteristics and varied clearly in their ability to adsorb K (Tab. 2.1). The K adsorption (ΔK) determined in the batch experiment was positively correlated with the *CEC* ($R^2 = 0.84$), which ranged from 0.3 to 8.4 mol_c kg^{-1}, but not with the clay content of the samples ($R^2 = 0.20$) or their absolute K_2O amount ($R^2 = 0.51$).

The clays 04S, 01S and 06B were selected for a more detailed characterization of the K adsorption and desorption dynamics because of their clear differences in ΔK (Tab. 2.1). The maximum adsorption capacity (K_{max}) of the three clays determined from the adsorption isotherms (Fig. 2.1) was in the same order as determined in the batch experiment (Tab. 2.1).

It was 4 and 40 times higher in clay 06B than in the clays 01S and 04S, respectively. The isotherm of clay 06B also had the steepest slope and a plateau was not reached within the tested conditions. Clay 01S showed a high K adsorption up to a K concentrations in the equilibrium solution (K_e) of about 20 mg K L^{-1}, but afterwards the isotherm plateaued. The isotherm of clay 04S had a very flat curve progression and the clay did not adsorb considerable amounts of K.

Tab. 2.1: Physical, chemical and mineralogical properties of seven clay samples from the Westerwald area, Germany, representing saprolitic (S), bentonitic (B), relocated clays (U) and blends (M). Marked clays were used for further investigations and in the plant experiment.

Clay	Clay content[a]	CEC[b]	K_2O[c]	Fe_2O_3[c]	ΔK[d]	Mineralogical composition[e]
	[wt %]	[mol_c kg^{-1}]	[wt %]	[wt %]	[mg kg^{-1}]	d = dominant; t = traces
04S	21	0.3	2.8	2.8	95	d: illite, kaolinite
36M	63	1.0	1.9	2.0	514	d: kaolinite, illite
28U	80	2.3	2.0	5.1	1338	d: kaolinite, illite
01S	13	0.6	4.2	8.9	1670	d: illite, kaolinite; t: chlorite, quartz
38M	35	4.9	1.6	10.3	2359	d: kaolinite, illite
06B	21	7.4	1.2	13.4	4137	d: smectite; t: illite, kaolinite
07B	13	8.4	1.4	12.9	4306	d: smectite; t: illite, kaolinite

[a] Particle size distribution according to DIN ISO 11277: 2002-08

[b] Cation exchange capacity (*CEC*) determination with *Cu-trien*

[c] Chemical composition determined by x-ray fluorescence

[d] K sorption determined in a batch experiment with 600 mg K L^{-1} solution

[e] Mineralogical composition of clay fraction determined by X-ray diffraction analysis of oriented samples after removal of Fe-oxides

Furthermore, the clays also differed in their equilibrium K concentration at which neither K adsorption nor desorption occurred, ΔK = 0 (K_{e-0}). The clays 04S and 01S started to release K when the K_e was lower than 1.2 and 1.5 mg K L^{-1}, respectively, whereas K desorption in clay 06B already occurred below 7 mg K L^{-1}. Because of these differences in K_{e-0}, the absolute ΔK was higher in clay 01S than in 06B at low equilibrium concentrations (<20 mg K L^{-1}).

The K desorption capacity of the clays could not be characterized sufficiently by the adsorption isotherms. Therefore, a desorption experiment was conducted and the pure clays, not loaded with K were constantly percolated with a K-free $CaCl_2$-solution. The by far highest K desorption was observed in clay 06B (Fig. 2.2-A). It released 5-10 times more K than the clays 01S and 04S, respectively.

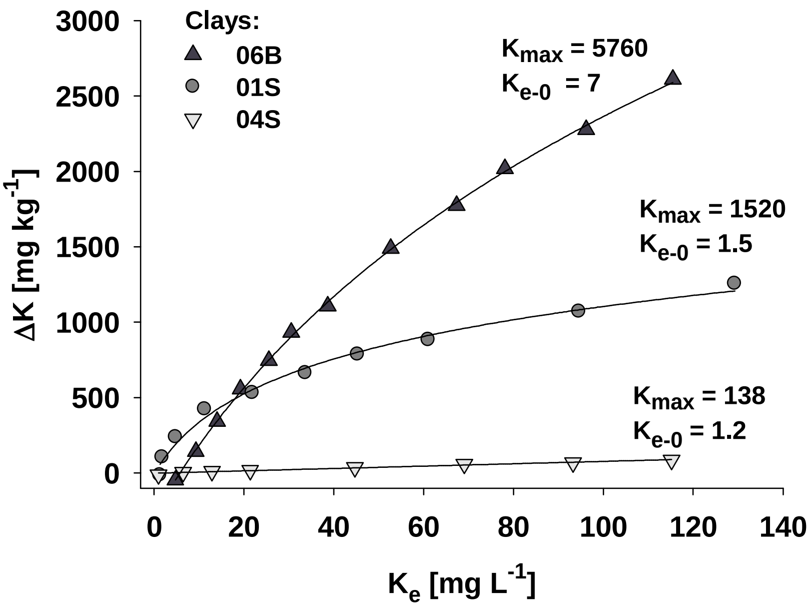

Fig. 2.1: Sorption isotherms of the three selected clays. With ΔK = the adsorbed/desorbed K amount; K_{max} = the calculated maximum K adsorption capacity [in mg kg^{-1}]; K_e = the equilibrium concentration in the shaking solution; K_{e-0} = the equilibrium concentration at which neither adsorption nor desorption occurred [in mg L^{-1}].

The dynamic of K desorption from the clays could be clearly divided into an initial fast release and a subsequent slower release (Fig. 2.2-B). In the first phase, about 90% of the maximal desorbable K was already released, lasting for only ~10 h in the clays 04S and 01S, while in clay 06B considerably high amounts of K were released for more than 20 h. The K concentration in the percolation solution (K_{perc}) fell to values <0.2 mg K L^{-1} within two days in all clays and afterwards the rate of release of adsorbed K stayed very low.

For the mixed substrates the K buffering curves were prepared in order to determine the fertilizer amount necessary for reaching the targeted CAT-extractable K concentration (K_{CAT}) in the different substrates (Fig. 2.3-A). The K_{CAT} increased with increasing K fertilizer amounts in the order peat > peat + clay 04S > peat + clay 01S > peat + clay 06B as indicated be the slope of the curve. However, the K fertilization required to obtain the targeted value of 60 mg K L^{-1} substrate was lower for clay 06B than for clay 01S since 06B already contained clearly more K_{CAT} without any K fertilization.

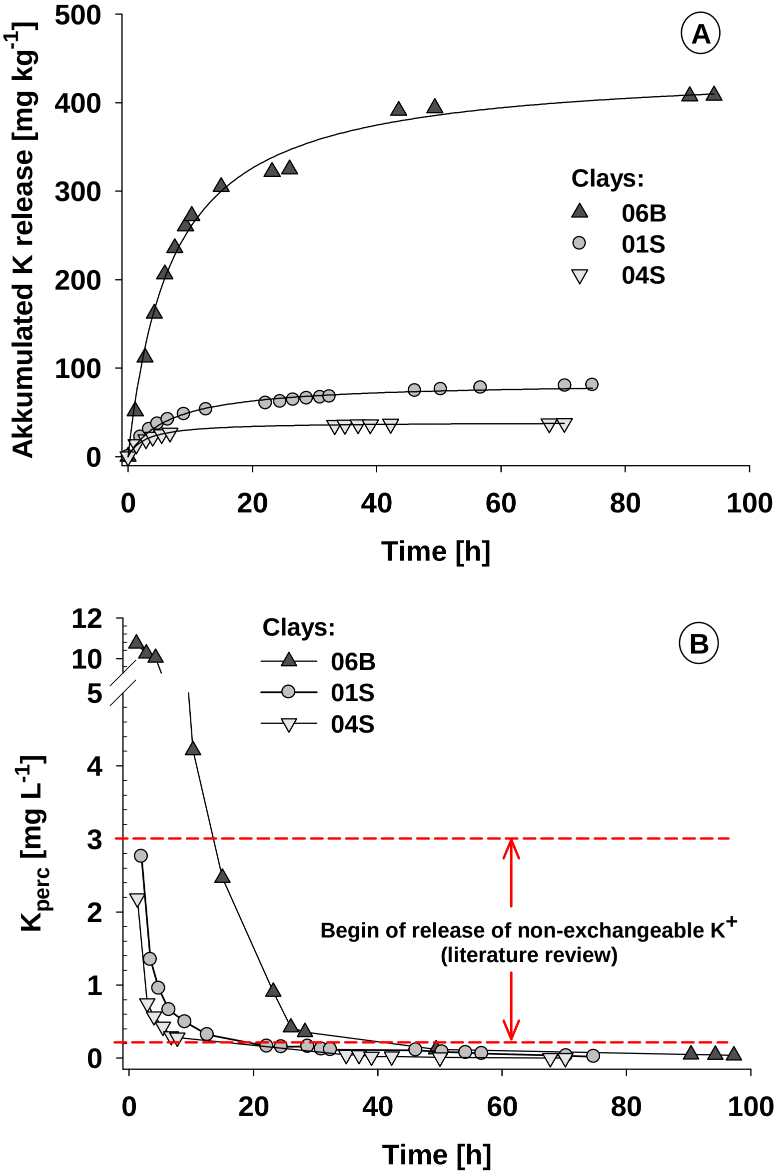

Fig. 2.2: K release of the clays which were constantly percolated with 3-5 mL 0.01 M $CaCl_2$ solution per hour. (A) Accumulated K release and (B) K concentration in the percolation solution (K_{perc}) during the course of the experiment. The range of solution concentrations at which the release of non-exchangeable K is believed to begin is marked in red.

At the beginning of the plant experiment all substrates contained 60 ± 10 mg K_{CAT} L^{-1} substrate (Fig. 2.3-B). In contrast, the K concentration in the substrate solution (K_{sol}) differed widely from ~120 mg L^{-1} in peat to ~20 mg L^{-1} in the blend with clay 06B, resulting in an increasing buffer power (*b*) in the order: peat < peat + clay 04S < peat + clay 01S < peat + clay 06B.

At the end of the plant experiment both K_{CAT} and K_{sol} were strongly depleted to values of <5 mg K L^{-1} substrate and <2 mg K L^{-1} substrate solution, respectively, in all treatments (data not shown).

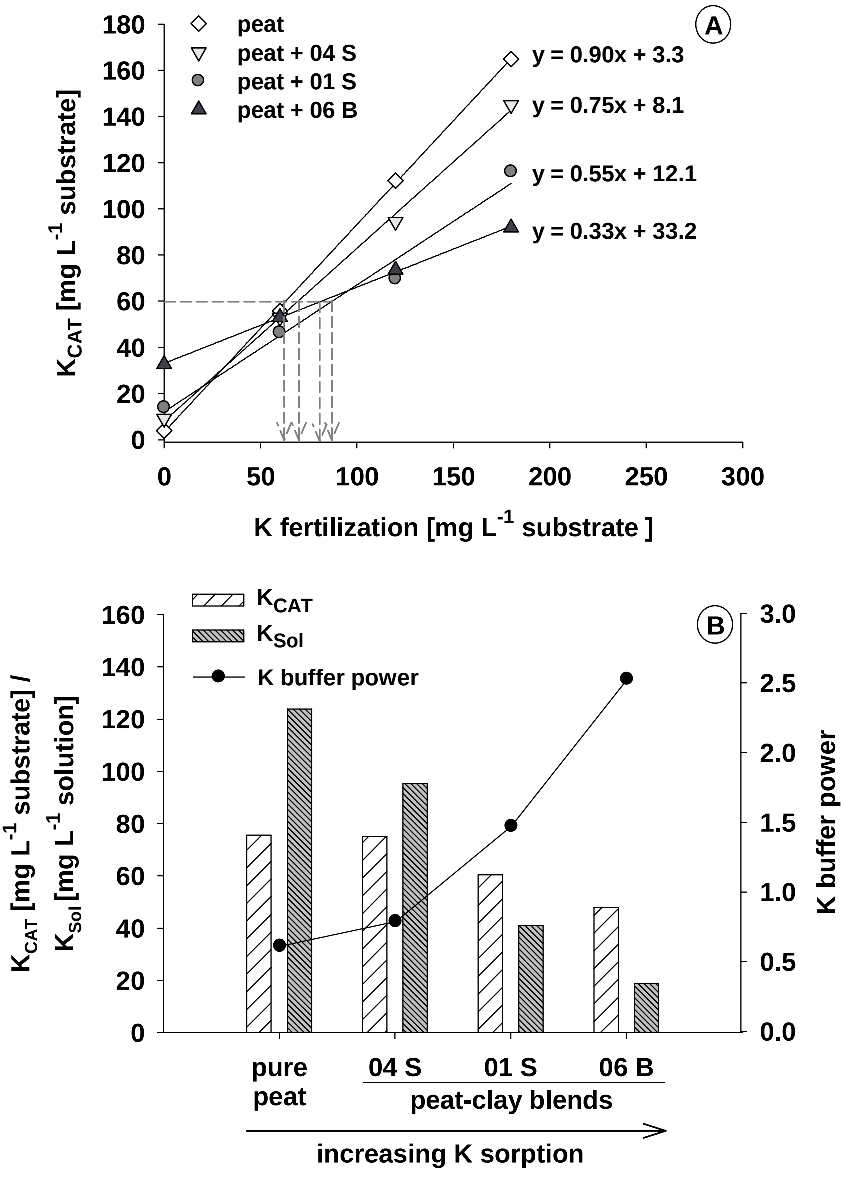

Fig. 2.3: K buffering curves of peat and three peat-clay mixtures. Curves were used for the determination of the K fertilization to obtain a CAT extractable K concentration (*K_{CAT}*) of 60 mg L^{-1} substrate (A). *K_{CAT}*, K concentration in the substrate solution (*K_{Sol}*) and the resulting buffer power of peat and three peat-clay mixtures at the beginning of plant cultivation (B). Data are adapted from *Meyer* (2012).

2.4.2 Plant growth and K in plant matter

After ten weeks cultivation the varied K top dressing resulted in clear differences in plant quality and DM yield among substrates. The elongation of shoots (Fig. S.2, supplementary data) and the DM yield of plants were enhanced by increasing K fertilization in the order none < delayed < immediate top dressing in all substrates, but the effect was clearest in the substrates with a low K sorption capacity, peat and peat + clay 04S (Fig. 2.4-A). Differences between substrate types were most evident in the treatment “no top dressing”, where plant DM was increased with increasing K adsorption capacity of the clays in the order peat = peat + clay 04S < peat + clay 01S < peat + clay 06B. In this treatment plants grown in peat, in the peat-clay mixture 04S and in some cases also in 01S showed clear symptoms of K deficiency like chloroses on old leaves, leaf shedding and wilting (Fig. S.3, supplementary data). The plants grown in blend 06B were free of symptoms.

At delayed K top dressing the differences between substrates were diminished and when K fertigation was started immediately plants reached the same DM yield in all substrates.

An earlier start of K top dressing resulted in increased K concentrations in plant matter in all substrates (Fig. 2.4-B). Without K top dressing, K concentrations in shoots were lowest in peat and increased with increasing K sorption of substrates. When K top dressing was begun delayed or immediately the differences between the substrates were diminished but peat-clay blend 06B still had a significantly higher shoot K concentration than the other blends. In all substrates plants reached their maximum shoot weight at about 17-20 mg K g^{-1} shoot DM.

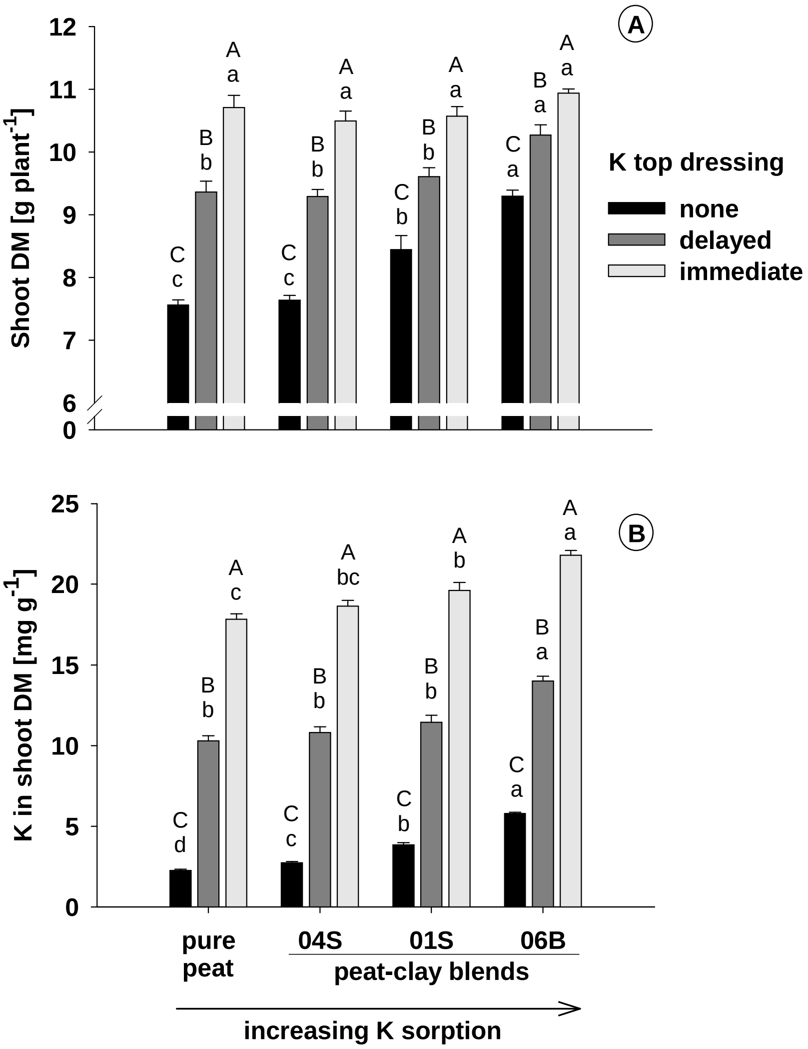

Fig. 2.4: Shoot dry matter (A) and shoot K concentration (B) of *Chrysanthemum indicum* depending on substrate type and beginning of K top dressing. Error bars illustrate standard errors. Different capital letters indicate significant differences between fertilization treatments within the same substrate and different small letters indicate significant differences between substrates at the same K fertilization level ($p<0.05$). Data are adapted from *Meyer* (2012).

Because K deficiency was first visible in old leaves the distribution of K in different development stages of leaves was analysed (Fig. 2.5).

In the treatments “no” and “delayed” K top dressing K concentrations were highest in young leaves and decreased with increasing leaf age. With immediate K top dressing the pattern was the other way round. Here old leaves had higher K concentrations than middle and young leaves independent of the substrate type. Differences between the fertilization treatments were most obvious in the old leaves. Independent of the K treatments all leaf stages of plants grown in peat-clay blend 06B had significantly higher K concentrations than those grown in the other blends or pure peat.

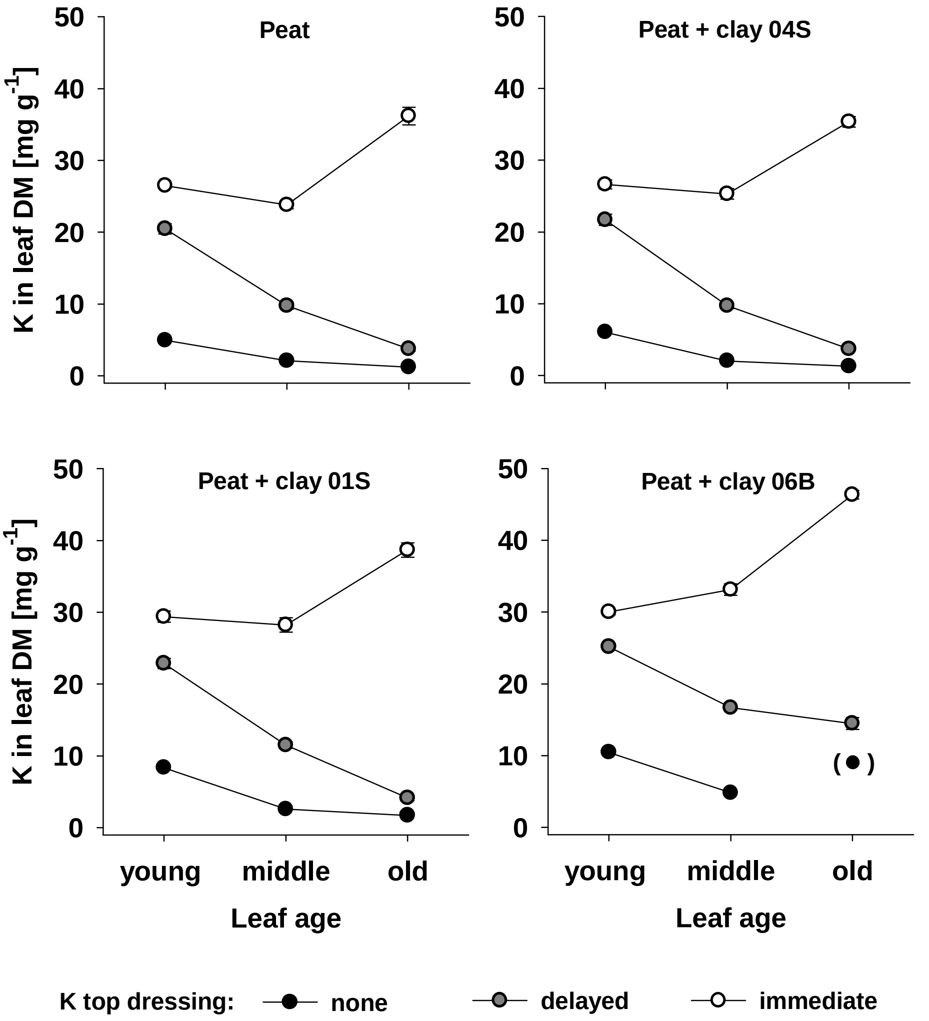

Fig. 2.5: K concentration in young, middle and old leaves of *Chrysanthemum indicum* grown in peat and three different peat-clay blends at varying K top dressing. Error bars illustrate standard errors. (•) = data not reliable. Data are adapted from *Meyer* (2012).

To characterize the capacity of the different clays to supply the plants with K the K amount contained in the plant DM was calculated for the treatments without K top dressing and compared to the fertilized K per pot as well as the K amounts determined with the different substrate extraction methods (Fig. 2.6). In the weakly buffered substrates peat and peat + clay 04S the CAT extraction approximately determined the fertilized K amount while in the peat-clay blends 01S and 06B not all of the fertilized K could be detected. When CAL or NH_4OAc were used more K could be extracted than with CAT in all substrates. In blend 01S the two extracting agents only determined the fertilized K amount whereas in the other substrates the dissolved K clearly exceeded the fertilized K. This effect was strongest in peat-clay blend 06B. In all substrates both methods showed comparable results but in peat-clay blend 06B much higher K contents were determined by NH_4OAc than by CAL. Plant K uptake increased clearly with increasing K sorption of substrates in the order peat < peat + clay 04S < peat + clay 01S < peat + clay 06B, but in all substrates plants were able to take up more K than was fertilized or CAT-extractable before. In peat-clay blend 06B the K amount taken up exceeded the fertilized and CAT-extractable K amount, respectively, by three and four times, respectively. In the substrates peat and peat + clay 04S plant uptake was equal to the CAL and NH_4OAc extractable K, while in the blends 01S and 06B considerably more K could be taken up than was extractable with these methods.

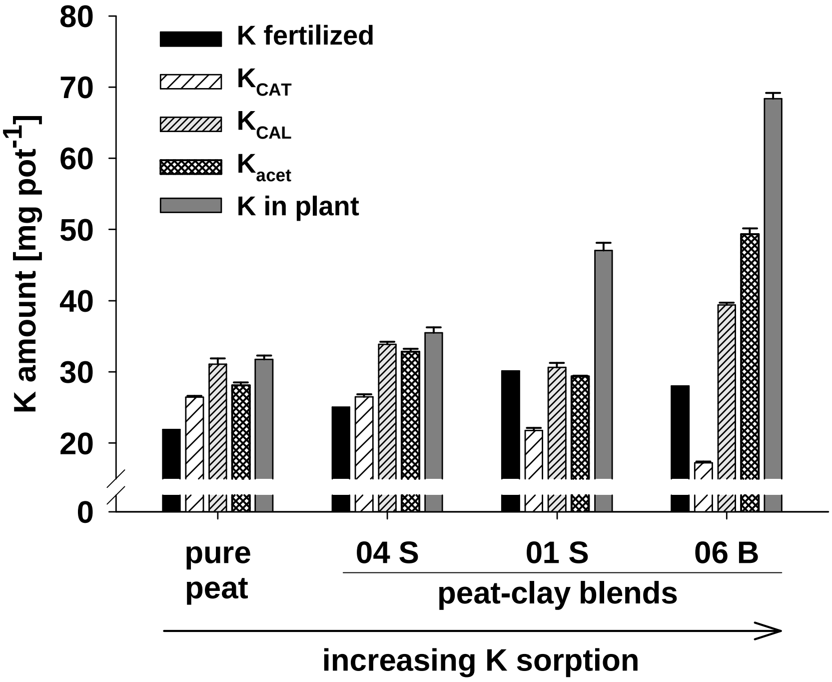

Fig. 2.6: Amounts of K fertilized, K extracted by CAT, CAL and NH_4OAc per plant container (0.35 L substrate) at the beginning of cultivation and K contained in DM of *Crysanthemum indicum* plants grown in pure peat and three different peat-clay blends without K top dressing. Error bars illustrate standard errors. Data are adapted from *Meyer* (2012).

2.5 Discussion

2.5.1 Growth and quality of *C. indicum*

Growth and quality of *C. indicum* plants were influenced by the K fertilization as well as the substrate clay. Without K top dressing plants in substrates pure peat, peat + clay 04S and peat + clay 01S suffered from K deficiency illustrated by typical symptoms such as suppressed growth, chloroses and necroses, especially on old leaves, and even dieback of leaves (*Bestford*, 1978; *Dong* et al. 2004) while the intensity of symptoms was diminished with increasing buffer power of substrates (Fig. 2.4-A + Fig. S.3, supplementary data).

The critical K concentration for optimal yield (90% of maximum yield) was about 17-20 mg K g^{-1} shoot DM and 30-50 mg g^{-1} in the DM of old leaves, respectively, which is in the same range as described in literature for many plant species (*Leigh* and *Jones*, 1984). This concentration was reached with immediate K fertigation in all substrates (Fig. 2.4-B). In contrast, *Deiser* (1996) recommended a shoot K concentration of 35-50 mg g^{-1} DM for optimal nutrition of *Chrysanthemum indicum* plants.

The distribution of K between different leaf ages was a better indicator of the nutritional status of the plant than the K concentration of the whole shoot, because K is highly phloem mobile and is relocated from old to young, growing leaves under K deficiency. At missing or delayed K top dressing the K concentrations in young leaves were higher than in the old ones indicating K deficiency (Fig. 2.5). Only with immediate top dressing the concentrations were highest in old leaves. Thus, it can be concluded, that plants were sufficiently supplied with K in this fertigation treatment.

The same discrepancy between young and old faba bean leaves was observed by *Aini* and *Tang* (1998) under K deficiency and *Pérez Melián et* al. (1977) could not detect weak K deficiency by analysis of the shoot K concentration of lettuce plants although the DM production was already significantly reduced compared to sufficiently supplied plants.

The differences in concentrations between leaf ages were more evident in pure peat and peat-clay blends 04S and 01S than in blend 06B emphasizing the observed difference in plant quality and growth between the substrate treatments. In horticultural practice, K deficiency could be best detected by a K analysis of old, but not senescent leaves. Here, greatest differences in the nutritional status of the plants were observed, either between the K fertilization levels or the substrate treatments.

2.5.2 Characterization of the potassium adsorption of clays

The K adsorption of the 7 clays could be easily determined by a single point batch experiment and correlated positively with the *CEC* of the clays, which is in agreement with similar findings described in literature (*Bouabid* et al., 1991; *Sardi* and *Csitari,* 1998; *Ghiri* and *Abtari*, 2012). Therefore, the *CEC* can be a helpful parameter for the comparison and pre-selection of different clays with regard to their K sorption capacity. *Ghiri* and *Abtari* (2012) additionally related the K fixation capacity of 24 calcareous soils to their clay and smectite content. However, the clay content of our 7 clays had no influence on the K binding, but highest K adsorption was also measured in the smectite-rich clays 06B and 07B. In contrast to kaolinitic clays, where only planar external surface sites are available for ionic exchange, the interlayer space of smectitic clays is able to swell with adequate hydration and thus also interlayers contribute to K adsorption (*Sparks* and *Carski*, 1985). Thus, it can be concluded that rather the type instead of the content of the clay mineral is important for the K adsorption behavior.

More detailed information about the adsorption process were obtained by the adsorption isotherms (Fig. 2.1). The three tested clays differed clearly in their maximum adsorption capacity (K_{max}). For the clay 04S and 01S K_{max} agreed well with the ΔK determined in the single-point batch experiment, but in 06B the calculated K_{max} was much higher than the one measured in the batch experiment. Thus, the K concentration used in the batch experiment was not high enough to reach K saturation in this clay.

Furthermore, the K concentration in solution at which $\Delta K = 0$ ($K_{e\text{-}0}$) for the different clay was derived from the isotherms. In the clay 06B the $K_{e\text{-}0}$ was much higher than in the clays 04S and 01S (Fig. 2.1). Due to this shifting of the isotherm of clay 06B to higher K_e values, the absolute K adsorption of clay 01S was higher than that of 06B at K_e <20 mg K L^{-1}.

A high $K_{e\text{-}0}$ value may prohibit a decrease of the K concentration in the soil solution to very low concentrations, and thus, ensure a more stable nutrient supply of the plants, as long as the amount of desorbable K is sufficiently high.

The results illustrated that the batch experiment performed with a single high dose of K was suitable to characterize possible differences in the K sorption capacities of clays, even if K_{max} was not achieved, because the solution concentrations in mixed substrates are often lower than required for K_{max} (Fig. 2.1 and Fig. 2.3-B). However, the K adsorption capacity should not be the only criterion for the evaluation and selection of a clay for the use in a horticultural substrate, but also the concentration at which the clay starts to desorb K ($K_{e\text{-}0}$) and the adsorption behavior at low solution concentrations should be considered, which can be best described by adsorption isotherms (*Beyme* and *Richter*, 1984; *Schneider* et al., 2013).

However, the K adsorption of the clays in mixed substrates may be different from the expected ΔK determined for the pure, untreated clays. It has to be considered that the K adsorption is time dependent and strongly affected by the concentration of competing cations such as Ca^{2+} and Mg^{2+} (*Moritsuka* et al., 2004; *Schneider* et al., 2013). In mixed substrates different other cations occur in high concentrations, originating from fertilization and liming. Thus, the ΔK determined by the laboratory methods is only a representative for the given conditions.

2.5.3 K availability in peat-clay substrates

The determined order in K sorption of the clays, 06B > 01S > 04S, was also reflected in the substrates blended with the clays, where the buffer power determined by K_{CAT} / K_{sol} (Fig. 2.3-B) was also ranked in this order, but the differences between the mixed substrates were not as pronounced as the differences of K_{max} between the pure clay samples. Furthermore, the amount of K_{CAT} without K fertilization was much higher in peat-clay blend 06B compared to the other blends (Fig. 2.3-A), which is in line with the higher value of $K_{e\text{-}0}$ determined with the adsorption isotherm in this clay (Fig. 2.1). Therefore, the fertilizer amount necessary for reaching the targeted K_{CAT} was lower in this peat-clay blend than in the blend amended with clay 01S although the latter had a lower K_{max} and a lower buffer power (Fig. 2.3-A).

The K concentration in the substrate solution (K_{sol}) at the beginning of plant culture differed clearly between the substrates according to the K binding capacity of the clays, although K_{CAT} was similar in all mixtures (Fig. 2.3-B). In blends 04S and 01S the amount of K_{sol} was almost equivalent to the amount of K_{CAT}, whereas in 06B it was only 20% of K_{CAT}. In outdoor cultivation systems or with overhead irrigation substrates with a low buffer power bear a higher risk of K leaching especially at the beginning of plant culture when the K concentrations in the substrate solution are very high and plant uptake is still very low (*Heming* and *Rowell*, 1997; *Jalali* and *Kolahchi*, 2008; *Rosolem* et al., 2010). Additionally, a high K sorption can also prohibit a supra-optimal K_{sol} leading to a deficiency of competing cations (*Jakobsen*, 1993)

During the cultivation *Chrysanthemum* plants strongly depleted the K_{CAT} and K_{sol} to very low values independent of substrate type and fertigation beginning, but it can be assumed that the K_{sol} of peat-clay blends 01S and 06B was held at the initial level over a longer time period than in peat and mixture 04S as their puffer power was much higher (Fig. 2.3-B). The strong K depletion of the substrate solution even with immediate K top dressing shows that the amount of fertilized K was not high enough to meet the plants demand and at the same time maintain the initial K status of the substrates.

Without top dressing uptake of plants clearly exceeded the K fertilization in all substrates (Fig. 2.6) indicating that the fertilized K was bound in exchangeable and easily available forms and no K fixation occurred. The K release from the initial K pool of the clays in the mixed substrate was calculated as the difference between the fertilized and taken up K minus the K release from peat, which was already about 10 mg K pot^{-1}. In the blends 04S, 01S and 06B about 2, 10 and 30 mg K pot^{-1}, respectively, were additionally released by the clays, which corresponds to ~30, 150 and 450 mg K kg^{-1} clay (data not shown).

Thus, the amount of K released from the initial K pool of the clays in mixed substrates was in the same range as the K desorption (K_{des}) determined in the percolation experiment (Fig. 2.2). In the blends amended with the clays 01S and 06B this additional K release could not only be attributed to exchangeable K but also to a high proportion to non-exchangeable K, which could not be extracted by NH_4OAc (Fig. 6). In sum, the non-exchangeable K

accounted for up to 30-40% of the K taken up by the plants without K top dressing in these blends, which is in line with results described in literature (*Kong* and *Steffens*, 1989; *Hinsinger* and *Jaillard*, 1993; *Meyer* and *Jungk*, 1993).
A release of non-exchangeable K from interlayer positions of clay minerals was supposed to occur, when the solution concentrations decreased below 5-80 µM K (~0.2 – 3.1 mg L^{-1}) (*Claassen* and *Jungk,* 1982; *Hinsinger* and *Jaillard*, 1993; *Springob* and *Richter*, 1998b). Thus, it can be concluded that the K_{des} in the percolation experiment was not only composed of exchangeable but also of non-exchangeable K (*Meyer* and *Jungk*, 1993; *Askegaard* et al., 2005; *Jalali* and *Zarabi*, 2006), and the non-exchangeable K was probably already released at concentrations in the upper range described in literature, as the release rates at solution concentrations below 0.2 mg K L^{-1} were too low to account for the high amounts of non-exchangeable K determined in the plant experiment (Fig. 2.2-B). A similar pattern of an initial fast release and a subsequent slower release of K was also observed by *Ghosh* and *Singh* (2001) and *Jalali* and *Zarabi* (2006) who determined K release rates for different soils.

The absolute K release from the clays was in the order 04S < 01S < 06B (Fig. 2.2-A) and could be related to the mineralogical composition of the clays (Tab. 2.1). The saprolitic clays 04S and 01S consisted mainly of illites. Pure illitic clays are characterized by a relatively high negative layer charge of 0.6-0.9 per half unit cell $[O_{10}(OH)_2]$ (*Mermut* and *Lagaly*, 2001) and interlayers are predominantly taken by K ions. In clay 01S higher concentrations of Fe_2O_3 than in clay 04S (Tab. 2.1) imply that high amounts of Fe are present in the octahedron positions of the silicates, causing a more labile crystal structure and thus, leading to a facilitated K release in this clay compared to clay 04S (*Felix-Henningsen*, 1990). The bentonitic clay 06B consisted to a large extent of smectites, which have a much lower negative layer charge of 0.2 - 0.6 per half unit cell $[O_{10}(OH)_2]$ and may contain different exchangeable interlayer cations besides K. The lower negative layer charge leads to a weaker K binding and an enhanced K release (*Sawhney* ,1973; *Inoue*; 1983; *Kong* and *Steffens*, 1989).
However, for the three clays used in our experiment the rate of K release at low K solution concentrations and the absolute amount of desorbable K were far too low to ensure optimum growth of plants as can be shown by severe growth depressions at the end of the plant experiment (Fig. 2.4-B).

2.5.4 Characterization of plant available K by different extraction methods

The differences in the K amounts, which could be extracted by the plants in the different peat-clay blends without K top dressing, could not be determined by the used substrate extraction methods (Fig. 2.6). CAT, which is commonly used for the evaluation of the nutritional status in horticultural substrates in Germany, clearly underestimated the plant available K amounts in all substrates. Here not even the initially fertilized K amounts could be extracted simulating K fixation by the clays. In contrast, CAL and NH_4OAc detected clearly more K than CAT, because NH_4^+ and H^+, which are used for K^+ exchange in the former methods, have a higher extraction power for K^+, bound on/in edge positions of interlayers, than the Ca^{2+} ion, used in the CAT procedure (*Jalali* and *Zarabi*, 2006).

However, when suffering from K deficiency, plants were able to take up 30-60% more K than characterized as plant available by CAL and NH_4OAc in the substrates blended with clays 01S and 06B. Furthermore, similar K amounts were extracted in the substrate blends 04S and 01S, although the actual K availability differed clearly between theses substrates. A poor correlation between the exchangeable K and crop response was also described by several other authors (*Cox* et al., 1999; *Askegaard* et al., 2005).

For the release of non-exchangeable potassium a high concentration gradient between K in the solid phase and K in the solution is needed, which cannot be provided by the presented batch-methods, where equilibrium conditions are fast reached (*Springob* and *Richter*, 1998a). Furthermore, K from interlayers is only slowly replenished to the substrate solution und is thus not extracted by the presented batch-methods, having shaking times of maximal 1.5 h (*Sparks* and *Carski*, 1985).

In contrast, the actual K release from the clays could be reliably predicted by the percolation experiment (Fig. 2.2), imitating the process of continuous depletion by plant roots. However, the method is very time consuming and susceptible to disturbances and therefore not applicable for standard use in horticultural practice.

2.6 Conclusions

The *CEC* of different clays already hinted at possible differences in their K adsorption behavior and should therefore be used for a first pre-selection of suitable substrate clays. The absolute extent of K adsorption could be well described by a single point batch experiment and, in more detail, by adsorption isotherms.

In peat-clay blends amended with highly K adsorbing clays, the K concentration in the substrate solution was much lower than in substrate blends with a low K sorption capacity, although the concentration of CAT-exchangeable K was similar. This could contribute to a reduction of K leaching.

The initially fertilized K could be fully taken up by the plants in all substrates indicating that no K fixation occurred. Without K top dressing considerable amounts of exchangeable and non-exchangeable K were additionally released from the initial K pool of the clays, especially in the substrate blend with the smectite-rich clay 06B, resulting in an enhanced plant quality and DM yield. Nevertheless, the K release was not sufficient to enable optimal growth of plants and to compensate for the missing K top dressing.

The actual magnitude of K desorption by the clays could be well predicted by the percolation experiment.

Chapter 3

Mn contained in substrate clays – harmful for plants?

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This is the pre-peer reviewed version of the following article

Binner, I. and Schenk, M.K. (2013): Mn contained in substrate clays – harmful for plants? *Journal of Plant Nutrition and Soil Science* 176, 809-817. DOI: 10.1002/jpln.201200433.

which has been published in final form at:
http://onlinelibrary.wiley.com/doi/10.1002/jpln.201200433/abstract

3.1 Abstract

Mixtures of peat and substrate-clays are commonly used as growing media for horticultural plant production and a quality protocol for substrate clays defined a threshold value of active manganese (Mn_{act} = sum of exchangeable and easily reducible Mn) in substrate clays of <500 mg kg^{-1} to prevent toxic reactions of pot plants. This threshold value was validated in experiments with peat-clay blends under different growing conditions, and nutrient solution experiments were additionally conducted to investigate the effects of silicic acid and dissolved organic matter on the occurrence of Mn toxicity. Common bean and hydrangea plants were cultivated in different peat-clay substrates and in peat under different moisture and pH levels. The clays varied in their Mn_{act} content from 4 to 2354 mg kg^{-1}. The results of the substrate experiments revealed that a threshold value for Mn in substrate clays is not justified, as plants grown in all peat-clay substrates did not develop any Mn toxicity even at high substrate moisture or low pH conditions which are known to increase the Mn availability. The extraction of active Mn did not well reflect the Mn concentrations in plant dry matter and substrate solution. As plants tolerated high Mn concentrations in the substrate solution compared to the nutrient solution without toxicity symptoms, the influence of silicic acid and dissolved organic matter (DOM) on Mn toxicity was characterized in a nutrient solution experiment. Manganese toxicity was clearly diminished by silicic acid application, but not by DOM. This most probably explains the tolerance of bean plants in peat-substrates where high silicon concentrations in the substrate solution were observed. Peat-clay blends even provided up to five times more silicon to plants than pure peat.

3.2 Introduction

Manganese is an essential micronutrient for plants, but it can become harmful when it occurs in excess. In aerated soils it predominantly occurs as Mn(III) and Mn(IV) (hydr)oxides, which are of low solubility. Thus, the Mn concentration in the soil solution is generally very low under aerobic conditions (*Mundus* et al., 2012). The bioavailability of Mn is mainly influenced by the level of easily reducible Mn oxides, pH and redox conditions. At low pH (< 5.5) Mn oxides can be reduced increasing the concentration of Mn(II) in the soil solution, which is also the form taken up by plants (*Millaleo* et al., 2010). At higher pH values Mn oxidation is favored. Under reducing conditions, which can be induced e.g. by waterlogging or soil compaction, the Mn availability can also be increased even at higher pH values (*Hue*, 1988). While the process of oxidation is catalyzed by chemolithotrophic bacteria, Mn reduction can be promoted by both microbial and chemical processes in the presence of protons and electron carrying reducing agents, which are excreted by plant roots and microorganisms or produced during the decomposition of organic matter (*Hue* et al., 2001; *Marschner* et al., 2003; *Uren*, 1981). Thus, Mn toxicity can become a problem in soils or substrates with high Mn reserves at low pH and under reducing conditions.

The critical Mn toxicity level in plant tissue varies widely between 200 and 4000 mg Mn kg^{-1} dry matter (DM) since plant species, genotype, age, temperature, light intensity, and nutritional interactions greatly affect plant tolerance (*El-Jaoual* and *Cox*, 1998). Wheat (*Fageria, 2001*) and common bean (*González* and *Lynch*, 1999), for example, are known to be relatively sensitive to excess Mn, while rice tolerates comparably high Mn concentrations without yield reduction (*Alam* et al., 2003).

The estimation of plant available Mn is difficult because of the high redox sensitivity of solution Mn and its various interactions with microorganisms in the rhizosphere (*Mundus* et al., 2012). Many chemical extraction methods have been proposed to determine the phytoavailability of Mn (*Başar,* 2009). Differentiation can roughly be made between methods used for the assessment of water-soluble Mn, exchangeable Mn and active Mn (Mn_{act} = sum of exchangeable and easily reducible Mn; *Baser* and *Saxena*, 1971). *Schachtschabel* (1957) found a good correlation between the Mn_{act} and the occurrence of Mn deficiency in oat plants. For the determination of Mn_{act} a reducing agent, e.g. hydroquinone, is added to the extraction solution, but the extraction procedure and the reagents used are not standardized. Recently, the technique of Diffusive Gradients in Thin-films (DGT) has been proposed as an alternative to the soil extractions with solutions (*Davison* et al., 2005), but *Mundus* et al. (2012) observed only a weak correlation between the Mn measured by DGT and plant tissue concentrations under aerobic conditions. So, soil tests do often not reflect the Mn availability properly since soil properties, plant species, environmental conditions and temporal fluctuations over a growing season are not considered (*Başar,* 2009; *Baser* and *Saxena*, 1971; *Mundus* et al., 2012).

In horticultural growing media clay minerals are frequently used for specific applications as additives to improve the chemical and physical properties of substrates. Application rates of 10-100 kg clay m^{-3} substrate are common. However, clays may contain high Mn concentrations which may become problematic for plant production. A threshold for Mn in substrate-clays of < 500 mg active Mn kg^{-1} clay was defined in a quality protocol for growing media raw material (*Stichting RHP,* 2010) in order to prevent toxicity in pot plants. However, results of *de Kreij* et al. (1993) indicated that the usage of Mn-rich clays is unproblematic for plant cultivation. So far only little is known about the potential for Mn toxicity in peat-clay substrates and the threshold given was never proven.

Clay minerals are also one of the major silicon (Si) pools in soils since Si is contained in crystalline silicates (*Sommer* et al., 2006). Silicon occurs mainly as monosilicic acid ($Si(OH)_4$) in the soil solution at concentrations between 2.5 and 20 mg L^{-1} and is taken up by plants in this form (*Epstein*, 1994). All plants contain Si in their tissues, although the concentrations vary considerably with species, ranging from 0.1 to 10% of leaf matter (*Ma*, 2004). According to *Epstein* (1994) plants with more than 1% Si in leaf DM can be considered as Si accumulators, e.g. rice, maize and cucumber. However, most plant species can be classified as non-accumulators with less than 1% Si in their leaf matter. Although Si is not considered as essential, it has a number of beneficial effects, including an enhanced resistance of plants to fungal and bacterial diseases and the alleviation of various abiotic and chemical stresses (*Ma, 2004*). It has been demonstrated that Si increases the tissue tolerance to Mn for many plant species including both, Si accumulators such as rice, barley and pumpkin, and non-accumulators such as common bean (*Ma*, 2004; *Maksimović* et al., 2012), but the interactions between Mn and Si seem to be species-specific. The mechanisms of Si in reducing Mn toxicity include a more homogenously distribution of Mn in the plant tissue (*Horst* and *Marschner*, 1978), a modified cation binding capacity of the cell wall (*Horst et* al., 1999), a lowering of the Mn concentration within the symplast (*Rogalla* and *Römheld*, 2002) or a significant reduction in membrane lipid peroxidation caused by excess Mn (*Shi* et al., 2005; for more details see review of *Liang* et al., 2007).

The aim of this study was to characterize the Mn availability in peat-clay substrates containing clay with high Mn reserves under normal growing conditions and under conditions which favor a high Mn solubility in order to validate the proposed Mn threshold for substrate clays. Furthermore, the effects of Si and peat derived dissolved organic matter on the occurrence of Mn toxicity were examined.

3.3 Materials and methods

3.3.1 Preparation of substrates

Mineral components with different textures were used for all substrate experiments. Although differing in their clay fraction (particle size < 2 µm), they will be referred to as (substrate-) clays in this paper. Six clays were selected according to their concentration in Mn_{act} in a preliminary screening experiment (Tab. 1). The clays 07B and 11B exceeded the Mn threshold of the quality protocol (500 mg Mn_{act} kg^{-1} clay). Clays were mixed with white peat at a ratio of 100 kg clay per m^3 peat. Additionally pure peat was used for control treatments. All substrates were fertilized with 1.1 g L^{-1} substrate of the compound fertilizer PG-Mix (14% N, 16% P_2O_5, 18% K_2O - YARA GmbH & Co. KG, Germany). The control plants in peat were additionally supplied with 1, 50, 100, 200, and 400 mg Mn L^{-1} substrate, respectively, in the form of $MnSO_4 * H_2O$ in order to establish concentrations in the range of the active Mn in peat-clay substrates (Tab. 3.1). The pH of the substrates was adjusted to 5.5 by the addition of $CaCO_3$ according to pH calibration curves. After storage for two weeks at room temperature, the substrates were compacted into plastic pots (∅ 13 cm; volume 0.8 L) to the bulk density previously determined as described in section 3.3.6.

Tab. 3.1: Active Mn concentrations (determined according to *Stichting RHP,* 2003) of selected substrate clays and mixed substrates

Substrate	Mn_{act} clay [mg kg^{-1}]	Mn_{act} substrate [mg L^{-1}]
Peat + Mn supply[a]		
Mn 1	-	1
Mn 50	-	38
Mn 100	-	67
Mn 200	-	182
Mn 400	-	351
Peat-clay mixtures[b]		
Peat + 15B	4	1
Peat + 36M	18	2
Peat + 01S	29	6
Peat + 38M	298	31
Peat + 07B	591	59
Peat + 11B	2354	266

[a] Mn supply in mg Mn L^{-1} substrate

[b] B = bentonitic clay; M = clay mixture; S = saprolitic clay

3.3.2 Evaluation of substrate clays under normal growing conditions

Manganese sensitive common bean plants (*Phaseolus vulgaris nanus* cv. “Saxa”) were grown in the different peat-clay blends and in peat enriched with Mn as controls to validate the Mn threshold for substrate clays. The bean plants were directly sown into the different substrates (1 plant pot^{-1}) and harvested four weeks after germination. During the experiment, plants were fertigated with a solution containing (in mg L^{-1}) 120 N, 20 P and 100 K in form of NH_4NO_3, $K_2HPO_4 * 3H_2O$ and K_2SO_4, and micronutrients (50 mg Ferty® 10 L^{-1}; Planta Düngemittel GmbH, Germany). All plants were grown in a greenhouse at day/night temperatures of 25°C/18°C, respectively, during a 1 6 h photoperiod. Additional light of 5 klx was supplied when the light intensity was below 25 klx.

3.3.3 Evaluation of substrate moisture

Bean plants were grown in the five peat treatments and in the two peat-clay treatments 01S + 11B under “normal” and “moist” substrate conditions to investigate the influence of the substrate moisture on the Mn availability in peat-clay substrates. Five pots per treatment were irrigated moderately on the substrate surface and another five pots stood continuously in a 1-2 cm deep water layer, so the substrates were constantly saturated with water. Fertigation was carried out as described. The plants were harvested four weeks after germination.

3.3.4 Evaluation of substrate pH

The impact of a low substrate pH on the risk of Mn toxicity in peat-clay substrates was investigated in a substrate experiment with *Hydrangea macrophylla* cv. “Early Blue”. Plants were grown for eight weeks in peat with 1 and 200 mg Mn L^{-1} substrate, respectively, and in peat-clay mixture 11B. The pH of the substrates was adjusted to 5.5 and 4.3, respectively. Fertilization of other nutrients and fertigation was carried out as described.

3.3.5 Silicic acid and Mn toxicity

The effects of dissolved organic matter (DOM) and silicic acid on the occurrence of Mn toxicity were characterized in a nutrient solution experiment. Mn-sensitive cowpea plants (*Vigna unguiculata* (L.) Walp. cv. Tvu 91; *Horst* et al., 1999) were used for this experiment because of difficulties in the cultivation of the common bean plants in growth chambers. Plants were grown in a growth chamber under controlled environmental conditions at day/night temperatures of 30/27°C, respectively, 75 % relative humidity and 200 µmol $m^{-2}s^{-1}$ PAR during a 16 h photoperiod. Seeds were placed between two layers of filter paper standing in 1 mM $CaSO_4$ for seven days for germination. Afterwards, seedlings were transferred to a constantly aerated nutrient solution with two plants per 3 L pot. The composition of the nutrient solution was (in µM): 1000 $Ca(NO_3)_2$ * 4 H_2O, 250 $(NH_4)_2SO_4$, 200 KH_2PO_4, 325 K_2SO_4, 800 MgSO4 * 7 H_2O, 500 $CaCl_2$, 40 Fe-EDTA, 25 H_3BO_3, 0.5 $CuSO_4$ * 5 H_2O, 1.5 $ZnSO_4$ * 7 H_2O, 0.1 $NaMoO_4$ * 2 H_2O, and 1.8 $MnSO_4$ * H_2O. After a preculture of seven days, the plants were transferred to the differently treated nutrient solutions and grown for five days. The solutions were prepared as follows: Demineralized water was mixed with silica gel for ten days yielding a concentration of 15 mg Si L^{-1} (+Si). The Si-enriched water and demineralized water with 0.1 mg Si L^{-1} (-Si) were used for the preparation of two types of nutrient solutions: peat solution (peat sol.) and normal nutrient solution (norm. sol.). The peat sol. was prepared by mixing white peat with the +Si and -Si solutions, respectively, in the ratio 1:5 (v/v) for 48 h at 5°C (to suppress microbial activity) and repeated stirring followed by filtration. The norm. sol. was not mixed with peat. The same nutrient concentrations were adjusted in both solution types as described above. The variation of the Mn concentrations was (in mg L^{-1}): 0.1 (low), 5 (medium) and 15 (high). The pH of all solutions was adjusted to 6.0 ± 0.1 by the addition of 10 % (v/v) H_2SO_4 or 0.75 M

KOH. Manganese toxicity symptoms were rated in five levels from 0 (= no toxicity symptoms) to 4 (= severe symptoms on old and young leaves).

3.3.6 Substrate analyses

The pH of the substrates was measured in 0.01 M $CaCl_2$ at a substrate:solution ratio of 1:2.5. The bulk density of the substrates was determined by a defined compaction of the samples by repeated tamping according to *VDLUFA* (1991). The Mn_{act} of the clays and substrates was determined according to *Stichting RHP* (2003). Air-dried and ground clay or substrate was shaken for 1 h at 180 rpm in 1 M NH_4OAc with 0.2% hydroquinone quinol (w/v) at a ratio of 1:20 (w/v) and a pH of 7. The extraction solution was filtered within 3 h after the addition of hydroquinone quinol to the NH_4OAc solution.

To obtain substrate solution all substrates were watered or dried to the same volumetric water content of 50 % 48 h before the centrifugation (3000 g for 20 min) to ensure comparable conditions. All solutions were filtered through 2 µm pore sizes before analysis.

3.3.7 Plant analyses

Plant material was dried at 60℃ for 4 d and ground. Manganese in plant tissue was determined after dry ashing at 480℃ for 8 h, dissolving the ash in 6 M HCl with 1.5% (w/v) hydroxylammonium chloride and then diluting (1:10 v/v) with double demineralized water. Measurements of Mn concentrations in all solutions were carried out by ICP-MS (7500 Series, Agilent Technologies, Japan). For silicon analysis plant material was digested overnight in a 1:2 mixture of 1 M HCl and 2.3 M HF (*Novozamsky* et al., 1984). The silicon concentration in solutions was determined photometrically at 811 nm, after the addition of 3.2% boric acid, dye reagent (0.08 M sulfuric acid and 2% ammonium heptamolybdate), 3.3% tartaric acid, and 0.4% ascorbic acid (all w/v). A standard sample with certified mineral contents (LGC Standards GmbH, Germany) was additionally analysed as quality control.

3.3.8 Statistical analysis

Treatments were arranged for each experiment in a completely randomized or a randomized block design and replicated five times for the substrate experiments and three times for the nutrient solution experiment, respectively. Statistical analysis was performed with the program R 2.13.2. Means of two treatments were compared by t-test and means of three or more treatments by Tukey´s test at $\alpha < 0.05$.

3.4 Results

3.4.1 Evaluation of clays under normal growing conditions

The plants grown in peat showed the typical symptoms of Mn toxicity starting at 100 mg Mn L^{-1} substrate. The intensity of symptoms increased with increasing Mn supply from brown spots on old leaves, partly surrounded by areas of chlorotic tissue, to necroses. Severe deformations of young leaves (“crinkle leaf”) were additionally observed beginning at 200 mg Mn L^{-1} (Fig. S.4, supplementary). Growth of bean plants in peat was already significantly reduced by 100 mg Mn L^{-1} substrate (Fig. 3.1-A). A further increase of Mn supply to 200 and 400 mg Mn L^{-1} resulted in strong growth depressions by 70% and 98%, respectively, of max. shoot matter. However, the plants grown in peat-clay substrates showed no toxicity symptoms or growth depression at all and this was independent of the Mn_{act} concentration of the used clays.

The growth reduction in peat was accompanied by increasing Mn concentrations in shoot DM and toxicity symptoms occurred at 1.0-1.2 mg Mn g^{-1} (Fig. 3.1-B). In all peat-clay mixtures the plant Mn concentrations stayed clearly below this value and did not differ significantly between the clays used.

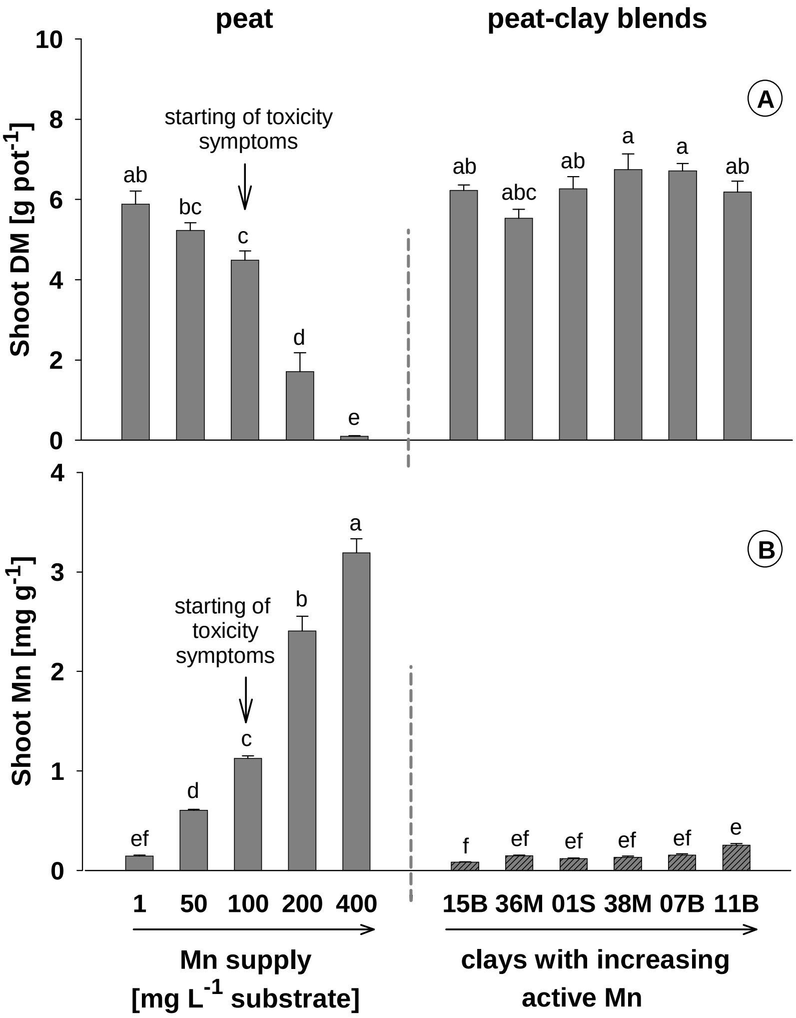

Fig. 3.1: Shoot dry matter (A) and Mn concentration in shoots (B) of common bean plants grown in peat with increasing Mn supply and in six peat-clay blends with increasing concentrations of active Mn. Error bars illustrate standard errors. Different letters indicate significant differences between treatments ($p<0.05$).

In peat about 80-100% of the applied Mn could be determined as active Mn (Tab. 3.1). The concentration of active Mn increased continuously with increasing Mn fertilization, which resulted in an equally constant increase in the Mn concentration in plant matter (Fig. 3.2). The plant Mn concentrations in peat-clay mixtures were all at the same level, but the concentration of Mn_{act} in the substrates differed widely. Thus, the Mn_{act} was not suitable to describe the Mn phytoavailability in peat-clay mixtures.

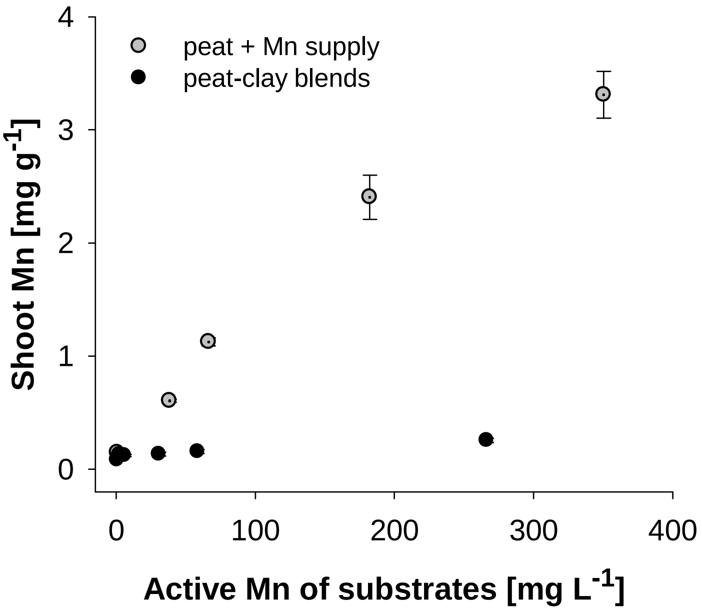

Fig. 3.2: Relationship between the active Mn content of peat with increasing Mn supply and peat-clay mixtures and the Mn concentration in shoots of common bean plants. Extraction was done at the beginning of plant cultivation. Error bars illustrate standard errors.

The Mn concentrations in the substrate solution (Mn_{sol}) of the peat substrates also increased with increasing Mn supply (Fig. 3.3-A). Toxicity symptoms were visible at about 14 mg Mn L^{-1} substrate solution. However, the Mn_{sol} of the peat-clay substrates did not reach this critical level, even though the substrate with the Mn-rich clay 11B had a 2-3-fold higher Mn_{sol} than the other peat-clay mixtures. Figure 3.3-B shows that the Mn_{sol} correlated well with the Mn concentrations in plants regardless of the substrate type.

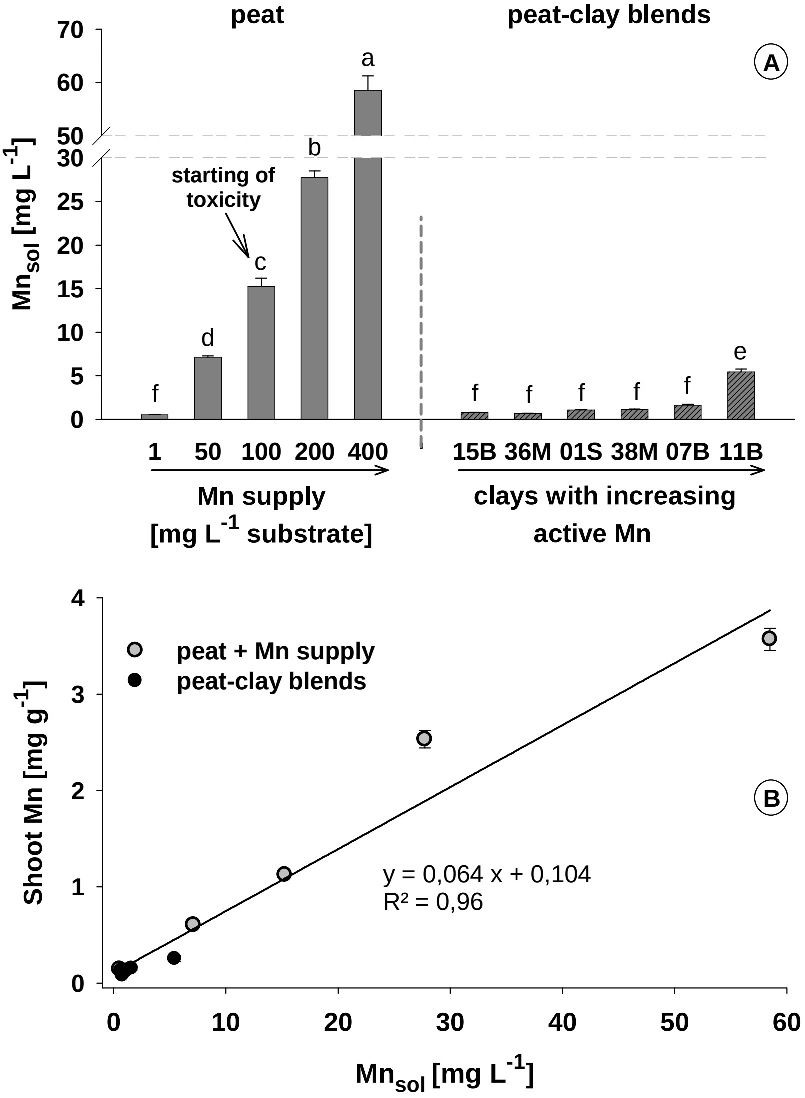

Fig. 3.3: Mn concentration in the substrate solution (Mn_{sol}) of peat with increasing Mn supply and six peat-clay blends with increasing concentrations of active Mn (A) and relationship between the Mn_{sol} of peat and peat-clay blends and the Mn concentration in shoots of common bean plants (B). Extraction of substrate solution was done at the end of plant cultivation. Error bars illustrate standard errors. Different letters indicate significant differences between treatments ($p<0.05$).

3.4.2 Substrate moisture and Mn plant availability

The plants grown in peat enriched with Mn showed the typical symptoms of Mn toxicity starting at 50 mg Mn L^{-1} substrate with “normal” and at 100 mg Mn L^{-1} with “moist” substrate conditions (Fig. 3.4-A).

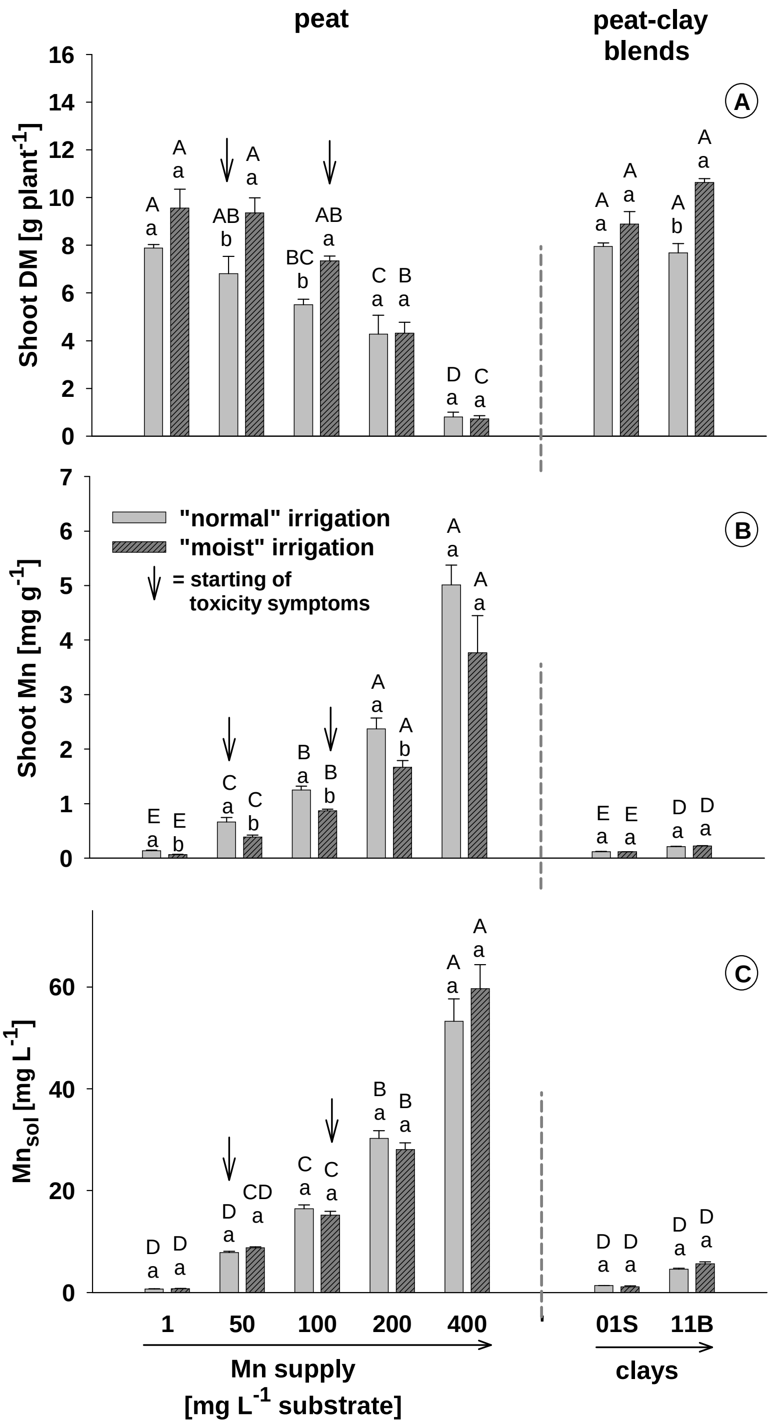

Fig. 3.4: Shoot dry matter (A) and Mn concentration in shoots (B) of common bean plants grown in peat with increasing Mn supply and in two peat-clay blends at different irrigation levels and Mn concentration in the substrate solution (Mn_{sol}) of these substrates at the end of the experiment (C). Error bars illustrate standard errors. Different capital letters indicate significant differences between substrates within irrigation levels and different small letters indicate significant differences between irrigation levels within substrates ($p<0.05$).

However, the plants grown in the peat-clay substrates showed no symptoms or growth depression compared to the lowest Mn treatment in peat independent of the substrate moisture. In all cases, the “moist” treatments even tended to have a higher DM. The shoot Mn concentrations of bean plants increased with increasing Mn supply and were significantly higher in the “normally” irrigated treatments in peat (Fig. 3.4-B). Toxicity symptoms occurred at 0.7-0.9 mg Mn g^{-1} in both moisture treatments. The Mn-rich clay 11B resulted in a slightly increased Mn concentration compared to the lowest Mn treatment in peat and the peat-clay mixture 01S. The substrate moisture level did not affect the Mn concentrations in plants grown in peat-clay blends. The Mn_{sol} at the end of the experiment were comparable to those given in Fig. 3.3-B and were not influenced by the moisture level, either (Fig. 3.4-C).

3.4.3 Substrate pH and Mn plant availability

The influence of a low substrate pH on the Mn availability for plants was characterized in an experiment with *Hydrangea macrophylla*. Plants did not show symptoms of Mn toxicity in any of the substrates and pH treatments. Dry matter production was also not influenced (data not shown), although the Mn concentration in shoots varied clearly (Fig. 3.5). The supply of 200 mg Mn L^{-1} peat at pH 5.5 increased the shoot Mn concentration up to seven times compared to the control treatment. At the same time, the amendment of the Mn-rich clay 11B to the peat only led to a doubling of shoot Mn. The lower pH of 4.3 resulted in increased plant Mn concentrations in all substrates, while the effect was strongest in absolute terms in peat + 200 mg Mn L^{-1}.

3.4.4 Silicic acid and Mn toxicity

The Si concentration in the substrate solution of peat was about 14 mg L^{-1} and the amendment of clay to the peat increased the Si concentration two to three times up to 40 mg Si L^{-1}, but differences between the clays were observed (Fig. 3.6). These differences were also reflected in the Si concentration in shoot DM of the bean plants which ranged from 0.8 mg Si g^{-1} in peat to 4.5 mg Si g^{-1} in mixture 07B (Fig. S.5, supplementary data).

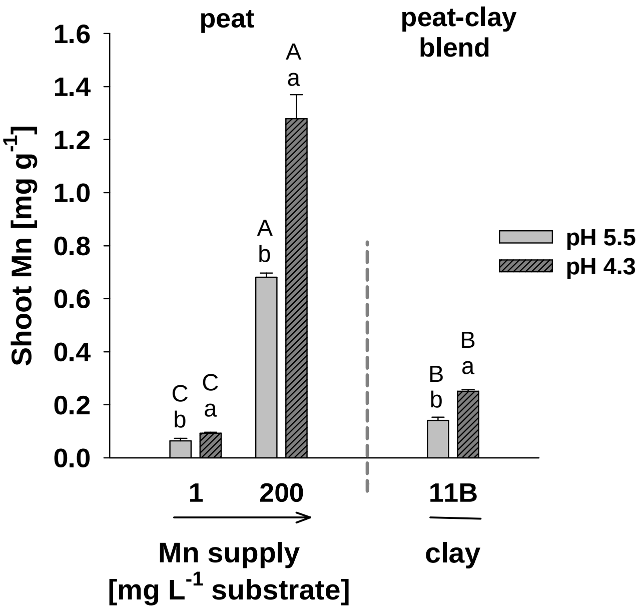

Fig. 3.5: Manganese concentration in shoots of *Hydrangea macrophylla* grown in peat with increasing Mn supply and in peat-clay blend 11B at different substrate pH. Error bars illustrate standard errors. Different capital letters indicate significant differences between substrates within pH levels and different small letters indicate significant differences between pH levels within substrates ($p<0.05$).

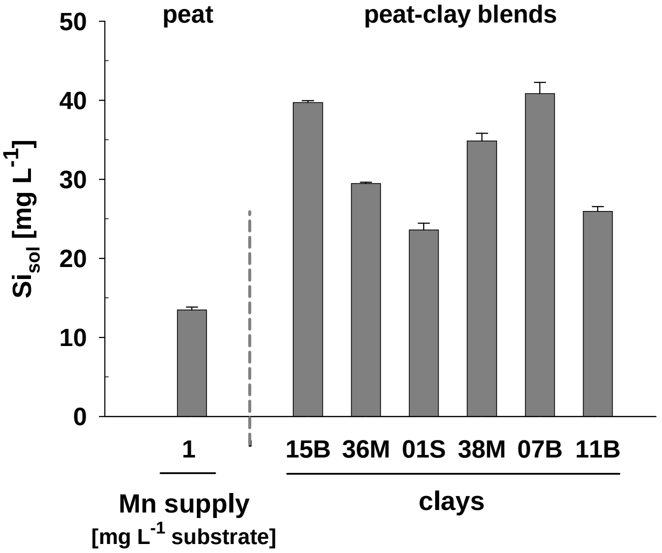

Fig 3.6: Silicic acid concentration in the substrate solution (Si_{sol}) of peat and six different peat-clay blends at the beginning of the plant experiment. Error bars illustrate standard errors.

In the nutrient solution experiment Mn toxicity symptoms already occurred at 5 mg Mn L^{-1} solution, increased with increasing Mn supply and were clearly more severe without Si application (Fig. 3.7-A). The intensity of Mn toxicity was similar in both solutions. However, shoot yield was not affected by the different treatments as the treatment time was only five days (data not shown).

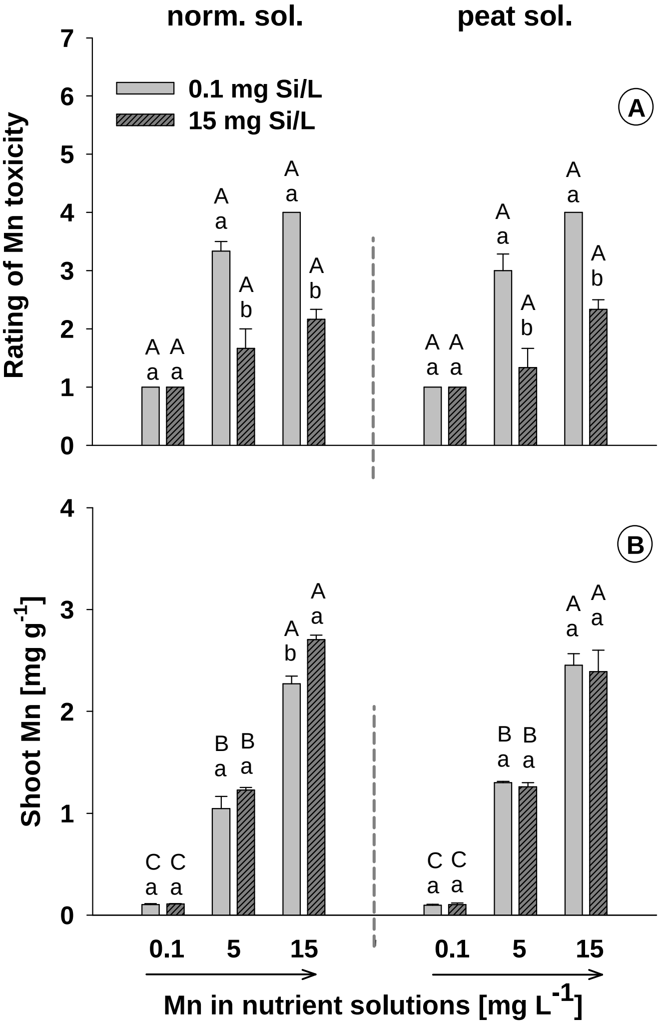

Fig. 3.7: Rating of Mn toxicity symptoms (1 = no symptoms; 4 = severe symptoms) (A) and Mn concentrations in shoots (B) of cowpea plants grown for 5 days in nutrient solution prepared from demineralized water (norm. sol.) and from peat solution (peat sol.) at different Mn and silicic acid concentrations. Error bars illustrate standard errors. Different capital letters indicate significant differences between Mn treatments within each nutrient solution type and Si level and different small letters indicate significant differences between Si levels within the nutrient solution type and Mn treatment ($p<0.05$).

The Mn concentration in plant matter was increased with increasing Mn supply and silicic acid supply did not reduce the Mn accumulation in plant shoots, but it was effective in preventing Mn toxicity (Fig. 3.7-B). Symptoms occurred at about 1.1-1.3 mg Mn g^{-1} DM in both solution types. The Si concentration in plants were just ~1 mg g^{-1} in the +Si treatment, since Si was only applied for a short time (data not shown).

3.5 Discussion

3.5.1 Development of Mn toxicity symptoms

The development of Mn toxicity symptoms was typical for common bean plants as described by *Horst* and *Marschner* (1978). First symptoms were observed at Mn supply of 50-100 mg L^{-1} substrate (Fig. 3.1-A + 3.4-A). The respective Mn_{sol} inducing Mn toxicity was 10-15 mg L^{-1} solution (Fig. 3.3-A + 3.4-C). In contrast, the cowpea plants grown in nutrient solution showed comparable symptoms already at 5 mg Mn L^{-1} nutrient solution (Fig. 3.7-A). *Fecht-Christoffers* et al. (2003) described the development of severe Mn toxicity in cowpea plants grown in nutrient solution at 50 µM Mn (~2.5 mg L^{-1}) and common bean plants were affected at even lower concentrations (*Horst* and *Marschner*, 1978).

Toxicity symptoms occurred in common bean and cowpea at about 1 mg Mn g^{-1} DM (Fig. 3.1-B, 3.4-B, 3.7-B), whereas *Hydrangea* did not show any symptoms at this concentration (Fig. 5). The results confirm the wide variation of critical toxicity levels in plant tissue (*El-Jaoual* and *Cox*, 1998). Obviously, bean plants are more sensitive than *Hydrangea*.

3.5.2 Plant available Mn in substrates

The Mn_{act} concentration in the substrate blend with the Mn-rich clay 11B was comparable to a supply of 200-400 mg Mn L^{-1} in peat (Tab. 3.1). However, this high concentration of Mn_{act} did not result in toxic Mn concentration in plants grown in the peat-clay substrate independent of all tested substrate conditions, but led to severe damage in plants grown in peat. Furthermore, the great differences in the concentration of Mn_{act} between the peat-clay blends were not reflected in the Mn concentration in plant dry matter. The extraction of Mn_{act} overestimated the Mn supply by the clays and was not suitable to characterize the Mn plant availability in peat-clay substrates. Similarly, *Baser* and *Saxena* (1971), *Roorda van Eysinga* et al. (1978) and *Başar* (2009) did not find a correlation between the Mn_{act} of different soils and the Mn uptake of different plant species. *Beyme* (1971) described a strong dependency of the quality of this relation on the soil composition and remarked that a comparison between different soil types is not possible. *De Kreij* et al. (1993) did not observe Mn toxicity in *Chrysanthemum* plants grown in a peat substrate mixed with a Mn-rich clay and found a good correlation between the Mn in water-extracts and the Mn in the plant, whereas NH_4OAc and DTPA strongly overestimated the Mn phytoavailability. As plants can only take up Mn dissolved in the substrate solution, the concentration of free Mn(II) is the relevant quantity for the evaluation of the Mn availability in a substrate. There was a good correlation between the Mn_{sol} and the Mn concentration in shoot matter in our experiments (Fig. 3.3-B). The Mn_{sol} of peat reached much higher values than the Mn_{sol} of peat-clay mixtures (Fig. 3.3-A). In mixture

11B the Mn_{sol} was clearly increased compared to the other peat-clay mixtures, but still stayed below the critical Mn concentration in peat where toxicity symptoms occurred. Thus, the Mn_{sol} was a reliable indicator for the evaluation of possible Mn toxicity. *Hernandez-Soriano* et al. (2012) also showed that the risk of Mn toxicity was clearly related to the Mn concentration in the soil solution.

3.5.3 Substrate factors affecting Mn availability

3.5.3.1 Influence of substrate moisture

Surprisingly, plants showed a higher DM production under “moist” than under “normal” substrate conditions and shoot Mn concentrations were even reduced, although the Mn_{sol} was not affected (Fig. 3.4). The biological reduction of Mn should be generally enhanced by the addition of fresh organic matter and by flooding. Thus, the availability of Mn(II) is usually highest in flooded soils which contain high levels of organic matter (*El-Jaoual* and *Cox,* 1998). *Jones* and *Etherington* (1970) determined significantly higher Mn concentrations in leaves of *Erica cinerea* plants grown under waterlogged conditions than under normal growing conditions. Similar results were obtained by *Hernandez-Soriano* et al. (2012) for barley grown under anaerobic conditions. But the authors observed a decrease in Mn reduction rates after an addition of peat to the soils. They concluded that the water repellence of peat may have resulted in localized more oxidized conditions. Significant Mn reduction can be expected when the redox potential is lower than 400 mV. Such low values (200-300 mV) were observed by *Agner* and *Schenk* (2006) only for 2-8 h after ebb and flow irrigation near the pot bottom but not in the upper parts of the pots. Obviously, the “moist” treatment did not sufficiently decrease the redox potential in the whole pot volume. Furthermore, nitrate from fertigation was probably available for the reduction by microorganisms and thus buffered the redox potential.

The lower Mn concentration in shoot DM under “moist” conditions may have been caused by a dilution effect, since shoot yield was enhanced or due to a reduced total quantity of plant available Mn since the substrate volume available for root development was probably lower because of the saturated zone at the pot bottom in the high moisture treatments. *Morvant* et al. (1997) described such a shifting of the main root mass from the pot bottom to the middle part of the pot when plants were irrigated by ebb and flow system compared to over-head irrigation.

Therefore, Mn from substrate-clays was not plant available in high amounts even under moist substrate conditions.

3.5.3.2 Influence of substrate pH

A decreasing pH in soils can lead to an increase in the Mn availability and thus to an increase in the Mn concentration in plant dry matter. *Markus* et al. (1984) found out that Mn toxicity occurred in *Chrysanthemum* plants grown in peat substrates at pH 4.5 at much lower Mn fertilization levels than at pH 6.5.

Hydrangea was chosen for this experiment since it is one of the few plant species in horticultural practice which is actually grown in peat-clay substrates at a quite low pH of about 4.1-4.6. The low pH of 4.3 during the cultivation increased the Mn concentration in shoots by about 50-80% in all treatments, but did not result in toxic reactions (Fig. 3.5). Nevertheless, the shoot Mn concentration of plants grown in the mixture with the Mn-rich clay 11B was only about 20% of the Mn content of the plants grown in pure peat with 200 mg Mn L^{-1} although the content of Mn_{act} in this substrate was even higher (Tab. 3.1), indicating the still restricted availability of Mn from the clay at such a low substrate pH. Furthermore, the Mn concentration in plant matter was far below the critical level which led to toxicity in bean plants (Fig. 3.1).

3.5.4 Silicic acid and Mn toxicity

The substrate experiments revealed that the Mn concentration in the substrate solution which led to the development of toxicity symptoms was very high compared to critical concentrations described in literature for nutrient solution experiments. It is well-known that silicon can alleviate harmful Mn effects by enhancing the tissue tolerance for Mn (*El-Jaoual* and *Cox,* 1998; *Iwasaki* et al., 2002; *Wiese* et al., 2007).

The silicic acid concentration in the substrate solution (Si_{sol}) of peat was remarkably high and was further increased by the addition of clay up to 40 mg Si L^{-1} (Fig. 3.6), which is already near to saturation (56 mg Si L^{-1} in water at 25℃). Although cowpea can be categorized as a Si non-accumulator according to *Epstein* (1994), a silicic acid concentration of 15 mg L^{-1} in nutrient solution, which was also found in the substrate solution of peat (Fig. 3.6), clearly reduced the susceptibility of cowpea plants to Mn toxicity, but not the Mn accumulation in the leaves (Fig. 3.7). This result agrees with observations for common bean, cowpea, maize, and other crops (*Liang* et al., 2007). Si leads e.g. to a more even distribution of Mn in plant tissue and enhances its Mn tolerance (*Horst* et al., 1999).

In contrast, the concentration of DOM in the solution did not influence the Mn tolerance or the Si effect on Mn tolerance (Fig. 3.7-A). This was not unexpected as complexes between Mn and humic substances are generally of low stability (*Finger* and *Klamberg*, 1993).

The result from the nutrient solution experiment indicates that the high silicic acid concentration in the solution of substrates was likely to be the main reason for the Mn tolerance observed in bean plants grown in peat-based substrates compared to nutrient solution. The silicic acid adsorbed to iron and aluminum oxides of clay minerals contributes greatly to plant Si uptake according to *Beckwith* and *Reeve* (1964) and *Sommer* et al. (2006). The use of a substrate-clay with a high concentration of soluble silicon can increase the silicic acid concentration in the substrate solution and thus, diminish possible toxic reactions of plants.

3.6 Conclusions

The method of Mn_{act} extraction overestimated the Mn supply by the substrate-clays. Even under conditions which are known to enhance the Mn availability in soils, the Mn_{sol} of peat-clay blends did not reach critical values and plant growth was not negatively affected. Additionally, the silicic acid derived from the clay additives will further prevent toxicity by excessive Mn supply. A toxicity threshold for active Mn in substrate clays is therefore not regarded as necessary.

General Discussion

Clay minerals are added to horticultural substrates in order to improve the physical and chemical properties of the substrate. In this study, the main focus was on the chemical characteristics of different clay amendments and their impact on the nutrient availability in peat-clay substrates and the resulting plant performance.

D.1 Beneficial effects of clay additives

D.1.1. P- and K-buffering

Clay amendments can increase the buffering capacity of pure peat for the nutrients phosphorus (P) and potassium (K), but the capability to adsorb P and K may vary widely between the different clay minerals available for the production of horticultural substrates. Therefore, a characterization of their P- and K adsorption behavior is necessary for the selection of suitable substrate clays. Possible methods and their prospects and limitations are discussed in the following section.

D.1.1.1 Characterization of the P- and K- adsorption capacity of clays

The different clays characterized in this study showed a high variation in their P- and K binding capacities.

The P adsorption was highly correlated with the NH_4-oxalate extractable amorphous Fe- and Al-oxides ($\sum Fe_{ox}+Al_{ox}$) (Fig. 1.1). The bonding between P and the surface of the oxides is of a specific nature and only slightly affected by competing anions such as sulfate or nitrate (*Weng* et al., 2012) but it can be reduced by high concentrations of dissolved organic matter or arsenate (*Antelo* et al., 2005, 2007). Thus, possible differences in the P binding capacities of several substrate clays could already be estimated from their contents of $\sum Fe_{ox}+Al_{ox}$, but a prediction of the absolute adsorption capacity is only possible with limitations since the relationships are not consistent and dependent on the soil type and pH conditions (*Borgaard* et al., 1990; *Freese* et al., 1992; *Börling* et al., 2001).

The K binding capacity of a clay was mainly dependent on its cation exchange capacity (*CEC*) and the mineralogical composition (chapter 2.4.1). A high *CEC* indicates a high K binding capacity, but nonetheless, the K adsorption may be restricted at lower K concentrations, if the binding sites on mineral surface are already covered by cations with a higher exchange power, such as Ca^{2+} (*Sivasubramananiam* and *Talibudeen,* 1972; *Bouabid* et al., 1991; *Ghiri* and *Abtari*, 2012). Therefore, the *CEC* can be used for a differentiation of the K binding capacity between several substrate clays, but the actual extent of K adsorption cannot be determined, since it is highly dependent on the concentration of competing cations.

The absolute P- and K- adsorption capacities of clays could be well characterized by a batch experiment with an application of a single high dose of the respective nutrient followed by the determination of the adsorbed amount, ΔP and ΔK, respectively (*Bache* and *Williams*, 1971) (P: Fig.1.1; K: Tab. 2.1). The batch experiments allowed a direct and quick comparison of the adsorption capacities of many different samples, provided that the applied nutrient amount was high enough to reach a high saturation of adsorption sites. If two or more clays show a similar ΔP and ΔK, respectively, although they differ clearly in their $\sum Fe_{ox}+Al_{ox}$ or *CEC*, it is possible that saturation was not reached in the clay with the higher $\sum Fe_{ox}+Al_{ox}$ or *CEC*.
Furthermore, the adsorption behavior of the clays at lower solution concentrations, as they are also present in the pore solution of horticultural substrates (P: Fig. 1.3; K: Fig. 2.3), could not be described by this approach. This may be of higher importance for K than for P, because the K adsorption is strongly influenced by the concentration of other cations in the solution, especially at low solution concentrations, and the clays may also differ in their equilibrium concentration at which they start to adsorb K, K_{e-0}. Thus, the actual adsorption may be much lower than expected from the determined ΔK in the batch experiment, as was the case for clay 06B, which showed a lower absolute K adsorption at low solution concentrations than the clay 01S, although it had a much higher ΔK than the latter (Tab. 2.1; Fig. 2.1).
These two restrictions could be overcome by the establishment of P- and K adsorption isotherms, where a great range of solution concentrations was included (P: Fig. 1.1; K: Fig. 2.1). The maximum adsorption capacity (q_{max}) could be calculated by fitting the data to the Langmuir equation, even if it was not reached within the tested concentration range. Furthermore, it was possible to identify the P- and K concentrations in the equilibrium solution at which neither desorption nor adsorption occurred, P_{e-0} and K_{e-0}, respectively, and to estimate differences in the P- and K-desorption between the clays by the extraction with a P- and K-free solution, respectively. However, the absolute extent of P- and K release could not be determined by this approach.

In general, all batch methods, single or multipoint, have the disadvantage that they may not properly reflect the actual sorption and desorption behavior of a soil or clay under "field" conditions, where adsorption and desorption are proceeding permanently and simultaneously and equilibrium conditions are never fully reached (*Holford*, 1997). Furthermore, the shaking procedure may lead to a breakdown of soil particles and change the reactive surfaces resulting in an increased ad- or desorption (*Sparks* and *Carsky*, 1985; *Springob* and *Richter*, 1998a).

For the selection of a clay according to its P- or K adsorption, the following clay properties should be evaluated:

The $\sum Fe_{ox}+Al_{ox}$ and the CEC hint at possible differences in the P- and K adsorption of the clays and can be used for a pre-selection. For the determination of the P- and K adsorption capacities a single point batch experiment was shown to be well suited, given the concentration in the shaking solution was high enough. More detailed information about the adsorption and also the desorption behavior of the sample, which may be helpful especially for the evaluation of the K adsorption at low solution concentrations, can be obtained by adsorption isotherms.

D.1.1.2 Influence of the P- and K- sorption capacity on the P- and K-buffer power in peat-clay substrates

For both nutrients, P and K, the observed differences in P- and K adsorption of the pure clays were also reflected in the calculated buffer power in mixed substrates (P: Fig. 1.3; K: Fig. 2.3). A higher P- and K sorption of the amended clay resulted in a lower P- and K concentration in the solution (P_{sol} and K_{sol}, respectively) of the respective peat-clay blend than with a weakly adsorbing clay, having the same CAT extractable nutrient concentration.

At a high buffer power of the substrate fluctuations in P_{sol} and K_{sol} are more balanced leading to a more stable P and K supply of the plants and a diminishment of nutrient losses due to leaching (*Owen* et al., 2007; *Rosolem* et al., 2010), which is of importance especially for outdoor cultivation systems and during early developmental stages of plants, when plant nutrient uptake is still low. Furthermore, a high buffer power can also prohibit supra-optimal and toxic levels of P_{sol} and K_{sol}, respectively (*Jakobsen*, 1993; *Hawkins* et al., 2008).

However, it is also possible that the behaviour of the clays may differ from the one expected from adsorption isotherms or batch experiments. Especially the pH value of the substrate, the high concentrations of dissolved organic matter (*DOM*) released from the peat and the presence of other cations and anions in the solution from fertilization and liming may influence the adsorption and desorption of P and K (*Hua* et al., 2008; *Weng* et al., 2012).

D.1.1.3 Impact of the P- and K sorption power of the peat-clay substrates on the nutrient supply of plants

The extent of P and K supply of the plants was dependent on both, the nutrient reserve which could be built up by the fertilization, and on the nutrient amount initially adsorbed to the clay mineral. The degree to which these two pools contributed to the nutrition of plants differed clearly between the nutrients, P and K (Tab. D.1).

In all peat-clay blends a more or less great portion of P and K from fertilization was bound in forms which were not extractable by CAT, but which were still plant available to a certain degree. In a highly buffered substrate a higher fertilization was necessary to reach the targeted CAT extractable nutrient concentration than in a weakly buffered one (Tab. D.1). Thus, the built-on nutrient stock possibly contributing to plant uptake was higher in the highly buffered substrates than in the weakly buffered ones. This effect was clearly more pronounced for P than for K. In the weakly buffered substrates peat and peat-clay blend 04S the fertilized K amount was even lower than the K_{CAT}, resulting in a “negative” K reserve, arithmetically speaking.

The contribution of CAT extractable and non-CAT extractable P- and K pools in the respective nutrient uptake differed widely between the nutrients and the used clays. The balancing of nutrient uptake and supply by the substrates was done in the treatments without P- and K fertigation, respectively, and is presented for the peat-clay blends 06B and 04S as examples for a highly and a weakly P and K buffering substrate (Tab. D.1).

In the weakly buffered peat-clay blend 04S the CAT extractable nutrient pool generally had a higher share in the total nutrient uptake than in the highly buffered blends and the latter were able to provide additional P and K, respectively, from non-CAT extractable pools. The non-CAT extractable pools could be subdivided into (i) P and K originating from the nutrient reserve built up by fertilization, (ii) P and K originating from the peat and (iii) P and K originating from the initial nutrient pool of the clay.

The P uptake of *Impatiens walleriana* plants not fertigated with P was covered to 68-100% by CAT extractable P forms, whereas in *Chrysanthemum indicum* the CAT extractable K accounted for only 25-77% of plant K uptake.

Tab. D.1: Balances of P- and K uptake from different P- and K pools in the peat clay blends 06B (high P- and K sorption) and 04S (low P- and K sorption)

	P		K	
	06B	**04S**	**06B**	**04S**
Absolute amounts [mg pot^{-1}]				
Fertilized	47	24	28	25
CAT extractable	15	15	17	27
Nutrient reserve [% of fertilized]	68	37	39	0
ratio: fertilized / CAT extractable	3.1	1.6	1.6	0.9
Plant uptake [a]	22	10	68	35
Proportion of … in plant uptake [%]				
...CAT extractable…	68	100	25	77
- from fertilizer	100	100	100	93
...non-CAT extractable…	32	0	75	23
- from fertilizer	100		22	0
- from peat [b]	0		20	100
- from the initial pool of the clay [c]	0		58	0

[a] Plant uptake was calculated as: (1) for P: P amount in shoot DM; (2) for K: K amount in shoot DM + K in roots (5% of K in shoots) + K loss by pruning – K in seedling

[b] P-/K-release from peat was calculated from the substrate treatment “pure peat” without P-/K-fertigation

→ for P: 0 mg P pot^{-1} ; for K: 10 mg K pot^{-1} (compare P: Fig. 1.5; K: Fig. 2.6)

[c] P-/K-release from the clay was calculated as: 100 - “P/K from fertilizer” - “P/K from peat”

In contrast to K, not the whole amount of P fertilized could be used by the plants, because the release rate of the non-CAT extractable P was too low, which is in line with results described in literature investigating the short-term effect of P fertilization on the P availability to plants (*Dias* et al., 2000; *Kwabiah* et al., 2003). Thus, a high proportion of P from fertilization was more or less “lost” for the nutrition of the plant in the short duration of a pot plant culture. Under field conditions this fixed P may still contribute to the P supply of plants as the growth period is generally longer and the plant growth rates are lower than for most pot plants under greenhouse conditions. Furthermore, plants only use about 20% of the soil volume around roots for P acquisition (*Jungk* and *Claassen*, 1997; *Claassen* and *Steingrobe*, 1999). Thus, the P utilization per unit soil volume is lower under field conditions than in a pot with a limited small substrate volume. This potential P loss should be considered for the choice of a suitable substrate clay due to ecologic as well as economic reasons.

The non-CAT extractable P taken up by the plants only consisted of the P fertilized at the beginning of the experiment as indicated by the calculation in Tab. D.1. Phosphorus that was initially adsorbed to the clays (P_{init}) was mathematically not necessary for plant P uptake (Fig. 1.5). Nevertheless, P_{init} contributed indirectly to the P release via the degree of P saturation (*DPS*), because the absolute extent of P release from the clays was mainly dependent on this factor (Tab. 1.1; Fig. 1.2-a). Providing that the P stock, consisting of the fertilized P and P_{init}, was at the same level, a higher *DPS* resulted in an enhanced P release. Thus, clay 06B showed a higher P release than clay 39W, although the latter had a higher buffer power and a higher P fertilization, but clay 06B had in sum a slightly higher P stock and a much higher *DPS*. Many authors described the *DPS* as a good indicator for the assessment of potential P losses of soils due to leaching (*McDowell* et al., 2000; *Casson* et al., 2006; *Abdala* et al., 2012).

For the K uptake of plants the CAT extractable K pool was of lower importance than for P. In the peat-clay blend 06B only 25% of the K taken up could be attributed to this pool (Tab. D.1). In contrast, considerable amounts of K were released from non-CAT-extractable pools (Fig. 2.5) and among these, the highest proportion could be attributed to the K originating from the initial K pool of the clay. In the peat-clay blend 06B the non-CAT extractable K pool consisted of almost 60% of K derived from the clay. Thus, this K source supplied > 40% of the K taken up by the plants in this blend. The actual extent of K release (Fig. 2.2-A) was mainly dependent on the mineralogical composition of the used clays (Tab. 2.1) and highest in the substrate amended with the smectite-rich clay 06B. Smectitic clays are characterized by a relatively low negative layer charge and good swelling properties compared to e.g. illitic or vermiculitic clays (*Sawhney*, 1973; *Inoue*; 1983), facilitating the release of interlayer K.

The variation in the observed P supply to the plants was mainly dependent on the level of P reserves due to fertilization in the different peat-clay blends, whereas the K supply was strongly influenced by the initial K pool of the used clay as the K reserve which could be built up by the fertilization was much smaller than for P (Tab. D.1).

However, the released P- and K amounts were not high enough to ensure optimal plant growth when no P and K, respectively, were fertigated during the experiment (P: Fig. 1.4; K: Fig. 2.4). This was even more evident for K than for P, because the K concentration in plant matter required for optimal growth was about 10 times higher than the one of P (P: Fig. 1.5; K: Fig. 2.4). For P the slow release rate of the non-CAT extractable pool (Fig. 1.2) was limiting plant P uptake and growth, even when the P stock available for plant nutrition was high enough. The K release rates at low K solution concentrations were also very low but additionally, the absolute releasable K amounts were far too low to sufficiently supply the plants (Fig. 2.2).

D.1.1.6 Determination of the P- and K-release from clays and mixed substrates

The nutrient release of pure clays and substrate blends was characterized by batch procedures, a percolation experiment and different chemical extractions.

As could be seen from the adsorption isotherms the P release from the initial P pool of the clay to a P-free $CaCl_2$-solution was negligible (Fig. 1.1). This was also calculated in the plant experiment, where no additional P was desorbed from the clays (Tab. D.1). When the clays were enriched with P, the P release could be determined by a desorption-batch-experiment with a stepwise decrease of the P concentration in the equilibrium solution (P_e) (Fig. 1.2). The proportion of the desorbable P in the primary adsorbed P amount determined by this approach was similar to the CAT extractable fraction of the fertilized P in the substrate blends (chapter 1.4.3). Thus, the P amount easily desorbable from the clays was reliably determined by the CAT extraction (*Khandan-Mirkohi*, 2009). Nevertheless, plants were able to take up a higher proportion of the fertilized P in the highly buffered blends. The actual P release could not be accurately predicted by the desorption experiment or the CAT-extraction, as it was not only affected by the binding capacity of the clay but also to a great extent by the *DPS*. Under field conditions, different plant factors may also influence the P desorption (*Raghothama*, 1999). But in general, the CAT extractable P was shown to be a good indicator for the easily plant available P pool ensuring optimal growth.

In contrast to P, K was released in considerable amounts from the initial K pool of the clays (Tab. D.1). The absolute extent of release could be reliably determined by a percolation experiment as proposed by *Meyer* and *Jungk* (1993) and *Springob* and *Richter* (1998b) (Fig. 2.2). The released K amounts measured by this approach were in the same range as the amounts provided by the clays in the plant experiment (chapter 2.5.3). However, the constant percolation of the clay samples is very time consuming and susceptible to disturbances and therefore seems not applicable for standard use. Possibly, cation resin methods are better suitable for the evaluation of the plant available K pool, as they also simulate plant K uptake by providing a constant sink for the cation (*Askegaard* et al., 2005). Nevertheless, the procedure is very labor-intensive and the extraction power is highly dependent on the used cation to be exchanged on the resin (e.g. Ca-resins or H^+-resins) (*Springob* and *Richter*, 1998a).

The chemical extractions of the mixed substrate, CAT, CAL and NH_4OAc, are fast and easily performed, but seem not to be very promising, as not all K pools, which were shown to contribute to plant K nutrition, are determined (*Kong* and *Steffens*, 1989; *Hinsinger* and *Jaillard*, 1993; *Meyer* and *Jungk*, 1993) (Fig. 2.6). However, it could not be clarified by the experiment, how much of the non-exchangeable K may be used by the plants without growth depressions and in most of the literature cited no control treatments with optimal K fertilization were integrated in the experimental design for a comparison of plant K uptake and plant growth.

Worldwide, NH_4OAc is commonly used for the estimation of plant available K in soils and substrates. Among the chemical extraction methods used in this study, NH_4OAc also had the highest extraction power as it determines more K in interlattice positions than CAL and CAT, and is therefore probably better suited for the determination of plant available K in substrates than the latter methods, although the actual K release from the substrate may still be underestimated. The K amount additionally released could be considered as a safety reserve for the nutrition of the plants.

D.1.1.5 Do clays contribute to the safety of plant cultivation?

The results of the plant experiments with *Impatiens walleriana* and *Chrysanthemum indicum* concerning the P- and K-availability in peat-clay substrates showed, that the usage of clays with a high P- and K-binding capacity, respectively, clearly led to an enhanced plant growth and an improved plant performance when the P- and K fertigation, respectively, was insufficient (P: Fig. 1.4; K: Fig. 2.4). However, the contribution of the P- and K-release of the clays in the total P- and K-uptake of the plants is highly dependent on the proportion of clay in the mixed substrate. The nutrient amount available for plant uptake would decrease with decreasing clay application rates.

In our experiments a proportion of 200 kg clay m^{-3} substrate was used. Such high clay contents of substrates are also found in horticulture practice nowadays (*www.einheitserde.de*; as at December 2nd 2013), but increased costs of carriage and the fact, that the improvement of most physical substrate characteristics as the rewettability can already be achieved with clay application rates of 20-30 kg clay m^{-3} substrate (*Verhagen*, 2004) led to a decrease of application rates in many substrate mixtures (e.g. *Klasmann-Deilmann GmbH*, Germany).

Thus, the rate of the clay amendment to the substrate has to be adapted to the area of application. A considerable P- and K-buffering of the substrate can only be reached by the addition of a sufficiently high amount of clay, while most physical properties can already be improved by much lower application rates (*Verhagen*, 2004; *Schellhorn* et al., 2013).

D.1.2 Silicon availability in peat-clay substrates

In our experiments the clays released considerable amounts of Si to the substrate solution (Fig. 3.6). In the solution of peat-clay blends the concentration of silicic acid was more than twice as high as in pure peat.

In soils clay minerals are one of the major sources of plant available silicon. Especially, silicic acid adsorbed onto Fe- and Al oxides contributes to plant nutrition (*Sommer* et al., 2006). It can easily be exchanged by other anions such as phosphate and become plant available. *Weng* et al. (2012) and others could show a strong decrease of the silicic acid adsorption onto goethite with increasing concentrations of added phosphate. Thus, it can be assumed that a higher P fertilization of highly P buffered peat-clay substrates would result in an even higher release of adsorbed Si due to competition.

Therefore, clay minerals with a high Si release could be applied systematically as Si sources for pot plants, especially since the use of other Si-fertilizers is only possible with limitations. Different industrial waste materials (e.g. coal fly ash or slags), which are mostly used as Si sources for the fertilization of soils, may not be used in horticultural substrates, as they have a great pH increasing effect (*Haynes* et al., 2013). The usability of other Si fertilizers, especially K_2SiO_3 and $CaSiO_3$, in sufficiently high amounts may also be restricted for this reason.

An improved Si supply of pot plants would have many positive effects (reviewed by *Ma*, 2004 and *Liang* et al., 2007):

It was shown that silicon can enhance the tolerance to salinity of many plants by decreasing their Na uptake. Si is also effective in enhancing the resistance to different insect pests and fungal diseases and in diminishing the risk of heavy metal toxicity in plants, as could be shown for Mn in this work. Furthermore, Si deposited on the leaf surface and stems accounts for a higher stability of plants decreasing the risk of breaking. Additionally, Si alleviates various physical and climatic stresses like drought and heat stress.

Up to now, very little is known about the Si uptake of most ornamental and other pot plants, but many of the positive Si effects were observed not only in Si accumulators but also in non-accumulators (*Ma*, 2004). Thus, the higher concentration of available Si in peat-clay substrates could positively influence the plant quality in many different ways.

D.1.3 Favourable physical effects of clay amendments

Clay amendments have many positive effects on the physical properties of horticulture substrates. The influence of different clays on the rewettability and the coherence of substrates was investigated by *Schellhorn* et al. (2013) for several clays which were also used in this study. It could be shown that all clay amendments led to an enhanced stability of press-pot substrates and to an improved rewettability of dry substrates compared to pure peat. However, not all clays were comparably well suited for the different applications. Saprolitic clays e.g., like the clays 01S and 04S, showed stronger effects on the water uptake than bentonitic clays, like clay 06B.

The appropriate clay should be selected according to its subsequent application. A clay which has the desired physical properties may only show a low P adsorption or the other way round. The bentonitic clay 06B was best suited for enhancing the P- and K-buffering capacity of peat and was also effective in improving the physical substrate properties (*Schellhorn* et al., 2013). Thus, it may be used for different applications in horticultural substrates.

D.2 Undesirable effects of clay additives

Due to their genesis, clay minerals may also contain elements and chemical compounds, which may become toxic to the environment, plants, animals or humans, when occurring in excess.

D.2.1 Heavy metals

In Germany, the *Düngemittelverordnung* (*DüMV*) (2012) gives thresholds for heavy metals in fertilizers and substrate components, which may also occur in clay minerals, including cadmium, chrome, lead, nickel and zinc, in order to prevent their release to the environment.

Additionally, the Dutch foundation *RHP* (*Stichting RHP*, 2010) defined quality standards for substrate raw material for guaranteeing an optimal plant growth and quality (Tab. S.1, supplementary data). Here, thresholds for manganese, iron, boron and other minor plant elements in clay minerals are given to prevent toxic reaction of pot plants. So, in some cases a clay may not be used as substrate amendment although it shows the desired physical or chemical properties. However, most of the defined thresholds have not been tested in plant experiments.

The threshold for Mn was validated in several plant experiments with bean and hydrangea plants (chapter 3). The results indicated, that the threshold value for Mn in substrate clays is not justified, as plants grown in a substrate amended with a Mn-rich clay did not develop any Mn toxicity even at conditions which increased the Mn availability. Furthermore, the used extraction of `active Mn´ in the substrates did not reflect the Mn concentration in plant dry matter well (Fig. 3.2), whereas the Mn concentration in the substrate solution was a good indicator for the availability to plants (Fig. 3.3).

D.2.2 Dioxins

In the newly revised *DüMV* (2012) a threshold for polychlorinated dibenzo-dioxins (PCDD) in clay additives was integrated for the first time. Dioxins and dioxin-like compounds have negative impacts on the immune-, the nervous- and the endocrine system as well as the reproductive functions and are also suspected of causing cancer (*Dumortier* et al., 2012). Clay minerals may contain considerable contents of PCDD originating from natural (e.g. forest fires) or anthropogenic (e.g. contained in herbicides and composts) sources (*Ferrario* et al., 2000; *Dumortier* et al., 2012). *Liu* et al. (2009) could show that smectites have a higher affinity for these dioxins than soil organic matter. Dioxins in the soils are mostly resistant to degradation and may accumulate in living organisms via the food chain. Several studies revealed that PCDD is taken up via the roots by different plant species (e.g. pumpkin and zucchini) while others take up only airborne dioxins via the leaves (e.g. cucumber, grasses) (*Hülster* et al., 1994; *Collins* et al., 2006).

Therefore, the transfer of PCDD from clay containing substrates to the plants and the consumer has to be investigated thoroughly in the future in order to prevent possible risks for human health or the environment.

Acknowledgments

We thank Eva Schmidt and Dr. Matthias Schellhorn from Stephan Schmidt KG and Gerald Schmilewski from Klasmann-Deilmann GmbH for the provision of substrate raw materials and the helpful discussions. The team in the laboratory is gratefully acknowledged for their excellent technical assistance. This work was supported by the Bundesministerium für Bildung und Forschung (BMBF) in the frame of the GEOTECHNOLOGIEN program `Mineral Surfaces – From Atomic Processes to Industrial Application´ (grant 03G0722A).

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Supplementary Data

Fig. S.1: Appearance of *Impatiens walleriana* plants grown in the highly P buffered peat-clay blend 06B and in the weakly buffered blend 04S without P fertigation.

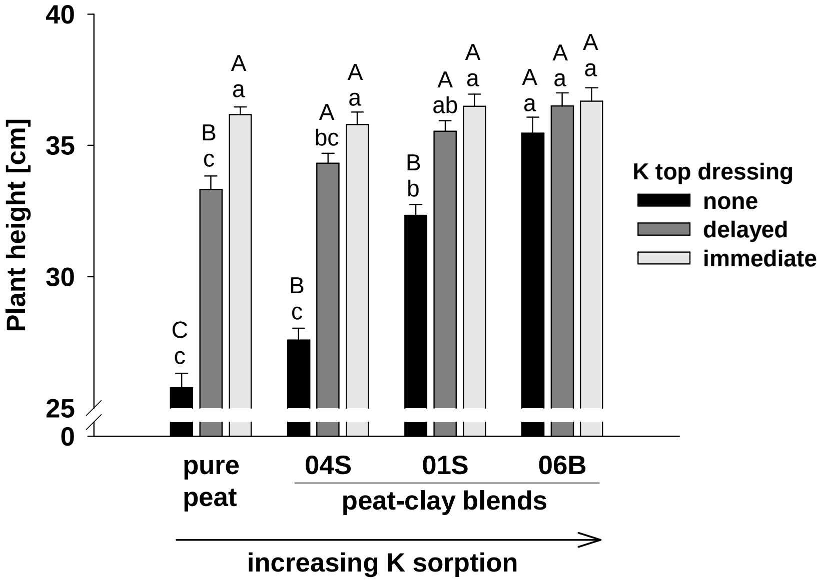

Fig. S.2: Plant height of *Chrysanthemum indicum* depending on substrate type and beginning of K top dressing. Error bars illustrate standard errors. Different capital letters indicate significant differences between fertilization treatments within the same substrate and different small letters indicate significant differences between substrates at the same K fertilization level ($p<0.05$). Data are adapted from *Meyer* (2012).

Fig. S.3: Appearance of *Chrysanthemum indicum* plants grown in peat and three peat-clay blends with increasing K sorption capacity (from left to right) without K top-dressing.

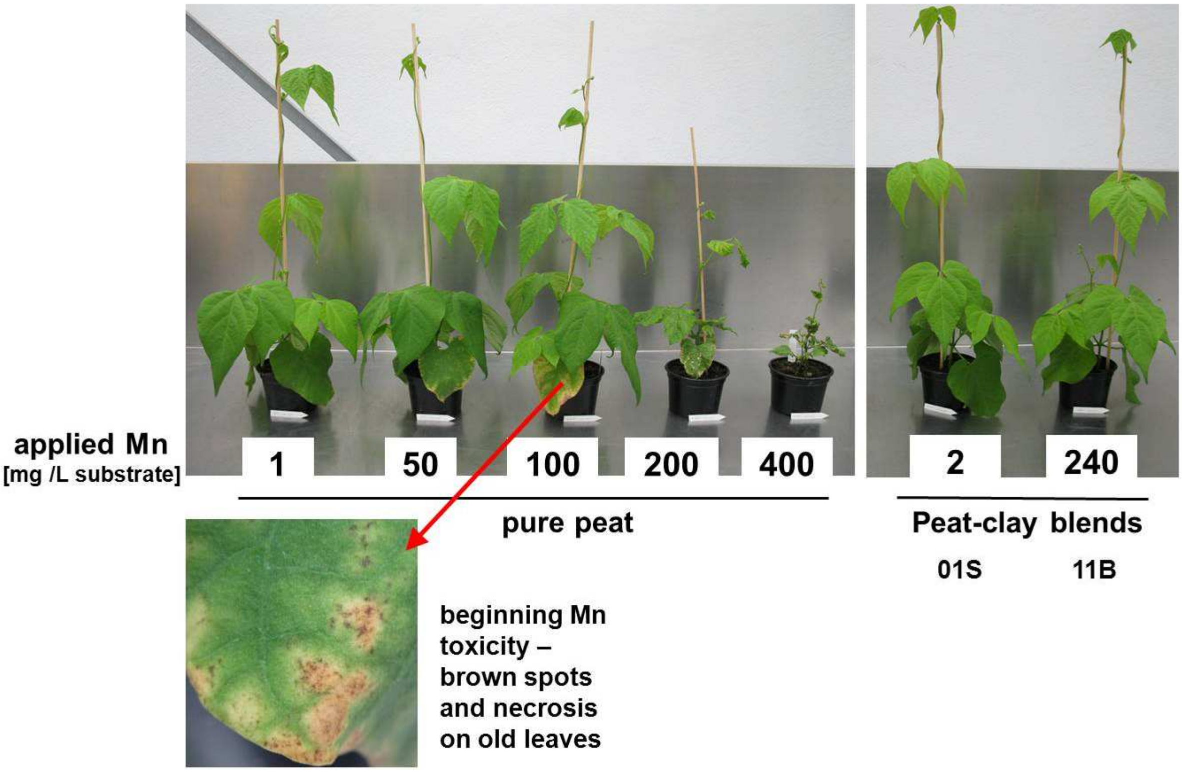

Fig. S.4: Appearance of bean plants grown in peat and two peat-clay blends with increasing Mn supply (characterized by the active Mn).

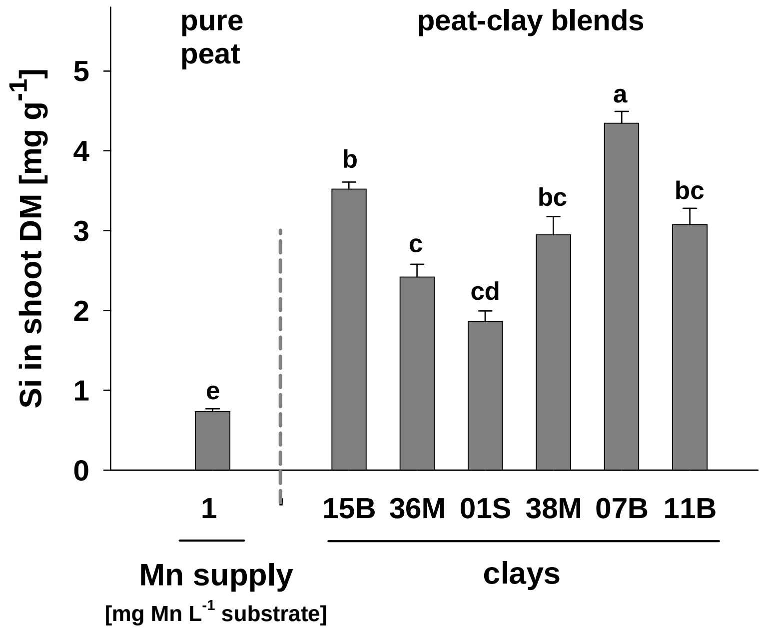

Fig S.5: Silicon concentrations in shoot DM of bean plants grown in peat and six different peat-clay blends. Error bars illustrate standard errors. Different letters indicate significant differences between treatments.

Tab. S.1: Quality standards for clay amendments to horticultural substrates defined by the *RHP* (*Stichting RHP*, 2010 - excerpt)

Quality trait	**Threshold RHP**
pH	3,5 – 9,0
EC	< 35 mS/m
$CaCO_3$	< 1,5 % (> 50 kg/m³) < 6 % (< 50 kg/m³)
Mn-active	< 500 mg/kg
CEC	0 – 10 (class 1) 10 – 20 (class 2) 20 – 30 (class 3) >30 (class 4)
Heavy metals:	
Cr	< 250 mg/kg
Ni	< 200 mg/kg
Cu	< 120 mg/kg
Zn	< 365 mg/kg
As	< 105 mg/kg
Cd	< 3,6 mg/kg
Hg	< 1,2 mg/kg
Pb	< 325 mg/kg
Dissoluble salts	Extraction 1 :5
Na	< 70 mg/l
Cl	< 110 mg/l
Mn	< 1,0 mg/l
B	< 1,2 mg/l

Wissenschaftliche Publikationen

Artikel:

Binner, I., Schenk, M.K. (2013): Mn contained in substrate clays – harmful for plants? *Journal of Plant Nutrition and Soil Science* 176, 809-817.

Mündliche Präsentationen:

Binner, I. (2011): Mn in substrate-clays – harmful for plants? ISHS International Symposium on Growing Media, Composting and Substrate Analysis, Barcelona, Spain.

Poster Präsentationen:

Dombrowski, I., Schenk, M.K (2009): Leaf damage of Helleborus niger is caused by phosphorus toxicity. Jahrestagung der Deutschen Gesellschaft für Pflanzenernährung, University of Applied Science, Osnabrück, Germany

Dombrowski, I., Schenk, M.K (2010): Manganese toxicity in peat/clay blends used as growing media? DGP Symposium „Genetics of Plant Mineral Nutrition“, 30.9. -2.10.2010, Leibniz Universität Hannover, Germany.

Binner, I., Schenk, M.K (2011): Influence of P buffering capacity of peat/clay-substrates on the safety of plant cultivation. ISHS International Symposium on Growing Media, Composting and Substrate Analysis, Barcelona, Spain.

Binner, I., Schenk, M.K (2012): Gypsum amendment to peat substrate reduces P availability. Jahrestagung der Deutschen Gesellschaft für Pflanzenernährung, Universität Bonn, Germany.

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