

# Control mechanisms of clays and their specific surface area in growing media – assessment of clay properties and their parametrization for the optimization of plant quality

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## Summary

The addition of clay to growing media aims at constant supply of potassium, phosphorus and micro nutrients, pH-buffering, improvement of rewettability, and cohesion of growing media. The identification of suitable clays and their classification is a prerequisite for product and cultivation safety. A range of different clays highly variable in their mineral parameters were selected for experiments on nutrient buffering (P) and Mn toxicity, their ability to improve the rewettability and binding capacity of growing media. From batch experiments and growth trials it was derived that a threshold value for the sum of exchangeable and easy reducible Mn in clays for growing media is not justified, as even very high Mn contents in clay were not phytotoxic. The P binding capacity of clays was strongly correlated with the oxalate extractable Fe and Al content. A newly developed capillary rise method (WOK) was used to characterize the rewettability of growing media. The speed of rewetting mainly depends on the fineness of the amended clay. Surface free energy (SFE) data of the growing media indica-

te that those with a good rewettability show also high values for SFE. Compared to the kaolinitic and illitic clay amendments, bentonites show no significant increase in the SFE. Surfaces of clay minerals exhibiting originally polar and hydrophilic surfaces, can render hydrophobic when coated with weakly or non-polar organic matter moieties. Dissolved organic carbon (DOC) sorption was found to be positively correlated with the specific surface area (SSA), cation exchange capacity (CEC) and amount of dithionite extractable Al and Fe. Clays containing expandable clay minerals with high CEC and SSA (e.g. smectites) and those rich in Al- and Fe-oxides seem to be less effective for improving rewettability, whereas an addition of non-expandable clays with lower SSA, CEC (e. g. kaolinitic and illitic clays) and amorphous oxide content appears more promising. New insights on the adsorption of DOM on clay mineral's surfaces will be obtained in the third year by chemical analysis of the surface with X-ray photoelectron spectroscopy (XPS), surface topography analysis and contact angle measurements. A new method for the determination

Table 1: Properties of growing media and their constituents that pertain to »quality« (adapted from *Schmilewski, 2008*).

Chemical	Physical	Biological	Economic
pH	structure and stability	pathogens	availability
nutrient content	water and air capacity	weeds	price
buffering capacity	bulk density	microbial activity	consistency of quality
noxious substances	wettability	storage life	cultivation technique

of the binding capacity of clays in blocking media is currently being tested and will be studied together with determinations on K-dynamics.

## Introduction

### **Concept on function und effect of clays in growing media related to practice**

A suitable rooting medium is fundamental for plant growth. Horticultural crops have certain requirements which the grower needs to fulfil with the help of individually tailored growing techniques and cultivation measures. For the selection of growing media constituents each should possess optimum characteristics for the specific culture. Modern horticulture with computer-controlled irrigation and fertilisation programmes, potting machines, pricking robots, climate-controlled greenhouses and just-in-time production requires dependable, quality-assured growing media. Specialist companies rely on ready-made growing media which are either part of the manufacturer's standard range or special mixtures produced at the grower's request. For the development of formulations and the production of growing media suitable for this market a large number of chemical, physical, biological and economic characteristics of the constituents must be taken into account (Table 1).

Due to its characteristics Sphagnum peat has been the most important constituent of organic growing media for several decades. A high water and air capacity in combination with other favourable features make peat ideal for this purpose. After fertilising and liming, peat is the sole constituent of many growing media. Nonetheless, peat has also some drawbacks

arising from the relatively poor wettability when dry, limited nutrient buffering capacity, and structural stability. Mineral amendments, especially those rich in clays, are commonly incorporated into the organic media in order to improve physical and chemical conditions.

In horticultural practice, clays are amended to peat in amounts of 10-80 kg/m<sup>3</sup>. The amendment aims mainly to improve the following three different properties of the growing media:

1. Buffering of nutrients. Clay amendment shall ensure that optimum conditions adjusted at start of the crop remain constant during cultivation. Relative large amounts of clay are needed.
2. Rewettability during irrigation. Due to the large specific surface area and charged surface sites, hydrophilic mineral surfaces of clay minerals coating the surfaces of peat should have a positive effect on the wettability of inherently water repellent growing media and the amount of plant available water. Relative low amounts of clay are needed.
3. Binding capacity. For the use of pricking robots when transplanting young plants and also for the production of peat blocks (e.g. 4 x 4 x 4 cm) for mechanical sowing the cohesion of the growing media shall be improved by the amendment of a suitable clay. Relative low amounts of clay are needed.

As a certain clay can hardly support all of the required properties, also blends of different clays are used in growing media industry. Clays available show great differences in their mineral parameters, e. g. texture, mineralogical composition, layer charge, and oxide content. Chemical as well as physical characteristics of the growing media strongly depend on the kind of clay amendment. Currently no proven

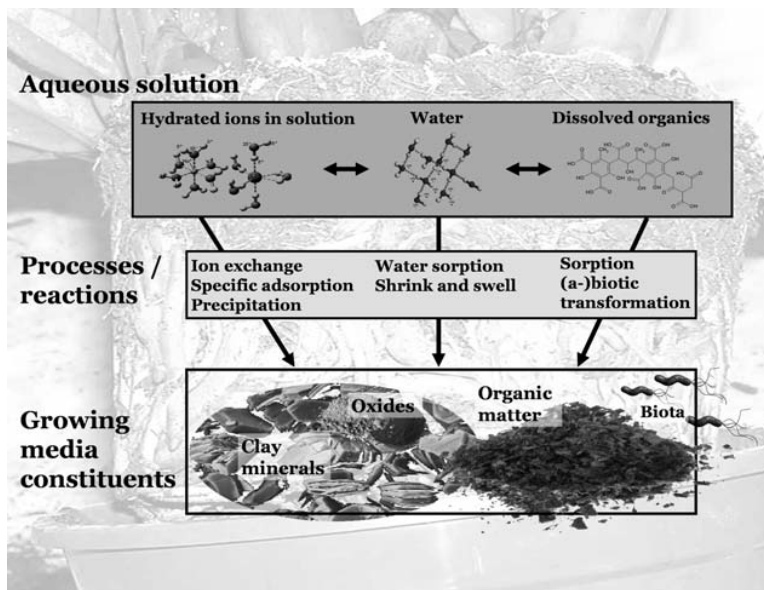


Figure 1: Scheme for the interactions growing media constituents with solution.

standards are available for evaluation of clay for use in growing media and to design growing media perfectly for specific crops and production methods. Here improved knowledge of the mechanisms and processes of these clays in growing media helps to identify suitable clays and to make the prognosis of clay properties more reliable.

### **Surface chemistry of growing media constituents**

The amendment of clays or clay blends to peat together with the addition of fertilizers and lime in a growing medium has a strong effect on the surface chemistry of its constituents. Clay and peat stem from very different environments and a distinct number of exchange reactions can be assumed. E. g. the clays used in this project from Mesozoic-Tertiary weathering mantle of the Rhenish Massif are undersaturated for the binding of dissolved organic matter (DOM), whereas peat is known to be a source for DOM. For this reason the external surfaces of clay minerals might act as a sink for DOM, whereby in turn the adsorption of DOM can modify the surface properties of the clay minerals. Here the interaction of water with peat and clay minerals defines the physical and chemical properties of the growing medium, as virtually all chemical and biological reactions take place at the solid-water interface. A sche-

me of the interactions of water with the growing media constituents is shown in Fig. 1.

The solid-water interface is important because it controls the retention and transport of nutrients and pollutants and provides physical support for plants. Also contained in the pore solution besides inorganic solutes is DOM, its fate and transport highly depending on interactions of the solid-water interface. On addition, many chemical species in the growing media solution can interact with each other. Solute behaviour is controlled by multiple solid phases, different clay minerals, oxides and organic matter, which have a complex and heterogeneous nature. The type of surface reaction has a decisive role for the potential of the solid phase for the desired properties listed above.

### **Water repellent surfaces of growing media**

Water repellent (hydrophobic) growing media can cause problems as, after drying out, they require a long time to rewet (Michel *et al.*, 2001). For that reason the rewettability could become a property with major repercussions for plant growth (Doerr *et al.*, 2000). Organic material in peats used for growing media comprises many substances which are only weakly or non-polar. As a consequence they are not able to form hydrogen bonds with water mole-

cules and hence exhibit often distinct water repellence (hydrophobicity). On the other hand, charged mineral surfaces are usually hydrophilic as they are capable of forming hydrogen-bonds. Thus, when incorporated into a water repellent sandy soil or a growing medium, it is expected that charged clay minerals show a positive influence on the wettability, by increasing the surface area, masking hydrophobic organic surfaces and exposing hydrophilic clay surfaces (McKissock et al., 2002; Lichner et al., 2006). The effect of mineral amendments on the wettability of soils was subject to several studies. Nevertheless, the results were somewhat inconsistent. Indication was obtained that the variations observed depend to a great extent on the formation of organic coatings on mineral surfaces. The adsorption of weakly or non-polar organic matter moieties can render a hydrophilic mineral surface hydrophobic (Chenu et al., 2000; Doerr et al., 2000). The hydrophilic reactivity of mineral surfaces and accordingly their positive influence on wettability can be reduced or even lost, when the minerals tend to accumulate hydrophobic organic compounds derived from soil organic matter or peat on their external surfaces.

For soils sorption of dissolved organic matter onto mineral surfaces was found to be affected by the parameters CEC, SSA and content of amorphous oxides (e. g. Kaiser and Guggenberger, 2000; Kahle et al., 2004). The stability of organic coatings depends on the type of bond, which is not only dependent on the chemical composition of DOM, but also on mineral surface properties. Basically it has to be assumed that wettability is largely influenced by the sorption of DOM and, as the wettability is a dynamic property, also desorption processes.

In the study on rewettability of growing media, the effect of certain clay amendments, highly different in their mineral parameters (mineralogical composition, specific surface area, oxalate and dithionite soluble Fe- and Al-oxides, texture) was determined. Processes and reactions responsible for the variations in growing media wettability are assessed and used to rate the effectiveness of the amendment. The results

will be used to find reliable criteria for the selection of suitable clays for improving wettability.

### **Clays for improving P buffering capacity**

The amendment of clay to peat-based growing media is supposed to improve both physical and chemical properties of growing media. Pure white peat is nearly non-buffered and the buffering capacity for the nutrients potassium and phosphorus can be increased by the addition of clay. A buffered growing media can absorb nutrients in large amounts by binding them and is able to release them again in the solution of the growing media when plants deplete the nutrient concentration. By this, fluctuations of plant demand or fertigation can be balanced and optimal growing conditions can be maintained.

The buffering capacity of a clay in growing media is mainly caused by its contents of amorphous Fe- and Al-oxides. Therefore P fixation varies widely between clay minerals and the choice of the »right« clay is very important. In horticultural practice the basic fertilization of a growing media is generally not sufficient to supply the plants over the whole vegetation period with nutrients and subsequent fertigation is necessary. The nutrient concentration in the fertigation solution should reflect the nutrient demand of plants. Growth rate and nutrient uptake of plants differs widely between species and cultivars and is dependent on environmental conditions. Therefore optimum fertigation concentration can be determined only with uncertainties.

Thus, i) clay characteristics affecting P buffering capacity were determined and ii) the influence of the buffering capacity of peat/clay-growing media on the safety of plant cultivation at varied concentrations of P fertigation was investigated.

### **Progress within the project**

The work in the first two years focused on the two sections »Buffering of nutrients« (1) and »Rewettability during irrigation« (2). In preliminary studies in the section »Binding capacity« (3) different methods were tried out and extensive experiments on blocked growing me-

Table 1: Physical, chemical and mineralogical properties of seven clay samples from the Westerwald area, representing saprolithic clay (S), bentonite (B), translocated clays (U) and blends (M).

Sample	sand/silt/clay (wt%)	CEC (mmol/kg)	SSA (m <sup>2</sup> /g)	Al <sub>ox</sub> (g/kg)	Fe <sub>ox</sub> (g/kg)	Mineralogical composition <2 μm fraction (d = dominant, t = traces)
01S	42 / 45 / 13	287	11	0.34	0.61	illite, kaolinite (d); chlorite, quartz (t)
06B	41 / 38 / 21	840	106	2.24	2.96	smectite (d); illite, kaolinite (t)
07B	46 / 41 / 13	881	92	1.77	1.53	smectite (d); illite, kaolinite (t)
27U	2 / 52 / 46	223	20	0.09	0.02	kaolinite, quartz (d)
28U	2 / 18 / 80	435	44	0.26	0.11	kaolinite, illite (d)
36M	2 / 35 / 63	256	30	0.16	0.33	kaolinite (high crystallinity), illite (d)
38M	25 / 40 / 35	572	62	1.06	0.87	kaolinite, illite (d)

dia by mechanical agitation will be carried out in the third year.

Determinations on Manganese toxicity (section 1) on clays with different contents of active Mn (sum of exchangeable and easy reducible Mn) reveal that a threshold value for Mn in clays for growing media is not justified (*Dombrowski and Schenk, 2010*). Even very high Mn contents in clays only resulted in small increase of Mn concentration in the solution of the growing medium. Additionally plants tolerated high Mn-concentrations in the growing media solution because, i) Mn was complexed by DOM and thus is less phytotoxic ii) silicic acid dissolved in growing media solution alleviated the harmful Mn effects. Results on the P binding capacity of clays, strongly correlated with the oxalate extractable Fe and Al content of clays, are described in detail in the result section.

For the determination of the rewettability of growing media the capillary rise method was used. For this purpose a WOK-apparatus allowing 8 simultaneous measurements was installed at Klasmann-Deilmann GmbH. The effectiveness in improving the wettability of growing media was found to depend on the surface properties of the clay minerals amended which govern the binding of DOM. Amendments with non-expandable clay minerals with low SSA, CEC (e.g. kaolinite and illite) and clays with a low amorphous oxide content appear most promising (*Walsch and Dultz, 2010*). The fineness of the clay was observed to be a decisive factor for improving the rewettability.

## Material and Methods

### Rewettability

Seven clay samples with distinct differences in mineral parameters (Tab. 1) and a blend of different Sphagnum peats with a moderate degree of decomposition were used.

The growing media was limed (6.0 kg/m<sup>3</sup>) and fertilized (1.1 kg NPK 14-16-18 standard fertilizer per m<sup>3</sup> growing media). The rewettability of the growing media mixtures was assessed in terms of capillary water uptake (WOK, Dutch RHP foundation) and contact angle (CA) measurements (OCA 20, Data Physics). In the WOK apparatus dry samples are placed in cylindrical rings (500 cm<sup>3</sup>) on a layer of water and the increase in water content is logged over time for 24 h (Fig. 2).

Hydration of particles in the growing media was determined in an environmental scanning electron microscope (ESEM; Quanta 200, Fei). As peat surfaces consisting mainly of C are covered with clay minerals rich in Si, the degree of coverage of the peat surface can be described by the C/Si ratio. By energy dispersive X-ray spectroscopy five different sections each of 6 mm<sup>2</sup> size were determined.

The adsorption of peat derived DOM on mineral surfaces was determined in batch adsorption experiments. DOM solutions for adsorption experiments were extracted from limed and fertilized peat. Batch adsorption experiments were carried out for 24 h at 20 °C in the dark. DOC concentrations were measured with a total organic carbon analyser (liquiTOC, elemental). Aromaticity of the adsorbed DOC and DOM-fractionation phenomena due to adsorption

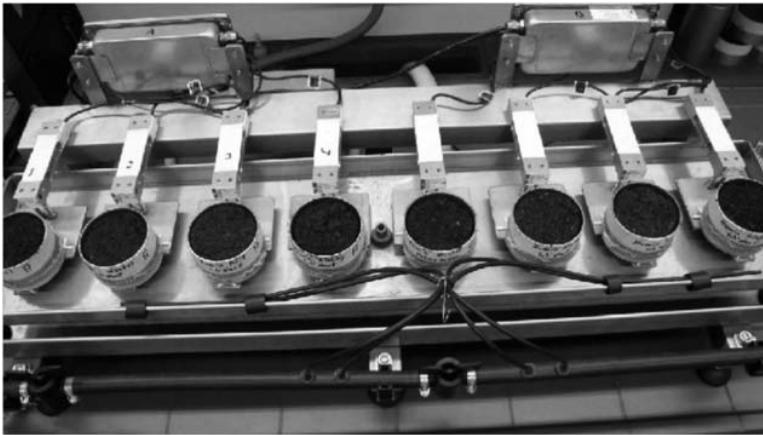


Figure 2: WOK apparatus used for the determination of the time dependent water uptake capacity.

were determined with a Cary 50 UV-Vis spectrometer (Varian). According to *Chin et al. (1994)* absorbance values were recorded at a wavelength of 280 nm, where electron transitions occur for a number of aromatic substances.

#### **P buffering capacity**

The influence of P buffering of peat/clay growing media on the safety of plant cultivation was characterized in a plant experiment. At first nine clays with different P fixation capacity were selected for the determination of plant availability of P in peat/clay growing media. To assess the P fixation clays and growing media were shaken in a P solution (1000 mg P L<sup>-1</sup>) at a ratio of 1:10 for 24h. Oxalate soluble Fe and Al were extracted using 0.2 M oxalate solution. Based on these data two clays with a low P fixation (04S and 01S) and two with a high P fixation (06B and 39W) were selected for the plant experiment and mixed with peat (80 vol-% peat, 20 vol-% clay).

For each growing media a calibration curve was established to determine the amount of P needed to obtain a CAT extractable P concentration of 25 mg P/L growing media, which is usually adjusted in horticultural practice. CAT (0.01 M CaCl<sub>2</sub> + 0.002 M DTPA) is commonly used for the extraction of potentially plant available P in horticultural growing media (*Alt & Peters, 1992*). The growing media were equilibrated in an oven at 50°C for 48 h, then at room temperature for another 48 h prior to determining the CAT extractable P concentration. Previous work showed that this incuba-

tion procedure is highly correlated with CAT soluble P after 9 weeks of storage.

Seedlings of *Impatiens walleriana* F1 »Candy® Coral Bee« were planted in 600 ml plastic pots (Ø 12 cm) filled with the different growing media and pure white peat as control. Volume weight of growing media was determined according to standard method of VDLUFA (1991). All growing media were fertilized with 1.5 g L<sup>-1</sup> of a P free compound fertilizer (Ferti 8® – N : P<sub>2</sub>O<sub>5</sub> : K<sub>2</sub>O = 20 : 0 : 16 + micronutrients) and pH was adjusted with CaCO<sub>3</sub> to pH 6 (0.01 M CaCl<sub>2</sub>). The CAT soluble P content of 25 mg P/L growing media was obtained by addition of Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> according to the calibration curves. The fertigation solution contained in mg/L solution: 120 N as KNO<sub>3</sub> and NH<sub>4</sub>NO<sub>3</sub>, 130 K as KNO<sub>3</sub>, K<sub>2</sub>SO<sub>4</sub> and KH<sub>2</sub>PO<sub>4</sub>, 10 Mg as MgSO<sub>4</sub>\*7 H<sub>2</sub>O and 200 Flori® 10. The P concentration of the fertigation solution was varied (in mg P/L solution): 0 (= *no P*), 17 (= *sufficient P*) and 35 (= *excess P*). Plants were harvested after 10 weeks cultivation after measuring plant height and diameter and length of internodes. The P concentration in plant d.m. was measured after wet digestion and the P concentration in the solutions was determined with the ammonium-vanadate-molybdate method. Treatments were replicated five times (each replicate consisted of 5 plants) in a completely randomized design and statistical analysis was performed with the program R 2.8.1. Means were compared between treatments at  $\alpha = 0.05$  using Tukey-Test.

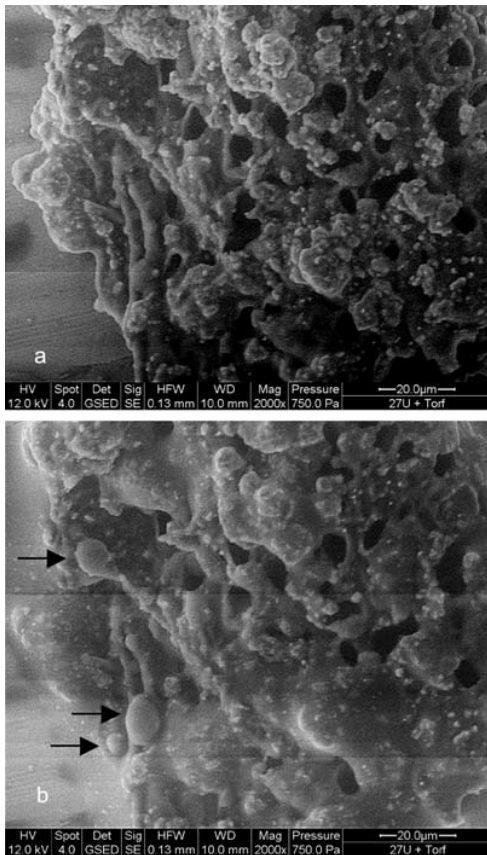


Figure 3a, b: Environmental scanning electron microscope (ESEM) observation of a peat-based growing media amended with a translocated clay (27 U) submitted to hydration conditions. The image shows a leave of Sphagnum moss peat covered with clay platelets in the dry state (a) and directly after beginning of condensation (b). Note that condensation starts at sites where clay minerals coat the peat's surface. Water droplets are marked with arrows.

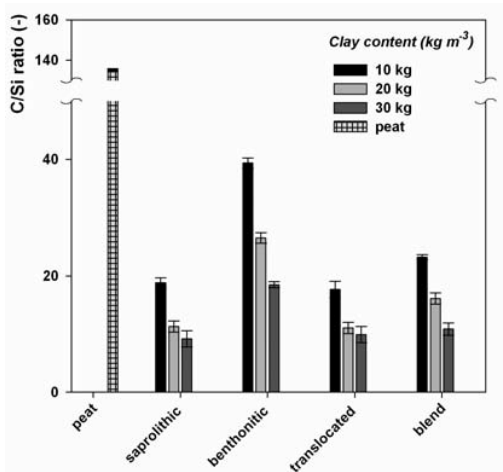


Figure 4: Coverage degree of peat surfaces with clay minerals expressed by the C/Si ratio (n=5). Low values indicate highly covered surfaces.

## Results

### Rewettability

#### ESEM observations

Growing media submitted to hydration show clearly that the condensation of water starts on the hydrophilic clay particles coating the external surfaces of the peat compounds (Fig. 3a, b). The formation of water drops on the surface of peat indicates high contact angles and strongly hydrophobic properties.

Saprolithic and translocated clays have the strongest effect on surface coverage of peat compounds with clay minerals (Fig. 4). Here already 20 kg/m<sup>3</sup> are sufficient to reach lowest C/Si ratios indicating maximum coverage degree. Bentonites and clay blends still increase the coverage degree of the peat's surface by the addition of 30 kg/m<sup>3</sup>. Bentonites show small effects even at the largest amended amount. Here C/Si-ratios are comparable with growing media amended with saprolithic and translocated clays in amounts of 10 kg/m<sup>3</sup>.

Water uptake is improved for all samples by the amendment of clay (Fig. 5), strongly depending on the clay parameters. Clays consisting mainly of illite and kaolinite (saprolithic and translocated clays) show fastest water uptake (50 vol.% within 10 min).

At C/Si ratios <20, where the surfaces of peat are most completely coated with clay minerals, all clay-peat systems show the highest water uptake rate. Highest variability is observed for a saprolithic clay rich in illite and kaolinite, where the water uptake rate ranges from 2.6 to 15.5 (%v/v)/min. Bentonites show only minor effects, water uptake ranges from 1.47 to 3.63 (%v/v)/min. The translocated clay is most effective to improve water uptake rate with small amended amounts. Larger added amounts show only slight improvements. For the clay blend and bentonite, the absolute amount of amended clay showed minor effects, but water uptake rate is quite higher than that of original peat (1.3 (%v/v)/min). The results show a good

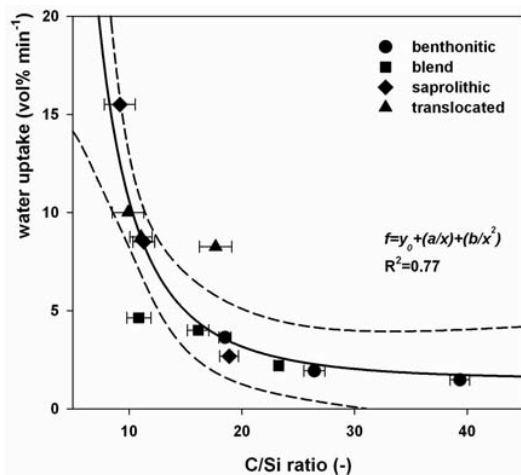


Figure 5: Effect of four different clays on the water uptake rate. Growing media are amended in amounts of 10, 20 and 30 kg/m<sup>3</sup> clay. Water uptake rate is determined by the time (min) needed to 50% saturation. The dashed line is the 95% confidence interval of the linear regression (solid line).

correlation of the surface coverage degree expressed by the C/Si ratio and rewettability determined by the capillary rise »WOK« method. The determination of the C/Si ratio in a relatively short procedure is a suitable method to identify suitable clays and the amount of clay needed.

#### *Effect of clay particle size on water uptake characteristics*

Time dependent water uptake measurements on growing media with clays of different particle size fractions reveal that the initial particle size of the amended clay has a strong influence on the water uptake rate. For fine aggregate sizes <0.5 mm the fastest water uptake was observed (Fig. 6). Note that in horticultural practice irrigation is often performed in the ebb and flow mode. If the uptake rate is high the time needed for irrigation can be shortened. After the total duration of the experiment of 1440 min (24 h) in the WOK apparatus the differences in water uptake rate are low. This is not relevant for horticultural practice, where the differences at the beginning of irrigation are most important. Here the growing media where the smallest aggregate size (< 0,5 mm) and the highest amount of amended clay (20 kg/m<sup>3</sup>) shows the fastest water uptake rate in the time period up to 15 min.

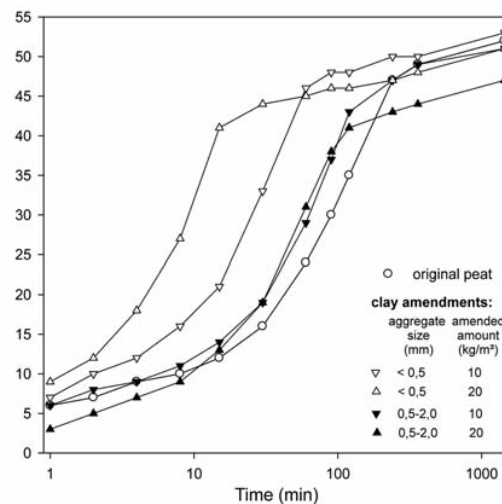


Figure 6: Time dependent water uptake of a growing media (fineness of peat: 0-10 mm) to which translocated clay 36M was added in two different amounts (10 and 20 kg/m<sup>3</sup>) and two particle size fractions (<0.5 and 0.5-2.0 mm).

#### *Effect of different clays on water uptake characteristics*

From the water uptake curves, it becomes evident that the growing media differ significantly in their rewetting behaviour (Fig. 7). Pure peat showed the slowest water uptake, whereas the increase in the volumetric water content of mineral amended growing media was generally faster. Up to 50 % water saturation, also marked variations in the rewetting behaviour among the different mineral amendments were observed. Amendments of smectite rich clays (06B and 07B) caused only a minor increase in water uptake velocity, while kaolinitic and illitic mineral amendments notably enhanced the rewetting. It can be concluded that the wettability of a growing media is a dynamic property, which is to a great extent influenced by the clay mineralogy and also other mineral parameters.

#### **Formation of hydrophobic coatings on clay mineral surfaces**

Mineral surfaces provide a variety of reactive functional groups on their surface, which allows strong interaction with dissolved organic and inorganic substances. Consequently, batch adsorption experiments with peat derived DOM revealed that both, the bulk samples



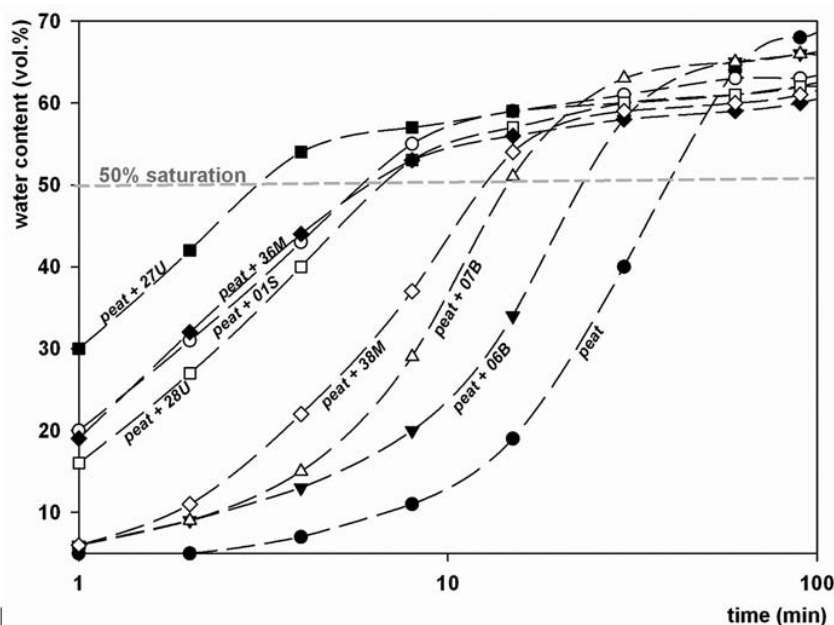


Figure 7: Time dependent water uptake of peat-based growing media amended with different clays in an amount of 30 kg/m<sup>3</sup>. For comparison, the water uptake of the pure peat is shown.

as well as the clay fractions adsorb relatively high amounts of dissolved organic substances (Fig. 8). For the samples under investigation, the adsorbed C content varies between 20 and 180 mmol C kg<sup>-1</sup>, with the highest amount being adsorbed by the samples rich in smectite (06B and 07B).

The composition of the organic coatings on the mineral phase was determined by UV-Vis analyses of the equilibrium solutions after the batch adsorption experiments (Fig. 9). Here, a decrease in light absorbance values (Abs<sub>280</sub>) indicates a high removal of aromatic organic substances from the solution due to the sorption onto mineral surfaces.

The extent of sorption was found to be dependent on the mineral parameters of the samples (Fig. 9, a, b, c). Linear regression analysis showed that sorption of aromatic compounds correlates well with the SSA, CEC and amount of oxalate soluble Al and Fe, which is consistent with findings reported elsewhere (e.g. Kaiser and Guggenberger, 2000; Kahle et al., 2004). Absorption at 280 nm shows strongest correlation to the SSA ( $r^2 = 0.86$ ), which is most likely due to the higher surface area available for

DOC sorption. Considering liming and fertilization, it can be suggested that DOM sorption is most likely also mediated by the solution chemistry. For instance Feng et al. (2005) found that sorption of peat derived humic acid onto kaolinite and montmorillonite increased with increasing ionic strength and decreasing pH, and that the presence of Ca<sup>2+</sup> largely enhanced the sorption. Subsequently, DOC linkage to negatively charged mineral surfaces via cation-bridges appears to be an important binding mechanism, which is also indicated by the positive correlation ( $r^2 = 0.66$ ) between adsorbed DOC and the CEC of the clay amendment. The correlation with the sum of oxalate extractable Al and Fe ( $r^2 = 0.71$ ) is indicative for DOC binding onto poorly crystalline Fe and Al minerals (Mikutta et al., 2005). It can be assumed that the amount and composition of adsorbed DOM as well as the mineral parameters are the key to explain the observed variations in wettability and accordingly the differences in the effectiveness of the mineral amendments.

#### Effect of hydrophobic mineral coatings on water uptake rate

Adsorption of peat derived DOM onto mineral

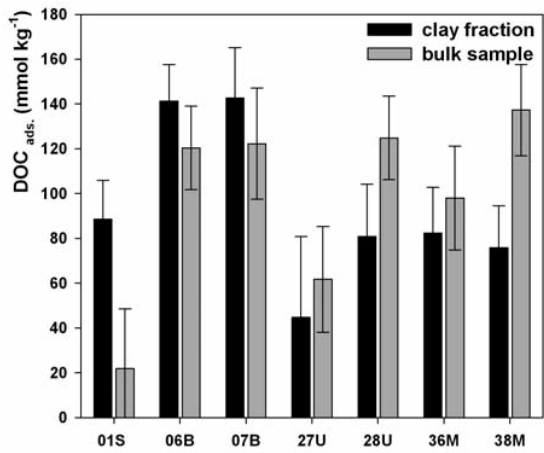


Figure 8: Sorption of peat derived DOM on bulk clay samples and the clay fractions.

surfaces influences the wettability of the growing media in a negative way (Fig. 10). From the non-linear regression it becomes evident that variations in wettability of the growing media can be attributed to a high extent to differences in the affinities of the mineral surfaces for aromatic DOM compounds. Most probably the hydrophilic behaviour of the mineral surfaces is affected by the adsorbed organic compounds forming hydrophobic surface coatings, diminishing their positive effect on the wettability.

#### Conclusions on rewettability

It was shown that the absorption of aromatic organic compounds changes the hydrophilicity of clay mineral surfaces. The intermolecular interactions involved in the formation of hydrophobic coatings can be very complex. However, significant effects can be expected if specific properties of the dissolved organic matter is varied (molecular size, configuration and polarity or hydrophobicity) and also specific surface properties of the adsorbents (texture, mineralogical composition and the distribution of reactive functional groups). Additionally, the properties of the organic and inorganic reactants can be affected by aqueous phase processes (e. g. hydrolysis, hydration, dissolution, and precipitation). Here the composition and properties of the aqueous solution (e. g. pH, ionic strength, presence of bridging-cations or competitive anions) have to be considered as well.

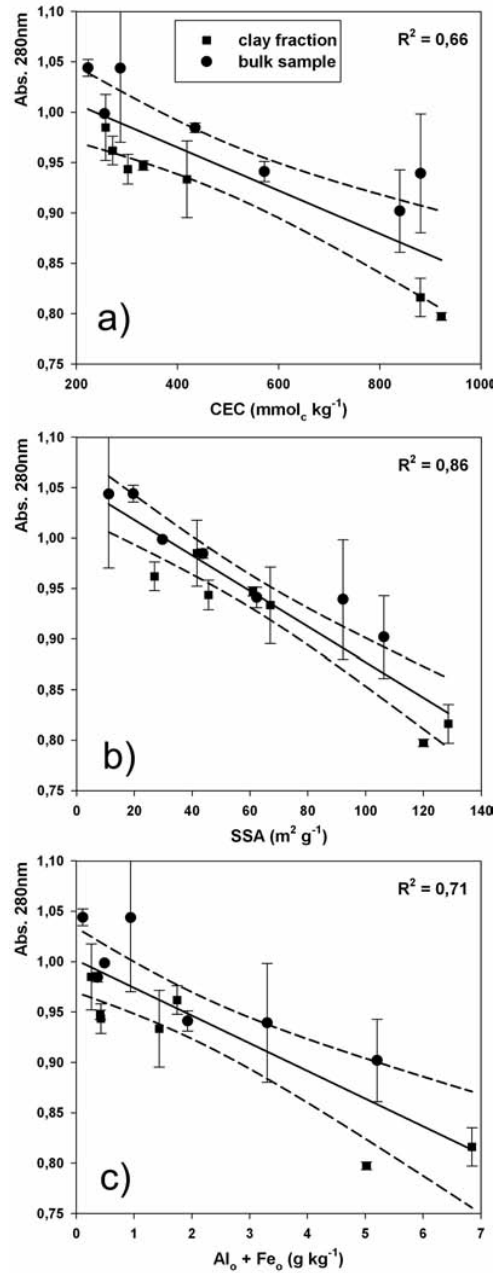


Figure 9: UV-Vis light absorbance values of the equilibrium solutions after batch adsorption experiment. Note, a decrease in the Abs<sub>280</sub>-values indicates a high removal of peat derived aromatic organic substances due to sorption onto mineral surfaces. Abs<sub>280</sub>-values are shown in relation to mineral properties a) CEC, b) SSA and c) oxalate soluble Fe and Al. The dashed line is the 95% confidence interval of the linear regression (solid line).

For instance, *Tarchitzky et al.* (2000) explained the role of polyvalent cations for water repellency with the enhanced formation of coatings on mineral surfaces, resulting in a reduction of the hydrophilic reactivity. Additionally it has

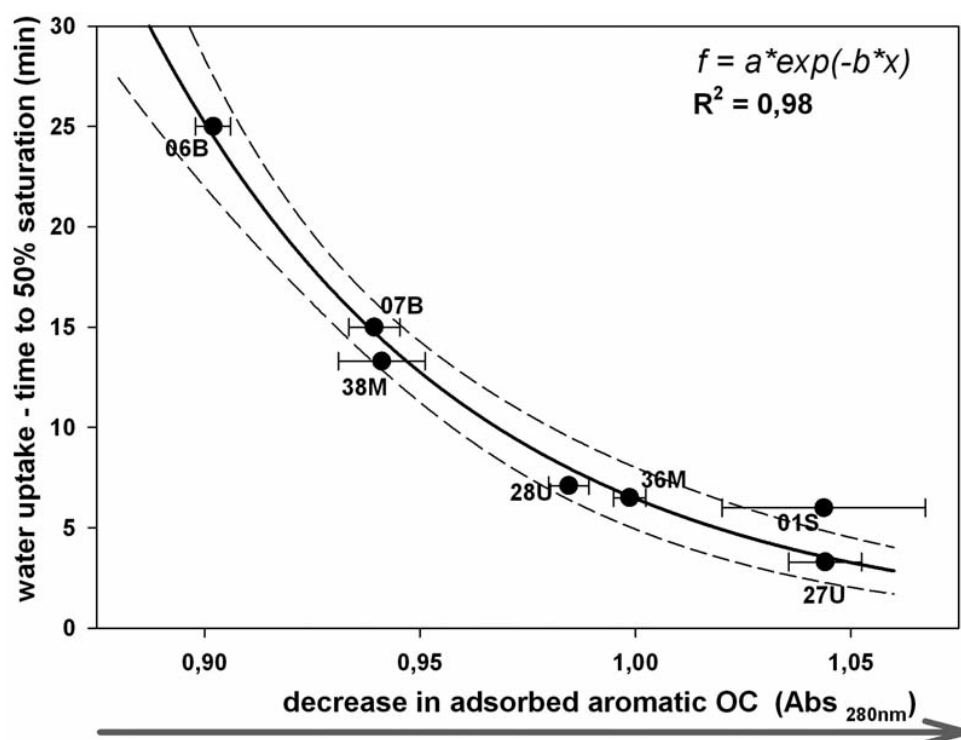


Figure 10: Water uptake of growing media amended with different clays in relation to the adsorption of aromatic compounds from peat derived DOM. The measure for the absorption of aromatic organic compounds from the equilibrium solution is the absorbance at 280 nm.

been suggested by Hurraß and Schaumann (2006) that bridges by polyvalent cations may cause an aggregation of the humic substances that would also result in a lower wettability.

The results of our study show that the observed differences in rewettability can be mainly attributed to the extent and kind of organic coatings on the mineral surfaces. Obviously the formation of these coatings relies on differences in the sorption properties of the minerals and, in turn on distinct mineral properties. Mineral amendments containing expandable clay minerals with high CEC and SSA (e. g. smectites) and amendments rich in amorphous Fe and Al compounds seem to be less effective, due to their high affinity for peat derived DOM, especially for hydrophobic DOM constituents (Fig. 11). Accordingly, an addition of non-expandable clays with lower SSA, CEC and amorphous oxide content (e.g. kaolinite and illite) seems more promising.

### **P buffering capacity**

The nine selected clays differed clearly in their P binding capacity and content of  $\Sigma\text{Fe}_{\text{ox}}+\text{Al}_{\text{ox}}$  (Fig. 12). The P binding of the clays correlated positively with the  $\Sigma\text{Fe}_{\text{ox}}+\text{Al}_{\text{ox}}$ , but could not fully explain the whole variation in P fixation. It is assumed that the surface of the oxides differs widely, which will be investigated in further experiments.

After ten weeks cultivation the varied P fertilization resulted in clear differences in plant growth and quality among the treatments and growing media.

Without P fertilization the elongation of shoots was reduced in pure white peat and the two clays with low P binding capacity 04S and 01S, compared to peat/clay blends containing clay 06B and 39W. Also P fertilization increased internode length in these blends (Fig. 13). The same trend was observed in plant diameter and height (data not shown).

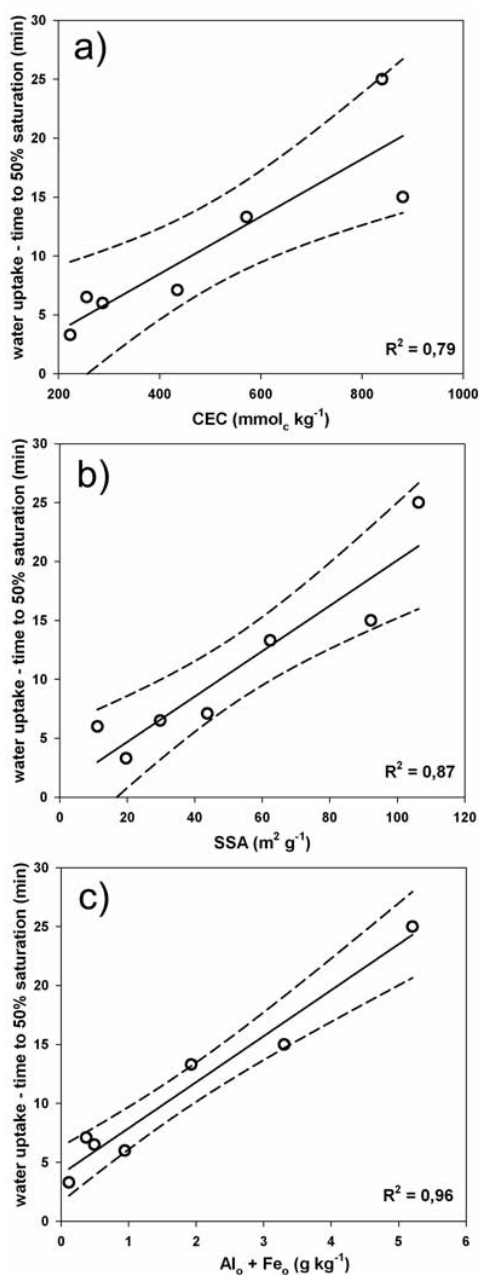


Figure 11: Water uptake of peat-based growing media mixtures amended with different clays with an amount of  $30 \text{ kg m}^{-3}$  and its relation to mineral properties a) CEC, b) SSA and c) oxalate soluble Fe and Al. Dashed line is the 95% confidence interval of the linear regression (solid line).

In all growing media the dry matter yield of the plants not fertigated with P was reduced compared to those receiving P. Without P fertigation yield of treatments in pure white peat and in the peat/clay blend 04S was lower than in the other three peat/clay mixtures (Fig. 14).

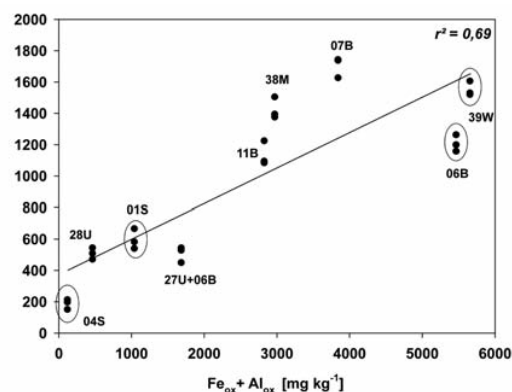


Figure 12: Relationship between the content of oxalate soluble Fe and Al and the P binding of nine different clays in a batch experiment with a P supply of  $10000 \text{ mg kg}^{-1}$ . Marked clays were used in the plant experiment.

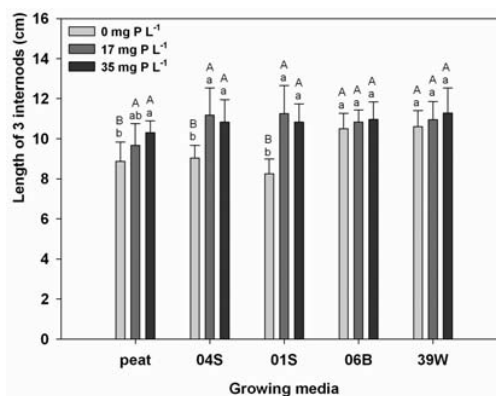


Figure 13: Length of internodes of *Impatiens walleriana* depending on growing media type and P conc. in fertigation solution. Different capital letters indicate significant differences between growing media at the same P fertigation level and different small letters indicate significant differences between fertigation treatments ( $p < 0.05$ ).

The increasing P supply via fertigation resulted in increased P conc. in plant d.m. in all growing media. Without P fertigation, P concentration in shoot d.m. was the lowest in treatment pure white peat and the peat/clay blend 04S and the highest P concentration was obtained in the treatment 06B. The same differences between growing media were observed with fertigation concentration  $17 \text{ mg P L}^{-1}$  solution, but no longer at the highest P fertigation level (Fig. 15).

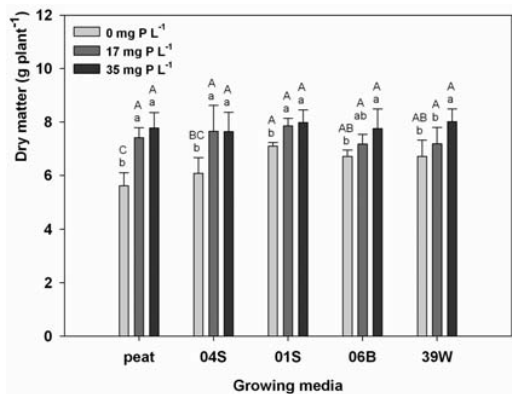


Figure 14: Dry matter of *Impatiens walleriana* depending on growing media type and P conc. in fertigation solution. Different capital letters indicate significant differences between growing media at the same P fertigation level and different small letters indicate significant differences between fertigation treatments ( $p < 0.05$ ).

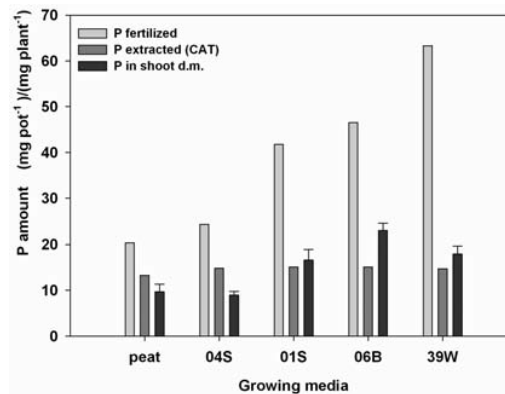


Figure 16: Amounts of fertilized and CAT-extractable P per plant container (0.6 L growing media) and P contained in shoot d.m. of *Impatiens walleriana* depending on growing media type.

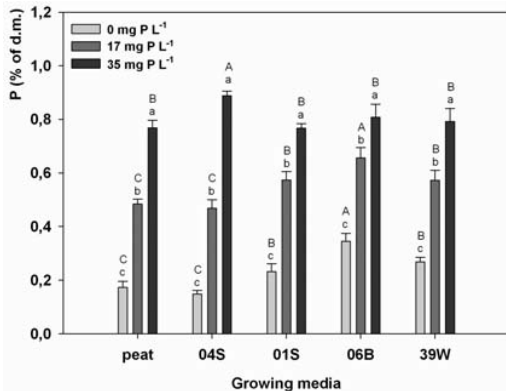


Figure 15: Phosphorus conc. in d.m. of *Impatiens walleriana* depending on growing media type and P conc. in fertigation solution. Different capital letters indicate significant differences between growing media at the same P fertigation level and different small letters indicate significant differences between fertigation treatments ( $p < 0.05$ ).

To characterize the capacity of different clays to supply P to plants the P amount contained in shoot d.m. was calculated for the treatment without P fertigation (Fig. 16). The clays 01S, 06B and 39W supplied about twice as much P to plants compared to pure peat and peat/clay blend 04S. In the latter treatments plants did not exhaust the P amount determined by CAT extraction whereas in the other treatments even more P was taken up than characterized as plant available by the extraction. In all growing media more P was fertilized than determined as plant available or taken up in shoot

d.m., which was more pronounced in blends with clays having a high binding capacity (01S, 06B and 39W). At the same CAT level, in this case 25 mg/L growing medium, peat/clay blends containing clay with a high P binding capacity supplied more P to plants indicating the capacity to buffer fluctuating P supply. In horticultural practice P availability in growing media is characterized by CAT extraction procedure.

#### Conclusions on P buffering capacity

The P binding capacity of clays was strongly correlated with the oxalate extractable Fe and Al content. However, this factor did not fully explain the observed variability. Low availability of P reduced internode length and supported compaction of plants. But at the same time d.m. production was decreased indicating that shortage of P is not a successful strategy to produce more compact and better shaped plants. Peat-clay blends containing clay with a high P binding capacity provided up to twice as much P to plants than those with a lower binding capacity, thus buffering fluctuations in P uptake and P fertigation. The common extraction procedure for horticultural growing media tended to underestimate the plant available P in peat-clay blends with high binding capacity. To improve the understanding of P binding of clays specific surface of oxides will be investigated.

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