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# Phosphorus sorption onto selected structured porous substrates

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## List of abbreviations

| | |
|---|---|
| P | Phosphorus |
| WRB | World reference base for soil resources |
| FAO | Food and agriculture organization |
| HNT | Halloysite nanotube |
| SEM | Scanning electron microscopy |
| XRF | X-ray fluorescence |
| RMSE | Root mean square errors |
| OM | Organic matter |
| SOM | Soil organic matter |
| NOM | Natural organic matter |

## Summary

Phosphorus (P) is an essential nutrient controlling plant growth and it is fundamental for the productivity of agricultural ecosystems; however, excess P in an environment causes eutrophication. Long-term accumulation of P in soils may cause environmental problems for decades even after reducing the anthropogenic P input into agro-ecosystems. A better understanding of the processes and characteristics that influence P adsorption, desorption, and solute transport in porous media is helping in assessing the availability of P for a sustainable agricultural production and productivity. The adsorption of P onto porous substrates can be a convincing strategy to reduce the non-point source pollution, for instance, from agricultural runoff. Many studies have addressed the importance of various substrates for the adsorption of P, although the impact of the structural characteristics of these substrates is unknown. The objectives of this thesis are to improve our knowledge on i) the P sorption onto structured soil; ii) the effects of soil aggregate size and stability on P sorption; and iii) halloysite nanotubes as an adsorptive material for P removal from aqueous solution.

Over decades soil-solution interactions were studied employing the slurry batch technique in which soil and solution is subjected to intensive mixing employing mechanical shakers. In a first step, a new experimental procedure was developed allowing to test the adsorption capacity of intact soil aggregates. The approach was termed ‘diffusion approach’ because the penetration of soil aggregates by solutes is basically diffusion controlled.

The P adsorption onto bulk soil, soil aggregates, powder, and granular halloysite nanotubes were evaluated by different initial phosphate concentrations ranging from 1 to 100 mg $L^{-1}$ over 24 hours. The results illustrate that the adsorption of phosphate onto soil aggregates was elevated as compared with unstructured bulk soil. The overall retention capacity of intact aggregates was higher than that of the disturbed soil because the inner-aggregate pore space accommodated a certain fraction of phosphate in addition to the adsorbed phosphate at the surface of the soil particles. The maximum adsorption efficiency of the granular halloysite nanotubes was more than that of powder halloysite nanotubes. It is assumed that the pore space of the granular halloysite nanotubes accommodates physico-chemically-bound phosphate at surfaces. The presented experimental approach allows studying diffusion-controlled adsorption processes in structured and bulk soil. The experimental design more intimately depicted the natural situation than the classical slurry batch technique that is frequently used for soil P interactions.

Studying the effect of initial phosphate concentration on the phosphate adsorption dynamic applying the diffusion approach with bulk soil and soil aggregates revealed that the first rapid adsorption was followed by a slower adsorption reaction onto soil aggregates compared with the bulk soil at later stages. A modified diffusion process and lower accessibility of sorption sites of soil aggregates could cause differences in the temporal dynamics of P adsorption.

The interaction between soil structural elements and phosphate was further investigated by considering aggregate size. The more pronounced adsorption of phosphate onto larger aggregates illustrates the importance of the inner aggregate pore spaces for the adsorption process. The intra-aggregate pore space appears as additional adsorption sites for phosphate besides physico-chemical reactions at soil particle surfaces. The nth-pseudo sorption rate equation provided a superior fit to the data, explaining the idea of the heterogeneity of soil surfaces for phosphate sorption. Finally, aggregate stability was related to the extent of phosphate adsorption presumably because aggregate stability and accessibility of the inner pore space are linked. The results highlight the applicability of the diffusion approach to a wide range of structured soil samples.

## Zusammenfassung

Phosphor (P) ist ein essentieller Nährstoff mit grundlegender Bedeutung für das Pflanzenwachstum in landwirtschaftlichen Ökosystemen. Phosphor im Übermaß verursacht jedoch Umweltprobleme wie beispielsweise die Eutrophierung von Gewässern. Ein besseres Verständnis der Prozesse, welche die Adsorption, die Desorption und den gelösten Transport in porösen Medien beeinflussen, hilft die Verfügbarkeit von P in Böden einzuschätzen und damit die Nachhaltigkeit der landwirtschaftlichen Produktion zu stärken.

Die Langzeitakkumulation und der Transport von P in Böden und Sedimenten können auch nach Verringerung des anthropogenen Phosphoreintrags als Dünger noch zu Umweltproblemen führen. Die Adsorption von P an poröse Filtermaterialien kann eine Strategie zur Reduzierung von diffusen Phosphorquellen darstellen (z.B. im Ablauf von landwirtschaftlichen Dränanlagen). Viele Studien haben sich mit der Bedeutung von verschiedenen Substraten für die Adsorption von P beschäftigt, jedoch ist der Einfluss der Strukturmerkmale der untersuchten Materialien noch weitestgehend unbekannt. Wissenschaftliches Ziel der vorliegenden Arbeit war die Verbesserung des Wissens über i) die Phosphatsorption an strukturierten Böden; ii) die Auswirkungen der Größe und Stabilität von Bodenaggregaten auf die Phosphorsorption und iii) Halloysit-Nanomaterialien als adsorptives Material zur Phosphorentfernung aus wässrigen Lösungen.

Phosphor-Boden-Interaktionen werden üblicherweise in sogenannten Batch-Versuchen, in denen Boden und Lösung intensiv geschüttelt werden, untersucht. Dabei wird jedoch die Struktur des Bodens zerstört und der Einfluss der Bodenstruktur auf Sorptionsprozesse kann nicht überprüft werden. In einem ersten Schritt wurde ein Versuchsansatz entwickelt, mit dessen Hilfe intakte Bodenaggregate mit Phosphorlösungen unterschiedlicher Konzentration in Kontakt gebracht werden konnten. Der experimentelle Ansatz wurde als ‚Diffusionsversuch' bezeichnet, weil der Transport der Phosphationen ins Aggregatinnere weitestgehend diffusionskontrolliert erfolgt.

Die Phosphoradsorption an Gesamtboden, Bodenaggregaten sowie Feinboden und granulatförmigen Halloysit-Nanoröhren wurde anhand verschiedener Ausgangsphosphatkonzentrationen im Bereich von 1 bis 100 mg $L^{-1}$ über 24 Stunden

bewertet. Die Ergebnisse zeigen, dass die Adsorption von Phosphat an Bodenaggregate im Vergleich zu unstrukturiertem Feinboden erhöht war. Die Retentionskapazität intakter Aggregate ist insgesamt höher als im Vergleich zu gestörtem Boden. Es kann angenommen werden, dass der Porenraum innerhalb der Aggregate einen bestimmten Anteil an P enthält zusätzlich zu dem adsorbierten P an der Oberfläche von Bodenpartikeln. Darüber hinaus war die maximale Adsorptionseffizienz für Granulat-Halloysit-Nanoröhren höher als die von Pulver-Halloysit-Nanoröhren. Es wird angenommen, dass der Porenraum von Granulat-Halloysit-Nanoröhren physikalisch-chemisch gebundenes Phosphat an Oberflächen aufnehmen kann. Der vorgestellte experimentelle Ansatz ermöglicht die Untersuchung diffusionskontrollierter Adsorptionsprozesse in strukturierten und unstrukturierten Böden. Die gewählte Versuchsanordnung gibt die natürlichen Verhältnisse in Böden besser wieder als die klassische Slurry-Batch-Technik, die häufig für die Wechselwirkungen zwischen Boden und Phosphor eingesetzt wird.

Die Untersuchung der Auswirkung der anfänglichen Phosphatkonzentration auf die Phosphatadsorptionsdynamik unter Verwendung des Diffusionsansatzes zeigt, dass in einer ersten schnellen Adsorptionsreaktion der gestörte und aufbereitete Feinboden zunächst mehr adsorbiert als die Bodenaggregate. Mit zunehmender Dauer des Experiments übersteigt allerdings die Adsorptionskapazität der Bodenaggregate die des Vergleichssubstrats. Unterschiede in der zeitlichen Dynamik könnten durch einen modifizierten Diffusionsprozess und weniger zugängliche Sorptionsstellen bei Bodenaggregaten verursacht worden sein.

Die beobachtete stärkere Adsorption von Phosphat an größere Aggregate hebt die Bedeutung innerer Porenräume von Strukturelementen in strukturierten Böden hervor. Intraaggregaträume bieten zusätzlich zu Partikeloberflächen, die für die Adsorption von P zur Verfügung stehen, Platz für die Phosphatretention. Dabei ist das Phosphatanion in der Lösung im inneren von Aggregaten nur ‚scheinbar' adsorbiert; es ist der Außenlösung, die für die Bemessung der Adsorption herangezogen wird, entzogen. Die Gleichung der n-ten Pseudosorptionsrate lieferte eine gute Anpassung an die experimentellen Daten und erklärte die Idee der Heterogenität der Bodenoberflächen für die Phosphatsorption. Schließlich zeigten die Untersuchungen, dass die Aggregatstabilität in Beziehung zur Höhe der Phosphatadsorption an Bodenaggregate steht. Es ist zu vermuten, dass größere

Aggregate leichter zugänglich sind. Die Ergebnisse belegen die generelle Anwendbarkeit des hier entwickelten experimentellen Diffusionsansatzes für strukturierte Böden.

# 1

# Introduction

## 1.1 Motivation

Phosphorus is an essential production-limiting nutrient encouraging plant growth that is fundamental for the productivity of agricultural ecosystems (George et al., 2016). Besides the convincing effects of phosphorus on crop growth, it is clearly required for crop development owing to its critical function in plant metabolism, the structure of nucleic acids and the expression of information (DNA and RNA) and energy transfer pathways, especially for ATP, phospholipids, and cell membrane (Childers et al., 2011; Elser, 2012).

Excess phosphorus causes environmental problems – in particular eutrophication – if released in higher concentrations to water resources (Barrow, 2015a; Van Der Salm et al., 2016). Environmental concerns related to the quality of surface waters due to phosphorus enrichment remain an increasingly important challenge in the world (Sharpley et al., 2015). An increasing world population size has led to an acceleration in the rate and extent of eutrophication through point-source discharges and the loading of limiting nutrients such as phosphorus into aquatic solutions (Carpenter et al., 1998; Barrow, 2015a; Van Der Salm et al., 2016). Recovering wastewater from the point of source of pollution – especially relating to nitrogen and phosphorus – is considered to be practical for many European countries through the use of different treatments. However, long-term accumulation and the transportation of accumulated phosphorus in soils and river sediments can be detected, even after reducing the anthropogenic phosphorus input in the form of fertilisers (Powers et al., 2016).

The uncontrolled growth of algal blooms in rivers, stream and coastal ecosystems has been recognised as a consequence of increased nutrient concentrations. Apart from limiting light penetration – which hinders predation on the part of hunters – the consumption of dissolved oxygen, raised pH levels, and increased rates of photosynthesis can be distinguished throughout the day. In severe stages of eutrophication, the algal blooms die down, and microbial decomposition critically squanders oxygen in the water (Chislock et al., 2013). Moreover, the consumption of harmful algae bloom is toxic for both plants and animals, and it can alter and threaten their food chains (Strokal et al., 2014).

In recent years, strong interest has been focused on nutrient status in the Baltic Sea, and elevated nutrient concentrations have been monitored since the 1970s (Bonsdorff et al., 1997). The treatment of eutrophication in the Baltic Sea has frequently been considered since the Baltic Sea basin has an area four times larger than the Baltic Sea itself (Stålnacke et al., 2015). Annual assessment of phosphorus transmission to the Baltic Sea revealed that the majority of sources of P entering the Baltic Sea originated from the state of Mecklenburg-West Pomeranian (Behrent and Bachor, 1998). Although some valuable efforts have been made to mitigate Baltic Sea eutrophication, a certain degree of turnover has been noted in some parts of the Baltic Sea (Andersen et al., 2017). This illustrates that the application of moderating strategies through non-point sources to remedy the situation facing surface waters is essential for sustainable agriculture (Jarvie et al., 2013; Kleinman et al., 2015; Sharpley et al., 2015).

Sorption processes in porous media including adsorption, chemisorption, biodegradation, and ion exchange alter the flow by which a contaminant becomes distributed between the solution and the solid phase. The sorption of inorganic solutes in porous media is a function of the area available for adsorption, as well as the accessibility of the ion exchange sites provided by porous media. In many studies, the convection-dispersion equation has been modified to consider the effect of solutes that are removed from a solution by sorption, chemical reaction and biological biodegradation. Some of the aforementioned reactions can be characterised through equilibrium reactions and some of the aspects needed to deal with the kinetics of reactions.

In addition to the processes by which the flow and its solute can be affected, the characteristics of the porous substrate and their differences have attracted strong attention regarding a range of aspects of flow and mass transportation. Soil as a porous medium has been studied to illustrate the end result and transportation of dissolved contaminants, as well as materials such as fertilisers and pesticide that have been applied to the soil. The adsorption of phosphate onto soil is dramatically affected by physical and chemical soil characteristics including clay content, soil moisture, organic matter, Al- and Fe-oxide content, and pH, as well as the redox conditions under which the adsorption process takes place (Xiao et al., 2017; Ho and McKay, 1998; Del Bubba et al., 2003; Samadi and Gilkes, 1998; Singh and Gilkes, 1991). Many studies have revealed how soil chemical characteristics and heterogeneous soil constituents affect the adsorption of phosphate. However, by contrast there is little clear information concerning the extent to which the physical characteristics of soil – in particular soil structure – affect the adsorption process (Akhtar et al., 2003).

Among the natural adsorbents, nanoparticle clay mineral has received relatively stronger attention in terms of its high specific surface area, high adsorption rates compared with other adsorbents, low toxicity, smooth operation, and relatively acceptable cost efficiency. Some research findings have indicated the potential of clay materials (halloysite) to remove anionic and pollutants besides cationic ions (Joussein et al., 2005; Mallikarjun and Mise, 2013; Cataldo et al.,2015). Studies have suggested that halloysite can be utilised as an adsorbent of different chemicals, and different mineralogical composition and pollution remediation materials (Matusik, 2016). Although the tubular shape of halloysite nanotubes contributes to adsorption capacity, the interlayer is not easily accessible for the adsorption of ions and molecules. To find a way to improve the adsorption of phosphate onto halloysite nanotubes in terms of addressing the crucial role of soil structure, we hypothesise that the application of the modified granular form of halloysite nanotubes may promote the adsorption of halloysite nanotubes (Yuan et al., 2016).

## 1.2 Research objectives and thesis outline

The overall objective of the study was to evaluate the sorption processes of phosphorus and the importance of soil structure in well-structured and fine earth in conditions that perform better compared with the natural situation through the introduction of a new approach (a diffusion experiment). Moreover, there will be additional testing of the method for other porous substrates – e.g. halloysite nanotubes – to determine whether these could be utilised as adsorptive material for phosphate removal from aqueous solutions. In addition, the aforementioned approach is examined to explore the effects of soil aggregate size and aggregate stability on phosphorus adsorption onto structured soil.

**Chapter 1** provides some information regarding the background and motivation for the study.

**Chapter 2** is a manuscript published in Soil Systems (Switzerland) (Saki et al., 2020). It focuses on the effect of structure characterisation on the adsorption of phosphate onto the soil. The research aims to characterise the impact of soil structure on phosphate adsorption through the introduction of a diffusion approach to address the effect of initial phosphate concentration on the kinetics of phosphate adsorption and the equilibrium adsorption isotherms for phosphates onto soil aggregates.

**Chapter 3** supplies some evidence regarding the effects of soil aggregate size and aggregate stability on phosphorus adsorption by conducting diffusion experiments using different classes of soil aggregate. The aim was to explore how soil structure characteristics are related to adsorbed phosphate, and evaluate the quality of various kinetic models in depicting the experimentally-observed adsorbed data.

**Chapter 4** is a manuscript published in the Journal of Water (Switzerland) (Saki et al., 2019) that concentrates on the use of halloysite nanotubes as adsorptive material for phosphate removal from aqueous solution. The aim was to study the adsorption of phosphate onto the powder and the granular form of halloysite nanotubes using the classical batch method, as well as a diffusion experiment to validate the performance of halloysite nanotubes as an efficient adsorptive for phosphate from agricultural runoff.

**Chapter 5** synthesises the finding of studies involving different experiments. In particular, it focuses on the newly-introduced diffusion approach and future research needs.

## 1.3 Background

### *1.3.1 Sorption mechanisms*

Sorption is a fundamental process in the environment that affects the degradation, transportation, and biological activity of the compounds. Despite often being regarded as an instantaneous phenomenon, sorption may necessitate some time to reach equilibrium for modelling purposes. Sorption kinetics is crucial in modelling the transport of contaminants in groundwater. Serious research regarding the sorption kinetics of soils and sediments began in the mid- to late-1980s (Sawhney and Brown, 1989; Alexander, 1997). While sorption is involved in fate, transportation, and risk assessment models, an understanding of sorption is critical for accurate evaluation (Pignatello and Xing,1996).

Over recent decades, researchers have revealed that the uptake and release of organics are bimodal in most cases, and they occur in fast and slow stages. The division between the two steps is unclear, although it ranges from a few hours to a few days. The changes in solution-phase concentration during the slow sorption stage have been experimentally observed to be small over some hours, and they can be easily concealed by random analytical errors. Accordingly, in many sorption experiments the equilibrium time after some hours has been falsely chosen.

The mobility and availability of contaminants in the environment are related to the adsorption of these contaminants onto the soil. Conceptual depictions of sorption are frequently simplified by assuming the establishment of an instantaneous equilibrium. However, data differing from this assumption has been commonly reported, challenging the effectiveness of such a simplification (Gaillardon, 1996; Walker and Jurado-Exposito, 1998; Cox and Walker, 1999).

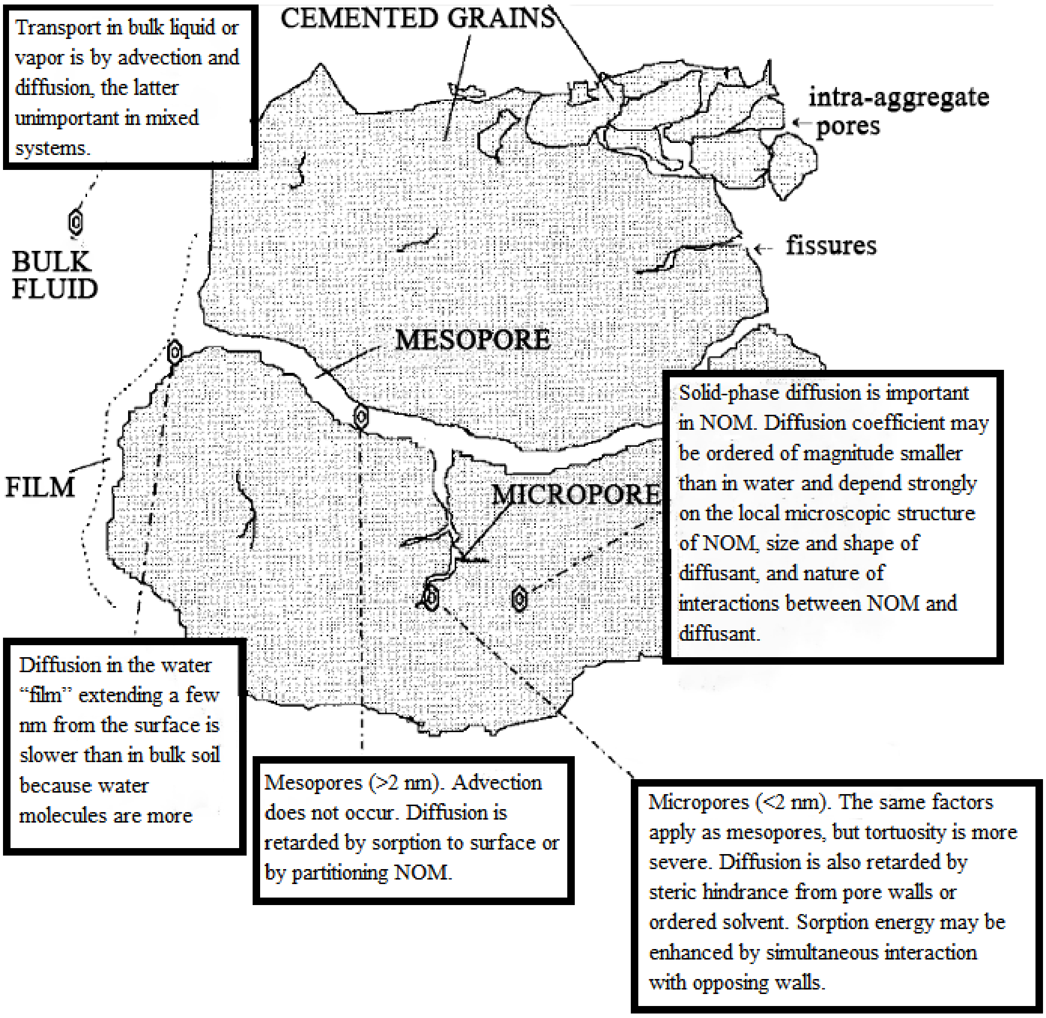
Time-dependent and non-optimal sorption behaviour has been assigned to numerous factors, including diffusive mass transfer resistance, rate-limited sorption reactions, non-linearity parameters in sorption isotherms, and sorption non-singularity (Brusseau and Rao, 1989a). The two dominant factors responsible for the non-ideal sorption of non-ionic or hydrophobic compounds are sorption non-equilibrium, resulting from physical non-equilibrium, and intraorganic matter diffusion (Brusseau and Rao, 1989b; Pignatello and Xing, 1995; Johnson et al., 1999). The availability of chemicals for transportation to surface or ground waters is related to any direct enhancement of the strength of sorption over time. Several authors have reported how pesticides and other chemical concentrations in leachate or groundwater diminish more rapidly than expected, solely based on the loss of chemicals via degradation (White et al., 1986; Lennartz et al., 1997; Jones et al., 2000; Walker et al., 2005).

Most sorption studies are conducted on sieved soils, and the number of sorption studies relating to intact soil aggregates is limited. Sorption behaviours using sieved soil do not necessarily resemble sorption behaviour in structured soils. Studying natural aggregates raises the practical difficulty that many aggregates would decompose when used in batch sorption studies. Sorption studies on aggregates within pesticide solution have been undertaken through batch equilibration (Novak et al., 1994), and by extracting available water from aggregates at different time intervals after the application of the pesticide (Walker et al., 1999; Beulke et al., 2004). However, moist aggregate applications in the field are more realistic and batch studies have the advantage of involving more controlled experimental conditions, which consequently allow differentiation between multiple causes of time-dependent sorption (Villaverde et al., 2009).

#### *1.3.1.1 Possible rate-limiting mechanisms*

The potential reasons for slow sorption are mass transfer limitations (molecular diffusion) and the activation energy of sorptive bonds. Sorption occurs through the physical adsorption on a surface or via partitioning (dissolution) into a phase; for instance, natural organic matter. The frequent intermolecular interactions that are available in the case of neutral organic compounds for both adsorption and partitioning are van der Waals (dispersion), dipole-dipole, dipole-induced dipole, and hydrogen bonding. In the case of a flat, unhampered, and rigid surface, adsorption is typically unactivated or only marginally activated, and it consequently should be practically instantaneously (Adamson, 1976).

It is well known that slow kinetics contribute to some kind of diffusion constraint. This is almost definitely the case because sorbing molecules can actively diffuse constraint limitations throughout the entire sorption period, due to the porous structure of particles. Diffusion is known as a random movement depending on the concentration gradient (Crank, 1975). Particles are porous depending on their aggregated nature, and the lattice of individual grains in the aggregate that could possibly be fractured.



Transport in bulk liquid or vapor is by advection and diffusion, the latter unimportant in mixed systems.

Solid-phase diffusion is important in NOM. Diffusion coefficient may be ordered of magnitude smaller than in water and depend strongly on the local microscopic structure of NOM, size and shape of diffusant, and nature of interactions between NOM and diffusant.

Diffusion in the water "film" extending a few nm from the surface is slower than in bulk soil because water molecules are more

Mesopores (>2 nm). Advection does not occur. Diffusion is retarded by sorption to surface or by partitioning NOM.

Micropores (<2 nm). The same factors apply as mesopores, but tortuosity is more severe. Diffusion is also retarded by steric hindrance from pore walls or ordered solvent. Sorption energy may be enhanced by simultaneous interaction with opposing walls.

**Figure 1. 1** Schematic of varied diffusion processes in a soil particle aggregate (Pignatello and Xing, 1995).

The conceptualisation of possible diffusion processes into a soil or sediment aggregate is shown in Figure 1.1. All sorption sites of the aggregates would be accessible if diffusing molecules crossing bulk liquid, the proportionately immobile liquid "film" extending from the solid surface (in the form of film diffusion), through the interior pores of the particle (in the form of pore diffusion), and porous solid phases (in the form of matrix diffusion). In the case of natural particle systems, some data indicates that the diffusion coefficients of organic molecules could be assumed to decrease similarly with the exclusion of bulk aqueous diffusion. One or more diffusion constraints could be visualised in series or parallel in the observed kinetics in any region of the sorption over time.

### *1.3.1.2 Kinetic behavior*

Some mathematical models including first-order, multiple first-order, Langmuir-type second-order (i.e. first-order each in solute and "site") and different diffusion rate laws have been proposed to study kinetic behaviour. Most sorption kinetic models fit the data in a superior way by involving an instantaneous, non-kinetic fraction, which is described via the equilibrium sorption constant. When comparing kinetic models, none is dominant, although diffusion models are more successful than first-order models (Pignatello et al., 1993; Pedit and Miller, 1994). To apply to transportation and degradation models, first-order kinetics are more accessible given that they do not necessitate a knowledge of particle geometry. Pedit and Miller (1994) have modelled the months-long uptake of diuron using a stochastic model that considers the inter- and intra-particle heterogeneity of soil, which processed sorbate concentration and a first-order rate constant as continuously-distributed random parameters.

### *1.3.1.3 Sorption-retarded pore diffusion*

The sorption-retarded pore diffusion model (Figure 1.2) hypothesises the rate-limiting process to involve molecular diffusion in pore water, namely retarded, chromatographic-like, through local sorption on pore walls (Wu and Gschwend, 1986). Most scientists have assumed instantaneous local sorption, uniformly porous particles, and constant sorption parameters in the soil pores. According to the aforementioned model, rates are expected to be negatively correlated with the square of the particle radius, the tortuosity of pores, the constrictivity of pores (steric hindrance), and the solution-phase distribution coefficient.

Observations that indicate sorption-retarded pore diffusion include faster rates after particle pulverisation, which reduces the length of the pore path for natural particles (Steinberg et al., 1978; Ball and Roberts, 1991; Pignatello, 1990) and – after acidification – a disaggregation of the grains that hold the aggregates together due to dissolving the inorganic oxide cements (Pignatello, 1990). The correlation between the diffusion rate and particle size is merely qualitative at best. On the other hand, there is some evidence regarding a rough correlation (Wu and Gschwend, 1986), as most experiments occurred over a few hours. In another case, coarse aquifer sand particles equilibrated some chemicals generally faster than was the cases with fine particles (Ball and Roberts, 1991), in the sense that the particles comprised cemented aggregates with calcite that had a significant surface area and internal porosity (Ball et al., 1990). The dependence of desorption on particle size is entirely absent in many systems (Pignatello et al., 1993; Steinberg et al., 1987; Carroll et al., 1994; Farrell and Reinhard, 1994; Novak et al., 1994).

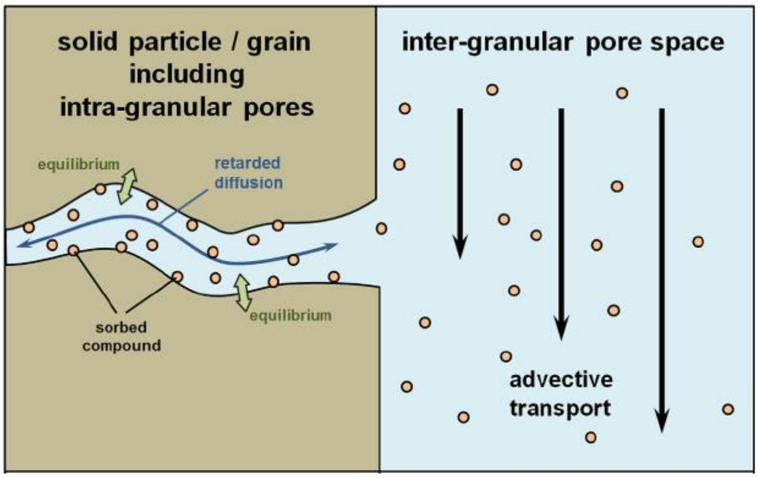


**Figure 1. 2** Sorption-retarded pore diffusion model (Finkel at al., 2016)

#### 1.3.1.4 *Significance of sorption mechanism to remediation and bioavailability*

The bioavailability to microbes, plants, and animals of chemicals in soil has attracted strong attention regarding the perspective of remediation and risk assessment. The clean-up of soil in situ or ex situ demands the mass transportation of contaminants through the materials, which in turn is dependent on sorption kinetics. Bioavailability has been described as a significant limitation when it comes to accomplishing the bioremediation of contaminated soils (Loehr and Webster, 1995; Environmental Protection Agency (EPA), 1991). In situations in which the soil contaminant degradation system is dynamic and interdependent, a mechanistic-based biodegradation model has been utilised regarding the mechanisms governing sorption, apart from the biological mechanisms leading to cell growth and substrate usage in the matrix.

### *1.3.2 Study sites and sampling*

#### *1.3.2.1 Soil aggregates*

Soil samples for the study of soil structure were obtained from an agricultural field site at Dummerstorf (site 1; Figure 1.3), located near the city of Rostock in north-eastern Germany. According to FAO classification, the soil type was categorised as a Stagnosol (IUSS Working Group WRB, 2015). The climate of the study ranges from Atlantic to continental, with average annual precipitation and annual mean temperature of 660 mm and 9.1°C, respectively. Sugar beet (*Beta vulgaris L.)* is intensively cultivated at the study site. All experiments were carried out with soil samples from both surface and subsurface horizons, which displayed various bulk density and organic matter content. Soil aggregates were obtained by dropping a block of soil onto the ground from a height of 1 m to achieve natural-structured aggregates. An aggregate size of 4-6 mm was obtained using a standardised sieve, with the results being separated for the purposes of the diffusion experiment, which involved exploring phosphate adsorption onto the structured soil. Different classes of soil aggregates including 4-6 mm, 1 cm, and 2 cm were used to assess the effects of soil aggregate size on the adsorption of phosphate onto structured soil. Disturbed soil samples that were obtained from grinding and passing through a 2 mm sieve were used as bulk soil in this study.

**Figure 1. 3** Location of study site

### *1.3.2.2 Halloysite nanotubes*

Among the natural adsorbents, halloysite nanotubes (HNTs) have been considered in this study as a promising adsorbent of pollutants. HNTs are a natural clay mineral of nano-size, with a predominantly tubular structure belonging to the 1:1 kaolin group of clay minerals. The structural formula of this adsorbent can be written as ($Al_2SiO_5(OH)_4.2H_2O$). Compared with the 1:1 kaolin group of clay minerals, each layer of HNTs accommodates tetrahedral (Si-O) and octahedral (Al-OH) sheets, and one aluminium octahedron sheet. The promising adsorption potential of the HNTs is attributed to their relatively small particle size and large surface area. The modified HNTs used in this study attracted attention due to internal and external surface modifications. The HNT material used in this study was prepared by the Durtec Company (Neubrandenburg, Germany).

**Figure 1. 4** Halloysite nanotubes at granular and powder form

A compaction process was used to prepare the granular HNTs by employing an EIRICH machine, producing a grain size of between 4 and 6 mm for the investigated HNT grains. Prior to the experiments, the morphology, size and elemental composition of the HNTs were characterised using scanning electron microscopy (SEM). In addition, the chemical composition and the specific surface area of the HNTs was ascertained by X-ray fluorescence (XRF) spectrometry and $N_2$ gas BET analyses, using a thermo Sorptomatic 1990 Analyzer.

## 1.4 Data analysis

The adsorption kinetics of phosphate onto bulk soil, soil aggregates, HNTs and granular HNTs was examined with the use of a number of mathematical models including pseudo-first-order (Lagergren, 1898), pseudo-second-order (Ho and McKay, 1998) and pseudo-nth-order equations (Özer, 2007). In addition, the two most-widely used isotherms – the Freundlich and Langmuir equations – were applied to describe the data of the adsorption isotherm. This data can represent the distribution of phosphates between the solid and liquid phase via linear or empirical exponential functions (Barrow, 1983) (**Chapters 2 , 3 and 4**).

MS Excel 2007 version was employed for fitting the kinetic and isotherm equation parameters. A T-test was used comparisons of phosphorus adsorption between fine soil and soil aggregates, and between topsoil and subsoil, at a significance level of 95%. An F-test was performed to examine differences regarding different variables as presented in the tables and figures. All statistical analyses were performed using SPSS Statistics 22.0 software (SPSS Inc. Chicago, IL, USA) (**Chapters 2 and 3**).

# 2

# Phosphate sorption onto structured soil

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## Abstract

Soil–phosphorus interactions are frequently studied employing the slurry technique, in which soil samples are intensively mixed with phosphate solutions of various concentrations. The result of such experiments is a “phosphate sorption potential” because the thorough mixing of soil and phosphate solution as obtained by overhead or horizontal shaking of the slurry would probably not occur under natural conditions, especially if the soil is structured. Here, we wanted to test the impact of soil structure on phosphorus (P) removal from aqueous solution. Soil aggregates of a defined size class were prepared by carefully sieving the soil. The soil aggregates were individually wrapped in an inert fabric and placed on a sieve, which was lowered into a basin containing a phosphate solution of a given concentration. The decrease of the phosphate solution concentration with time was registered at fixed intervals, and adsorbed amounts were quantified by differences between initial concentrations and concentrations at the time of sampling. Pre-tests on fine earth revealed that sorption was more pronounced in the classical slurry batch experiment than in the approach used in this study. Differences between methods were more pronounced at lower initial phosphate concentrations. The increase in P sorption in the classical batch experiment continued over 24 h to 140 mg kg$^{-1}$, while the adsorbed P amount remained constant (64 mg kg$^{-1}$) after 6 h in the diffusion experiment. Interestingly, it was observed that the sorption onto soil aggregates was elevated as compared to unstructured fine earth. The sorption capacity of aggregates was approximately one third higher than that of the fine earth samples according to optimized Freundlich adsorption coefficients. This was unexpected since it was assumed that the soil surface area available for sorption processes is greater or at least far more accessible if the unstructured fine earth is exposed to the phosphate solution. We conclude that if the inner pore space of soil aggregates is readily accessible and diffusion is not hindered, the overall retention capacity of intact aggregates might be higher than that of the disturbed soil because the intra-aggregate pore space can accommodate a certain fraction of phosphate in addition to the adsorbed amount at particle surfaces. The presented experimental approach allows for studying sorption processes in well-structured and fine earth in conditions that perform better compared to the natural situation. Additional testing of the method for different soil types is advisable.

**Keywords:** phosphorus; structured soil; sorption isotherm; soil aggregate; kinetic model; diffusion experiment

## 2.1 Introduction

The process of phosphate sorption onto soils is of significant relevance, because phosphorus (P) is an essential plant nutrient driving growth and causes environmental problems if released in higher concentrations to water resources (Barrow, 2015a; Van Der Salm et al., 2016; Xia et al., 2020). The sorption process of phosphate onto soil depends on physical and chemical soil characteristics including clay, organic matter and Al- and Fe-oxides content, soil moisture, pH, and moreover, on the redox conditions at which the sorption process takes place (Xiao et al., 2017; Ho and McKay, 1998; Del Bubba et al., 2003; Samadi and Gilkes, 1999; Singh and Gilkes, 1991). While a solid body of literature is available on how soil chemical properties and various soil constituents affect the sorption of phosphate, little is known as to what extent soil physical characteristics, in particular, soil structure, influence the sorption process (Akhtar et al., 2003).

Soil aggregates are formed in soil by the arrangement and organization of soil particles, and the tendency of individual soil units, including clay minerals and organic substances, to bind together (Lal and Shukla, 2004). The formation of soil peds results in an intra- and inter-aggregate pore space, with an according fractionation of flow pathways for water, gases, and solutes (Peth et al., 2008; Kausch et al., 2012). Soil aggregates differ from the fine earth with respect to density, and they are more tortuous because of the dominance of finer pores (Horn, 1990). The accessibility of the pore space of aggregates for solutes depends on the composition of the soil (clay content) and the pore size classes.

In the majority of batch sorption studies, the adsorbed amount of a compound is indirectly determined by calculating the difference of compound mass prior to and after thorough mixing of the compound solution and a soil sample, taking the soil-solution ratio into account (Prutton and Maron, 1953). In cases in which porous substrates are used as an adsorbent, the pore space may accommodate molecules in addition to the actual sorption process, in which a molecule is bound to the surface of soil particles via a variety of binding mechanisms such as Van-der-Waals forces, hydrogen bonding, ion-induced dipole forces, and ion-dipole forces. The release of adsorbed phosphorus from the interior of soil aggregates to the soil solution is a prerequisite to maintain the phosphorus flux to plant roots (Temminghoff et al., 2008). Some studies have addressed the importance of diffusion into intra-aggregate pores as the rate-limiting process in the mass transfer of reactive solutes for some ions between sorption site within porous adsorbents and bulk solutions (Trivedi and Axe, 2000; Lin and Wu, 2001; Kravchenko et al., 2015).

The sorption isotherm is a functional relationship quantifying the adsorbed amount as a function of the solution concentration in a dynamic equilibrium (Southam et al., 2004; Liu et al., 2008; Yang et al., 2019). It is intensively used to describe the behavior of P in a wide range of soils and environmental conditions (Van Der Zee et al., 1986). Sorption isotherms were obtained by agitating soil samples with solutions of different concentrations (Barrow, 1978; Streck et al., 1995). Shaking is continued until it is believed that an equilibrium between molecules in the solution and attached to solid surfaces is attained (e.g., 24 h) (Köhne et al., 2002). Empirical as well as more thermo-dynamic-based equations, including Freundlich and Langmuir models, are commonly used to describe the sorption behavior of phosphate in soils (Zhou and Li, 2001; Naeem et al., 2013; Abdelwaheb et al., 2019).

The result of a phosphate sorption study is a function of the chosen experimental duration (to obtain equilibrium between dissolved and adsorbed amount), the temperature, the solution:soil ratio, the mixing method, as well as the concentration of initial phosphate solution, among others (Barrow, 1978). All of the mentioned experimental conditions and their effect on phosphate sorption have been thoroughly investigated (Barrow, 2015b; Barrow and Debnath, 2014); soil structure effects, however, remain unconsidered. We can currently refer only to a very few phosphate sorption isotherms, which were obtained from structured soil (Barrow, 2015b; Linquist et al., 1997).

The specific objectives of this study were to (i) establish and examine an applicable method allowing us to quantify sorption effects as caused by soil structure, (ii) characterize the effect of soil structure on phosphate sorption and the effect of initial phosphate concentration on the kinetics of phosphate sorption, and (iii) derive equilibrium sorption isotherms for phosphate onto soil aggregates.

## 2.2 Materials and methods

### *2.2.1 Study site and soil samples*

Soil samples were obtained from an agricultural field site, which is located near the city of Rostock, in northeastern Germany. The soil type was classified as a Endostagnic Luvisol, according to the World Reference Base for Soil Resources (WRB) (IUSS Working Group WRB, 2015). The climate of the study site ranges from Atlantic to continental, with an average annual precipitation of 660 mm and an annual mean temperature of 9.1 °C. The study site was under intensive agricultural use, with sugar beet (*Beta vulgaris* L.) as the dominant crop.

All experiments were conducted with soil samples from two horizons of the experimental site. Soil aggregates were obtained by letting a soil block fall onto the ground from a 1 m height. Aggregates were separated by sizes of 4–6 mm using a standardized sieve. Fine earth in this study refers to disturbed soil samples which were passed through a 2 mm sieve. Selected physical properties of the soil are listed in Table 2.1 and some chemical characteristics of the studied site are summarized in Supplementary Table S1. The initial moisture content of fine earth and aggregates samples was 2.62 ± 0.04 and 5.07 ± 0.6 (wt%) respectively.

**Table 2. 1** Soil physical properties of the soil at the study site

| **Soil Horizon** | **Depth** | **Clay (≤2 µm)** | **Silt (2–63 µm)** | **Sand (63–2000 µm)** | **Bulk Density** | **Organic Matter Content** |
|---|---|---|---|---|---|---|
| | **cm** | | **%** | | **g cm$^{-3}$** | **%** |
| Topsoil | 0–40 | 7.6 | 48.5 | 43.6 | 1.44 ± 0.32 | 3.22 ± 0.04 |
| Subsoil | 40–70 | 15.7 | 35.2 | 48.8 | 1.77 ± 0.02 | 1.88 ± 0.03 |

### *2.2.2 Classical batch experiment (Pre-Test)*

The classical batch experiment for testing phosphate sorption onto soil samples was performed by the agitation of 4 g of air-dried fine earth with 100 mL of phosphate solution of various concentrations (1, 5, 10, 20, 50, and 100 mg L$^{-1}$) using plastic flasks (soil:solution ratio = 1:25). The batch containers were shaken using a horizontal shaker with a speed of 200 rpm to homogenize the samples and to promote the reaction within 24 h at a constant temperature of 22 ± 1°C and a natural pH (6.68 ± 0.12). Twenty-four hours has been preferred for sorption experiments providing the 48 h pre-test experiments for fine earth and soil aggregates (Supplementary Figure S1). After shaking the samples, the suspension was filtered through a 0.45 µm nylon mesh. The solution concentration of residual phosphate at equilibrium time was determined by the photometric method (Murphy and Riley, 1962) and a spectrophotometer (Specord 40) at 850 nm. All sorption experiments were carried out with three repetitions, and all calculations are based on the average ± standard deviation.

The effect of contact time onto P sorption was investigated by sampling the soil-solution mixture at appropriate time intervals ranging from 30 s to 24 h and analyzing the solution as described above.

### *2.2.3 Diffusion experiments*

In comparison to the classical batch experiment, we named the approach tested in this study ‘diffusion experiment’ as it is believed that diffusion is one of the controlling factors contributing to the overall P retention. The diffusion experiments to quantify phosphate sorption onto fine earth and aggregates were carried out as a function of time with six initial phosphate concentrations (1, 5, 10, 20, 50, and 100 mg $L^{-1}$) and a soil:solution ratio of 1:25 using $KH_2PO_4$. A metal mesh was placed into a container in such a way that the soil samples were just in contact with the phosphate solution. A magnetic stirrer adjusted at a low speed of 100 rpm below the mesh ensured a slow motion of the P solution, preventing the establishment of concentration gradients within the solution (Figure 2.1). Aliquots of the solution (20 mL) were withdrawn at various contact times ranging from 30 s to 24 h. The samples were passed through a 0.45 µm nylon mesh and the phosphate concentration was determined photometrically (Murphy and Riley, 1962). The soil aggregates were individually wrapped using an inert nylon fabric to support cohesion and soil structure. The wrapped soil aggregates were capillary saturated with distilled water for 12 h prior to the onset of the diffusion experiments (Fig. 2.1) (Köhne et al., 2002). In the case of fine earth, the sample was placed directly on the metal mesh covered with an inert fabric and lowered into the phosphate solution. The soil:solution ratio was equal for both fine earth and aggregates. Repeated sampling of the solution slightly modified the soil:solution ratio, which was explicitly accounted for in all calculations (Köhne et al., 2002).

**Figure 2. 1** Soil aggregates wrapped in an inert nylon mesh on a sieve during the diffusion experiment

### 2.2.4 *Evaluation of experimental data*

Selected mathematical models, including pseudo-first order (Lagergren, 1898), pseudo-second order (Ho and McKey, 1998), and pseudo-nth order equations (Özer, 2007), were used to simulate the sorption kinetics of phosphate onto fine earth and aggregates:

$$q_t = q_e(1 - e^{-k_1 t}), \text{ pseudo-first order} \tag{2.1}$$

$$q_t = \frac{{q_e}^2 k_2 t}{1 + k_2 q_e t}, \text{ pseudo-second order} \tag{2.2}$$

$$q_t = q_e - [{q_e}^{1-n} - (1-n)k_n t]^{1/(1-n)}, \text{ pseudo-nth order} \tag{2.3}$$

where $q_t$ is the amount of adsorbed phosphate at time t, $q_e$ is the amount of adsorbed phosphate at equilibrium time (both in mg kg$^{-1}$ soil), and $k_1$, $k_2$, and $k_n$ are the pseudo-first-order rate constant of sorption (h$^{-1}$), the pseudo-second-order rate constant of sorption (kg mg$^{-1}$ h$^{-1}$), and the pseudo-nth order rate constant of sorption (kg$_n$ mg$^{-n}$ h$^{-1}$), respectively.

The sorption isotherm can represent the distribution of phosphate between the solid and the liquid phase via linear or empirical exponential functions (Barrow, 1978). Often, the plot of the logarithmic adsorbed amount versus the logarithmic equilibrium concentration follows a linear function in the case of phosphate. In this research, the two widely used isotherms, Freundlich and Langmuir equations in the nonlinear form, were applied to describe the data owing to their practical model parameters, simplicity, and interpretability (Tran and You, 2017; Hubbe et al., 2019).

$$\mathrm{q_e} = \frac{\mathrm{K_L Q C_e}}{1+\mathrm{K_L C_e}}, \text{ Langmuir} \tag{2.4}$$

$$\mathrm{q_e} = \mathrm{K_F {C_e}^n}, \text{ Freundlich} \tag{2.5}$$

where $\mathrm{q_e}$ is the amount of adsorbed phosphate at equilibrium (mg kg$^{-1}$), $\mathrm{C_e}$ represents the equilibrium concentration of phosphate in the solution (mg L$^{-1}$), Q is the Langmuir parameter, which is associated with the sorption density (mg kg$^{-1}$), and $\mathrm{K_L}$ and $\mathrm{K_F}$ are the Langmuir and the Freundlich coefficients, respectively. $\mathrm{K_L}$ expresses the maximum sorption capacity when n approaches infinity (L mg$^{-1}$) and $\mathrm{K_F}$ expresses the total sorption capacity (L kg$^{-1}$), while n is the Freundlich constant parameter representing the sorption intensity (dimensionless) (Goldberg, 2005; Freundlich and Heller, 1939). The Freundlich isotherm is an empirical model assuming that the sorption takes place on heterogeneous surfaces being predominantly chemisorption, while the Langmuir sorption considers the sorption onto homogeneous layers (Freundlich and Heller, 1939; Langmuir, 1918).

Moreover, the Langmuir equation is used to obtain the separation factor, $\mathrm{R_L}$:

$$\mathrm{R_L} = \frac{1}{1 + \mathrm{K_L C_0}} \tag{2.6}$$

where $\mathrm{C_0}$ (mg L$^{-1}$) is the initial concentration of phosphate in contact with the soil. $\mathrm{R_L}$ values are representative for the shape of the isotherm, as $0 < \mathrm{R_L} < 1$ imply favorable sorption, and $\mathrm{R_L} > 1$,

$\mathrm{R_L} = 0$ or 1 correspond to unfavorable, irreversible, and linear sorption (Alemayehu et al., 2011).

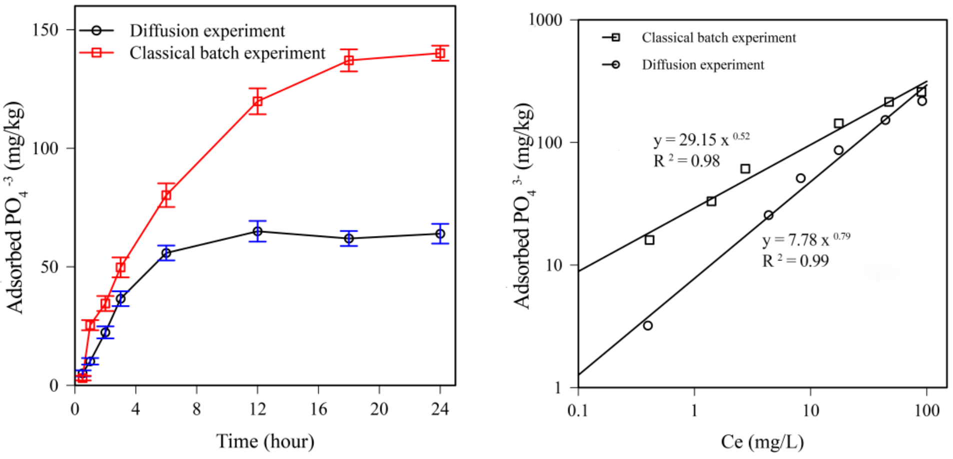
The data validity of phosphorus sorption onto soil aggregates was checked exemplarily through the determination of the phosphorus mass balance. The total phosphorus content of soil samples after conducting the experiments was determined using microwave-assisted digestion. Subsamples of 0.5 g of dry soil (<2 mm) were shaken with 100 mL $HNO_3$, and HCl solutions for 30 min and samples were centrifuged for 10 min and filtered (Whatman no. 42 filter). The concentrations of phosphorus were ascertained with inductively coupled plasma-optical emission spectroscopy (ICP-OES) at wavelengths of 215 nm (JY 238, Jobin-Yvon, France). The phosphorus amount, as determined from the soil samples, was compared to the calculated adsorbed amount using aqueous solution concentrations from the sorption experiments. In all test cases, the adsorbed phosphorus amount, as determined by soil extraction, was below the calculated amount but was always above 91% of the calculated value. This is taken as a proof, despite minor discrepancies, that the developed approach for testing phosphorus sorption onto soil aggregates is operational. MS-Excel version 2007 was employed for the fitting of kinetic and isotherm equation parameters. A T-test has been used for the comparison of phosphorus adsorption between fine soil and soil aggregates and between topsoil and subsoil at a significance level of 95%. An F-test was performed to examine the differences of different variables as presented in Tables and Figures. All statistical analyses were performed using SPSS Statistics 22.0 software (SPSS Inc. Chicago, IL, USA).

## 2.3 Results and discussion

### *2.3.1 Pre-test with fine earth*

At first, we wanted to test how the thorough shaking of a sample, as it is performed in the classical slurry batch approach, impacts the sorption process in comparison to an equilibration by diffusion. Fine earth was taken for a classical batch as well as for a diffusion experiment, and the sorption dynamic was studied over a time period of 24 h. The differences between the moisture contents of fine earth and soil aggregates was considered throughout the experiments and the results of phosphate sorption have been adjusted accordingly. The adsorbed P amount similarly increased for both set-ups for the first 6 h, although sorption of phosphate was slightly stronger if the samples were shaken (Figure 2.2a). Interestingly, the increase in P sorption in the classical batch experiment continued over the entire 24 h period by around 140 mg $kg^{-1}$, while the adsorbed amount remained constant in the diffusion experiment after 6 h, at just around 64 mg $kg^{-1}$. Differences between approaches varied among the investigated concentration range after 24 h equilibration time (Figure 2.2b). At higher solution concentrations, discrepancies diminish, which could be explained by higher diffusional gradients at higher solution concentrations.

It is likely that the shaker-facilitated energy input enhances sorption in general. The reason behind this is probably three-fold. The continuous shaking of the soil might rearrange soil particles, especially breaking micro-aggregates that have passed the 2 mm sieve intact during soil sample preparation. As a result, additional surfaces became available for sorption. In addition, constant shaking provides unlimited transport of phosphate anions in a well-mixed system to potential sorption sites, while the availability of anions might be limited in the diffusion set-up. As an additional factor, the shaking process provides an energy input into the system, which might increase the sorption capacity of phosphorus onto soil.



**(a)** **(b)**

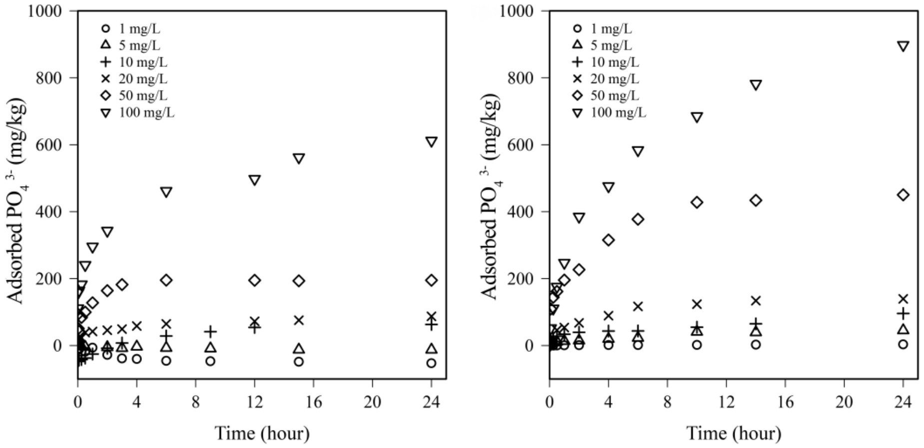
**Figure 2. 2** Impact of experimental conditions on adsorbed phosphorous (P) amount and P sorption dynamic. (**a**) Temporal development of adsorbed P amount in classical batch and diffusion experiment, (**b**) sorption isotherm (Freundlich) from the fine earth obtained from classical batch experiment and diffusion method (Ce; equilibrium concentration; $PO_4^{3-}$; phosphate; topsoil)

The observed differences in adsorbed P amount between approaches questions the representativeness of the classical batch sorption experiments (Linquist et al., 1997; Van Grinsven and Van Riemsdijk, 1992). Doubtlessly, the intensive mixing of soil and solution in the shaking experiments gives a sorption potential rather than a depiction of what would happen in the field (Van Grinsven and Van Riemsdijk, 1992; Pačes, 1983; Velbel, 1987). It has to be additionally considered that experimental conditions hardly ever resemble natural conditions concerning temperature and ionic strength (Pačes, 1983). Depending on the purpose of the investigation, it has to be carefully weighed as to which approach is most suitable. The diffusion experiment presented here might be a reasonable alternative for both bulk and aggregated soil.

### *2.3.2 Sorption kinetic and effect of initial concentration*

All soil aggregates remained intact throughout the experiment. For both fine earth and aggregates, a comparable temporal sorption behavior can be observed independently of the initial concentration (Figure 2.3). The sorption dynamic is characterized by a rapid first phase (1 to 4 h) in which at least 50% of the final amount is adsorbed. In the second phase of the process, the adsorbed amount increases slowly, approaching a maximum value in an asymptotic manner (Barrow, 2015a; Fink et al., 2016; Do Carmo Horta and Torrent, 2007). Twenty-four hours seems to be sufficient to reach an equilibrium, which is according to pre-test experiments and in agreement with earlier studies (Köhne et al., 2002; Yao et al., 2011). The visual inspection of the concentration course in Figure 2.2a reveals that the first rapid sorption is almost similar in both experimental approaches. At later stages, however, sorption onto soil aggregates increases at a slower pace as compared to the fine earth. Differences in the temporal dynamic might have been caused by a modified diffusion process and less accessible sorption sites in case of soil aggregates.

The results show that at low initial concentrations (1 and 5 mg $L^{-1}$), P sorption is negative, and P is released into the solution. Similar effects have been observed earlier in studies with agricultural soil (Barrow, 2015a; Barrow, 2015b). Phosphorus desorption is to be expected if fertilized soils are investigated (Barrow, 2015b; Barrow and Debnath, 2014). Interestingly, according to the F-test, the final adsorbed P amount was greater or at least equal in the aggregate case as compared to the fine earth samples, at least for the higher initial concentrations.

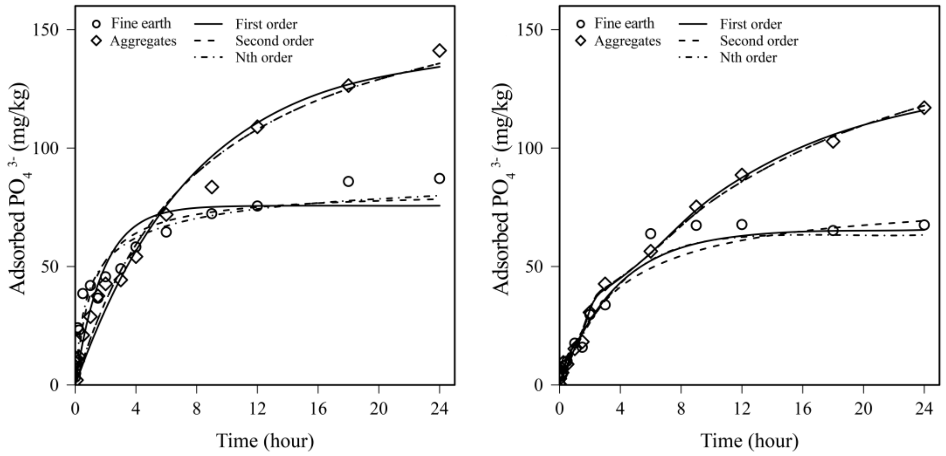


(**a**) (**b**)

**Figure 2. 3** The effect of initial phosphate concentration on the phosphate sorption dynamic employing the diffusion approach with (**a**) fine earth and (**b**) soil aggregates (topsoil)

### *2.3.3 Evaluation of sorption kinetics*

Different models were fitted to the experimental data in order to get more insight into the kinetics of the sorption process. The pseudo-first order, pseudo-second order, and the pseudo-nth order equations were tested and the parameter values, as obtained for the rate constants, are listed in Table 2.2.



(**a**) (**b**)

**Figure 2. 4** Phosphate sorption kinetic data and optimized model equations for aggregates and fine earth for the (**a**) topsoil and (**b**) subsoil (initial phosphate concentration of 20 mg L$^{-1}$)

All tested models describe the experimental data reasonably well (Figure 2.4). Expectedly, among all applied models, the pseudo-nth order equation performed better than the pseudo-first and pseudo-second order, especially in the case of soil aggregates with the highest $R^2$ values (0.984 to 0.996) and lowest root mean square errors (RMSE). It should be noticed that the pseudo-nth order model has one more parameter compared to the other tested models and a better optimization outcome is expected. Interestingly, the fitting criteria indicated that, in general, the optimization procedure was more successful for the datasets from the subsoil samples, independent from the aggregation status of the soil.

**Table 2. 2** Optimized parameter values of the various kinetic models

| **Model** | | **Fine Earth** | | **Aggregates** | |
|---|---|---|---|---|---|
| | | **Topsoil** | **Subsoil** | **Topsoil** | **Subsoil** |
| Pseudo-first-order kinetic | $q_e$ | 76 | 70 | 141 | 130 |
| | $k_1$ | 0.55 | 0.27 | 0.13 | 0.09 |
| | RMSE | 154 | 41 | 65 | 53 |
| | $R^2$ | 0.90 | 0.97 | 0.98 | 0.996 |
| Pseudo-second-order kinetic | $q_e$ | 82 | 84 | 183 | 188 |
| | $k_2$ | 0.01 | $3.41 \times 10^{-3}$ | $6.07 \times 10^{-4}$ | $3.70 \times 10^{-4}$ |
| | RMSE | 83 | 40 | 66 | 53 |
| | $R^2$ | 0.93 | 0.96 | 0.98 | 0.995 |
| Pseudo-nth-order kinetic | N | 3.59 | 0.84 | 3.14 | 0.92 |
| | $q_e$ | 97 | 63 | 238 | 126 |
| | $k_n$ | $8.72 \times 10^{-6}$ | 0.5 | $8.20 \times 10^{-7}$ | 0.137 |
| | RMSE | 55 | 37 | 66 | 53 |
| | $R^2$ | 0.95 | 0.98 | 0.984 | 0.996 |

$q_e$: The amount of adsorbed phosphate at equilibrium time (mg $kg^{-1}$); $k_1$: Pseudo-first-order rate constant of sorption ($h^{-1}$); $k_2$: Pseudo-second-order rate constant of sorption (kg $mg^{-1}$ $h^{-1}$); $k_n$: Pseudo-nth-order rate constant of sorption ($kg_n$ $mg^{-n}$ $h^{-1}$); RMSE: root mean square error

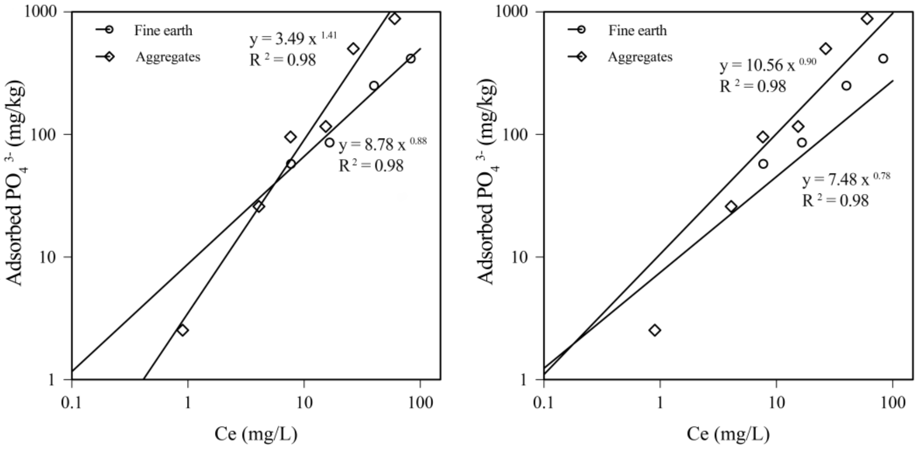
For topsoil, $q_e$ values, as derived from the pseudo-first order equation, were 76 mg $kg^{-1}$ and 141 mg $kg^{-1}$ for fine earth and soil aggregates, respectively. The elevated values of $q_e$, as found for aggregates, indicate that phosphate sorption was more pronounced for the structured soil samples than for fine earth, and statistical data from the T-test has confirmed these differences for topsoil and subsoil. The values of $k_1$, $k_2$, and $k_n$ parameters obtained from sorption kinetic models for fine earth were consistently higher, although total sorption was elevated for the soil aggregates. k values are interpretative for the rate of phosphate sorption: higher values indicate a steeper curve, especially at the beginning of the experiment. The more pronounced phosphate sorption of the soil aggregates that was observed is consistent with the proposed hypothesis that phosphate is not only adsorbed at accessible soil surfaces but is also retained by the intra-aggregate pore space. The assumption of a more pronounced phosphorus adsorption onto soil aggregates as compared to fine earth because of intra-aggregate retention is in agreement with Cui et al. (2019), who described that macro-aggregates showed a considerable capacity to retain phosphorus in restored wetlands.

### *2.3.4 Sorption isotherms*

Experimental sorption data along with the Freundlich and Langmuir model optimization are given in Figure 2.5. It was found that for both tested soil materials, sorption onto aggregates was more pronounced than onto fine earth. Both optimized sorption equilibrium models confirm this relation. The observed impact of soil structure onto sorption capacity can probably be attributed to the inner aggregate pore space, which might accommodate phosphate molecules independent of any reactions at soil particle surfaces (Lee at al., 1997; Wang et al., 2020). It is hypothesized that the diffusional transport of phosphate into soil aggregates lowers the phosphorous concentration in the solution, which then is counted as the adsorbed amount. It is also to be considered that the soil composition of the accessible and inner part of the aggregates might differ from the fine earth. The, in general, great heterogeneity of soil in physical, chemical, and mineralogical aspects in the solid-state, and also regarding soil solution, has to be considered in explaining the data (Van Der Zee et al., 1986; Santos et al., 2011). Although the sorption process is predominantly assumed to be a surface phenomenon (Köhne et al., 2002; Wang et al., 2001), structured soils may withdraw molecules from the advectively moving soil water. In experimental solute transport studies, the combined effect of surface sorption and diffusional retention into aggregate pore space results in a later breakthrough and probably stronger tailing of a breakthrough curve (Lee et al., 1997).

Phosphorus sorption was found to be higher for the subsoil, for fine earth and soil aggregates, which is in agreement with the clay content of the two tested materials (Table

2.1). It has been clearly demonstrated earlier that the adsorbed phosphate amount is firmly, positively related to the clay content because of the high surface area and according soil buffering capacity (Cox, 1994). Although the subsoil had a higher clay content, less phosphate was adsorbed. The reason behind this is not fully understood but might be related to the blockage of reactive clay surfaces for adsorption of phosphorus through coating of the specific sorption sites by soil organic matter (Linquist et al., 1997; Dubus et al., 2001).



(**a**) (**b**)

**Figure 2. 5** Sorption isotherms of phosphate for samples from (**a**) topsoil and (**b**) subsoil horizons.

The parameter values computed employing the isotherm models and the coefficients of determination are displayed in Table 2.3. Both models were capable of describing the experimental data, although the Freundlich approach gave more accurate results according to the greater values of $R^2$. As anticipated, the Freundlich sorption capacity, $K_F$, of soil aggregate (12.61 L $kg^{-1}$ for topsoil and 16.95 L $kg^{-1}$ for subsoil) is large compared with that of fine earth (7.66 for topsoil and 11.48 for subsoil).

In the case of the Langmuir model, the $K_L$ values ranged from 0.02 to 0.05 (Table 2.3), which implies favorable sorption conditions for phosphate on fine earth and aggregates. The sorption density, $Q_L$, ranged from 114.7 to 272.3 mg $kg^{-1}$ and was greater for aggregates than for the fine earth for both tested materials. The $R_L$ values fell between 0 and 1, which demonstrates the favorable sorption of phosphate onto fine earth and aggregates. Furthermore, the $R_L$ values show that the sorption of phosphate was more favorable for the lower than for the higher concentrations, $C_0 = 1$ mg $L^{-1}$: $R_L = 0.97$ (fine earth, topsoil), 0.98 (fine earth, subsoil), 0.95 (aggregates, topsoil), 0.98 (aggregates, subsoil), and $C_0 = 100$ mg $L^{-1}$: $R_L = 0.25$ (fine earth, topsoil), 0.33 (fine earth, subsoil), 0.17 (aggregates, topsoil), 0.25 (aggregates, subsoil), which is due to the decrease of surface affinity at increasing phosphorus concentrations. This is a well-known phenomenon, generally attributed to the saturation of high-affinity binding sites and the increasing of the electrostatic barriers as negatively charged phosphate binds to the surfaces of soil (Celi et al., 1999).

**Table 2. 3** Sorption Freundlich and Langmuir isotherm data

| | | Freundlich | | | | Langmuir | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $K_F$ | $n_F$ | RMSE | $R^2$ | $K_L$ | $Q_L$ | $R_L$ | RMSE | $R^2$ |
| Fine earth | Topsoil | 7.66 | 0.80 | 246.7 | 0.976 | 0.03 | 161.8 | 0.25–0.97 | 14.07 | 0.965 |
| | Subsoil | 11.48 | 0.56 | 139.2 | 0.989 | 0.02 | 114.7 | 0.33–0.98 | 10.48 | 0.957 |
| Aggregates | Topsoil | 12.61 | 0.94 | 505.9 | 0.966 | 0.05 | 272.3 | 0.17–0.95 | 20.64 | 0.960 |
| | Subsoil | 16.95 | 0.85 | 343.2 | 0.997 | 0.03 | 190.9 | 0.25–0.98 | 16.68 | 0.977 |

## 2.4 Conclusions

In this study, the phosphate sorption onto fine earth and aggregates was investigated to clarify the importance of soil structure on the process. The results showed that the sorption onto soil aggregates was elevated as compared to unstructured fine earth, even if the same experimental time period was observed. Compared to fine earth, the more pronounced sorption of phosphate onto aggregates demonstrates the importance of soil structure for soil chemical processes in general. We assume that the inner pore space of soil aggregates is an accommodation space for phosphate molecules besides the adsorbed amount. In such a situation, the sorption capacity of intact aggregates might be higher than that of the disturbed soil. The nth-pseudo sorption rate equation provided a superior fit to data, explaining the idea of the heterogeneity of soil surfaces for phosphate sorption. Moreover, the sorption of phosphate onto fine earth and aggregates was found to be strongly dominated by the initial phosphate concentration. The present study introduced a new approach to investigate sorption phenomena in structured soil, which is believed to more closely compare to natural circumstances as they might occur in the field. Many open questions remain, however. The results highlighted the importance of soil structure onto phosphate sorption for a soil with low organic and clay content. A thorough testing of the new approach shall reveal its applicability to a wide range of soils and chemical compounds. Also, aggregate size and according diffusion path length should be more closely considered in future studies, as some studies have highlighted that the distribution and release of phosphorus in restored wetlands are associated with the size of soil aggregates (Wang et al., 2020). Soil studies at the molecular level and phosphorus chemisorption on a number of soil minerals can improve insights into the phosphorus adsorption mechanism in soil for the proposed experiment.

**Supplementary Materials:** The following materials are available online at www.mdpi.com/2571-8789/4/2/21/s1: Figure S1: Adsorbed phosphate amount as a function of experimental duration for fine earth and soil aggregates, Table S1: Some chemical characteristics of the experimental field.

# 3 Effects of soil aggregate size and stability on phosphorus sorption

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## Abstract

Soil structure is one of the fundamental features affecting the productiveness of soils and the environmental side-effects of agricultural lands. A new experimental framework via a diffusion experiment that permits an accurate determination of adsorbed phosphate onto structured soil was applied to clarify the importance of soil structure on the sorption of phosphate. This study aims to investigate the effect of the soil structure characteristics on phosphorus (P) sorption. We investigated two main physical properties including soil aggregate size and aggregate stability to examine their effects onto structured soil through intra-aggregates. Different soil aggregate size fractions were wrapped in an inert fabric for diffusion experiments. Diffusion approach was used to illustrate the impact of soil aggregate size on the sorption of phosphate onto structured soil. Moreover, a wet-sieving method was applied for assessing the soil aggregate stability. The decrease of the phosphate solution concentration over time was recorded at fixed time intervals and adsorbed amounts were quantified at the time of sampling. Here, the aggregate size had a comprehensive affinity with the adsorbed phosphate. The bigger the size of soil aggregates, the much higher concentration of adsorbed phosphate at the same equilibrium time. The higher contents of water-stable aggregate in Ah soil were correlated with the amount of intra-aggregate in structured soil. This is in line with the amounts of adsorbed phosphate onto soil that was consistent with the greater presence of intra-aggregate in Ah soil. The soil aggregate size thus induced changes in the sorption of phosphorus onto structured soil that could be beneficial for sustainable agriculture and environmental protection. The results indicate enhancing soil larger aggregate formation increase P sorption thereby alleviates soil phosphorus contribution to freshwater eutrophication.

**Keywords:** phosphorus; structured soil; soil aggregate size; soil aggregate; kinetic model; diffusion experiment, soil aggregate stability

## 3.1 Introduction

Precise estimation of P availability in soils is becoming ever more critical concerning the sustainability perspectives of agriculture and protection of the environment. Prediction of P requirements remains inaccurate, while the influences of soil chemical characteristics on P release from soil and uptakes by plants are thoroughly investigated (Chen et al., 1997). For instance, the Fox and Kamprath recommended more than 500 kg P ha$^{-1}$ for crop production (Fox and Kamprath, 1970); however, Cassman et al. (1993) recommended 100 kg P ha$^{-1}$ for soybean production. A better understanding of the processes adjusting P adsorption onto soil can give an alternative solution to such an imprecision recommendation, especially for soils of diverse structure. There is comprehensive literature on how soil chemical and physical properties including clay, organic matter, soil moisture, Al- and Fe-oxides content, pH, and moreover, the redox conditions affect the sorption of P onto unstructured soil (Xiao et al., 2017; Ho et al., 1998; Del Bubba et al., 2003; Samadi and Gilkes, 1999; Singh and Gilkes, 1991), but the P sorption onto structured soil are far from being comprehensively understood.

Soil aggregates are considered as the fundamental unit of soil structure and are formed in soil through the binding and arrangement of micro-aggregates and soil particles with decomposed fungal hyphae, organic materials and roots (Lal and Shukla, 2004; Tisdall and Oades, 1982; Wei et al., 2014). Varied aggregate size fractions have disparate effects on how soil aggregates maintain and provides soil nutrient for plant growth (Chen et al., 1994). Numerous studies have confirmed the close association between the aggregate size fractions and the concentration of phosphorus by acting on the sorption and desorption of soil P (Linquist et al., 1997; Wang et al., 2001; Fonte et al., 014; Nesper et al., 2015). Moreover, studies depicted that soil aggregate size had a strong influence on bioavailability and P sorption (Wiersum, 1962; Gunary et al., 1964; Cornforth, 1968; Misra et al., 1988; Linquist et al., 1997). The more pronounced phosphate sorption onto the soil aggregates compared to that of unstructured bulk soil, representing that the intra-aggregate pore space is readily accessible for P and provides more sorption capacity in addition to the accessible surface area (Saki et al., 2020). Concerning the inner pore space of soil aggregates, one might expect that P sorption onto larger aggregates may be higher if P diffuses profoundly into the aggregates (Wang et al., 2001).

Soil's physical quality is represented by the ability of a soil to contribute water, aeration and strength to both plants and the ecosystem (Saffari et al., 2020). One of the most important soil biological indices which illustrate a soil's physical quality is soil aggregate stability (Reynolds et al., 2009; Shrestha et al., 2007; Zhu et al., 2017; Wang et al., 2019). Aggregate stability serves as a sustainable indicator of soil structural stability for clarifying many environmental issues and soil quality (Six et al., 2002). In agroecosystems, some studies have pointed out that the distribution of soil aggregates, soil aggregate stability, and aggregate associated with soil organic matter under various forms of land management, including fertilization, no-tillage, converting natural ecosystem into agriculture land (Six et al., 1999; Six et al., 1998; Garland et al., 2017; Jiang et al., 2017; Bhattacharyya et al., 2010). Although soil aggregate stability and soil organic matter have predominantly related characteristics (Villasica et al., 2018), their interaction with the sorption of phosphate onto structured soil remains unclear.

The most widely used approaches for the determination of P are based on the slurry batch experiment in bulk soil (Barrow, 1978; Streck et al., 1995; Álvarez-Esmorísa et al., 2020), in which soil samples are thoroughly mixed with various concentrations of P solution. The diffusion experiment was used in our investigations because it represents that the pore space in the soil aggregates provide more spaces for P sorption beyond the actual sorption process of bounding a molecule to the surface of soil particles. There is a wide range of binding mechanisms of P sorption, such as hydrogen bonding, Van-der-Waals forces, ion-dipole, and ion-induced dipole forces. The above-mentioned experimental approach allows the study of sorption processes in bulk soil and well-structured soil in conditions that perform better compared to the natural situation (Saki et al., 2020).

The objectives of this study were: (i) to investigate the effect of aggregate size on P sorption through diffusion experiment for different soils; (ii) to examine the hypothesis that increased aggregation increases P sorption through diffusion experiment; and (iii) to explore the relationship between soil aggregate stability and P sorption onto soil aggregates.

## 3.2 Materials and methods

### *3.2.1 Study site and soil samples*

The agricultural field site of Dommertsorf is situated in Northern Germany near the city of Rostock. The soil type is characterized as Stagnosol, according to the Food and Agriculture Organization of the United Nations (FAO). The study site's climate was characterized as ranging from Atlantic to continental. An average annual temperature of 9.1 ºC and average annual precipitation of 660 mm were recorded for the study site. The study site was characterized by intensive sugar beet (*Beta vulgaris* L.) production.

The soil samples were taken at two different soil depths as soil blocks, and soil aggregates were obtained through letting a soil block fall onto the ground from a height of 1 m. Obtained soil aggregates were separated using standardized sieves, and three varied sized of aggregates (4-6 mm, 1 cm and 2 cm) were investigated during this research. The selected physical characteristics of the soil aggregates are presented in Table 3.1. The initial moisture content of soil aggregates was determined as 5.07 ± 0.6 (wt%).

**Table 3. 1** Selected physical characteristics of the soil at the research site

| **Soil horizon** | **Depth** | **Clay (≤2 µm)** | **Silt (2-63 µm)** | **Sand (63-2000 µm)** | **Bulk density** | **Organic matter content** |
|---|---|---|---|---|---|---|
| | cm | | % | | g cm$^{-3}$ | % |
| Ah | 0-40 | 7.6 | 48.5 | 43.6 | 1.44 ± 0.32 | 3.22 ± 0.04 |
| AhSw | 40-70 | 15.7 | 35.2 | 48.8 | 1.77 ± 0.02 | 1.88 ± 0.03 |

### *3.2.2. Diffusion experiments*

The diffusion experiments were used in this study to illustrate that diffusion is one of the controlling factors which contributes to the overall P retention. The diffusion experiment to quantify phosphate sorption onto different classes of soil aggregates was carried out as a function of time, with an initial phosphate concentration of 20 mg L$^{-1}$ and a soil:solution ratio of 1:25 using $KH_2PO_4$. Diffusion experiments were conducted at a room temperature of 22±1°C under constant and regular agitation using a magnetic stirrer at a low speed of 100 rpm to prevent the formation of concentration gradients within the solution. The soil aggregates were just in contact with the phosphate solution by placing a metal mesh into a container. Cohesion and soil structure of the soil aggregates were preserved during the experiments by wrapping each aggregate individually with an inert nylon fabric. Prior to the onset of the diffusion experiments, the wrapped soil aggregates were capillary saturated with distilled water for 12 hours (Figure 3.1) (Southam et al., 2004). Aliquots of the solution were withdrawn at various contact times ranging from 5 min to 24 h, and after passing through nylon mesh 0.45 µm, the phosphate concentration was determined according to the photometric method (molybdenum blue) in a filtered solution (Barrow and Debnath, 2014).

**Figure 3. 1** Soil aggregates wrapped up in an inert nylon mesh placed on a sieve throughout the diffusion experiment

### *3.2.3 Soil aggregate stability test*

The aggregate stability of soil samples were investigated for both soil horizons using a wet-sieving method (DIN 19683- 16, 2009). Prior to the experiment, the soil samples were dried, and 2.00–3.15 mm soil aggregates were separated through sieving. Approximately 25 g of the mentioned fraction were situated on a round-hole sieve (mesh size: 1.0 mm) and immersed gently into the water for 2 min with 72 vertical lifts of 8 cm high. The residual of soil aggregates on the sieve (AS) was dried at 105 ºC and weighted. We also characterized the proportion of sand (1.0–2.0 mm); the remaining dried aggregates were re-watered and crushed. The sand (S) was dried at 105 ºC and weighted. The water-stable aggregates (%) were the percent of the difference between AS and S fraction.

### *3.2.4 Evaluation of experimental data*

The mass balance equation has been applied in this research to estimate the amount of phosphate adsorbed at time t.

$$q_t = (C_0 - C_t) * \frac{V}{M}, \tag{3.1}$$

where $C_0$ is the initial concentration of phosphate in contact with soil aggregates, $C_t$ is the mass concentration of phosphate in the liquid phase at time t and $q_t$ is the amount of adsorbed phosphate per unit mass of soil aggregates (mg kg$^{-1}$), and V the volume of solution (L) and M is dry mass of the soil (kg).

Several mathematical models, including pseudo-first-order and pseudo-second-order have been proposed to investigate the sorption kinetics of phosphate onto soil aggregates. The equations are expressed as:

$$q_t = q_e(1 - e^{-k_1 t}), \text{ pseudo-first order} \tag{3.2}$$

$$q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t}, \text{ pseudo-second order} \tag{3.3}$$

$$q_t = q_e - [q_e^{1-n} - (1-n)k_n t]^{1/(1-n)}, \text{pseudo} - \text{nth order} \tag{3.4}$$

where $q_t$ is the amount of adsorbed phosphate at time t (mg kg$^{-1}$), $q_e$ is the amount of adsorbed phosphate at equilibrium time (mg kg$^{-1}$), and $k_1$, $k_2$ and $k_n$ are the pseudo-first-order rate constant of adsorption (h$^{-1}$), the pseudo-second-order rate constant of adsorption (kg mg$^{-1}$ h$^{-1}$) and the pseudo-nth order rate constant of sorption (kg$_n$ mg$^{-n}$ h$^{-1}$), respectively.

MS-Excel version 2007 was applied for the fitting of kinetic and isotherm equation parameters. A T-test has been used for the comparison of P sorption between different aggregate soil classes for Ah and AhSw soil at a significance level of 95%. All statistical analyses were accomplished with the software SPSS Statistics 22.0 (SPSS Inc. Chicago, IL, USA).

## 3.3 Results and discussion

### *3.3.1 Sorption kinetics and effect of initial concentration*

Throughout the experiment, all soil aggregate classes preserved their structures. Both Ah and AhSw behaved similarly towards phosphate sorption with time, $q_t$ increasing rapidly in the first 4h, in which at least 50% of the final amount was adsorbed. In the second stage of the sorption procedure, the phosphate was slowly adsorbed as equilibrium was approached (Figure 3.2). Temporal sorption behaviour of the phosphate sorption was independent of the aggregate size for both Ah and AhSw soils (Barrow, 2015; Fink et al., 2016; Do Carmo Horta and Torrent, 2007). The shaking time was set to 24 hours, while the increase was not significant after 24 h for both soil horizons that agreed with the findings of earlier studies (Köhne et al., 2002; Yao et al., 2011). At the initial stage, the remarkable initial sorption rate could be attributed to the availability of a large number of sorption sites, including specific surface area and inner pore space of soil aggregates. At later stages, as the sites were progressively filled up, sorption rates diminished, and the kinetic became more related to the rate at which the phosphate was adsorbed onto soil aggregates. The phosphate sorption in the second phase was diffusion-controlled and time dependant. Among the soil aggregates studied, the amount of phosphate adsorbed onto soil aggregates was in accordance with soil aggregate size. The bigger the size of soil aggregates, the much higher amount of adsorbed phosphate at the same equilibrium time of 24 hours (Figure 3.2).

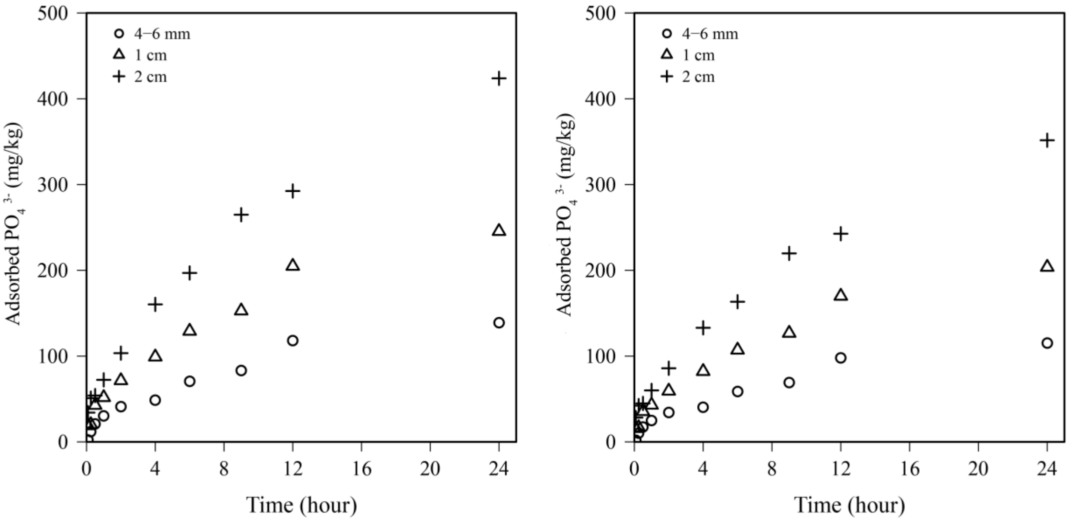

**Figure 3. 2** The effect of soil aggregate size on the phosphate sorption dynamic employing the diffusion approach for Ah (**a**) and AhSw soil (**b**)

### *3.3.2 Evaluation of sorption kinetics*

Different kinetic models were fitted to the experimental data to get further insight into the kinetics of the phosphate sorption process onto soil aggregates. The values of the parameter derived from the pseudo-first-order, pseudo-second-order, and the pseudo-nth order equations were analysed, and the coefficients of kinetic models acquired, are listed in Table 3.2.

The calculated equilibrium phosphate values were agreed with the experimental data for all soil aggregate classes (Figure 3.3). In general, excellent fits ($R^2 > 0.96$, Table 3.2) for all soil aggregate classes were observed implying that all kinetic models are applicable; however, among all applied models, the pseudo-nth order equation performed better than the pseudo-first and pseudo-second order concerning the higher $R^2$ values (0.98 to 0.99) and lowest root mean square errors (RMSE). It should be pointed out that among the kinetic models, the pseudo-nth order model has one more parameter compared with the other tested models and a better optimization performance is expected. Interestingly, the fitting criteria revealed that the optimization procedure was in agreement with the aggregation status of the soil, and the T-test for the comparison of P sorption between the two different soil aggregate classes.

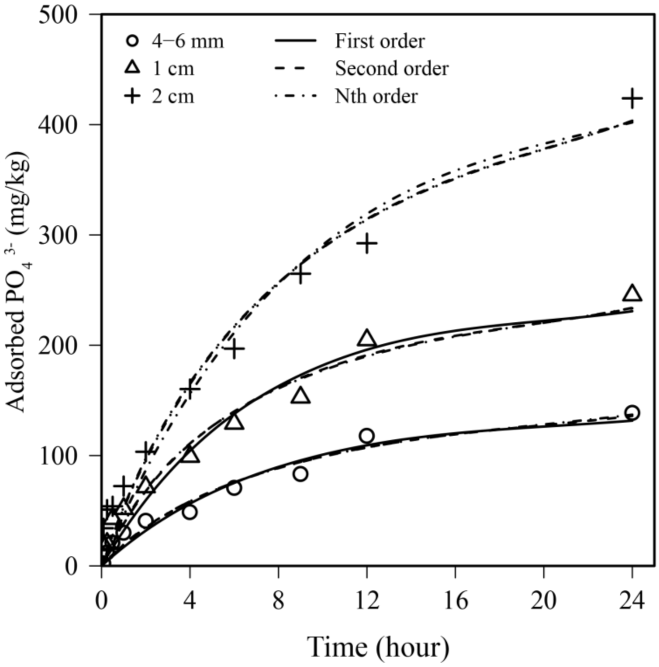

**Figure 3. 3** Phosphate sorption kinetic data and optimized model equations for different soil aggregate classes (Ah soil)

For Ah soil, $q_e$ values, as derived from the pseudo-first-order equation, were 139.40 mg kg$^{-1}$, 238.44 mg kg$^{-1}$ and 431.09 mg kg$^{-1}$ for 4-6 mm, 1-cm, and 2-cm soil aggregates, respectively. In the case of AhSw soil, $q_e$ values respectively acquired from the pseudo-first-order equation were 126.00 mg kg$^{-1}$, 197.84 mg kg$^{-1}$ and 357.67 mg kg$^{-1}$ for 4-6mm, 1-cm, and 2-cm soil aggregates. The elevated values of $q_e$, as found for 2-cm soil aggregates, demonstrate that phosphate sorption was more prominent for the 2-cm soil aggregates compared to other soil aggregate classes, and statistical data from the T-test has confirmed these differences for topsoil and subsoil. The amounts of $k_1$, $k_2$, and $k_n$ parameters achieved by sorption kinetic models for Ah were higher k parameters and total P sorption was following the soil aggregate sizes; 4-6 mm < 1-cm < 2-cm soil aggregates. The k values represent the rate of phosphate sorption: the higher amounts imply an abrupt curve. The more pronounced phosphate sorption of the soil aggregates associated with the soil aggregate sizes could be attributed to the quantity of phosphate adsorbed not only at surfaces of aggregates but also onto the intra-aggregate pore spaces. Higher P sorption onto soil aggregates due to the intra-aggregate is in agreement with Cui et al. (2019), who described that macro-aggregates showed a considerable capacity to retain P in restored wetlands. Likewise, it has been demonstrated that large soil macro-aggregates store dramatically higher amounts of C, N, and P than aggregates of smaller sizes (Wang et al., 2020).

**Table 3. 2** Optimized parameter values of the various kinetic models.

| Model | | Ah | | | AhSw | | |
|---|---|---|---|---|---|---|---|
| | | **4-6mm** | **1-cm** | **2-cm** | **4-6mm** | **1-cm** | **2-cm** |
| Pseudo-first-order kinetic | $q_e$ | 139.40 | 238.44 | 431.09 | 126.00 | 197.84 | 357.67 |
| | $k_1$ | 0.13 | 0.14 | 0.12 | 0.08 | 0.10 | 0.09 |
| | RMSE | 79.02 | 65.33 | 97.28 | 54.40 | 68.89 | 98.78 |
| | $R^2$ | 0.956 | 0.965 | 0.973 | 0.959 | 0.965 | 0.985 |
| Pseudo-second-order kinetic | $q_e$ | 184.92 | 300.35 | 565.06 | 173.43 | 249.20 | 468.78 |
| | $k_2$ | $6.25\times10^{-4}$ | $4.85\times10^{-4}$ | $1.84\times10^{-4}$ | $5.53\times10^{-4}$ | $4.84\times10^{-4}$ | $2.22\times10^{-4}$ |
| | RMSE | 66.32 | 82.55 | 80.32 | 45.65 | 75.67 | 98.65 |
| | $R^2$ | 0.969 | 0.973 | 0.983 | 0.974 | 0.972 | 0.992 |
| Pseudo-nth-order kinetic | N | 2.44 | 2.37 | 1.78 | 2.49 | 2.86 | 1.80 |
| | $q_e$ | 209.18 | 327.42 | 533.99 | 175.26 | 303.01 | 445.66 |
| | $k_n$ | $4.86\times10^{-5}$ | $4.88\times10^{-5}$ | $7.89\times10^{-4}$ | $4.77\times10^{-5}$ | $3.14\times10^{-6}$ | $7.89\times10^{-4}$ |
| | RMSE | 64.65 | 79.67 | 93.55 | 44.41 | 68.02 | 86.60 |
| | $R^2$ | 0.980 | 0.984 | 0.993 | 0.980 | 0.985 | 0.994 |

$q_e$: The amount of adsorbed phosphate at equilibrium time (mg $kg^{-1}$); $k_1$: Pseudo-first-order rate constant of sorption ($h^{-1}$); $k_2$: Pseudo-second-order rate constant of sorption (kg $mg^{-1}$ $h^{-1}$); $k_n$: Pseudo-nth-order rate constant of sorption ($kg_n$ $mg^{-n}$ $h^{-1}$); RMSE: root mean square error.

### *3.3.3 Evaluation of soil stability*

A significantly lower proportion of water-stable aggregates for AhSw compared to Ah soil (Figure 3.4) indicated the sensitivity of AhSw soil physical stresses. The proportions of water-stable aggregates increased significantly for Ah soil might be explained through the increased input of leaf residue and root litter in this horizon (Tisdall and Oades, 1982). Furthermore, the mycorrhizal networks of residual plants might have increased the aggregate stability by their hyphal (Baum et al., 2009). The higher contents of water-stable aggregate in Ah Soil were correlated with the amount of intra-aggregate in structured soil. Moreover, this is in line with the observation that the amounts of adsorbed phosphate onto soil are consistent with the more significant presence of intra-aggregate in Ah soil.

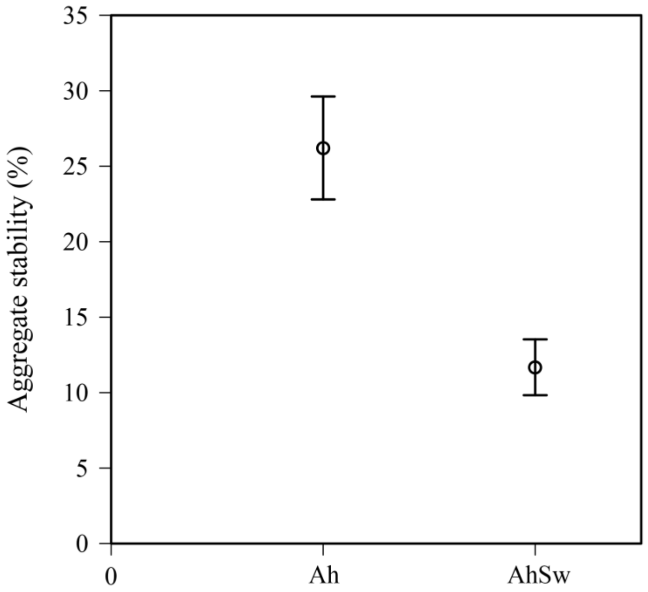

**Figure 3. 4** The proportion of water-stable soil aggregates at the Dummerstorf test site (different letters indicate significant differences between the treatments).

## 3.4 Conclusion

In the present study, we explored the interaction between soil structure and the adsorbed phosphate, with the aim to identify critical factors controlling the sorption of P onto structured soil. The phosphate sorption onto soil aggregates was elevated when the aggregate sizes of surface and subsurface horizons were increased. In general, the more pronounced sorption of phosphate onto larger sizes of aggregates demonstrates the importance of inner pore spaces as accommodation spaces for phosphate molecules, in addition to surface sorption onto structured soil. The aggregate stability was found to be related to the amount of phosphate sorption onto soil aggregates owing to the importance of the inner pore spaces beside the available surface for phosphate sorption. The nth-pseudo sorption rate equation provided a superior fit to data, explaining the idea of heterogeneity of soil surfaces for phosphate sorption. Many questions remain open, however. The results highlighted the importance of soil structure on phosphate sorption. Thorough testing of the diffusion approach should reveal its applicability to a wide range of soil aggregates.

# 4

# Halloysite nanotubes as adsorptive material for phosphate removal from aqueous solution

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## Abstract

In this study, we were aiming at testing halloysite nanotubes as an efficient adsorbent for the removal of phosphate from agricultural runoff. Sorption of phosphate onto powder and granular form of halloysite nanotubes has been examined by using the classical batch method and diffusion experiments at room temperature. Different forms of halloysite nanotubes were investigated to explore the effect of structure on the sorption of phosphate. The maximum sorption efficiency was obtained for powder halloysite nanotubes (79.5%) and granular form (94.7%). It is believed that the pore space of the granular halloysite nanotubes accommodates P in addition to physico-chemically bound phosphate at surfaces. The pseudo-first order and pseudo-second order model fitted well the experimental kinetic data for both powder and granular form of halloysite nanotubes. The fit of the Freundlich isotherm model was superior as compared with the Langmuir approach, implying that the halloysite nanotubes are heterogeneous because of multiple surface groups and different pore structures. The two forms of halloysite nanotube tested have the abundant potential for removal of phosphate from agriculture runoff. Additional investigations at the pilot scale are, however, required to draw definite conclusions.

**Keywords:** phosphate; halloysite nanotubes; sorption; isotherm; kinetic

## 4.1 Introduction

Excessive phosphate discharge from manure, sludge sources and chemical fertilizer applied to agricultural soils to runoff is the prominent source of water quality deterioration and nutrient enrichment. Heavily phosphate laden waters impose hazardous risk to the aquatic ecosystems (Tabbara, 2003; Tarkalson and Mikkelsen, 2004; Daverede et al., 2004; Hart et al., 2004). Although P concentrations in runoff from agricultural fields are, in general, below 1 mg $L^{-1}$, the elimination of P is considered as a crucial environmental sustainability concern to halt rapid degradation of water quality (Hart et al., 2004; Boesch et al., 2001; Márquez-Pacheco et al., 2013; Duranceau et al., 2016; Southam et al. 2004). A wide range of P concentrations has been investigated in P sorption studies (Tabbara, 2003; Márquez-Pacheco et al., 2013; Lewis et al., 2011). Chemical precipitation, coagulation, ion exchange, biological and physical treatments have been reported to remove P from aqueous solution before it discharges to agricultural runoff (Farmer, 2001; Valsamy-Jones, 2004; Shilton et al. 2006). Although chemical treatment involving Al, Fe and Ca is a traditional approach to remove phosphate from wastewater, these methods lead to huge sludge treatment and disposal problems (Zhang et al., 2014). Physical treatment containing electrodialysis, reverse osmosis and sorption seem to be highly promising as compared to chemical treatments to remove phosphate from aqueous solutions (Yao et al., 2011). However, except sorption, most of these methods involve high capital cost with recurring expenses, which are not suitable for many parts of the world (Gupta et al., 2009; Johansson Westholm 2006; Hylander et al., 2006; Cucarella et al., 2008). Several adsorbents have been investigated in various studies for the removal of phosphate from aqueous solution such as nanoparticle (Joussein et al., 2005; Prashantha Kumar et al., 2018), nanoscale zero-valent materials (Cataldo et al. 2018), activated red mud (Baraka et al., 2012), biogenetic calcium carbonate minerals (Liu et al., 2012), hybrid impregnated polymeric sorbent containing hydrated ferric oxide (You et al., 2016), industrial acidified laterite by-product (Glocheux et al., 2014), mixture of sand and dolomite (Prochaska and Zouboulis, 2006), slag and fly ash (Ragheb 2013), steel slags (Barca et al. 2012), silicate hybrid materials (Zhang et al., 2011), schwertmannite (which is ferric oxyhydroxide sulphate) (Eskandarpour et al., 2006), and volcanic rocks (Fetene, 2015). Nanoparticle clay mineral receives much more attention among the natural adsorbents duo to the high specific surface area, high sorption rates compared to other adsorbents, low toxicity, easy operation and to some extent cost-effectiveness. The potential of clay materials (Halloysite) to remove both anionic and cationic pollutants has been reported (Joussein et al., 2005; Mallikarjun and Mise, 2013; Dong et al., 2012; Cataldo et al., 2015). In recent studies, it was found that halloysite of different chemical and mineralogical composition can be used as an adsorbent and pollution remediation material (Matusik, 2016).

Halloysite is a widespread clay mineral in soils and weathered rocks where it appears in a variety of particle configuration and hydration states (Joussein et al., 2005; Yuan et al., 2015; Pasbakhsh et al., 2013). Though halloysite particles occur in a variety of morphologies, the dominant morphology is tubular form (Joussein et al., 2005). Halloysite nanotubes (HNTs) are formed as a result of strain caused by lattice mismatch between adjacent silicon dioxide and aluminum oxide layers. Chemically tubular halloysite can terminate from deformation of platy kaolinite ($Al_2SiO_5(OH)_4.2H_2O$), or it is derived from crystallization of Micas and Feldspar (Joussein et al., 2005; Furumi et al., 2009; Singh and Gilkes, 1992).

HNTs were selected as a compelling candidate for removal of phosphate, and it can be fabricated in a diversity of shapes and varied lattice planes (Prashantha Kumar et al., 2018). Despite the tubular shape of HNTs that contribute to sorption capacity, the interlayer is scarcely accessible for adsorption of ion and molecules. Therefore the application of the modified granular form of HNTs should be considered to improve the sorption of HNTs (Yuan et al., 2016). Granular HNTs might have a higher or lower sorption capacity as compared to the powder form. Theoretical calculations demonstrate that the aggregation of nanotubes lead to a specific reduction in surface area, but at the same time the pore volume is enlarged due to interstices trapped in the aggregated nanotubes (Zhang and Shao, 2009).

However, no information is available about the sorptive interactions between phosphate in the aqueous system and HNTs in the aggregated form. Therefore, the objectives of this study were: (1) to examine the characteristics of the HNTs (2) to investigate the phosphate sorption capacity of HNTs under a batch sorption setup, (3) to determine kinetics of the sorption reaction onto HNTs, and (4) to predict the sorption process by using isotherm models.

## 4.2 Materials and methods

### *4.2.1 Adsorbent characterizations and preparations*

All HNT material used in this study was provided by Durtec Company (Neubrandenburg, Germany). Granular HNT was prepared through compaction employing an EIRICH machine; water was used as reagent. The size of investigated HNT grains was between 4-6 mm. The HNTs were also characterized by scanning electron microscopy (SEM) to study morphology, size and elemental composition (Figure 4.1). The chemical composition and the specific surface area of the HNTs was determined by X-ray Fluorescence (XRF) spectrometry and $N_2$ gas BET analyses using a thermo Sorptomatic 1990 Analyzer (Thermo Fisher Scientific, Milan, Italy).

All chemicals used in this experiments for preparing phosphate solutions and for analyzing adsorbed phosphate, such as $KH_2PO_4$, $C_6H_8O_6$, $(NH_4)_6Mo_7O_{24}.4H_2O$, $(SbO)K(C_4H_4O_6).1/2H_2O$ , $H_2SO_4$ were analytical reagent grade chemicals from Carl Roth (Karlsruhe, Germany). The varying concentrations of phosphate solution for sorption experiments were prepared by diluting the stock solution (1000 mg $L^{-1}$ phosphate).

The determination of inorganic phosphate in aqueous solution is based on the reaction of the phosphate ions with the acidic molybdate reagent producing a phosphomolybdate complex. This complex is reduced to a favourably coloured blue compound (Molybdenum Blue Method) (Murphy and Riley, 1962).

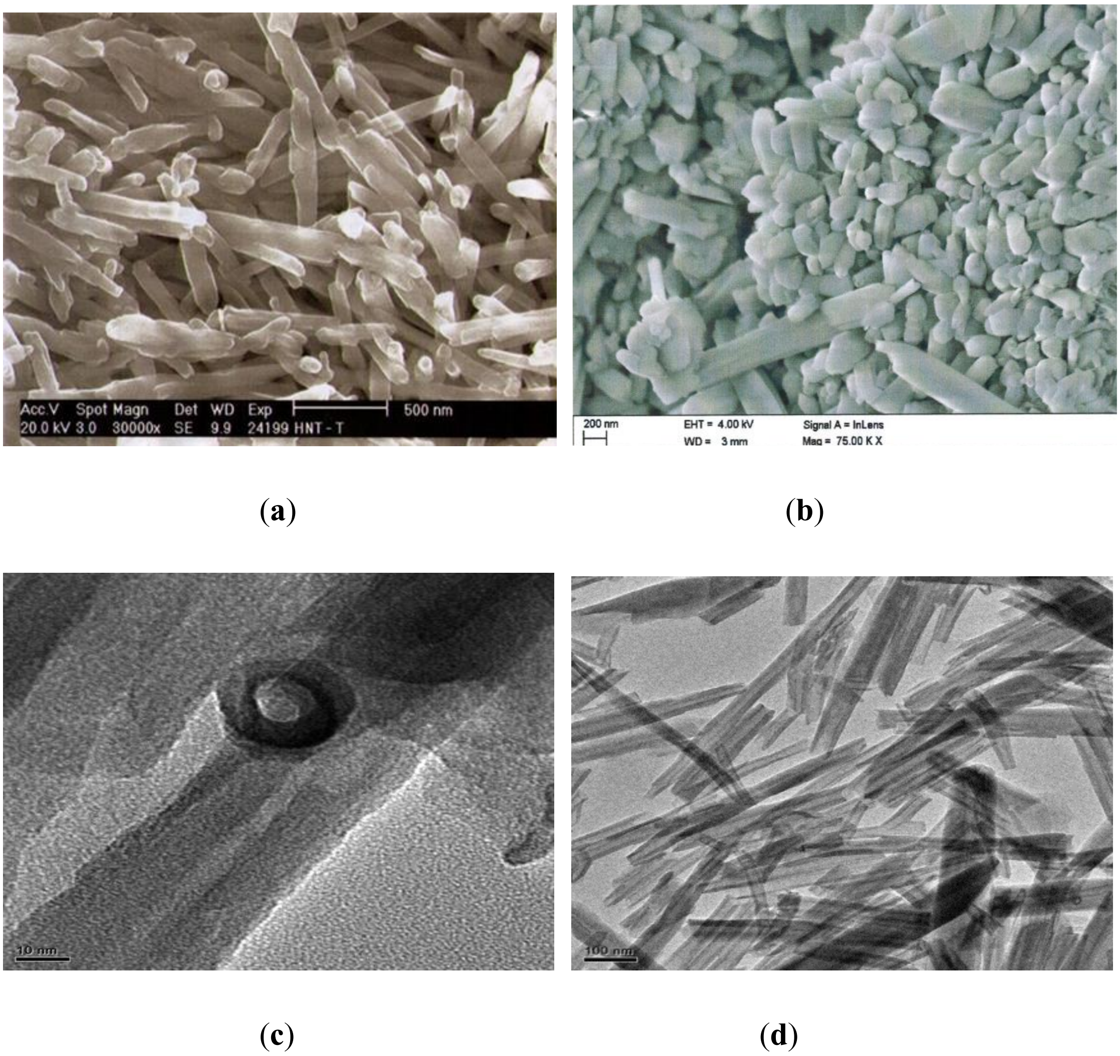

**Figure 4. 1** Scanning electron microscope images of halloysite nanotubes (**a**) HNT-MF4; (**b**) HNT-MF2; (**c**) and (**d**) HNT-MF7.

### *4.2.2 Classical batch experiments*

The classical batch experiment was conducted by agitating 4 g of each adsorbent with 100 mL of phosphate solution of known concentration ranging from 1 mg $L^{-1}$ to 100 mg $L^{-1}$ in plastic acid-washed polypropylene bottles (adsorbent:solution ratio, 1:25 g:mL). The batch containers were shaken using a horizontal shaker with the speed of 200 rpm to homogenize the samples and to accelerate the sorption at a temperature of 22 ± 1 °C and a natural pH (7.014 ± 0.09). At the end of equilibrium time (24 h), the mixtures were filtered through 0.45 µm nylon mesh and the concentration of residual phosphate at equilibrium time was determined by the photometric method (Molybdenum blue method) and a spectrophotometer (Specord 40, Analytik Jena AG, Jena, Germany) at 850 nm

(Murphy and Riley, 1962). Each experiment was conducted triplicate to check the repeatability of the experimental data, and data represent the mean value of the individual results. The variance in the data of repetition was consistently less than 5%. The amount of phosphate adsorbed at time t and the adsorbed amount $q_t$ were calculated from the mass balance equation:

$$q_t = (C_0 - C_t) \times \frac{V}{M} \tag{4.1}$$

where $C_0$ is the initial concentration of phosphate in contact with halloysite nanotubes, $C_t$ is the mass concentration of phosphate in the aqueous phase at time t and $q_t$ is the amount of adsorbed phosphate per unit mass of HNTs (mg kg$^{-1}$), M is dry mass of the adsorbent (kg), and V the volume of solution (L).

### *4.2.3 Kinetic experiments and data presentations*

Several models have been proposed to investigate the mechanism of sorption onto several HNTs (Joussein et al., 2005; Cataldo et al. 2018).

In order to evaluate the kinetic sorption parameters, mathematical models including pseudo-first order (Equation (4.2)) and pseudo-second order (Equation (4.3)) equations were used to analyze the experimental data of phosphate sorption onto HNTs. The equations are expressed as:

$$q_t = q_e\left(1 - e^{-k_1 t}\right), \tag{4.2}$$

$$q_t = \frac{{q_e}^2 k_2 t}{1 + k_2 t q_e} \tag{4.3}$$

where $q_t$ is the amount of adsorbed phosphate at time t, $q_e$ is the amount of adsorbed phosphate at equilibrium time (both in mg kg$^{-1}$), and $k_1$ and $k_2$ are the pseudo-first order rate constant of sorption (h$^{-1}$) and the pseudo-second order rate constant of sorption (kg mg$^{-1}$ h$^{-1}$) respectively.

To evaluate isotherm parameters, non-linear isotherm models were fitted to the equilibrium sorption data. In order to estimate sorption constants that indicate the sorption capacity and affinity of the adsorbents, the Langmuir (Equation (4.4)) and Freundlich (Equation (4.5)) sorption isotherms were applied to the data. The isotherm equations have been optimized using the root mean square errors (RMSE).

The equations are expressed as a non-linear function as follows:

$$q_e = \frac{K_L Q C_e}{1 + K_L C_e} \tag{4.4}$$

$$q_e = K_F {C_e}^n \tag{4.5}$$

where $q_e$ is the amount of adsorbed phosphate at equilibrium (mg $kg^{-1}$), $C_e$ correspond to the equilibrium concentration of phosphate in the solution (mg $L^{-1}$), Q represents the Langmuir parameter, which is associated with the sorption density (mg $kg^{-1}$) and $K_L$ represents the Langmuir coefficient of sorption energy (L $mg^{-1}$) and $K_F$ is the Freundlich coefficients expressing the sorption energy ($mg^{(1-n)}$ $L^n$ $kg^{-1}$), while n is the Freundlich constant representing the sorption intensity (dimensionless).

## 4.2 Results and discussions

### *4.2.3 Morphology and characterizations of HNTs*

Table 4.1 represents the structural characteristics of HNTs from Durtec GmbH, Neubrandenburg, Germany. As expected, the $Al_2O_3$ content was more magnificent than $Fe_2O_3$. Surface characterization depicts that the specific surface area of HNTs ranges from 25 to 35 $m^2$ $g^{-1}$, which is principally appealing for phosphate sorption. Chemical analysis of HNTs reveals that the amount of $Fe_2O_3$ is up to 23%. This observation suggests that Fe oxides like hematite and maghemite are associated and/or the partial substitution of $Fe^{3+}$ for $Al^{3+}$ in the octahedral sheet (Joussein et al., 2005; Yuan et al., 2016). However, further work is needed to better understand HNTs and their properties.

**Table 4. 1** Characteristic of the halloysite nanotubes (HNT) powder materials

| **Adsorbent** | **$Al_2O_3$ (%)** | **$Fe_2O_3$ (%)** | **Specific Surface Area ($m^2$ $g^{-1}$)** | **Morphology** | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | **Length (µm)** | **Diameter (nm)** | | **Aspect Ratio** | **Grain Size** |
| | | | | | **Inner** | **Outer** | | |
| HNT-MF2 | 25.0 | 23.0 | 35 | 0.3–1.0 | 25 | 120 | 8 | <2 µm |
| HNT-MF4 | 37.5 | 0.4 | 25 | 0.6–1.2 | 20 | 100 | 10 | <7 µm |
| HNT-MF7 | 35.9 | 1.3 | 25 | 0.5–3.5 | 15 | 60 | 30 | <7 µm |

(Joussein et al., 2005; Zhang et al., 2011) proposed that morphological variability of halloysite is attributed to various factors including crystal structure, the degree of alteration, chemical composition, and the effects of dehydration. SEM image of HNTs illustrates tubular morphology with different lengths, covering a range from 0.3 to 3.5 µm and the diameter varies from 15 nm to 120 nm, which explains the mesoporous (2–50 nm) and even macroporous scale (>50 nm) (Yuan et al., 2015; Pasbakhsh et al., 2013).

### *4.2.4 Phosphate sorption kinetics*

Principally, the kinetics of phosphate sorption by HNTs illustrates two different steps of sorption with different slopes. The sorption dynamic is characterized by a fast first phase (first 4 h of the experiment) in which 50% of the final amount is adsorbed onto HNTs. The second step corresponds to slower kinetics reaching maximum sorption at a constant rate beyond 18 h of the experiment (Figure 4.2). The data indicate that the equilibrium is attained at 24 h. The shaking time for the equilibrium tests was chosen accordingly. A 24 h kinetic experiment appears to be adequate to reach equilibrium, which is in agreement with prior studies (Tabbara, 2003). Differences in the temporal dynamic can be attributed to less accessible adsorption site of phosphate and a limited diffusion process in case of granular HNTs. Among studied adsorbents, the amount of phosphate adsorbed on HNT-MF4 (G) (549 mg $kg^{-1}$, 94.7%) was much higher than the values obtained for all other adsorbents at the same interaction time of 24 h.

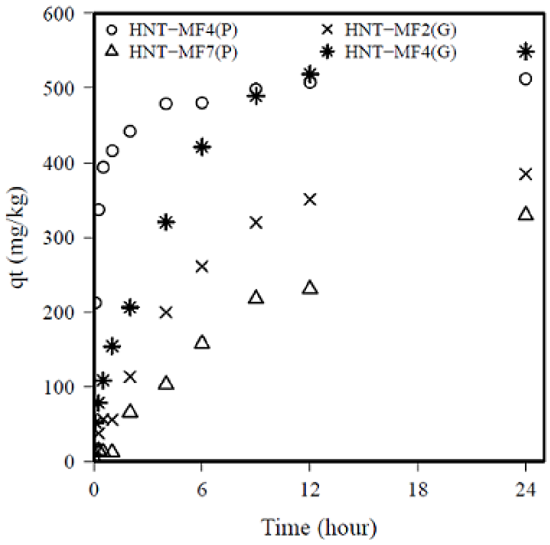

**Figure 4. 2** Kinetic experiments for the sorption of phosphate onto halloysite nanotubes (HNT) material in powder and granular form.

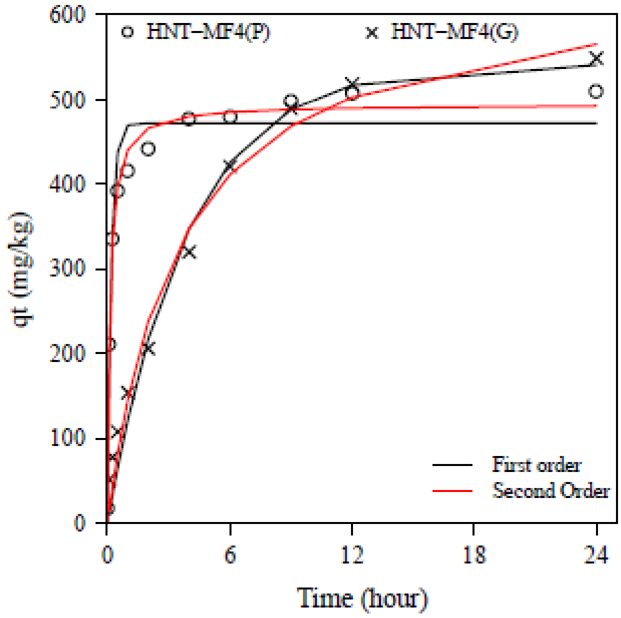

**Figure 4. 3** Phosphate sorption kinetic data and optimized model equations for powder HNT-MF4(P) and granular form of HNT-MF4(G).

To get more comprehension of the kinetics of phosphate sorption onto HNTs, different models were fitted to the experimental data. The pseudo-first and pseudo-second order equations were applied in this study, and the parameter values for the kinetic experiment as acquired are reported in Table 4.2. For all HNTs, the calculated equilibrium capacity values were very close to the experimentally determined values ($q_e$). The $k_1$ and $k_2$ represent the steepness of the curve and describe the rate of phosphate uptake. From Table 4.2 it is evident that the sorption of phosphate onto HNT-MF4(P) is faster than onto the other HNTs. In powder form, the sorption sites of the HNTs are instantly accessible. In general, excellent fits ($R^2 > 0.90$, Table 4.2) for all HNTs were observed indicating that both kinetic models are applicable. All adsorbent favorably adsorb phosphate efficiently.

For the mentioned HNTs (HNT-MF4), $q_e$ values as derived from the pseudo-first order equation are 541.1 mg kg$^{-1}$ and 472.1 mg kg$^{-1}$ for granular form and powder form, respectively indicating a slightly higher sorption capacity (around 10%) for the granular form at time of equilibrium, although the rate of phosphate uptake of the powder form was higher than that of the granular form at early stages of the experiments ($k_1$ = 5.25 vs. 0.256 h$^{-1}$) (Figure 4.3).

**Table 4. 2** Pseudo-first and second order parameter values of phosphate sorption onto different halloysite nanotubes.

| Model | | Adsorbent halloysite nanotubes | | | |
|---|---|---|---|---|---|
| | | **HNT-MF2 (G)** | **HNT-MF4 (P)** | **HNT-MF7 (P)** | **HNT-MF4 (G)** |
| Pseudo-first order | $q_e$ experiment | 384.5 | 511.6 | 329.5 | 549.0 |
| | $q_e$ model | 369.9 | 472.1 | 328.5 | 541.1 |
| | $K_1$ | 0.19 | 5.25 | 0.087 | 0.256 |
| | RMSE | 440.1 | 1459 | 143.9 | 1077 |
| | $R^2$ | 0.98 | 0.87 | 0.99 | 0.99 |
| Pseudo-second order | $q_e$ model | 384.6 | 492.3 | 331.9 | 565.6 |
| | $K_2$ | 0.0004 | 0.016 | 0.0001 | 0.0004 |
| | RMSE | 260.1 | 251.8 | 136.4 | 589.6 |
| | $R^2$ | 0.98 | 0.97 | 0.99 | 0.98 |

### *4.2.5 Adsorption isotherms*

Analysis of the relationship between the sorption capacity of the materials (HNTs) and different phosphate concentrations at equilibrium was performed using the equations of Langmuir (Equation (4.3)) and Freundlich (Equation (4.4)). The isotherm plots of the equilibrium sorption of phosphate are graphically presented in (Figure 4.4), and the parameters values derived from the isotherm models and the parameters of determination are demonstrated in Table 4.3. It was found that among the tested materials, sorption onto the granular form of HNTs was more pronounced than onto powder form. Freundlich equation relatively better describes the sorption of phosphate onto halloysite nanotubes as indicated by the greater value of $R^2$ (Table 4.3).

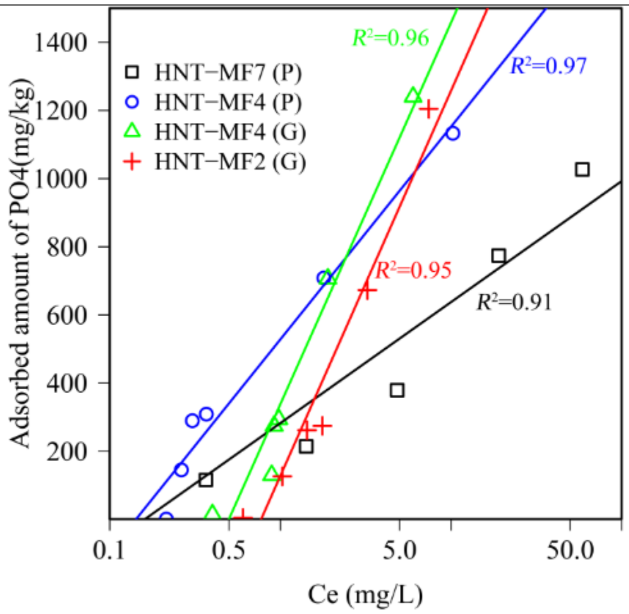

**Figure 4. 4** Sorption isotherms of phosphate for adsorbents HNT-MF4 (P), HNT-MF2 (P), and HNT-MF7 (P).

Nevertheless, in the case of HNT-MF2(G) and HNT-MF4(G), systems follow both Freundlich and Langmuir type sorption isotherms. The results confirm that the Freundlich sorption capacity, KF, of HNT-MF4 (P) is larger (415 L kg$^{-1}$; R$^2$: 0.983 for HNT-MF4 (G) and 380 L kg$^{-1}$; R$^2$: 0.982 for HNT-MF2 (G) as compared to that of other adsorbents (345 L kg$^{-1}$; R$^2$: 0.977 for HNT-MF7 (P) and 207 L kg$^{-1}$; R$^2$: 0.964 for HNT-MF4 (P)) (Table 4.3).

**Table 4. 3** Sorption Freundlich and Langmuir isotherm data.

| Adsorbent | Freundlich | | | | Langmuir | | | |
|---|---|---|---|---|---|---|---|---|
| | **$K_F$** | **$n_F$** | **RMSE** | **$R^2$** | **$K_L$** | **$Q_L$** | **RMSE** | **$R^2$** |
| HNT-MF2(G) | 380 | 0.934 | 112 | 0.982 | 0.918 | 184 | 438 | 0.978 |
| HNT-MF4(P) | 334 | 0.848 | 203 | 0.977 | 0.865 | 61.2 | 621 | 0.798 |
| HNF-MF4(G) | 415 | 0.968 | 153 | 0.983 | 0.937 | 204 | 215 | 0.966 |
| HNT-MF7(P) | 207 | 0.404 | 311 | 0.964 | 0.564 | 59.4 | 976 | 0.727 |

The Freundlich constant, $n$, can be considered a measure of deviation from linearity of adsorption. If $n$ = 1 the sorption is linear, indicating that the sorption sites are homogenous in energy and no interaction occurs between the adsorbed species (Panuccio et al., 2009). The results revealed that the $n$ values for all adsorbents were less than unity (Table 3.3), which indicates that increased sorption can modify the adsorbent and that a chemical rather than physical sorption was dominant (Jiang et al., 2002; Alemayehu and Lennartz, 2010).

## 4.3 Conclusions

The mechanism of phosphate sorption onto the powder and granular forms of halloysite nanotubes was studied via diffusion and batch experiments. Both powder and granular halloysite nanotubes are adequate of removing phosphate from agricultural runoff. At equilibrium time, the granular form of halloysite nanotubes had a slightly higher sorption capacity than the powder form. We postulate that the pore volume as formed by the production of grains can accommodate phosphate anions in addition to the adsorbed amount at solid surfaces. Sorption of phosphate onto granular halloysite nanotubes took place primarily at active sites of the surface area followed by a slow diffusion into the inner structure of the grains. The Freundlich isotherm model provided a superior fit to data indicating the irregular internal morphology of halloysite nanotubes particles and interrupted placement of the layers. The lab-scale phosphate sorption onto halloysite nanotubes offers interesting perspectives; however, the use of the halloysite nanotubes for phosphate-laden agricultural runoff requires more investigations deploying real runoff, which also contains dissolved and particulate organic matter and clay minerals possibly altering sorption behavior. Besides, clogging of filter materials in a flow-through-set-up is a severe problem and may be considered additionally in future studies (Loganathan et al., 2014).

# 5

# Synthesis and outlook

This dissertation has considered and outlined several objectives in terms of investigating phosphorus sorption onto selected structured substrates, aiming to ascertain the phosphorus sorption onto structured soil. It has also explored how soil aggregate size and aggregate stability can change P sorption onto different classes of soil aggregates. Besides, it has assessed the use of halloysite nanotubes as an adsorptive material for the removal of phosphate from aqueous solutions using different approaches involving halloysite nanotubes in powder and aggregated form. To achieve these goals, a simple and easy-to-reproduce method was established to quantify sorption effects based on structural characteristics. In this chapter, a consideration of the aforementioned objectives is followed by a review of relevant results from previous studies, which link to a discussion of how this project has answered the research questions. The overall conclusion also highlights ways in which future studies could improve knowledge and ignores the ambiguities in the contexts that require more precisely analysis.

## 5.1 Diffusion approach as a new alternative for P-sorption studies

The increasing concerns about the use of P as an essential nutrient driving plant growth has invigorated research efforts to gain comprehensive insight into the processes controlling phosphate sorption onto soils (Barrow, 2015a; Salm et al., 2016). Consequently, scientists have more prominently focused on physical and chemical soil characteristics including clay, organic matter and Al- and Fe-oxide content, soil moisture, pH, and redox conditions where the sorption process occurs (Xiao et al., 2017; Singh and Gilkes, 1991). Classical batch, kinetic and isotherm experiments have previously been performed on peaty soils to quantify the process of phosphate sorption onto such soils. However, the results of phosphate sorption onto soil are restricted to the classical batch experiments. The results of the phosphate sorption potential are unrealistic given that thorough mixing of the soil and phosphate solution as obtained by shaking in the slurry technique would probably not take place under natural conditions, principally if the soil is structured. From the results, it can be concluded that the shaker-facilitated energy input enlarges adsorption in general. Besides, the continuous shaking of the soil might rearrange soil particles. In particular, this might occur due to breaking up micro-aggregates that have passed intact through the 2 mm sieve during soil sample preparation. It provides additional surfaces for adsorption. In addition, constant shaking in the classical batch experiments encourages unrestricted transport of phosphate anions to potential sorption sites, whereas the availability of anions is limited in the diffusion setup. However, the promising results obtained in this study regarding the observed differences in adsorbed P amounts between the classical batch experiments and the diffusion approach question the representativeness of the classical batch sorption experiments (van Grinsven and van Riemsdijk, 1992; Linquist et al., 1997). The intensive mixing of soil and solution in the shaking experiments undoubtedly presents sorption potential rather than a depiction of what would happen in the field (Pačes, 1983; Velbel, 1987; van Grinsven and van Riemsdijk, 1992). Despite all of the promising results relating to phosphate sorption onto soil, it remains a controversial issue. As the first and fundamental step for assessing structure onto the sorption process, the temporal development of adsorbed P amount in classical batch and diffusion experiment, and sorption isotherm from the fine earth obtained from classical batch experiment and diffusion method has been thoroughly investigated (**Chapter 2**). In this thesis, the sorption of phosphate onto soil was quantified through the use of a 'diffusion experiment', as it is believed that diffusion is one of the controlling factors contributing to overall P retention. In this study, attempts were made to determine the effectiveness of the diffusion approach to explore how soil structure can change the sorption of phosphate. To the best of our knowledge, such experiments have not previously been conducted. Moreover, the effect of initial phosphate concentration on the phosphate sorption dynamic was highlighted employing the diffusion approach with fine earth and soil aggregates with six different phosphate concentrations **(Chapter 2)**.

We could clearly show that the phosphate sorption onto aggregates was more pronounced than was the case onto fine earth. The visual inspection of the concentration course illustrates that the initial rapid sorption is approximately alike in the two experimental approaches; however, at later stages, the adsorption onto soil aggregates rises at a slower pace compared with the situation regarding fine earth. Differences in the temporal dynamic might be attributed to a modified diffusion process, and the existence of less accessible sorption sites in the case of soil aggregates **(Chapter 2)**. The experimental sorption data could be obtained by the empirical and thermo-dynamic based isotherm models. The effect of structured soil on phosphate sorption reveals that more phosphate sorption is associated with increased amounts of inner-aggregate pore space. However, there is evidence that the diffusion approach is a reasonable alternative for fine earth and aggregated soil compared with classical batch experiments **(Chapter 2)**.

Remarkable emphasis is given to the sorption process to substrates, while it is a fundamental process influencing the transport and degradation of compounds in the environment. Since all transport, fate and risk assessment models comprise term of sorption, consequently a comprehensive understanding of sorption dynamics is essential. Ignoring kinetics accurately can result in underestimating the actual extent of sorption, sophisticated predictions of the mobility and bioavailability of contaminants, and feasibly the inappropriate clean-up technology.

As indicated in **Chapter 2,** the results obtained by classical batch experiments are imperfect when it comes to simulating phosphate sorption. However, the innovative diffusion experiment could also be improved by considering more parameters including pH, and temperature change regarding the soil being used. This would help to identify the mechanisms of P sorption under controlled laboratory conditions and achieve better simulation on the outcomes of P in soil. Moreover, regarding the performance of structured soil and different diffusion path lengths in the estimation of P in soil (**Chapter 2**), it would hold strong interest to use differently-sized aggregate fractions. More importantly, the new approach should be tested to affirm its applicability to a wide range of soils and chemical compounds.

As the next stage, assessing the alteration in the adsorbed amount of phosphate onto different soil aggregates of various sizes as a function of soil structure was crucial. This offers an insight into how soil structure as a fundamental feature affects the productiveness of soils and the environmental side-effects of agriculture. Two main physical properties – soil aggregate size and aggregate stability – were investigated to explore their effects on structured soil through a consideration of intra-aggregates. Therefore, in **Chapter 3**, phosphate sorption onto different classes of soil aggregates was systematically studied using diffusion experiments. The studies of different soil aggregate sizes illustrate that the amount of phosphate adsorbed onto soil aggregates is in accordance with soil aggregate size. The larger the size of the soil aggregate, the larger the amount of adsorbed phosphate at equilibrium after 24 hours. The more pronounced phosphate sorption of the soil aggregates is a useful indication that the adsorbed amount of phosphate was not only associated with the accessibility of soil surfaces but also with the intra-aggregate pore spaces. These changes in P sorption onto soil aggregates were in agreement with Cui et al. (2019), who outlined that macro-aggregates showed a considerable capacity to retain P in restored wetlands. Moreover, the results were parallel to those of other studies that likewise proved that large soil macro-aggregates store dramatically larger amounts of compounds compared with smaller-sized aggregates (Wang et al., 2020).

The excessive phosphate appearing in agricultural runoff from manure, sludge sources and chemical fertilisers applied has received strong attention due to the risk to aquatic ecosystems (Tabbara, 2003; Tarkalson and Mikkelsen, 2004; Daverede et al., 2004; Hart et al., 2004). Many approaches have been attempted, including chemical sorption, precipitation, coagulation, ion exchange, biological and physical treatments applied to remove P from aqueous solution before being released in the form of agricultural runoff (Farmer, 2001; Valsamy-Jones, 2004; Shilton et al. 2006). However, most of these methods involve high capital costs with recurring expenses and therefore they are not suitable for many parts of the world (Gupta et al., 2009; Johansson Westholm 2006; Hylander et al., 2006; Cucarella et al., 2008). In various studies, several adsorbents have been investigated for the removal of phosphate from an aqueous solution such as nanoparticles (Joussein et al., 2005; Prashantha Kumar et al., 2018).

The results of **chapter 4** provide important information in terms of making comparisons between the powder and granular form of halloysite nanotubes as an adsorptive for the removal of phosphate and assessing how the structured soil can affect phosphate adsorption. As a function of structure and in agreement with previous studies **(Chapter 2),** when equilibrium is achieved, the granular form of halloysite nanotubes had a slightly higher sorption capacity compared with the powder form. This was due to the pore volume as formed by the production of the granular form in addition to the amount adsorbed at the solid surface. According to the results obtained, both powder and granular halloysite nanotubes are effective when it comes to removing phosphate from agricultural runoff. In addition, the high contribution of the clay materials (halloysite) to remove both anionic and cationic pollutants has been reported in the runoff area (Joussein et al., 2005; Mallikarjun and Mise, 2013; Dong et al., 2012; Cataldo et al., 2015).

The lab-scale phosphate sorption onto halloysite nanotubes here evidenced new perspectives in terms of acting as an appropriate material for phosphate sorption from an artificial phosphate solution. However, the use of halloysite nanotubes for phosphate-laden agricultural runoff must also be improved by applying real runoff, given that it also contains dissolved and particulate organic matter and clay minerals, possibly altering sorption behaviour. General knowledge about adsorptive materials should be improved by considering the impact of the clogging of filter materials in a flow-through setup, considering that this can be a severe problem, and thus it should be considered in future studies (Loganathan et al., 2014).

## 5.2 Implications for future research

This thesis makes important contributions to a crucial aspect, namely the structural characteristics and their influence on the adsorption of phosphate onto selected porous media, as well as studying the methodology and implications of a diffusion experiment. Some of the findings from this research have been published in the peer-reviewed international journals Soil Systems (Saki et al., 2020) and Water (Saki et al., 2019).

The project described in this dissertation considered a diverse range of experimental works and analyses to evaluate the sorption of P onto some structured substrate. In the future, other important factors that can affect phosphate sorption onto structure substrates should be explored in forthcoming studies to identify how additional and advanced techniques can help to maintain, justify and improve the diffusion approach as a promising one that enables studying sorption processes in well-structured substrates in conditions that perform better compared with the natural situation.

The diffusion experiment should be additionally improved by considering more parameters regarding the soil under consideration. This can help to identify the mechanisms of P sorption under controlled laboratory conditions, as well as how to achieve better simulation regarding adsorbed phosphate in soil or other structured substrates. Soil studies at the molecular level and P chemisorption should be considered in future studies regarding a number of soil minerals to develop insights into the P sorption mechanism in soil by making use of diffusion experiments. Aside from aggregate size, the other soil parameters responsible for the length of the P sorption diffusion path require further investigation.

Moreover, regarding the performance of halloysite nanotubes as an adsorptive substrate for the removal of phosphate from agricultural runoff **(Chapter 4)**, it is advised that future researchers perform diffusion experiments that consider the clogging of filter materials in a flow-through setup, given that it is a severe problem. To verify the applicability of the diffusion experiment, a wide range of soils and chemical compounds should be considered. Since different aggregate sizes influence phosphate sorption differently **(Chapter 3)**, it would hold strong interest to use different aggregate size fractions for P from aqueous solution for contaminant remediation. More importantly, the best-sized class of aggregates (as perform best in the case of P sorption; **Chapter 4**) should be tested in field experiments as an introduction to practical agriculture.

In summary, this dissertation has consistently resolved some of the important aspects of diffusion experiments as a substitute for classical batch experiments for the first time, as well as demonstrating that the proposed approach is a promising method for considering the structure of substrates, and an outstanding alternative to classical batch experiments regarding natural condition in the field.

# 6

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# 7

# Appendix

# Supplementary materials

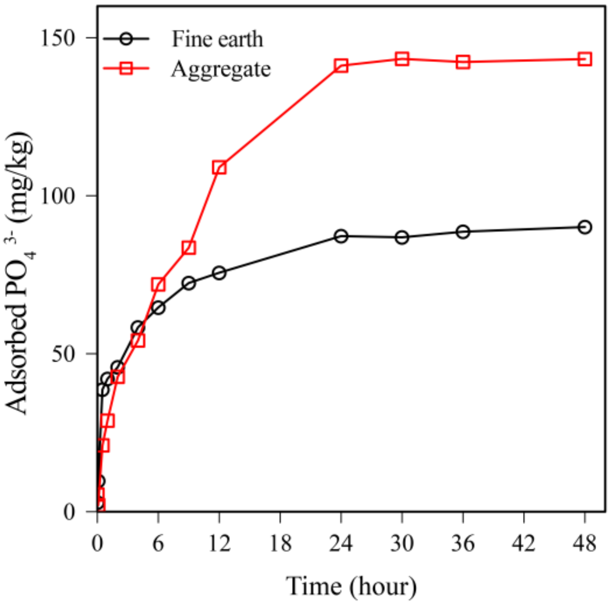

**Figure S. 1** Adsorbed phosphate amount as a function of experimental duration for fine earth and soil aggregates.

(**Chapter 2**)

**Table S. 1** Some chemical characteristics of the experimental field.

(**Chapter 2**)

| | **Soil horizon** | **Al**<br>(g/kg) | **Fe**<br>(g/kg) | **Ca**<br>(g/kg) |
|---|---|---|---|---|
| **Fine soil** | Topsoil | 9.85 ± 0.29 | 11.03 ± 0.02 | 3.10 ± 0.004 |
| | Subsoil | 8.78 ± 0.55 | 10.69 ± 0.20 | 2.76 ± 0.009 |
| **Aggregates** | Topsoil | 9.92 ± 0.84 | 11.52 ± 0.28 | 2.93 ± 0.07 |
| | Subsoil | 9.26 ± 0.27 | 11.49 ± 0.03 | 2.70 ± 0.03 |

# Curriculum vitae

## Personal Information

| | |
|---|---|
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## Academic Education

| | |
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| 04/2013 – now | PhD student, Soil Physics Professorship, Faculty of Agricultural and Environmental Sciences, University of Rostock.<br>Title of the thesis: “Phosphate adsorption onto selected structured porous substrates”. |
| 09/2006 – 06/2009 | Master of Soil Science, Faculty of Agricultural and Environmental Sciences, Islamic Azad University, Karaj, Iran.<br>Title of the thesis: ‘‘Prediction of the saturated hydraulic conductivity from primary particle size distribution in Karaj region”. |
| 09/2001 – 07/2005 | Bachelor of Soil Science, Faculty of Agricultural and Environmental Sciences, Guilan University, Iran.<br>Title of the thesis: “Soil classification of Lishavandan pedon concerning the physical and chemical characteristics of the soil.” |

## Work experience

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|---|---|
| 05/2017- 02/2019 | Research assistant at University of Rostock, Faculty of agricultural and environmental sciences, Chair of Soil physics, PhosWaM project. |
| 10/2010- 08/2012 | Soil and water engineering services company, Karaj, Iran. |

## List of publications

**Saki, H.**, Liu, H., and Lennartz, B. 2020. Phosphate sorption onto structured soil. *Soil Sys.,*4(2), 21, doi:10.3390/soilsystems4020021.

**Saki, H.,** Alemayehu, E., Schomburg, J., and Lennartz, B. 2019. Halloysite nanotubes as adsorptive material for phosphate removal from aqueous solution. Water. 11(2), 203, https://doi.org/10.3390/w11020203

Liu, H., Forsmann, D.M., Kjærgaard, C., **Saki, H.,** and Lennartz, B. 2017. Solute transport properties of fen peat differing in organic matter content. J. Environ. Qual. 46: 1106-1113. doi:10.2134/jeq2017.01.0031

## Selbständigkeitserklärung

Ich erkläre, dass ich die hier vorgelegte Arbeit selbständig und ohne fremde Hilfe verfasst, andere als die von mir angegebenen Quellen und Hilfsmittel nicht benutzt und die den benutzten Werken wörtlich oder inhaltlich entnommenen Stellen als solche kenntlich gemacht habe.

Rostock, den                                        Hermin Saki

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# Proof of individual contribution

| Manuscript included in the thesis | Author (H. Saki) | Co-authors |
|---|---|---|
| **Saki, H.**; Liu, H.; Lennartz, B:<br>*Phosphate adsorption onto structured soil.*<br>***Journal of Soil Systems*** (2020), 2 (21)<br>**Chapter 2** | Generating research idea, generating and evaluating data, writing the manuscript. | **H. Liu** (assistance during data evaluation, correcting the manuscript)<br>**B. Lennartz** (generating research idea, correcting the manuscript) |
| **Saki, H.**; Alemayehu, E.; Schomburg, J.; Lennartz, B:<br>*Halloysite nanotubes as adsorptive material for phosphate removal from aqueous solution.*<br>***Journal of Water.*** (2019), 11(2)<br>**Chapter 4** | Conducted the research, reviewed the literature, writing the manuscript. | **E. Alemayehu** (updated and revised the manuscript)<br>**J. Schomburg** (characterized the halloysite nanotubes)<br>**B. Lennartz** (generating research idea, supervised the study) |

# Theses

## Phosphate adsorption onto selected structured porous substrates

*Presented by Hermin Saki*

### Rationale and objectives of the research

Phosphorus (P) is a fundamental element for living organisms, plant growth, and food productions. It has also required for crop development, plant metabolism, and energy transfer. The phosphorus excess, which has been generated considerably from anthropogenic activities, leads to unfavorable water quality, in particular, eutrophication. Recent concerns over future phosphorus scarcity and water quality have promoted interest in recovering wastewater and remediation strategies.

The nutrient status of the Baltic Sea has received much more attention over the last two decades. The treat of eutrophication to the Baltic Sea has much considered owing to the broader area of the Baltic Sea and its basins. Annual assessment of phosphorus transmission to the Baltic Sea illustrates the importance of the sources which originated from the Mecklenburg-West Pomeranian. To deal with the impairments of surface waters, the application of moderating strategies seems indispensable for sustainable agriculture.

Among several restoration and remediation strategies that have been proved to diminish the non-point sources, sorption by some substrate has shown great potential and cost-effective performance. Sorption processes including adsorption, chemisorption, biodegradation, ion exchange will alter the distribution of phosphorus between the solution and solid phase. Sorption of inorganic solute in porous media is a function of the available area for adsorption as well as the accessible ion-exchange sites which provided by porous media.

In many studies, the convection-dispersion equation has been modified to consider the effect of solute that is removed from solution by sorption, chemical reaction and biological biodegradation. Some of the mentioned reactions can be characterized through equilibrium reactions and some part necessity to deal with the kinetic of reactions. Diffusion approach was developed to address this critical issue of the structure characteristics on the phosphorus adsorption onto a structured selected substrate.

In order to establish the novel of Solute transport properties of peat at various stages of degradation, miscible displacement experiments were conducted on various undisturbed soil columns under saturated steady state condition using tritium and bromide as a conservative tracer. This novel must be understood in detail, and this can be achieved by 1) exploring solute transport properties in fen peat soils, 2) evaluating the quality of various modeling approaches in depicting the experimentally observed transport behavior, and 3) assessment on how the transport parameter values vary for peat soils differing in organic matter content.

## Main research results

The new-introduced diffusion experiment conducted for different bulk soil and soil aggregates using and diffusion experiments on different initial phosphate concentrations. The results revealed that differences between methods were more pronounced at lower initial phosphate concentrations. The results indicate that adsorption onto soil aggregates was elevated as compared to unstructured bulk soil. This result was unexpected since it was assumed that the soil surface area available for adsorption processes is greater or at least by far more accessible for bulk soil. The results reveal that adsorption of phosphate onto structures soil is strongly dependent on the inner pore space of soil aggregates as extra accommodation for phosphate adsorption. Moreover, the phosphorus adsorption was related to the aggregate size and stability of soil aggregates.

Besides a significant correlation between the phosphate adsorption and the structure characteristics, some experiments were well-studied on halloysite nanotubes to clarify the importance of structure on the adsorption processes. The results illustrate that the overall retention capacity of intact aggregates is higher than that of the disturbed soil considering the inner-aggregate pore space accommodated a certain fraction of phosphate in addition to the adsorbed amount at particle surfaces. Besides, the maximum adsorption efficiency for the granular from of halloysite nanotubes was more than that of powder halloysite nanotubes.