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Nutrient recycling from animal slurries

Solutions for minimizing eutrophication and environmental pollution

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不论发生什么事都是有原因的

Everything happens for a reason

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Abstract

Economic development with a concomitant higher income as in China is often associated with a growing demand for protein rich food. This has led to high animal densities, especially large pig farms and consequently vast amounts of manure in peri-urban areas in China. As arable land available for direct manure application is limited, this leads to high nutrient (nitrogen (N), phosphate (P)) overloads. Leaching, direct discharge, and gaseous emissions from animal husbandry thus contribute finally to eutrophication of water bodies.

The present work focuses on the recycling of nutrients as a measure to minimize environmental pollution. The objective in this context was to test different techniques for the elimination of N and P from effluents of animal husbandry. The research focused on i) precipitation experiments for phosphate recovery in the form of struvite ($MgNH_4PO_4$), ii) the development of an ammonia stripping device consisting of rotating discs and iii) the identification of parameters influencing both processes most. P removal from effluents was assessed by comparing soluble P_i-concentrations before and after different treatments. In a comparison of different methods, I found that the monovanadate-yellow method tended to sometimes grossly overestimate P levels, whereas the molybdenum-blue method was superior.

i) Struvite precipitation in slurry or digestate samples was assessed by adding MgO at different molar ratios (Mg:P as 1:1 and 2:1). The PO_4-P concentration decreased significantly by around 80% in slurry as well as digestate samples through struvite precipitation. Struvite was identified via X-ray diffractometry. ii) Ammonia stripping was successfully carried out with a rotating disc system. Different surface areas (0.14 m^2, 0.28 m^2, 0.57 m^2 and 1 m^2), performed by varying numbers of discs, were rotated through containers with acid and digestate. Ammonium nitrogen (NH_4-N) removal efficiencies of up to 85% could be obtained within 4 days. iii) A higher surface area, achieved by more discs in the system or an increased rotating speed removed a higher percentage of the NH_4-N in a shorter time. However, an increased temperature did not affect ammonia stripping. Organic matter and suspended solids in the samples influenced struvite precipitation most.

The pretreatment (chemical oxidation) released large quantities of bound P, which could then be precipitated. Struvite precipitation was neither influenced significantly by an increased pH nor by an increased molar Mg:P ratio. During anaerobic digestion, large quantities of struvite precipitated spontaneously in the digester, thus reducing the PO_4-P concentration in the digestate. The main conclusions drawn from this research showed a huge N and P recovery potential through struvite precipitation and ammonia stripping in these particular slurry and digestate samples. The removal and subsequent conversion into a transportable form facilitates the nutrient export and redistribution to areas with nutrient shortages. This can thus help to reduce the threat on the environment in peri-urban areas.

Kurzfassung

Das rasante Wirtschaftswachstum der Volksrepublik China führte in den vergangenen 40 Jahren zu steigendem Wohlstand und damit auch zu einer Veränderung des Lebensstandards der vorwiegend städtischen Bevölkerung mit einer erhöhten Nachfrage nach proteinreichen Nahrungsmitteln wie Käse und Fleisch. Vor allem der vermehrte Schweinefleischkonsum führte zu einer Zunahme von Mastbetrieben in unmittelbarer Nähe von Großstädten und infolgedessen zu großen Mengen an tierischen Abwässern wie Gülle und Gärresten. Im Umfeld der immer größer werdenden Städte wird vermehrt Ackerland zu Bauland umgewandelt, was den Einsatz dieser Abwässer als organisches Düngemittel begrenzt und zu erheblichen Nährstoffüberschüssen von Stickstoff (N) und Phosphat (P) führt. Weitere Folgen der intensiven Tierhaltung sind erhöhte Ammoniakemissionen sowie Nährstoffauswaschungen, die zur Eutrophierung von Fließ- und Standgewässern führen.

Ziel der Doktorarbeit war das Nährstoffrecycling von N und P aus Gülle und Gärresten, die unter folgen Aspekten untersucht wurden: i) Fällungsexperimente zur Phosphatrückgewinnung in Form von Struvit ($MgNH_4PO_4$), ii) die Entwicklung einer Versuchsvorrichtung mit rotierenden Platten zur Ammoniakstrippung und iii) die Identifizierung der Haupteinflussparameter beider Prozesse. Der Phosphatentzug aus tierischen Abwässern wurde durch den Vergleich der gelösten P_i-Konzentrationen vor und nach den unterschiedlichen Behandlungen beurteilt. Der Methodenvergleich zur P-Bestimmung zeigte eindeutig, dass die Monovanadat-Gelbmethode dazu neigte die P-Gehalte deutlich zu überschätzen, wohingegen die Molybdän-Blaumethode unbeeinflusst von Matrixeffekten war. i) Die Struvitfällung in Gülle oder Gärresten wurde durch die Zugabe von MgO in unterschiedlichen molaren Verhältnissen (Mg:P von 1:1 und 2:1) analysiert. Die Orthophosphat-Konzentrationen nahmen in allen Proben durch Fällung um etwa 80% ab. Der Nachweis von Struvit erfolgte mittels Röntgendiffraktometrie. ii) Ammoniak konnte erfolgreich mit der neuen Versuchsvorrichtung aus rotierenden Scheiben gestrippt werden. Eine unterschiedliche Anzahl von Scheiben, und damit veränderte Oberflächen (0.14 m^2, 0.28 m^2, 0.57 m^2 und 1 m^2), rotierten abwechselnd durch Behälter mit Säure und Gärrest und erzielten eine Ammonium-Stickstoff (NH_4-N)-Entfrachtung von bis zu 85% innerhalb von 4 Tagen. iii) Eine größere Oberfläche (mehr rotierende Scheiben) oder eine erhöhte Umdrehungsgeschwindigkeit waren die maßgeblichen Einflussfaktoren der Ammoniakstrippung. Höhere Temperaturen beeinflussten die Ammoniakstrippung hingegen nicht. Die Struvitfällung wurde am stärksten von organischer Substanz und Schwebstoffen in den Proben beeinflusst.

Die Vorbehandlung des Probenmaterials durch chemische Oxidation setzte große Mengen an gebundenem P frei, das als Struvit ausgefällt werden konnte. Die Struvitfällung wurde weder durch einen erhöhten pH-Wert noch durch ein erhöhtes molares Mg:P Verhältnis signifikant beeinflusst. Ein Großteil des Orthophosphats fiel bereits spontan während des Biogasprozesses aus und reduzierte damit die Konzentration im Gärrest. Die Untersuchungen zeigten eindeutig, dass in den Gülle- und Gärrestproben ein hohes Potential zur Nährstoffrückgewinnung liegt und die vorgestellten Verfahren zu einer Verminderung der Umweltbelastung in stadtnahen Gebieten beitragen können. Die Rückgewinnung und anschließende Umwandlung der Nährstoffe in eine transportable Form erleichtert den Nährstoffexport und die Umverteilung in nährstoffarme Gebiete.

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List of Abbreviations

c_i	initial concentration
c_f	final concentration
DAP	di-ammonium phosphate
DHC	disc holding capacity
DM	dry matter
IAP	ion activity product
MAP	mono-ammonium phosphate
η	ammonia removal efficiency
NH_4-N	ammonium nitrogen
ODM	organic dry matter
P_i	solute inorganic phosphate
PET	polyethylene terephthalate
PO_4-P	orthophosphate-P
PO_4-P_f	final orthophosphate-P concentration
SI	saturation index
WSA	water-sparged aerocyclone

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I. General introduction

Worldwide, a higher household income and the resulting altered living standards lead to a changed consumption behavior. Especially relevant is the increasing demand for higher-valued and protein rich food such as meat, eggs and milk (FAO, 2003). This change in food demand and an unprecedented population growth, have led to large increases in the total demand for animal products in emerging countries. China, with a still fast growing economy and the highest absolute population growth with an increase from 554 million in 1950 to a projected 1395 million in 2050 (UN, 2009), is facing the problem to satisfy an increasing demand for meat. In China, meat consumption increased rapidly from approximately 20 kg per person and year in 1985 to 53 kg in 2006 (Schuchardt et al., 2011). In addition, the ongoing urbanization (McOrist et al., 2011) leads to the formation of megacities. This is accompanied by the phenomenon that food production is often carried out in big animal husbandries close to the consumers (Gerber et al., 2005) in order to avoid long transportation routes for meat resp. animals.

In peri-urban areas, though, arable land is limited and the available area is more and more diminished as a consequence of the ongoing urban expansion. High livestock densities, accompanied by decreased agricultural areas available for a prudent manure use, will thus lead to dumping far in excess of the needed rate on arable land. This then results in surface runoff, leaching of nutrients and their accumulation in adjacent water bodies, contributing to eutrophication (Bonmatí and Flotats, 2003a). The main nutrients in animal manures contributing to this environmental pollution are nitrogen (N) and phosphorus (P), which are, however, as well important macronutrients for crop growth. The export of animal manures from areas with high animal densities and thus nutrient overload to those regions with shortage is limited by the high water content of manures, which make long-distance transport uneconomical (Bonmatí and Flotats, 2003a).

Further, easily exploitable rock phosphate (e.g. for fertilizer production) is a finite resource and will last, according to different calculations between 115 years (Elsner, 2008) to 320 years (Gethke-Albinus, 2012). Nutrient extraction and recovery from animal slurries could thus help on the one hand to reduce environmental pollution and on the other hand to recycle valuable nutrients.

The main method for phosphate recovery in animal manures is the precipitation as solid phosphate salts (e.g. calcium or magnesium phosphates). The resulting product can then be used as valuable fertilizer and, due to the reduced volume, easily be transported and exported to areas where nutrients are lacking. Nitrogen removal from liquids is often obtained through ammonia stripping techniques. The resulting product is ammonium sulfate, a valuable fertilizer, too.

II. Phosphate recovery

1. Introduction

1.1 The chemical element phosphorus and the importance for organisms

The word phosphorus is derived from the ancient Greek words *phos*, meaning “light” and *phorus*, meaning “bringing” (Emsley, 2000) and was first discovered by chance by Henning Brand in 1669 when searching for an elixir for longevity – the philosopher’s stone. In 1974, the Russian-American biochemist Isaac Asimov summarized the importance of phosphorus in his publication “Asimov on chemistry” as follows: *“Life can multiply until all phosphorus has gone and then there is an inexorable halt which nothing can prevent. … We may be able to substitute nuclear power for coal, and plastics for wood, and yeast for meat, and friendliness for isolation—but for phosphorus there is neither substitute nor replacement.”*

With the first sentence of this statement, Asimov refers to Liebig’s Law of the Minimum, which explains that growth and yield are not controlled by the total amount of available resources, but by the scarce resource representing the limiting factor. Asimov defined phosphorus as the “life’s bottleneck”, even though it is, in no case, the rarest mineral element. Phosphorus is a macronutrient and even though organisms need only small quantities, it is in many cases a limiting nutrient for living organisms on earth and in water. Asimov observed further that plants can, compared to the surrounding environment, concentrate mineral elements.

Phosphorus is a chemical element, so that, compared to other resources like crude oil, it can only be used but not used up. After it is “used”, it transforms into another form – more precise into another chemical composition.

Phosphorus is an essential component for all living organisms and can be found in or is involved in the following processes (Marschner, 2012):

- nucleic acids (DNA), as carriers of the genetic information
- nucleic acids (RNA), responsible for the translation of the genetic information
- the metabolism of carbohydrates, fats and proteins

- as component in the biomembrane of plants (phospholipids)
- the intracellular power supplies (ADP/ATP)
- photosynthesis, carbohydrate and water balance
- improves the quality of fruit and vegetable crops

If phosphorus is deficient, leaf area is reduced and the leaves become rigid. This might be attributed to a changed carbohydrate conversion rate and a change in the size of cells and vacuoles. The leaves have a dark green color, as chlorophyll production is not reduced as much as leaf area. This coloration is additionally intensified by the accumulation of anthocyanins, which are built as a reaction of a decreasing pH in the cell. These anthocyanins have reddish to purple color in the then acidic vacuole sap. Further, some cells die off and the generative phase of the plant (blossom, seed) is delayed or diminished. Phosphorous deficient plants are smaller as root growth and tillering are reduced. Plants increase the root to shoot ratio or substitute phospholipids by glycolipids in order to increase the phosphorus availability for other processes in the plant. To prevent phosphorus deficiency, plants can store excess phosphorus as phytate (Amberger, 1984) and as inorganic polyphosphates in the vacuoles (Seufferheld and Curzi, 2010).

Phosphorus plant uptake is limited to

1. the direct plant available form as dissolved orthophosphate $H_2PO_4^-$ and HPO_4^{2-}
2. the labile form which is plant available after dissolving (P-fraction sorbed to iron or aluminum oxides or hydroxides and clay minerals; different forms of phosphates like ammonium phosphate, sodium phosphate; organic bound phosphates which are easily mineralized)
3. stable non-water soluble compounds which are hardly plant available (e.g. phytates)

The available phosphate (P) form and the concentration depend mainly on soil pH and, to a smaller extent, on temperature and soil structure. Higher pH values favor the adsorption to clay-humus complexes whereas lower ones favor nutrient leaching. P availability is reduced with increasing soil acidification ($pH < 5.5$) as the affinity of P adsorbing to aluminum and iron oxides or hydroxides increases

(Barekzai, 1984; Welp et al., 1983). In the presence of $CaCO_3$, i.e. under alkaline conditions (pH > 7), hardly soluble Ca phosphates are formed.

1.2 Phosphate resources, world trade and expected life span

Currently, the main proportion of the world's rock phosphate is used for fertilizer production and exploited through mining of phosphate ores. Rock phosphate is the raw material used for manufacturing most of the commercial P fertilizers. Processing of rock phosphate refers to the separation of P from the mix of clay, sand and phosphates. According to Gethke-Albinus (2012) and Elsner (2008), there are three types of deposits as P sources: marine-sedimentary phosphorite (rock phosphate) deposit, magmatogenous apatite deposits and guano deposits. Rock phosphate deposits developed mainly due to chemical-biological precipitation of phosphates when cold, phosphate-rich water met warm phosphate-poor water near the equator and settled at the bottom of ancient seas. Preferred areas can be found around the 40th latitude in USA, Morocco, Algeria, Tunisia and Kazakhstan. Magmatogenous apatite deposits consist mainly of apatite ores, which are part of nearly all magmatic rocks and can be found in South Africa and Sweden. Guano deposits are formed through the accumulation of bird feces on oceanic islands and through bat feces in caves (islands in Southern Pacific and Indian Ocean). However, these deposits are now almost exploited (Gethke-Albinus, 2012; Elsner, 2008).

Big economies like Japan, India or the European Union do not have their own, domestic supply of phosphates. They are highly dependent on P imports from the five main producing countries that control about 90% of the world's P reserves (China, USA, Russia and Morocco, which also controls the reserves of Western Sahara) (Ott and Rechberger, 2012). Further, smaller reservoirs can be found in Brazil, South Africa and Israel (Elsner, 2008). Worldwide annual mining of rock phosphates shares between China with 29%, USA 19%, Morocco 17%, Russia 7%, Tunisia 5% and to a smaller percentage by Brazil, Jordan, Syria and South Africa (Elsner, 2008).

The two terms P resource and P reservoir must be distinguished clearly. A resource is an economically mineable P source whereas a reservoir is not. Mined rock phosphate is a non-renewable, or better, finite resource and, depending on the calculations and the actual rate of exploitation, this resource will be depleted within 50 - 150 years if no other easily accessible P resources are identified or new mining technologies are developed (Isherwood, 2000; Steen, 1998). According to calculations from 2007, the world P resources, mineable below 40$ t^{-1} P_2O_5 (the actual level for economic benefit), were 18 billion tons. The P pool was, in 2007, expected to be 50 billion tons. Out of the 18 billion tons, 156 million tons were mined, so statistically P will be depleted within 115 years (Elsner, 2008). The discrepancy between the different depletion times is influenced by the estimation of the available P resources (Gethke-Albinus, 2012). Recalculations with a P pool of 50 billion t^{-1} P_2O_5, instead of 18 billion t^{-1} almost tripled the depletion time to 321 years. The depletion time for China's reservoir was estimated to be around 145 years (Gethke-Albinus, 2012). The quality of the mined product plays also an important role. Newly discovered rock phosphate deposits are more contaminated with cadmium and uranium (van Kauwenbergh, 1997). In order to avoid soil contamination, these products would require an expensive decadmiation process and further high costs for the removal of uranium.

1.3 Fertilizer consumption

Worldwide, the overall fertilizer consumption is still increasing. The invention of the Haber-Bosch process in the early 20th century led to a generous application of N fertilizers on soils during industrialization in Europe. This led, together with an intensified animal husbandry, to high P stocks on arable land in certain regions. Nowadays, these soils need P application only to substitute the losses, which occur through the harvested produce and leaching (the latter being in general rather low (below 1 kg $ha^{-1} \cdot a^{-1}$)). Therefore, in the late 1990s, the demand for P fertilizer application decreased and the developed countries cut down drastically their fertilizer consumption, reaching now a much lower level than before (Cordell et al., 2009). Thus, fertilizer consumption is reduced in developed countries whereas on the other hand, mainly in developing countries and emerging nations soils are poor in nutrients and thus the fertilizer consumption is still increasing. Elsner (2008) adapted data from the IFA (International Fertilizer Industry Association) and depicted an increase in the overall fertilizer consumption from 1960 to 2005 worldwide from 35 million tons (30 million tons in developed countries, 5 million tons in developing countries) to 155 million tons (105 million tons in developing countries and 50 million tons in developed countries). The overall fertilizer consumption (155.4 million tons) in 2006 was distributed on the three main nutrients as follows:

25.8 million tons K_2O, 36.4 million tons P_2O_5, 93.2 million tons N

The main fertilizer consuming countries are shown in Fig. II-1 with the biggest share of fertilizers used in China (29.7%).

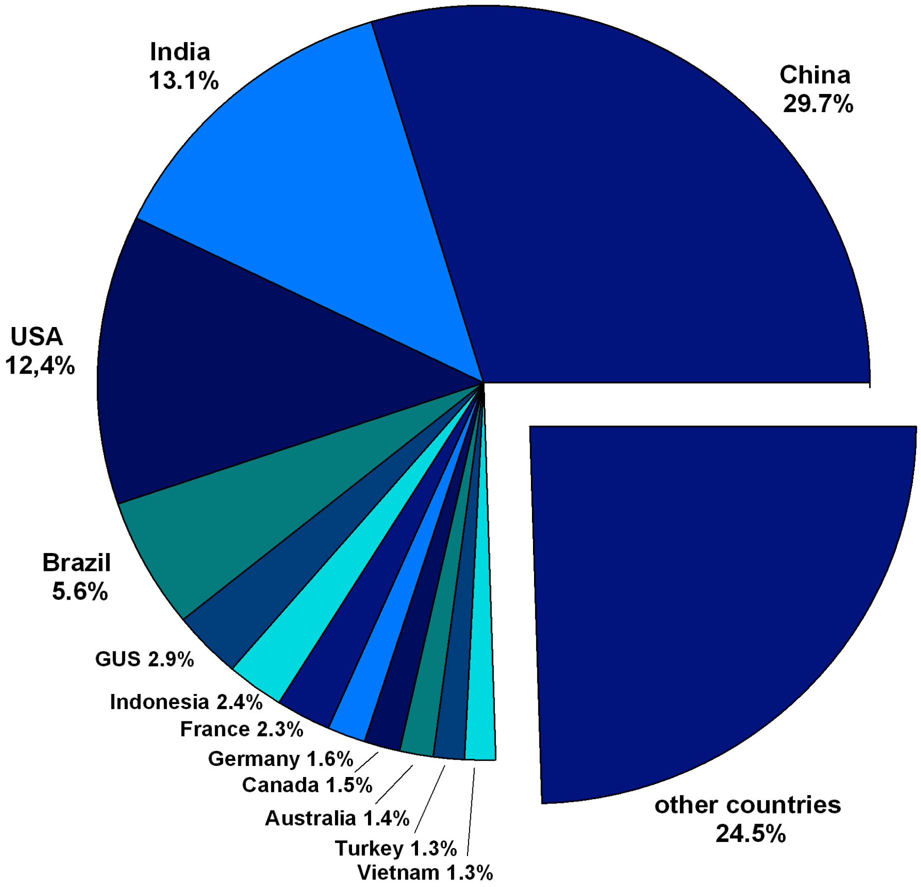


Fig. II-1: Fertilizer consumption worldwide (in %)

1.4 Phosphorus consumption in China

Industrialization and higher income came along with a change in living standards and an altered consumption behavior of the Chinese population towards a growing demand for protein rich food, i.e. meat, grains and corn for daily consumption. This led to pressure on the farmer’s production and thus an adoption of well-established foreign technologies for crop growth and fertilization and the import of genetic material from animals from USA as breeding stock. One of the main input factors for crop growth is phosphate fertilizer. According to Industrial Minerals, the price for phosphate ore increased from January 2012 to May 2012 by ten percent to US$ 98.40 t^{-1} (Industrial Minerals, 2012). Further, rock phosphate production in the country increased dramatically over the last years, starting with 30 million tons in 2000 to expected 80 million tons in 2011. Simultaneously to the increased production, the quality of the processed rock phosphate increased and shifted from lower-grade single super phosphate to higher-level mono-ammonium phosphate (MAP) and di-ammonium phosphate (DAP) (Wellstead, 2012; Baker, 2012). Baker (2012) emphasizes an increase in the DAP exports from insignificant amounts in 2000 to 4 million tons in 2010. For this reason, China's Ministry of Commerce specified phosphate as the third most important national strategic resource, resulting in export quotas and a specially designed reserve system in the main phosphate producing provinces (Hubei, Hunan, Yunnan, Sichuan and Guizhou). The Ministry planned also to restrict the number of phosphate producers by closing pits mining less than 150.000 tons and limit mining rights to several years (Wellstead, 2012).

1.5 Concentration of population growth, animal production and nutrients

Data from the Chinese Statistical Yearbook, evaluated by Schuchardt et al. (2011), revealed that China's economy was growing steadily at an average growth rate of 9.5% over the period 1997 - 2009. This economic growth led to higher household income and was accompanied by an increasing consumption of animal products. Meat consumption increased rapidly from approximately 20 kg per person and year in 1985 to 53 kg in 2006 (Schuchardt et al., 2011). These results were emphasized by estimations from the Chinese butcher association in 2012 that pig meat consumption doubled within the last 16 years. This might, on the one hand, be explained by the increase in income and on the other hand by the Chinese culture as 70% or more of the consumed meat products were made of pork. Every year, 38 kg pork is consumed per person and year in China and the demand is steadily growing at a yearly rate of 4% - 7%. Consumption increased, compared to the year 2000, by 23% mainly due to the growing population and the ongoing urbanization, as meat consumption is higher for urban residents (McOrist et al., 2011).

In China, pigs are either produced on a small scale where farmers grow a few pigs in the backyard or in large commercial farms where the system is “farrow-to-finish”, meaning that the pigs are produced, raised, fed and sold in one farm (McOrist et al., 2011; Mendoza-Huaitalla et al., 2011). According to estimates from the Food and Agriculture Organization of the United Nations (FAO), the number of pigs raised in China between 2009 and 2010 ranged from 490 million to 618 million pigs (FAO, 2012).

The industrialized and specialized pig farms were often built in close proximity to (mega) cities in so called pig belts (Gerber et al., 2005) in order to avoid long distances for the transport of meat and meat products. However, this leads to a concentration of pig farms in the sub-urban area of cities. As a consequence of the ongoing urban expansion, the arable land available for direct land application of manure is delimited, leading, besides the odor and hygienic risk for the population, to severe nutrient surpluses. This concentration of pigs can be seen in Fig. II-2, where the study area (North China Plain, located in the eastern part of China), is highlighted. This area is commonly known as China’s granary and produces around 30% of the overall animal products whereas it make up only 3.3% of China’s total land area (Zhang et al., 2010).

Figures II-2 and II-3 show the maps of the estimated pig density (animals km^{-2}) and the human population (persons km^{-2}), with a darker reddish-brown color indicating a higher pig or human population density.

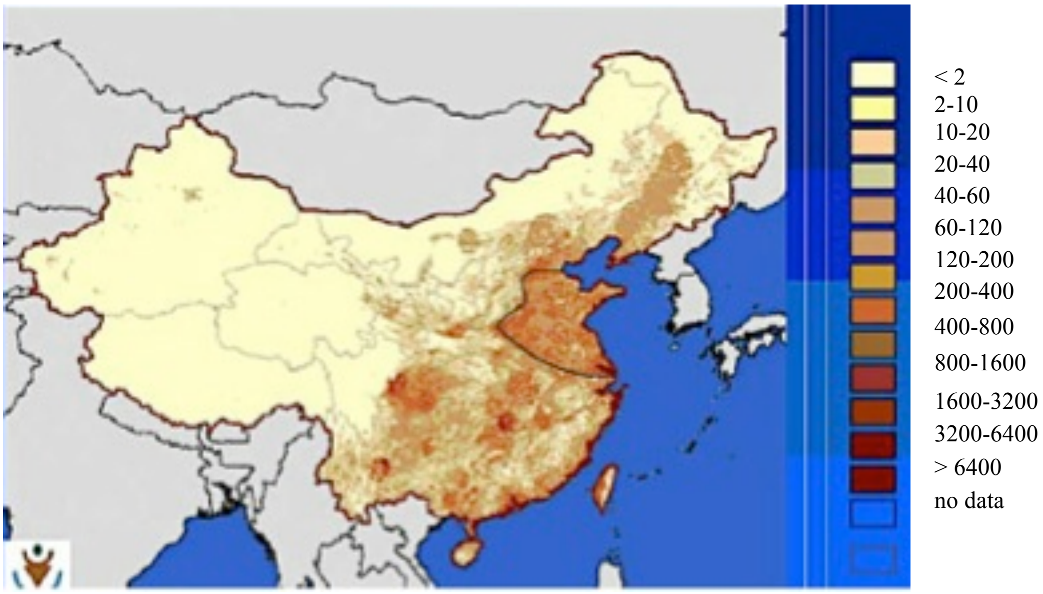


Fig. II-2: Estimated pig density in China (animals km^{-2}). The black encircled area highlights the North China Plain. (http://www.fao.org/DOCREP/005/AC801E/ac801e0d.jpg)

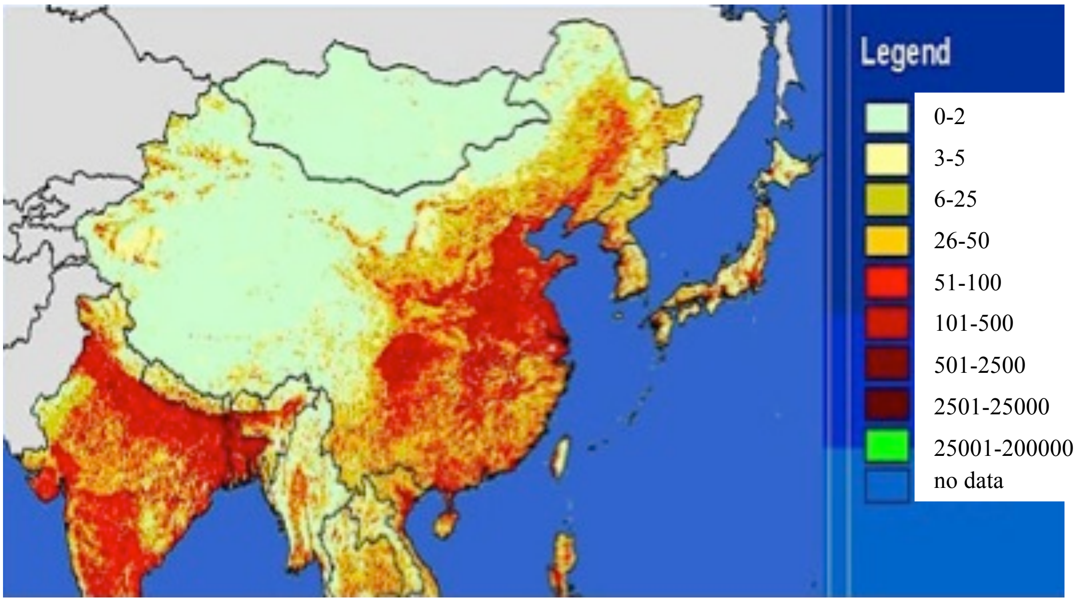


Fig. II-3: Estimated human population density in China (heads km^{-2}) (www.fao.org/DOCREP/005/AC801E/ac801e09.jpg)

By comparing the charts, it is obvious that high concentration levels are observed around urban centers (e.g. Chongqing in the center of China and Guangzhou in the South) and highly populated areas (e.g. coastal areas, Beijing, Shanghai). Low animal densities can be found in the less populated area in Western China (exception: the moderately populated Urumqi in the northwest). As the agricultural area for manure application is limited, nutrient imbalances are inevitable. The following maps illustrate the P_2O_5 mass balances (Fig. II-4) and the contribution of livestock to total P_2O_5 supply on agricultural land (Fig. II-5).

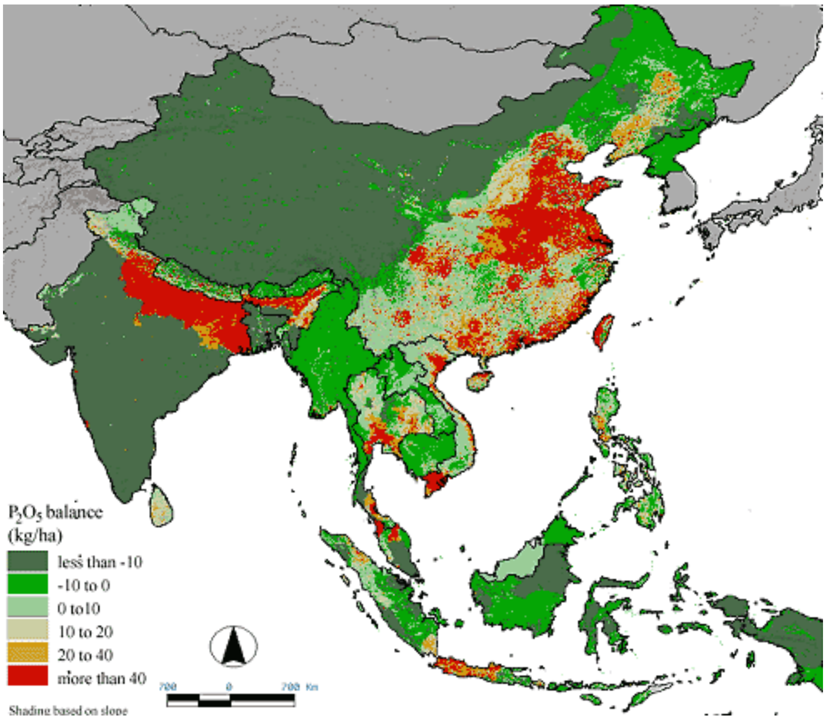


Fig. II-4: P_2O_5 mass balance (total quantity of P_2O_5 applied minus total P_2O_5 removed via the harvested crop) (Gerber et al., 2005).

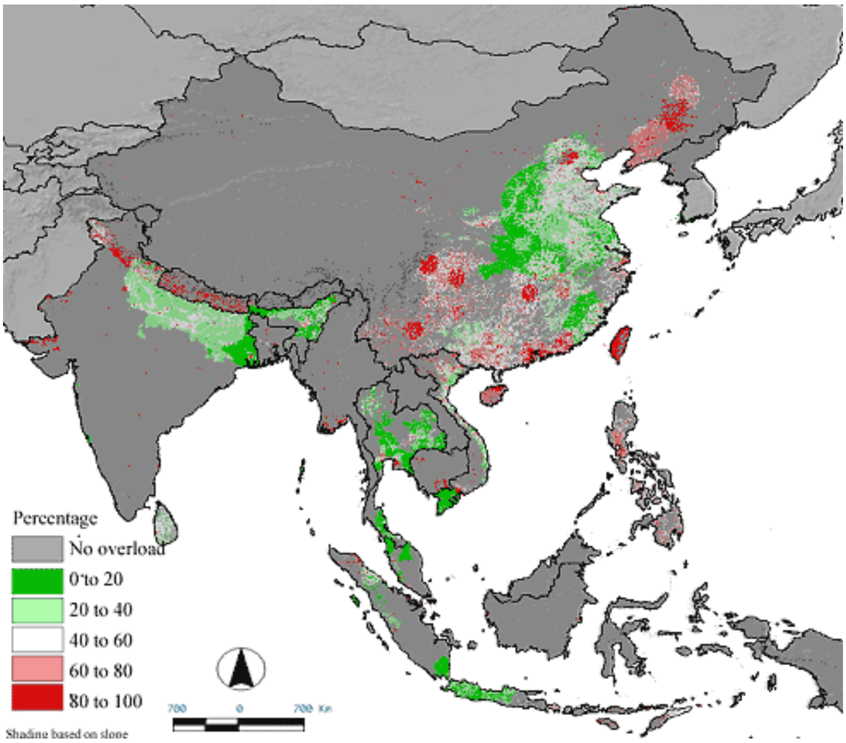


Fig. II-5: Estimated contribution of livestock (in %) to total P_2O_5 supply on agricultural land, in areas presenting a P_2O_5 overload (mass balance higher than +10 kg of P_2O_5 per hectare)(Gerber et al., 2005).

Fig. II-4 shows heterogeneity in the P_2O_5 balance within the country. Areas colored in green demonstrate a negative P_2O_5 balance and thus deficit as compared to the P_2O_5 input, revealing that more P_2O_5 was removed with the harvested crops than added by fertilization. In contrast, the areas colored in red show a high P_2O_5 surplus, indicating that more P_2O_5 was applied than removed. Gerber et al. (2005) characterized a mass balance lower than -10 kg of P_2O_5 per ha arable land as P_2O_5 deficient. In contrast to that, a mass balance higher than +10 kg of P_2O_5 per ha of arable land is characterized as P_2O_5 overload. Especially the areas in Western China, Tibet and Inner Mongolia show a negative P_2O_5 balance. These areas account for around 28.9% of the countries' cropped area (Zhang et al., 2010). The Chinese provinces in the northeast and south are estimated to have balanced P_2O_5 fluxes. In the North China Plain, as well as the coastal areas, a severe P_2O_5 overload can be observed.

The impact of livestock on the nutrient fluxes is illustrated in Fig. II-5, where the application of P_2O_5 excreted by livestock is compared with the application of P_2O_5 from chemical fertilizers. Gerber et al. (2005) compared therefore data for territories with an overload of more than 10 kg of P_2O_5 per ha of agricultural land. In eastern China (Jiangsu, Anhui and Henan provinces), where rice is the dominant crop, the bulk of the P_2O_5 load is represented by chemical fertilizers. In northeastern and southeastern China (Liaoning, Jilin, Sichuan, Hubei, Fujian and Guangdong provinces) manure represents more than half of the P_2O_5 surplus. Further, livestock excretion accounts for around 40% of the P_2O_5 load and peaks around urban centers where animal husbandry is located (Gerber et al., 2005).

2. Theoretical background

2.1 Strategies to avoid nutrient overload

Growing concerns on land use and thereby associated soil and water quality claimed for regulations limiting the amount of manure spread on the fields dependent on the crops' nutrient requirements (Shober and Sims, 2003). However, an increased pig production coincides with an increased quantity of wastewater loaded with nutrients and organic matter, which thus requires huge storage capacities. A solution could be the transport of animal wastes from areas with high livestock density and thus a nutrient surplus to those with nutrient deficiencies (Bonmatí and Flotats, 2003b; Bateman et al., 2011) i.e. from the huge animal production areas in sub-urban Beijing and other megacities to areas lacking nutrients like Western China. The dewatering of manure or digestate is an essential step for a better storage and an economically feasible transport. With a mechanical dewatering step using centrifuges or gravity belt, 20% - 30% of the solids (Bateman et al., 2011), which contain the majority of the phosphorus, can be removed. However, the resulting solid still contains 70% - 80% water and is bulky, requiring well-elaborated logistics for cost-effective routes for manure distribution. The further treatment of animal wastewater to extract phosphorus in a solid, mineral form could help to close the phosphate loop and make the long distance transport economically feasible.

An expected world population growth, mainly in Asia and Africa, from 6.5 billion in 2005 to 9.15 billion in 2050 (UN, 2009) accompanied by a higher income, will further increase the pressure on food production. Developing countries have an enormous potential to increase their yields by using appropriate technologies where the access to mineral fertilizers plays a key role (Tilman et al., 2002). However, without an appropriate management, this additional livestock and crop production will increase the negative impacts on agricultural land and water bodies worldwide.

Excessive nutrient concentrations in wastewaters pose a threat to the environment and may cause environmental damage with surface water pollution (e.g. algae growth, eutrophication), groundwater pollution (e.g. nitrates in groundwater) and soil pollution (e.g. leaching) (von Münch et al., 2001). This requires, against the background of non-renewable P resources, a good management of the already existing agricultural nutrient cycle. Further, an alternative way for P production, where recovery of phosphates gained from industrial and animal wastewaters may become an important (secondary) resource. The removal of phosphates from wastewater can reduce the nutrient load on agricultural fields in areas with high animal density and diminish the eutrophication problems in adjacent (surface) water bodies (Laridi et al., 2005).

2.2 Precipitation processes

Phosphorus can either be precipitated spontaneously (van der Houwen and Valsami-Jones, 2001) or be converted into a solid fraction (e.g. insoluble salt precipitates, plant biomass in constructed wetlands, or microbial mass in activated sludge (de-Bashan and Bashan, 2004)). In these just now mentioned cases, phosphorus is not recycled as a sustainable product but is rather gained together with a mixture of different other waste products of which some are toxic. Nowadays, P is removed from wastewater effluents mainly through chemical precipitation using aluminum, iron salts or lime (de-Bashan and Bashan, 2004) and fewer through biological removal e.g. by cultivation of microorganisms in wastewater. However, the use of aluminum or iron as precipitation source focuses only on the removal and not on the recovery of P from wastewaters.

The spontaneous formation and precipitation of phosphate salts in nutrient-rich wastewaters and sludge treatment plants, mainly in the form of magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4 \times 6\ H_2O$), MAP or struvite, was first observed by Rawn et al. (1939). The free, predominant ions (Mg^{2+}, NH_4^+ and PO_4^{3-}) precipitate spontaneously and minimize the need for the addition of chemicals to remove P from wastewater (Battistoni et al., 1997). Since the first discovery of struvite, various reports were published on mineral deposits associated with clogging of pipes and pumps in wastewater treatment plants (Doyle et al., 2002). The impact of uncontrolled struvite formation resulted in the need of e.g. manual removal of scale from pumps or the partially renewal of the pipework. Operators try to avoid or at least mitigate struvite formation by flushing the system with acid solutions in order to remove the clogging or by adding metal salts to reduce the precipitation potential of struvite. The annual costs for a mid-size treatment plant caused by struvite deposits may rise above US$ 100.000 (Doyle et al., 2002).

In general, wastewaters tend to have high ammonium concentrations whereas magnesium is deficient and has thus to be added to force struvite formation (Doyle et al., 2002). In wastewater, P is also present in excess of plant needs and thus precipitation processes can reduce the amount of leaching P and N compounds, leaving a nutrient-low fertigation (fertilization and irrigation) wastewater. By using struvite precipitation, the effect on the net content of N will be small but the impact on P in the wastewater will be big (de-Bashan and Bashan, 2004). The phosphate and ammonium concentrations are high in swine wastewater and form, in the presence of a high magnesium concentration or after the addition, struvite (Suzuki et al., 2007; Nelson et al., 2003). However, struvite precipitation on single farm scale is not viable (Zhao et al., 2010) as for example for dairy manure an expensive chelating agent had to be added in order to release phosphorus from calcium compounds. Therefore, the transport of animal wastewaters to regional struvite processing facilities could be a solution to increase phosphorus recovery while environmental and economic impacts are minimized (Bateman et al., 2011).

Struvite can be used in the fertilizer industry (Gaterell et al., 2000) and is a slow-release fertilizer (Zhang et al., 2010) comparable to superphosphate and is suitable for ornamentals, vegetables, orchard trees and potted plants. It showed excellent fertilizer qualities in controlled greenhouse experiments (Doyle et al., 2002). Further, these fertilizers have low leaching rates and release the nutrients slowly during the growing period (von Münch et al., 2001). Previous studies have also shown that struvite is approximately equal or even surpasses mono-calcium phosphate and di-calcium phosphate in efficiency (Barak and Stafford, 2006). The use of struvite is also economical as the struvite crystals can be recycled using final oxidation, resulting in $Mg_3(PO_4)_2$ (Stefanowicz et al., 1992).

A further major process and common method for P precipitation with recovery and recycling of the obtained product is the calcium-phosphate precipitation. Hydroxyapatite ($Ca_5(PO_4)_3OH$) is precipitated by adding calcite ($CaCO_3$) or calcium silicate hydrate (CaO-SiO_2-H_2O). This technique is widely used due to the simple handling and the low costs. Struvite crystallization is mainly adopted in nutrient rich wastewaters like effluents from animal production plants (piggeries, poultry, feedlots and aquaculture), domestic wastewater plants with anaerobic digesters (as these waste side-streams are high in nitrogen and phosphorus) and fertilizer production plants (von Münch et al., 2001). Adding $Mg(OH)_2$ to an anaerobic sludge digester resulted in a higher biogas production, a larger decrease in suspended solids and a lower concentration of ammonia and phosphate (de-Bashan and Bashan, 2004). Further, the pH of the wastewater influences phosphate precipitation as well as the concentrations of phosphate and magnesium, the ionic strength and the impurities of the solution.

The most significant solid form of P in slurry is struvite (Ohlinger et al., 2000). Hydroxyapatite ($Ca_5(PO_4)_3OH$) is not as much favored for P removal from wastewater and slurry as much calcium precipitated already as $CaCO_3$ (Hjorth et al., 2010). Bril and Salomons (1990) observed a difference between dissolved Mg and total Mg with traditional extraction and measuring techniques, as a major fraction of the Mg^{2+} ions is prone to form complexes with dissolved organic matter.

2.3 The effect of anaerobic digestion on pig slurry and precipitation characteristics

As described above, an increasing demand as well as good sales profits for pig meat leads to farms with thousands of pigs in China. As herds are increasing, the quantity of wastewater with nutrients and organic matter is also increasing, exceeding the capacity for direct land disposal. In order to avoid severe environmental impacts, the wastewater has to be treated. This treatment needs to cope with large quantities of liquids, residues and solids and a commonly used system for animal wastewater treatment is anaerobic digestion.

The biogas process will positively affect slurry characteristics, which thus favor struvite precipitation in digestate (Möller and Müller, 2012; Voća et al., 2005). During anaerobic digestion, the pH, which is mainly controlled by the equilibria $CO_2 \leftrightarrow HCO_3^- \leftrightarrow CO_3^{2-}$, $NH_4^+ \leftrightarrow NH_3$ and $CH_3COOH \leftrightarrow CH_3COO^-$ (Sommer and Husted, 1995), increases. This is attributed to the formation of ammonium carbonate ($(NH_4)_2CO_3$) and the removal of CO_2 as a result of the transformation of CO_3^{2-} and 2 H^+ to CO_2 and H_2O (Möller and Müller, 2012). pH is also increased by the addition of Fe^{III}-ions in order to remove hydrogen sulfide (H_2S) as well as due to the mineralization and reduction of multivalent ions (e.g. SO_4^{2-}, $Fe^{III}(OH)_3$) (Hjort et al., 2010). At the same time, digestate pH decreases due to the precipitation of carbonates ($CaCO_3$) (Hjorth et al., 2010) and Fe^{2+} phosphates, releasing protons ($3\ Fe^{2+} + 2\ HPO_4^{2-} \leftrightarrow Fe_3(PO_4)_2 + 2\ H^+$). Further, the reaction between the struvite forming ions (Mg^{2+} + NH_4^+ + HPO_4^{2-}) cause the release of H^+ ions in the solution and thus also a decrease in digestate pH.

Anaerobic digestion decreases the amount of volatile fatty acids, thus reducing the corrosive effect on plants and the odor. However, a higher pH enhances the risk of ammonia volatilization. Decomposing the organic matter decreases the viscosity and thus increases the flow characteristics, which thus leads to a faster infiltration in soil. Digestates often have a higher nutrient concentration as the undigested slurry.

2.4 Orthophosphate determination methods

In literature, orthophosphate (PO_4-P) determination is carried out according to two different methods. One is the molybdenum-blue method (Fiske and Subbarow, 1925), where the analysis is based on the photometric measurement of the product phosphomolybdenum blue formed during the reduction of phosphomolybdate. Adding ascorbic acid to the coloring solution refined the method as therewith the color formation phase was reduced (Murphy and Riley, 1962). Further, the presence of ions like iron, copper, silicate and arsenate did almost not interfere when phosphate was determined in seawater (Murphy and Riley, 1962). However, Stanton (1968) observed in his experiments that the presence of biological material and adenosine triphosphate in the sample interfered with the development of the blue color. The second commonly used and described method for phosphate determination is the monovanadate method, where orthophosphate ions build together with ammonium vanadate and ammonium heptamolybdate an orange-yellow colored molybdatovanadatophosphoric acid, which is analyzed photometrical, too.

Kaylor (1971) compared three methods for phosphate determination in solid wastes: original molybdenum-blue method based on Fiske and Subbarow (1925), molybdenum-blue method based on the variation of Murphy and Riley (1962) by adding additional ascorbic acid and the monovanadate-yellow method. Most of the solid waste samples used by Kaylor (1971) were either incinerated or digested with HNO_3 and H_2SO_4 before phosphate was determined. Further, the author used also liquid quench water samples, which were digested and filtered before phosphate determination. The monovanadate-yellow method was the most suitable method for the incinerated and digested samples as it was simple, free from interferences and, as phosphate concentrations are much higher in solid wastes, it could be used without large dilution (Kaylor, 1971).

The reduced phosphomolybdenum-blue is measured at about 815 nm, whereas the monovanadate-yellow method requires shorter wavelength (350 nm). This can be disadvantageous as the presence of finely dispersed particles increases the optical density of the solution due to the scattering of light (Stanton, 1968). According to the Rayleigh scattering law, the intensity of scattered lights is proportional to the reciprocal fourth power of the wavelength for colloidal particles, whose dimensions are an order of magnitude smaller than the wavelength of light. For this reason and to avoid any significant contribution of turbidity, the author recommended the use of long wavelength. Additionally, the probability of an interference by optical absorption due to electronic transition of substances present in the biological material is higher, the shorter the wavelength (Stanton, 1968).

2.5 Thermodynamic calculations

Chemical reactions follow the laws of thermodynamics, which describe the correlation between different forms of energy in a chemical reaction. Struvite formation is dependent on the concentration of Mg^{2+}, NH_4^+ and PO_4^{3-} and the solubility of these ions in (animal) wastewaters as the ions react in a molar ratio of 1:1:1 to form struvite.

A solution always tries to stay in equilibrium with the solutes. If a solution is overbalanced, the solution returns to the equilibrium state by precipitation of the excess solute. Supersaturation is a measure of this deviation. The product of the ion concentrations in the solution is called ion product or, in the context of struvite precipitation, sometimes described as saturation index (SI). The SI is a good measure to judge supersaturation with respect to the precipitate phase (Song et al., 2002a). The solution is in equilibrium when $SI = 0$. For an undersaturated solution no crystallization occurs as $SI < 0$. When $SI > 0$, the solution is supersaturated and precipitation occurs spontaneously.

The equilibrium ion-activity product (IAP_{eq}) is calculated according to equation II-1:

$$IAP_{eq} = (Mg^{2+})(NH_4^+)(PO_4^{3-}) = 7.08 \times 10^{-14} \qquad \text{(Eq. II-1)}$$

Thus, in a given solution, struvite precipitation is likely to occur if the product of Mg^{2+}, NH_4^+ and PO_4^{3-} activities (IAP) exceeds the IAP_{eq}. In the context of struvite crystallization, values of pK, the equilibrium constant, are published, ranging from pK = 12.06 to pK = 13.15 (Taylor et al., 1963; Buchanan et al., 1994; Hjorth et al., 2010). Bhuiyan et al. (2007) determined the solubility of struvite in deionized water, resulting in 169.2 mg L^{-1} at 25°C and a maximum solubility of 212.7 mg L^{-1} at 35°C.

In a supersaturated solution, the spontaneous precipitation does not automatically start fast. Song et al. (2002a) and Stumm and Morgan (1996) observed a metastable zone between the undersaturated zone and the spontaneous precipitation zone where no precipitation occurs over a long time although the solution is already supersaturated. This intermediate zone can be called critical supersaturation (Joko, 1984).

2.6 Influence of pH on chemical equilibria

Swine wastewater pH plays an important role in struvite precipitation. Although the concentration of H^+ does not directly enter equation II-1, the activities of NH_4^+ (see also III Nitrogen recovery, chapter 2.3) and PO_4^{3-} are highly pH dependent, and thus influence their availability for struvite precipitation. An increased pH shifts the chemical equilibrium from HPO_4^{2-} towards the formation of PO_4^{3-} i.e. an increase in pH from 7 to 9 decreases the total ammoniacal N, present as NH_4^+, from 99% to 64%, whereas the fraction of total PO_4-P present as PO_4^{3-} increases 250 fold (Stumm and Morgan, 1970). This huge increase in the proportion of total PO_4-P, present as PO_4^{3-}, shows a bigger influence of pH on the activity of PO_4^{3-} than on the activity of NH_4^+ when raising the pH from 7 to 9. The better availability of PO_4^{3-} at higher pH values and the anyway high NH_4^+ concentration cause then a spontaneous precipitation of calcium (e.g. $Ca_3(PO_4)_2$) or magnesium phosphates (e.g. struvite) (Hjorth et al., 2010; Möller and Müller, 2012).

Another important equilibria reaction is described in equations II-2 and II-3:

$$H^+ + CO_3^{2-} \leftrightarrow HCO_3^- \tag{Eq. II-2}$$

$$HCO_3^- + H^+ \leftrightarrow CO_2 + H_2O \tag{Eq. II-3}$$

The transformation of CO_3^{2-} and 2 H^+ to CO_2 and H_2O increases the pH by decreasing the concentration of free H^+.

2.7 N:P ratios of slurry and digestate and plant requirements

The available N:P ratio of swine lagoon liquid ranges between 2:1 and 4:1. The N:P ratio of the receiving crops range between 4:1 to 9:1. When using this liquid manure as fertilizer and the attempt to meet the N requirements of the crops will lead to a two to three fold oversupply of P. The resulting excessive application of P on agricultural land will thus increase the risk of leaching to nearby surface waters and contribute to eutrophication (Nelson et al., 2003). For digestate, Makádi et al. (2012) confirmed this with N:P ratios of 3:1 for digested swine manure and 6:1 for liquid cattle slurry. An increased N:P ratio of 15:1 when using food waste as substrate for the biogas plant and 16:1 when using livestock slurries was described by WRAP (2011).

Based on this knowledge the following hypotheses were developed:

I. **Phosphate in pig slurry from the experimental plant in China can be removed efficiently by struvite precipitation.**

II. **There is a (significant) difference in struvite precipitation between slurry and digestate, as conditions in digestate favor precipitation.**

III. **Struvite precipitation is influenced by slurry/digestate characteristics and components.**

3. Materials and Methods

3.1 Sampling site China

The pilot pig farm is situated in the sub-urban area of Beijing in *Shunyi District*, around 30 km northeast the city center of Beijing, Peoples Republic of China. The average altitude is 35 m, mean annual precipitation 622 mm and mean annual temperature 11.5 °C. In the north, *Shunyi District* borders on the Yan Mountains, in the south on the North China Plain. In 2008, total area of *Shunyi District* was 1.021 km^2 with a population of 732.000 inhabitants. There are 12 towns, 7 regional offices, 2 subdistrict offices, 428 natural villages and 27 neighborhood committees (Kamphuis et al., 2004) in *Shunyi District*. On the pilot pig farm, the permanent stock (including piglets, sows, breeding and fattening pigs) is around 8.000 pigs with a daily slurry production of 400 m^3 (summer), resp. 100 m^3 (winter) and a feces production of roughly 3 m^3 - 4 m^3 per day. Slurry production varies during seasons as manure is collected according to the “gan qing fen” (cleaning the manure dryly) method, where solid feces are separated manually from the liquid phase. This liquid phase slurry consists of a mixture of pig urine, some feed and fecal particles and high amounts of (washing) water. In summer, the overall slurry amount is considerably higher as washing water is also used for cooling the pigs and stables. This resulting washing water is low in organic matter but moderately high in nutrients as a high proportion of the P can be found in the excrements.

Once leaving the pig houses, the slurry is collected in an open storage pond and flows afterwards into the biogas plant for anaerobic treatment. There are 3 biogas plants on the farm, whereas plant 1 and 2 run simultaneously to digest the slurry. Management and hydraulic residence time in these 2 plants during the research periods in 2010 - 2011 were as follows: plant 1: 25 days and plant 2: 35 days. After anaerobic digestion, the effluents of both plants were mixed with small quantities of undigested pig slurry and transferred into biogas plant 3 for further digestion with a retention time of 5 days. In summer 2011, each plant was fed 10 times (in total 2 - 3 t) per month with slurry and additional solid feces to increase gas production. In winter, when the villagers used more gas, feces were added in higher amounts and more frequently to increase gas production. Total gas production was 500 m^3 per day. The addition of feces was regulated dependent on the gas consumption of the around 500 households (1.300 habitants) in the village neighboring the farm. The per capita consumption of each household is 1 m^3 gas per day and basically used for cooking. In summer, the surplus feces were composted in a composting plant nearby in order to produce fertilizer. In winter, the amount of feces produced on the farm was too low for a sufficient gas production. Therefore, the farm management had to buy manure from outside.

3.2 Sampling

During the three research periods in Beijing (March - May 2010, March - May 2011 and September - December 2011) samples of untreated as well as anaerobically digested pig slurry were taken at the pilot pig farm. Pig slurry samples from raw, undigested material were taken before feeding into the biogas plant. Digestate samples were taken from the 3 different biogas plants described above. Another sample was taken from the effluent, which was digested, afterwards aerated and left the farm for further storage in an open lagoon. Each sample was filled in 25 L plastic cans. The cans were stored in darkness at room temperature. Before taking slurry samples for the experiments, the cans were shaken in order to homogenize the material thoroughly. After sampling, the basic slurry parameters like pH, orthophosphate (PO_4-P), ammonium nitrogen (NH_4-N) concentration and dry matter (DM) content were analyzed and phosphate removal experiments were carried out in the laboratory at the College of Engineering at China Agricultural University, Beijing. As the research periods in Beijing were limited, slurry samples of each stay were transported to Germany in 0.5 L polyethylene terephthalate (PET) bottles in the cargo compartment of the airplane. Further experiments were then carried out at the "Institute for Crop Science and Resource Conservation", INRES, Division Plant Nutrition, Bonn University.

In general, the biogas effluent contained around 100 g L^{-1} ammonium nitrogen (NH_4-N), between 35 - 45 mg L^{-1} PO_4-P, 130 - 150 mg L^{-1} of total phosphorous (P_t) with a pH of 7 for untreated material and pH 7.5 - 8 for digestate.

3.3 Phosphate precipitation experiments

3.3.1 Material used for experiments

Precipitation experiments were carried out in 50 ml polypropylene centrifuge tubes (Carl Roth, Karlsruhe, Germany). The centrifuge tubes were filled with 25 ml of slurry. Experiments with bigger volumes were carried out in 500 ml or 1 L glass bottles (HXBL, China) with screw caps.

Centrifugation experiments were carried out using a Beckman centrifuge (Beckman J2-21, Krefeld, Germany) and a JA-14 rotor at 14.000 rpm (creating ≈ 30.000 g). Centrifuge bottles (NALGENE, PPCO) had a capacity of 250 ml.

Ultracentrifugation experiments were carried out in polycarbonate centrifuge bottles (Beckman, Palo Alto, California) with a capacity of 70 ml (38x102mm) in a Beckman ultracentrifuge (Beckman L7–55, Krefeld, Germany). Rotor used was a Ti 45 with 40.000 rpm, creating r_{av} 125.000 g, r_{min} 65.000 g and r_{max} 185.000 g.

3.3.2 Phosphate determination

The measured P-fraction in the untreated as well as anaerobically treated slurry is the solute-dissolved PO_4-P in the liquid phase. For the determination of dissolved PO_4-P there are two methods available:

- monovanadate-yellow method
- molybdenum-blue method

3.3.2.1 Monovanadate-yellow method

A „ready-to-use“ test kit from Merck (Spectroquant Phosphat-Test, 1 - 30 mg L^{-1} PO_4-P, Darmstadt, Germany) was used to measure the samples with the monovanadate method. In a sulfuric solution, orthophosphate ions build together with ammonium vanadate and ammonium heptamolybdat an orange-yellow colored molybdatovanadatophosphoric acid, which is analyzed photometrically.

The reaction is as follows:

$$H_3PO_4 + 6\,Mo\,(VI) \leftrightarrow (12 - MPA) + \ 9\,H^+ \qquad \text{(Eq. II-4)}$$

For the measurement, 5 ml of the prepared sample and afterwards 1.2 ml of the test reagent was pipetted in a test tube and shaken manually until it was mixed thoroughly. Afterwards it was transferred into a rectangular shaped cuvette (Hellma Präzisionsküvetten, 6030-0G, 10 mm) and measured photometrically at 410 nm (WTW, PhotoLab S12, Weilheim, Germany).

3.3.2.2 Molybdenum-blue method

The formation of molybdo-phosphoric acid and reduction in the presence of antimony by either ascorbic acid (in my experiments) or stannous chloride to the intensely colored molybdenum blue followed by colorimetric quantification is based on the method of Murphy and Riley (1962). A stock solution is mixed with ascorbic acid ($C_6H_8O_6$), acting as reducing agent, and then added to the sample where the orthophosphate ions form a complex with molybdenum, resulting in a bluish colored solution. The solution is measured photometrically at 578 nm (Eppendorf, ECOM 6122, Hamburg, Germany).

$$PO_4^{3-} + 12\, MoO_4^{2-} \rightarrow PMo_{12}O_{40}^{3-} + 12\, O^{2-} \overset{Sb}{\rightarrow} PSb_2Mo_{10}O_{40}^{3-} \qquad \text{(Eq. II-5)}$$

3.3.3 Addition of precipitating agent

All chemical reagents used were of analytical reagent grade. Water used in the experiments was ultrapure water. Phosphate precipitation was assessed in pig slurry and in anaerobically treated biogas effluents by using calcium oxide (CaO), magnesium chloride ($MgCl_2$), magnesium hydroxide ($Mg(OH_2)$) and magnesium oxide (MgO) as precipitating agents.

By adding a magnesium source ($MgCl_2$, $Mg(OH)_2$, MgO) the following struvite forming reaction is taking place:

$$Mg^{2+} + NH^{4+} + PO_4^{3-} \times 6\, H_2O \rightarrow MgNH_4PO_4 \times 6\, H_2O \qquad \text{(Eq. II-6)}$$

For the precipitation processes, measuring the PO_4-P concentration at the beginning of the experiments assessed the optimum ratios of free Mg- and Ca- ions. Magnesium and calcium powder was dosed in a molar Mg/Ca:P ratio of 1:1. Theoretically, all the solute inorganic P (P_i) present in the liquid could react with the

Mg^{2+}/Ca^{2+} and be precipitated. In order to find out whether there is a difference in precipitation behavior and velocity, the Mg:P ratio was raised to a slight surplus of 1.5:1 and 2:1. In a number of studies, I used excess Mg:P ratios of 5:1 and 10:1 but these experiments were not pursued further as the addition of such an excess of Mg is not economical. In some series, Mg^{2+} ions were added a second time in order to assess whether further P removal would be possible. All experiments were carried out with 2 replicates of the control sample and 3 replicates for the treated samples. pH value was adjusted using 1 M NaOH.

After determination of the initial, solute P_i concentration and the addition of the precipitating agent, centrifuge tubes were covered immediately to prevent ammonia losses. The centrifuge tubes were shaken manually to homogenize the sample, and thereafter shaken horizontally for 1 hour at 160 rpm - 175 rpm at 25 °C (GFL 3019, Burgwedel, Germany; Qilinbeier TS-1000 orbital shaker, China) to enhance chemical precipitation. Samples were subsequently incubated at room temperature for precipitation and struvite crystallization. The precipitates settled down at the bottom of the conical shaped centrifuge tube. After 17 hours, NH_4-N, PO_4-P and pH were determined from the supernatant of each sample in duplicates. Samples were taken from the supernatant 2 cm below the surface in order to avoid any disturbance and to reduce the risk of sucking slowly settling struvite crystals.

Final PO_4-P concentration (PO_4-P_f) was analyzed and removal efficiencies were calculated according to equation II-7 by the differences between initial concentration (c_i) and final concentration (c_f) divided by their respective initial concentration.

$$PO_4 - P_f = \frac{ci-cf}{ci} \qquad \text{(Eq. II-7)}$$

3.3.4 Ammonia determination

In China, ammonia was determined and reagents were prepared according to the “Chinese Standard Methodology Reference Book”. The samples were mixed with salicylic acid ($C_6H_4(OH)COOH$), sodium hypochlorite ($NaClO$), sodium hydroxide ($NaOH$), potassium sodium tartrate ($C_4H_4KNaO_6$) and nitroprussid ($Na_2[Fe(CN)_5NO]$ x 2 H_2O) and were shaken thoroughly until all components were dissolved. After a reaction time of 1 hour, the samples were transferred into a cuvette (10 mm) and analyzed photometrical at 697 nm (UV-VIS Spectrophotometer 756, Laipade Science Instruments, Shanghai, China).

3.4 Methods to remove organic matter and suspended solids in the samples

3.4.1 Centrifugation

In Germany, digestate samples (70 ml) produced at INRES, Plant Nutrition, Bonn, were treated in a Beckman centrifuge (2 h at 30.000 g). This treatment removed a great share of organic matter.

3.4.2 Ultracentrifugation

The samples used for the ultracentrifugation experiments (described in detail in chapter 4.5) differed in their dry matter (DM) contents with ≤ 1.5% DM in effluent 1 and 3.5% DM in effluent 2. Effluent 3 equals effluent 2 with 3.5% DM content, but it was treated additionally with hydrogen peroxide (H_2O_2) before centrifugation. After centrifugation, the digestate samples were treated at r_{av} 125.000 g for 2 hours in an ultracentrifuge to precipitate the smallest organic fractions and the suspended solids. Afterwards, samples for P_i determination were taken. Subsequently MgO was added and the samples were shaken for 1 hour.

The control samples did not receive MgO but were shaken simultaneously with the treated samples. Then, samples were incubated at room temperature for precipitation and forming of struvite. To assure that samples, taken after precipitation were free of slow-settling struvite crystals, the ultracentrifugation step was repeated after 17 hours and NH_4-N, PO_4-P and pH were determined in the supernatant of each sample in duplicates. In order to determine whether struvite precipitation is taking place when the already formed crystals were removed, precipitation was not disturbed for 24 hours. Afterwards, the samples were ultracentrifuged at r_{av} 125.000 g. Then, the same quantity of MgO in a molar Mg:P ratio of 1:1 was added to the samples and shaken for 1 hour. Again, 17 hours after the treatment, the samples were ultracentrifuged at r_{av} 125.000 g. The final PO_4-P concentration (PO_4-P_f) was calculated according to equation II-7.

3.4.3 Treatment with oxidizing agent (hydrogen peroxide)

A chemical measure for the removal of the organic fraction was the use of hydrogen peroxide (H_2O_2). H_2O_2 reduces the organic matter by breaking up the organic bonds by oxidation, thus releasing additional phosphate. H_2O_2 was added until the samples were more or less free of oxidizable organic material (100 ml biogas effluent treated with 185 ml H_2O_2).

3.5 pH determination

pH was measured using a pH meter (pH-100 ATC, Voltcraft, Hirschau, Germany). The electrode was calibrated with pH-buffer solutions 7.0 and 4.1 (Mettler-Toledo GmbH, Germany) before each measurement, in order to assure measurement accuracy.

3.6 Dry matter content (DM) / Organic dry matter content (ODM)

For determination of dry matter content, samples were dried at 105° C (cabinet dryer Heraeus instruments, helvitron®t) until constant weight was achieved.
DM was calculated according to equation II-8:

$$DM\ (\%) = \frac{m\ output\ weight\ (g)}{m\ initial\ weight\ (g)} \times 100 \qquad \text{(Eq. II-8)}$$

The organic dry matter (ODM) represents the organic fraction, which is degradable in the biogas process. For analysis, substrate was burnt in a muffle furnace (550° C, Carbolite AAF 1100) until constant weight was achieved. Calculation is based on the following equation:

$$ODM\ (\%) = \frac{m\ initial\ weight\ (g) - output\ weight\ (g)}{m\ initial\ weight\ (g)} \times 100 \qquad \text{(Eq. II-9)}$$

3.7 Standard addition

In the standard addition method, a standard P-solution with a known concentration of the analyte (here: 0, 0.1, 0.5, 1, 10, 20 mg P ml^{-1}) was added to the slurry samples, where the P_i-concentration was unknown. The calculation of the linear regression should generate a straight line equation $(y = m \times x + b)$ (Eq. II-10), where m is the slope and b is the intercept. The concentration of the analyte in the original sample can be calculated by determining the value of x, where the line crosses the x-axis and thus absorption is equal to zero. Solving the straight line equation for y = 0 yields in x = b/m. By using standard addition technique, mistakes emerging from measuring devices as well as from matrix effects (some sample components or impurities which can (re)act with the analyte or even produce an instrumental response) can be minimized. This technique was used to determine the most suitable method for PO_4-P determination in slurry.

3.8 Determination of total Kjeldahl nitrogen

For the measurement of total Kjeldahl nitrogen, 5 g of the slurry or digestate sample was weighed in a Kjeldahl tube. A pellet consisting of 5 g potassium sulfate (K_2SO_4), 0.15 g copper sulfate ($CuSO_4$) and 0.15 g titanium dioxide (TiO_2) was added to the sample. Afterwards, 10 ml sulfuric acid (H_2SO_4) was poured onto the sample. Chemical digestion was carried out in a Kjeldahl device (C. Gerhardt GmbH & Co KG, Vapodest, Germany). During digestion, organic components of the sample are removed and nitrogen is transferred to ammonium sulfate. By addition of 33% sodium hydroxide (NaOH) and 3% boric acid (H_3BO_3) ammonia (NH_3) is released from the solution, trapped in acid and can be determined titrimetrically. The amount is displayed as Kjeldahl nitrogen (TKN).

3.9 Digestate production in Germany

Pig manure from fattening pigs was collected at Frankenforst (experimental farm of the University of Bonn in Königswinter). With this raw material, biogas experiments with varying organic loading rates, temperatures and residence times were carried out in batch fermenters. The resulting anaerobically digested material was filled in

1 L plastic bottles and used for the precipitation experiments. Slurry samples were stored at +4°C.

3.10 Analysis of the nutrients

Precipitates were dried in a drying cabinet at 40°C - 50°C until constant weight was reached. Then samples were analyzed with an X-ray diffractometer at the Steinmann Institute for Geology at the University of Bonn. This method identifies the crystalline fraction of the mineral composition of a sample due to the scattering pattern of interacting X-rays. The mineral composition of the available quantity of the precipitate was analyzed and the distribution (in %) was estimated.

All precipitates obtained in China were collected and dried in a drying cabinet at 50°C for several days until constant weight was reached. Higher temperatures will lead to struvite instability and transform the product to dittmarite ($MgNH_4PO_4$ x H_2O) due to the evaporation of water. The samples were transferred back to Germany and decomposed by acid digestion with HNO_3. After filtration (Macherey-Nagel, ash-free filter, 640) the samples were analyzed on their nutrient contents by flame photometer (K and Ca) (ELEX 6361, Eppendorf, Germany) or atomic absorption spectrometer (Mg) (AAS, 1100B, Perkin Elmer, MA, USA). Phosphate was analyzed using the molybdenum-blue method.

3.11 Statistical evaluation

The statistical evaluation was carried out using IBM SPSS Statistics, version 21. In chapter 4.2, a one-way analysis of variance (ANOVA) was carried out in order to compare the significant effect of pH and the treatment (control or MgO addition) on the samples. Therefore, each pH was assigned a pH-code and the difference between the PO_4-P concentration before and after the treatment was calculated. Data was split to treatment; difference was set as dependent variable and factor was pH-code. Level of significance was $\alpha = 0.05$.

In order to statistically evaluate the effect of the MgO-treatment, control and treated samples were compared with an independent samples t-Test. The data was split to pH-code. The samples were assigned a treatment code

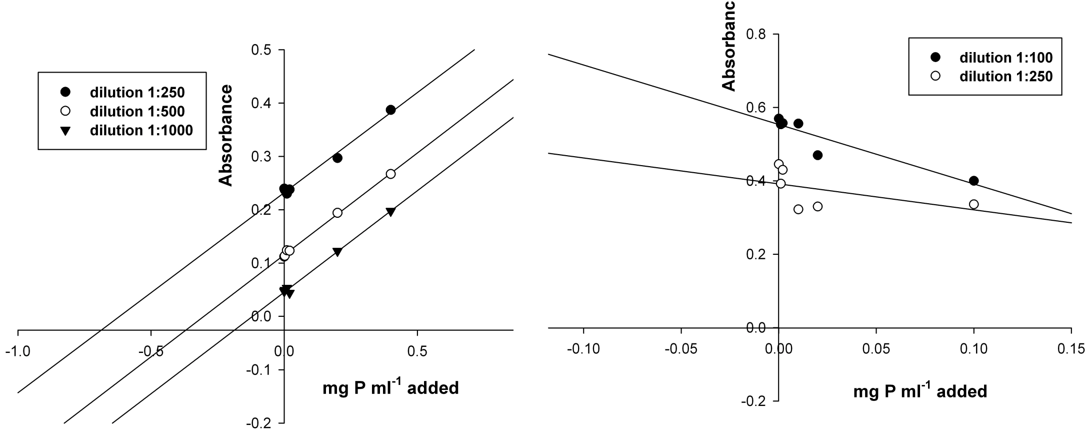
(1: control, 2: MgO treated), which then became the group variable. The test variable was the difference in the PO_4-P concentration before and after the treatment. Level of significance was $\alpha = 0.05$.

Splitting the data to pH-code and treatment and using PO_4-P as test variable evaluated the effect of the 17 hours settling time statistically. The PO_4-P concentration was the group variable, which was set to 1 (before the treatment) and 2 (after treatment). An independent samples t-Test with a level of significance of $\alpha = 0.05$ was carried out.

4. Results and Discussion

4.1 Comparison of the two main methods for orthophosphate (PO_4-P) determination

As described in chapter 2.4, there are two methods widely used for orthophosphate determination. In order to compare the practicability and the sensitivity of these methods (molybdenum-blue and monovanadate-yellow) when analyzing pig slurry or digestate, a standard addition test was carried out. Therefore, three different digestate samples were analyzed: two digestate samples from the Chinese biogas plants 1 & 3 and one sample from anaerobic digestion experiments carried out in Germany with intermediate organic matter content. The absorbance of both methods when using different dilution factors is compared and illustrated in the following.

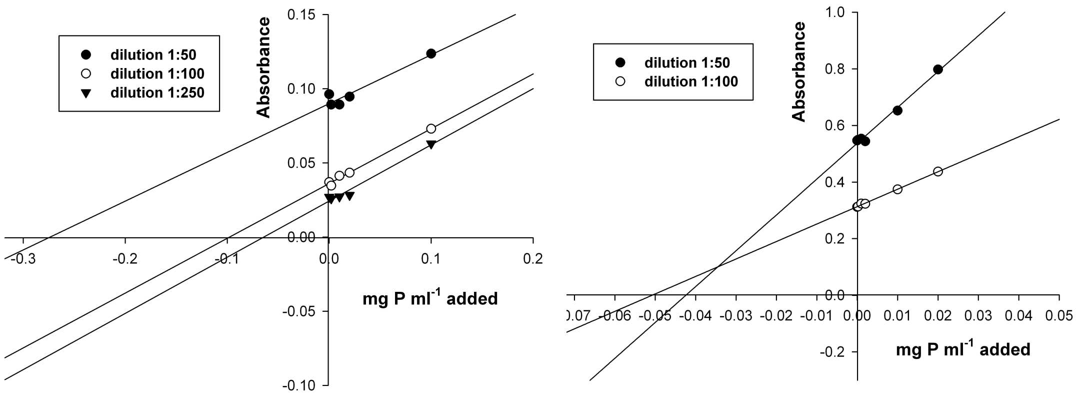


Figs. II-6 and II-7: The figures show the absorbance after the addition of a P-standard to the digestate from Chinese biogas plant 1. Digestate samples were analyzed with different dilution factors using the molybdenum-blue (left side) and monovanadate-yellow (right side) method. Regression lines are described by the equation: y = mx+b. The intercept, where the regression line intersects the x-axis, reflects the concentration of the digestate samples without adding the P-standard.

Fig. II-6 on the left side shows the plot of the absorbance of the digestate with different dilution factors versus the added P-concentrations. The calculation of the linear regressions yielded in straight lines, as the measured absorptions were proportional, just as was the added P-standard. A doubled dilution factor reduced the absorbance by half. The three straight lines run, due to the almost identical slope, in parallel. The coefficient of determination (r^2) was for each of the three straight lines $r^2 = 0.99$. Solving the equations resulted in similar phosphate concentrations, independent from the different dilution factors. These results clarify that there was no interference from the digestate matrix.

The different absorbances when using the monovanadate-yellow method are illustrated in Fig. II-7 on the right side and show clearly, that there is no coherence between the added P-standard and the resulting absorbance. It seems like the data was randomly grouped together and the regression line show rather a decrease even though an increased concentration of the P-standard was added. The calculation of the phosphate concentration resulted in different concentrations, dependent on the dilution factor. This indicates that the complex, slightly yellow colored digestate matrix interfered with the measurements. Further, I observed that this method is less sensitive as the dilution factors are 1:250 and 1:100, whereas the samples analyzed with the molybdenum-blue method had to be diluted more (up to 1:1000). The same results were observed for the digestate sample with intermediate organic matter content produced in Germany (data not shown).

Results from the standard addition experiments using digestate from Chinese biogas plant 3 (where slurry was digested twice) are illustrated in Figs. II-8 and II-9. In contrast to the above-mentioned results for the other two digestate samples, standard addition and PO_4-P determination worked well with both methods.



Figs. II-8 and II-9: Absorbance after the addition of a P-standard to the digestate from Chinese biogas plant 3 (digested twice). Digestate samples were analyzed with different dilution factors using the molybdenum-blue (left side) and monovanadate-yellow (right side) method. Regression lines are described by the equation: y = mx+b. The intercept, where the regression line intersects the x- axis, reflects the concentration of the digestate samples without addition of P-standards.

Fig. II-8 on the left side shows the absorbance when using the molybdenum-blue method for the double digestate samples. The calculation of the linear regressions yielded, similar as for the digestate samples described above, straight, parallel lines. In these samples, the digestate matrix did not affect the measurement. The graph on the right side (Fig. II-9) illustrates the absorbance using the monovanadate-yellow method for the double digested samples. For these samples, the calculation of the linear regressions resulted in straight lines. However, the lines do not run in parallel, as the slope was steeper for the samples with a lower dilution factor. Doubling the dilution factor reduced the absorbance by more than half. The main reason for the linearity of the data points might be the further reduction in organic matter and suspended solids present in the samples by the additional digestion. So in this special case, the measurement seemed not to be affected by matrix effects of the organic matter and suspended solids present in the sample.

When analyzing the samples with the monovanadate-yellow method, lower dilution factors (1:50 and 1:100) were sufficient for PO_4-P determination. These results are in accordance with findings from Kaylor (1971) who measured PO_4-P in pretreated waste and Gericke and Kurmies (1952) in steel samples. Gericke and Kurmies (1952) observed a delay in color development in the samples when high concentrations of anions like citric acid and oxalate were present. Further, the presence of H_2O_2 in the sample led to a reddish-brown coloration. We observed this change in color, when pig slurry or digestate samples were pretreated with H_2O_2 (Fig. II-10), too. The thus obtained measurements resulted in exaggerated values for the measured PO_4-P concentrations.

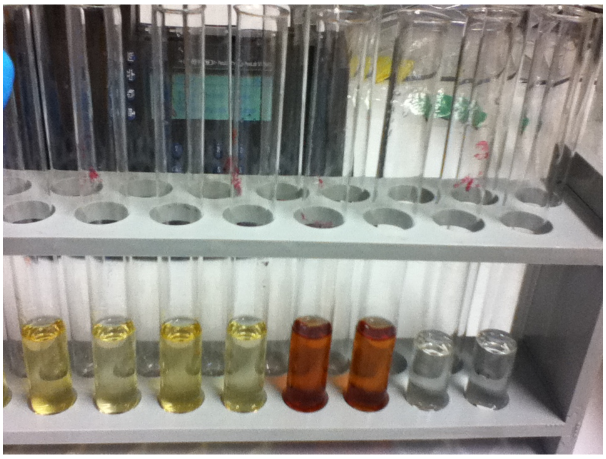


Fig. II-10: Digestate samples prepared for PO_4-P determination using the monovanadate-yellow method. The reddish-brown colored samples were pretreated with H_2O_2.

The authors observed also color variations when sulfate, silicone, iron and chromates were present in the samples leading to errors during measurement (Gericke and Kurmies, 1952).

However, the molybdenum-blue method is the most commonly used method for phosphate determination and showed no matrix effects in my standard addition experiments with different pig slurries and digestates. Further, I did not observe any turbidity or changing colors, resulting in unbiased PO_4-P data. In contrast, matrix effects of the organic material and suspended solids present in the sample influenced the measurement when using the monovanadate-yellow method. For the samples pretreated with H_2O_2, I observed a change in the coloration from yellow to reddish-brown when using monovanadate-yellow method and no discoloration when using the molybdenum-blue method. Further, I did, in contrast to Stanton (1968), not observe a delay or problems in the development of the blue color due to the presence of organic material. Therefore, I decided to use the molybdenum-blue method for all further experiments.

4.2 Determination of the optimum pH for struvite precipitation

In order to define the most suitable pH value for a high PO_4-P removal and struvite recovery, additional experiments with various kinds of untreated slurry (mixed pig slurry, slurry from fattening pigs, dairy cattle and cattle) were carried out in the laboratory in Germany. This served to check the influence of pH (chapter 2.6) and the activity of ions involved in struvite precipitation. As the slurry samples differed in their initial organic matter content, all samples were centrifuged for 1 hour at 30.000 g and the supernatant was used for the experiments. Experimental procedure was carried out as described in chapter 3.3.

Fig. II-11 shows the PO_4-P concentrations before and after the addition of MgO in mixed pig slurry. The control samples did not receive MgO but have been shaken as well for 1 hour like the samples with MgO added. The initial pH value of the slurry was pH 7.74 and the PO_4-P concentration was 1.06 mmol L^{-1}. 17 hours after the treatment, the PO_4-P concentration decreased in the control samples with initial pH slightly by 2% and in the corresponding samples, which received MgO, by 23%.

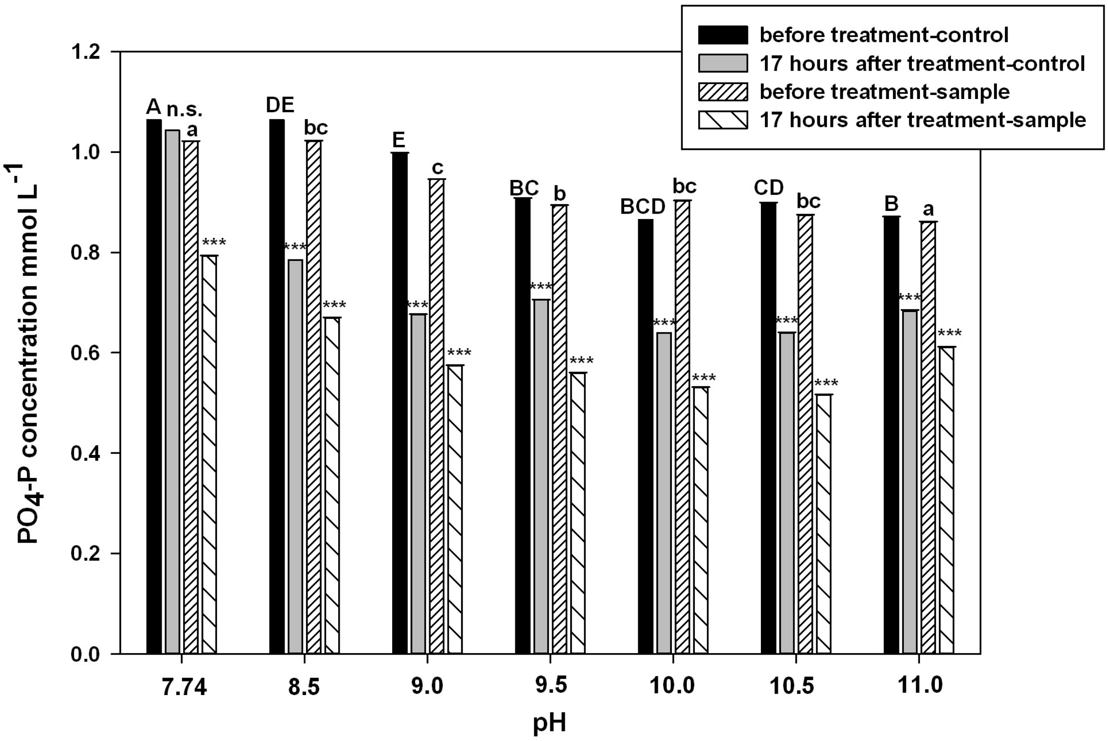


Fig. II-11: PO_4-P concentrations in mixed pig slurry samples before and 17 hours after the treatment. The control samples did not receive MgO whereas the treatment samples received MgO in a molar Mg:P ratio of 1:1. 7.74 is the initial pH; increased pH was adjusted using 1 M NaOH. Capital letters denote the statistical difference of the PO_4-P concentration difference values between the control samples, lower case denote the statistical difference of the PO_4-P concentration difference values between the treated samples (level of significance $\alpha = 0.05$). Asterisks denote the statistical significance between the control samples resp. the treated samples before and after the treatment (n.s. not significant, * $p \leq 0.05$, ** $p \leq 0.01$, *** $p \leq 0.001$).

Increasing the pH gradually to pH 11 yielded in a PO_4-P removal in the control samples by 21% - 34%, with lowest PO_4-P removal at pH 9.5 (21%), and 31% - 39% in the MgO added samples. Additionally, pH increased slightly after the addition of MgO and the subsequent shaking by 0.3 to 0.5 units. With an increasing pH, the initial PO_4-P concentration in the control samples decreased gradually by 20%. This decline is noticeable until pH 9.5 is reached and can be attributed to spontaneous struvite formation due to the improved conditions and enhanced availability of the required ions in the slurry. For this mixed pig slurry samples, the raise in pH had the biggest influence on PO_4-P removal. A slight increase to pH 8.5 - pH 9, followed by the subsequent shaking for 1 hour, was enough to achieve PO_4-P removal rates of 30% (visible in the control samples). Adding MgO to the slurry samples reduced the

PO_4-P concentration significantly further (to overall 55%) due to an additional struvite precipitation and should thus be favored.

My results are in good accordance with Buchanan et al. (1994) who modeled struvite precipitation with nutrient concentrations typical for anaerobic swine wastewater lagoons. The model predicted struvite precipitation between pH 7 and pH 11, with a minimum solubility and thus maximum struvite precipitation at pH 9. Further, Nelson et al. (2003) predicted and achieved almost complete (91% - 96%) PO_4-P removal in anaerobic swine lagoon liquid at pH 9. Beal et al. (1999) carried out struvite precipitation experiments with swine wastewater and, likewise as I did in my experiment, found out that a pH increased to > 8 enhances PO_4-P removal. Similar experiments were carried out with pig slurry from fattening pigs (Fig. II-12).

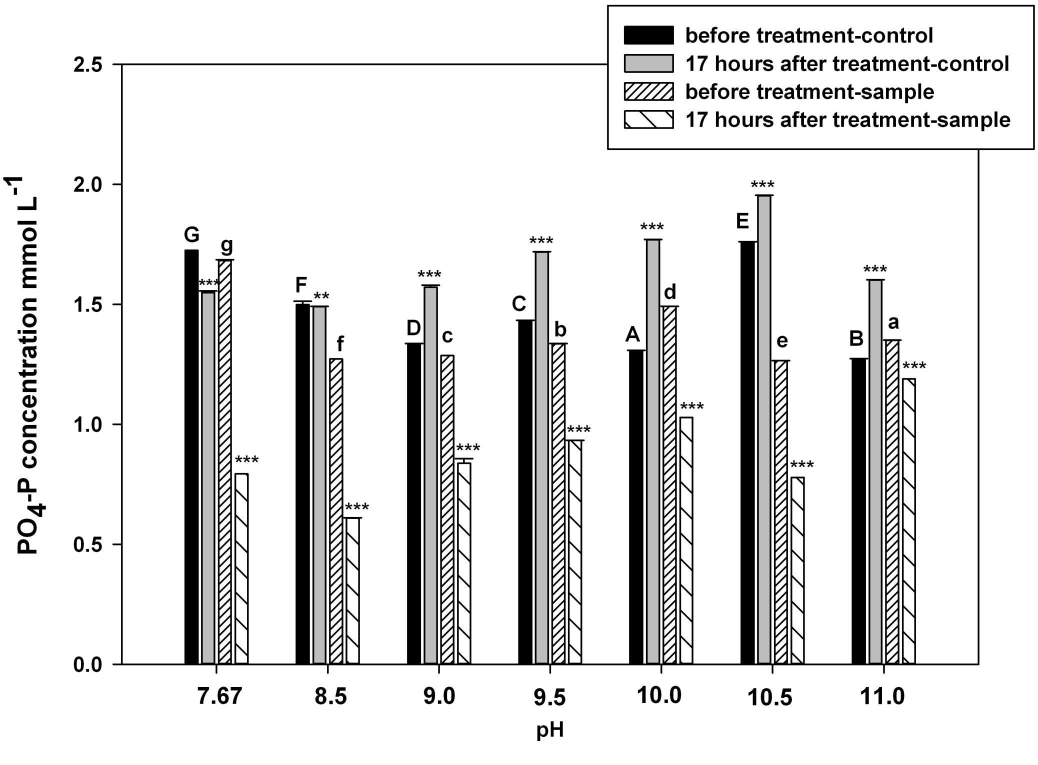


Fig. II-12: PO_4-P concentrations in slurry samples from fattening pigs before and 17 hours after the treatment. Control samples did not receive MgO whereas the treatment samples received MgO in a molar Mg:P ratio of 1:1. 7.67 is the initial pH; increased pH was adjusted using 1 M NaOH. Capital letters denote the statistical difference of the PO_4-P concentration difference values between the control samples, lower case denote the statistical difference of the PO_4-P concentration difference values between the treated samples (level of significance α = 0.05). Asterisks denote the statistical significance between the control samples resp. the treated samples before and after the treatment (n.s. not significant, * $p \leq 0.05$, ** $p \leq 0.01$, *** $p \leq 0.001$).

For higher pH values, PO_4-P removal was less efficient. Surprisingly, the control samples showed with increasing pH an increased PO_4-P concentration. A reason might be that the settling time was too short and that a major proportion of the spontaneously formed struvite crystals did not settle down at all. Probably during sampling, some remaining crystals were determined together with the soluble PO_4-P and thus increased the measured PO_4-P concentration. Highest PO_4-P removal rates were obtained with pH 7.67 and 8.5. This is in accordance with Laridi et al. (2005), who observed struvite formation in raw swine slurry at pH < 9 with best PO_4-P removal rates at pH 8.5. However, the authors pretreated their samples with Fe_2Cl, thus reducing the suspended solids and releasing Mg, which induced spontaneous struvite precipitation (Laridi et al., 2005).

The test with two different kinds of pig slurry did not reveal a clear result concerning the most suitable pH for struvite precipitation. In general, the composition and texture of pig slurry differs from cattle slurry. In cattle slurry, DM content and particle size are high due to the bedding material (e.g. straw or sawdust) and spilled feed. Further, pig slurry has a higher density at the same DM content than dairy cattle slurry (Hjorth et al., 2010). Due to this and as slurry composition and the content of suspended solids might play an important role in struvite precipitation, two cattle slurry samples (dairy cattle and cattle slurry) were also tested exemplarily.

Increasing the pH in dairy cattle slurry samples stepwise from pH 7.65 to pH 9 decreased the initial PO_4-P concentration by 10% due to spontaneous struvite precipitation (Fig. II-13). A further increase to pH 10 decreased the PO_4-P concentration, compared to the initial concentration, by almost 50%. Shaking had a higher effect in decreasing the PO_4-P concentration in the control samples with initial pH up to pH 9 (20%) than with higher pH 11 (9%). The PO_4-P concentration decreased significantly after the addition of MgO and removal was highest with initial pH (34%). 55% resp. 53% of the initial PO_4-P was removed in the control samples, where no MgO was added, with higher pH (pH 10 and pH 11) by shaking.

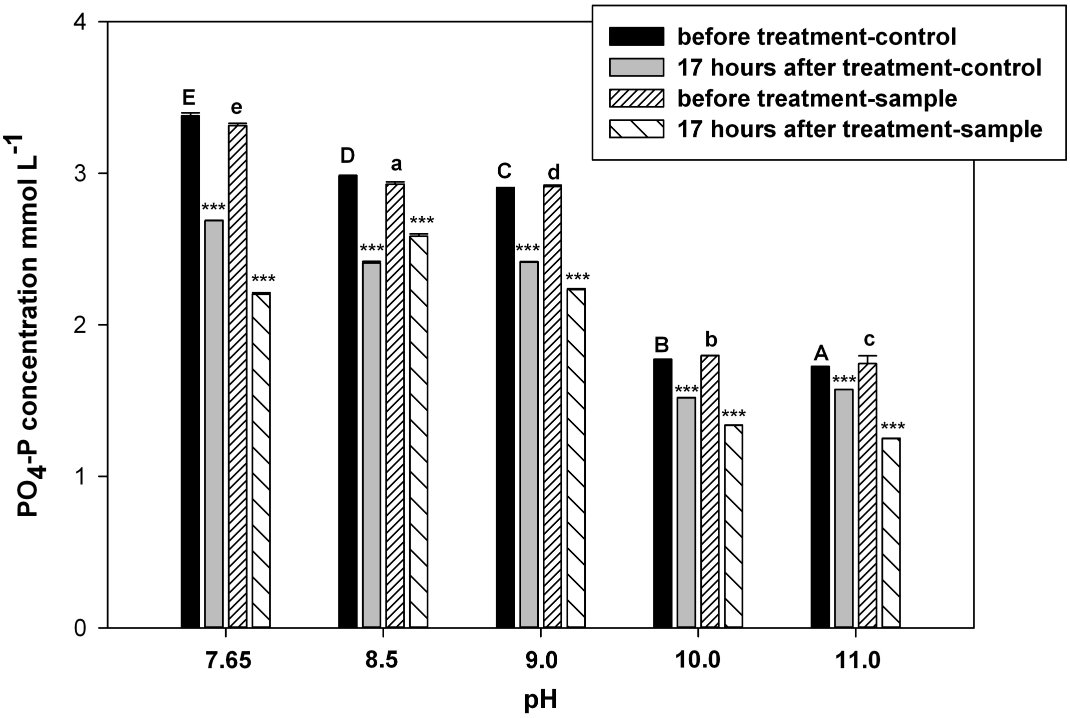


Fig. II-13: PO_4-P concentrations in samples from dairy cattle slurry before and 17 hours after the treatment. Control samples did not receive MgO whereas the treatment samples received MgO in a molar Mg:P ratio of 1:1. 7.65 is the initial pH; increased pH was adjusted using 1 M NaOH. Capital letters denote the statistical difference of the PO_4-P concentration difference values between the control samples, lower case denote the statistical difference of the PO_4-P concentration difference values between the treated samples (level of significance $\alpha = 0.05$). Asterisks denote the statistical significance between the control samples resp. the treated samples before and after the treatment (n.s. not significant, * $p \leq 0.05$, ** $p \leq 0.01$, *** $p \leq 0.001$).

The addition of MgO and the resulting decrease in PO_4-P was highly significant ($p \leq 0.001$) for all samples. However, the removal efficiencies in the samples with MgO added were only 6% - 15% higher compared to the control samples without MgO.

The cattle slurry described in Fig. II-14 had the lowest initial pH compared to the other pig and cattle slurry samples described above. Shaking had no significant effect on the control samples, except for pH 10, where 21% of the PO_4-P was removed. The addition of MgO resulted in a significant decrease in the PO_4-P concentration at initial pH by 36% and at pH 10 by 31%. Increasing the pH reduced the overall PO_4-P concentration in the samples by around 20% - 30%. Astonishingly, there was no further PO_4-P reduction in the samples with pH 8, pH 9 and pH 11 - neither in the control samples by shaking, nor in the samples receiving MgO. PO_4-P removal was highest with pH 10, where overall 47% of the initial PO_4-P was removed.

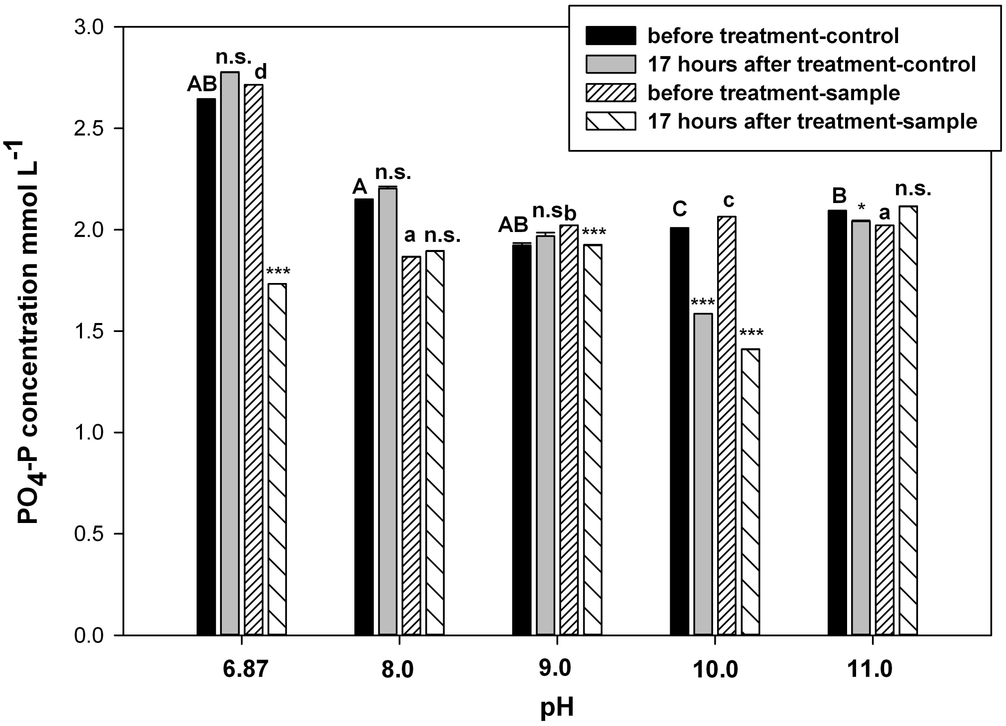


Fig. II-14: PO_4-P concentrations in samples from cattle slurry before and 17 hours after the treatment. Control samples did not receive MgO whereas the treatment samples received MgO in a molar Mg:P ratio of 1:1. 6.87 is the initial pH; increased pH was adjusted using 1 M NaOH. Capital letters denote the statistical difference of the PO_4-P concentration difference values between the control samples, lower case denote the statistical difference of the PO_4-P concentration difference values between the treated samples (level of significance $\alpha = 0.05$). Asterisks denote the statistical significance between the control samples resp. the treated samples before and after the treatment (n.s. not significant, * $p \leq 0.05$, ** $p \leq 0.01$, *** $p \leq 0.001$).

Overall, the PO_4-P removal for (dairy) cattle slurry was highest (50% - 60%) with pH 10 and pH 11. At lower pH, some struvite precipitated in samples from dairy cattle slurry, thus reducing the PO_4-P concentration. However, no precipitation occurred in the cattle slurry samples at the same pH. This heterogeneity of the results might be attributed to the varying organic matter content of the original samples, where P was associated with the particle fraction through inorganically binding or adsorption onto particles. This different quantity of the remaining suspended solids might have led to a spontaneous struvite precipitation in some samples when pH was adjusted or when the control samples were shaken, whereas in other samples at the same pH nothing happened.

My results obtained with cattle slurry are largely in accordance with Schulze-Rettmer (1991) and Kim et al. (2004), who reported pH values for maximum PO_4-P removal ranging, dependent on the ionic strength, from pH 9 to pH 10.7. Struvite solubility starts to increase when the pH increases above pH 9, as the PO_4^{3-} concentration increases and NH_4^+ concentration decreases (Kim et al., 2004). However, in my samples, the optimum was rather at higher pH (pH 10 - pH 11) and thus in better accordance with the predictions from Ohlinger et al. (1998). The authors' model predicts a maximum struvite precipitation at pH 10.3 to pH 10.7. This was confirmed in my results obtained with the dairy cattle slurry samples (pH > 10: 55% - 63% PO_4-P removal). The predictions are also true for the cattle slurry samples as in total 47% of the PO_4-P was removed with pH 10 compared to 36% with an initial pH of 6.8.

The four different slurries - two pig slurries and two cattle slurries - not only differed in their PO_4-P removal efficiency and thus the quantity of precipitated struvite but also in their optimum pH. Due to the heterogeneity in optimum pH values with the different animal wastes, each time before starting the precipitation experiments in China, the optimum pH value was determined.

4.3 Determination of the most suitable precipitating agent and Mg:P ratio

Usually, the limiting ion for struvite formation in animal wastewaters is magnesium. Therefore, to induce and force struvite precipitation, magnesium was added as a component in four different chemical compounds to the digestate. Possible sources that were often used for struvite precipitation are magnesium hydroxide ($Mg(OH)_2$), magnesium oxide (MgO) and magnesium chloride ($MgCl_2$) (Burns et al., 2003). CaO, another commonly used precipitating agent in literature (Song et al., 2006), was used for the means of a better classification of the obtained results. The precipitates with Ca^{2+} were not specified but expected to result in various forms of calcium phosphates e.g. $Ca(H_2PO_4)_2$, $CaHPO_4$, $Ca_3(PO_4)_2$ and ($Ca_5OH(PO_4)_3$ whose formation depends on the slurry pH (Hjorth et al., 2010). Besides the four different precipitating agents, three different molar ratios of Mg:P or Ca:P (1:1, 1.5:1, 2:1) were added to the digestate in order to determine the influence of an elevated ratio on struvite precipitation behavior. The samples received the same amount of MgO,

$MgCl_2$, $Mg(OH)_2$ and CaO a second time in order to test if the remaining PO_4-P could be precipitated further.

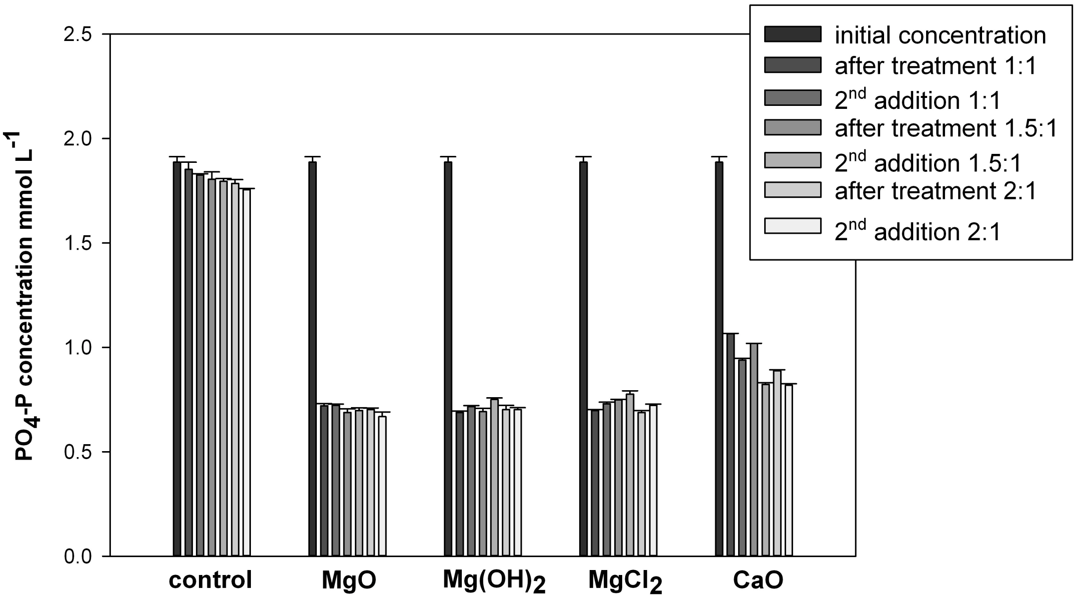


Fig. II-15: PO_4-P concentrations in digestate at initial pH 7.5 before and 17 hours after the addition of MgO, $Mg(OH)_2$, $MgCl_2$ and CaO in different molar Mg/Ca:P ratios of 1:1, 1.5:1 and 2:1. The same quantity of MgO, $Mg(OH)_2$, $MgCl_2$ and CaO was added a second time. The control samples did not receive Mg^{2+}/Ca^{2+} but were shaken simultaneously with the treated samples for 1 hour.

The initial PO_4-P concentration decreased slightly in the control samples (Fig. II-15) at initial pH 7.5. Turbulences created by the filling and shaking of the control samples led to a release of small amounts of CO_2 as a result of the transformation of CO_3^{2-} and 2 H^+ to CO_2 and H_2O (Eqs. II-2 and II-3, chapter 2.6). The release of CO_2 slightly increased pH, which thus favored the conditions for struvite precipitation and thus slightly decreased the PO_4-P concentration. The addition of MgO reduced the initial PO_4-P concentration by 62%. There was no difference in the PO_4-P removal between the three different molar Mg:P ratios 1:1, 1.5:1 and 2:1. PO_4-P was not reduced further when MgO was added in the same molar ratios a second time. Similar results were obtained for $Mg(OH)_2$ and $MgCl_2$. The addition of CaO achieved higher PO_4-P removal with a higher molar Ca:P ratio (43% for the ratio 1:1, 46% for the ratio 1.5:1 and 53% for 2:1). By adding CaO a second time, further PO_4-P was removed. The overall removal efficiency after two additions of Ca^{2+} was slightly lower compared to the ones obtained with Mg^{2+}. Raising the initial pH in digestate from 7.5 to 9 by

NaOH reduced the starting PO_4-P concentration by 10% due to spontaneous struvite formation (Fig. II-16).

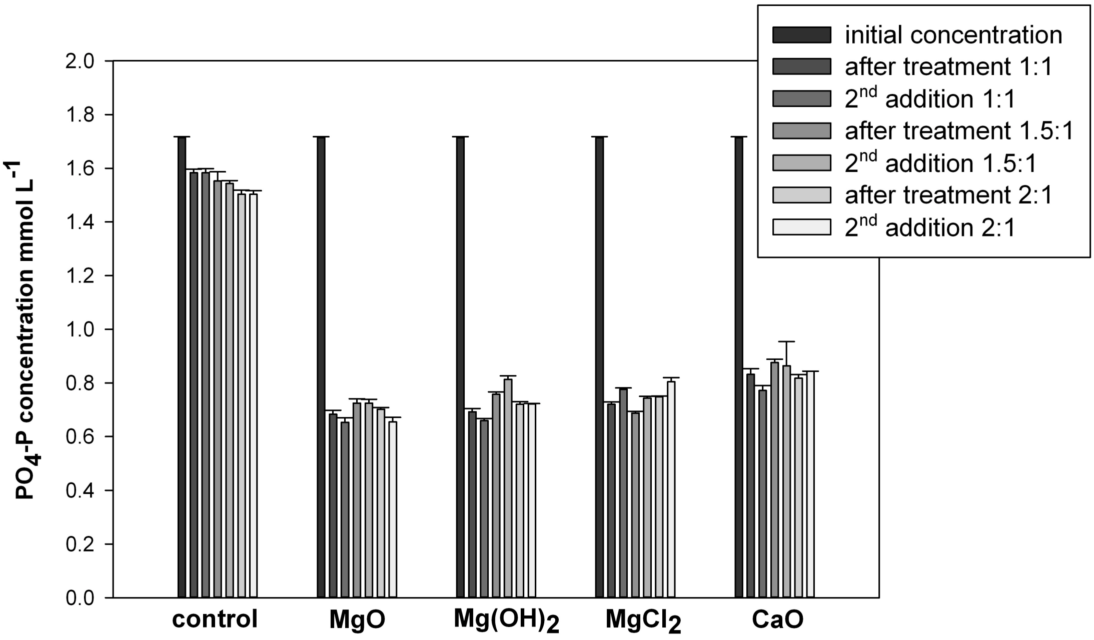


Fig. II-16: This figure shows the same digestate samples as described above in Fig. II-15, but pH was adjusted to pH 9 using 1 M NaOH. PO_4-P concentrations were illustrated before and 17 hours after the addition of MgO, $Mg(OH)_2$, $MgCl_2$ in different molar Mg/Ca:P ratios of 1:1, 1.5:1 and 2:1. The same quantity of MgO, $Mg(OH)_2$, $MgCl_2$ and CaO was added a second time. The control samples did not receive Mg^{2+}/Ca^{2+} but were shaken simultaneously with the treated samples for 1 hour.

Shaking of the control samples yielded higher PO_4-P removal with elevated pH 9 (7% - 12%) than with initial pH (2% - 5%). During shaking, the pH increased slightly more and thus favored additional struvite precipitation. For pH 9, the addition of MgO, $Mg(OH)_2$ and $MgCl_2$ yielded almost similar PO_4-P reduction (60%) as described above in Fig. II-15. The second addition did not reduce the overall PO_4-P concentration further and no difference was observed between the three Mg:P ratios. The elevated pH 9 influenced the precipitation behavior of the different molar ratios of CaO less than the initial pH 7.5, resulting in a uniform decrease between the treatments. With pH 9, CaO achieved a PO_4-P removal of 55% and was thus also slightly less efficient compared to the three Mg- sources. The different molar Ca:P ratios did not affect the PO_4-P removal and were in the same range for all samples.

My findings were in contrast to data described in the literature as I did not observe differences between the three Mg:P ratios. Also, there was no further PO_4-P reduction when Mg^{2+}/ Ca^{2+} ions were added a second time. Normally, by bringing new Mg^{2+}/ Ca^{2+} ions into the system, the remaining dissolved phosphate should at least be precipitated partially. The results above showed, however, that the repeated addition of Ca^{2+} ions at pH 7.5 precipitated only a small percentage (4% - 10%) of the initial PO_4-P as calcium phosphate. Instead, most of the added Ca^{2+} might have precipitated as $CaCO_3$ since slurry contains excessive levels of carbonate (CO_3^{2-}) (Hjorth et al., 2010). The second addition of Mg^{2+} or Ca^{2+} ions did not have any effect on the digestate at pH 9. In order to overcome the effects of complexing agents, which may bind to magnesium e.g. organic material, additional amounts of Mg^{2+} are required for struvite precipitation (Burns et al., 2003). This effect of complexing agents was not directly observed in these experiments as all molar Mg:P ratios (1:1, 1.5:1 and 2:1) removed similar quantities of PO_4-P. However, complexation might explain the fact that the second addition of Mg^{2+}/ Ca^{2+} did not remove any or at best small amounts of PO_4-P.

Nelson et al. (2003), for example, observed a further reduction in the PO_4-P concentration of swine lagoon liquid when increasing the Mg:P ratio from 1:1 to 1.6:1. These results were in good accordance with findings from Beal et al. (1999) who carried out struvite precipitation experiments using MgO in bench scale reactions where with an increasing Mg:P ratio the PO_4-P concentration decreased.

MgO as Mg^{2+} source had the additional benefit of an increase in pH, theoretically favoring struvite precipitation. However, MgO is almost insoluble in water and it therefore takes longer to react and leaves more residual MgO (Beal et al., 1999).

Burns et al. (2001) used $MgCl_2$ in experiments with swine manure slurry and described it thereupon as a good Mg^{2+} source for struvite precipitation. A reason was the easy handling and good solubility, which shortened the time required for bringing Mg^{2+} into solution. Nevertheless, $MgCl_2$ is slightly acidic (pH 5) and did not increase pH as MgO does. In their experiments, the addition of $MgCl_2$ resulted in a PO_4-P removal of 76% (Burns et al., 2003). Shepherd et al. (2009) used also $MgCl_2$ for their precipitation experiments with swine wastewater and achieved a PO_4-P reduction of 78%.

Miles and Ellis (2001) used phosphate fertilizer and a 50% $Mg(OH)_2$ solution to reduce ammonia through struvite precipitation in swine wastes. During their experiments, the authors faced insolubility problems with the $Mg(OH)_2$ and therefore changed to the use of MgO. The authors added supplemental magnesium and phosphate to the anaerobically treated swine waste and achieved almost complete PO_4-P removal in the form of struvite.

During the experimental procedure I observed the formation of small, encapsulated, insoluble globules after the addition of MgO and $Mg(OH)_2$, which sedimented immediately. Therefore, the almost insoluble MgO, $Mg(OH)_2$ and the soluble $MgCl_2$ were dissolved in water and the solution was added subsequently to the digestate in order to facilitate and thus enhance struvite precipitation. But this did not change struvite precipitation and resulted in similar PO_4-P removal efficiencies as if added as powder. The overall PO_4-P removal efficiencies varied in literature in raw swine wastewater and digestate from 76% - 90%, which is, in relative terms, 15% - 30% higher compared to our results. Therefore, further precipitation experiments were carried out in order to determine the factors influencing precipitation most and to find the most suitable conditions for struvite precipitation in Chinese biogas digestate. As MgO was the most efficient and most suitable precipitating agent in Chinese digestates, all further experiments were carried out with MgO.

4.4 Precipitation experiments with Chinese pig slurry and digestate

Further precipitation experiments were carried out with different samples from the pig farm in China: untreated pig slurry, digestates from the two different biogas plants and digestate that was digested a second time. Another sample was taken from the effluent that was, after the double digestion treatment, aerated before leaving the farm. These different samples were used in order to test whether there was a difference in precipitation behavior initiated through the treatment steps on the farm and to determine under which conditions struvite precipitation was best. Shaking the samples was a prerequisite, as the turbulences led to aeration, CO_2 was released and the pH increased. Further, the shaking led to a thorough mixing and bringing the Mg^{2+} into solution. No precipitation occurred when slurry or digestate samples were not shaken.

Initial PO_4-P concentration in the untreated pig slurry sample being fed into the biogas plant was 1.13 mmol L^{-1} (107 mg L^{-1}). The slurry samples were taken before the material entered the biogas plant and DM content was below < 1%. The control samples did not receive any MgO while the other samples received MgO at a molar Mg:P ratio of 1:1 and 2:1.

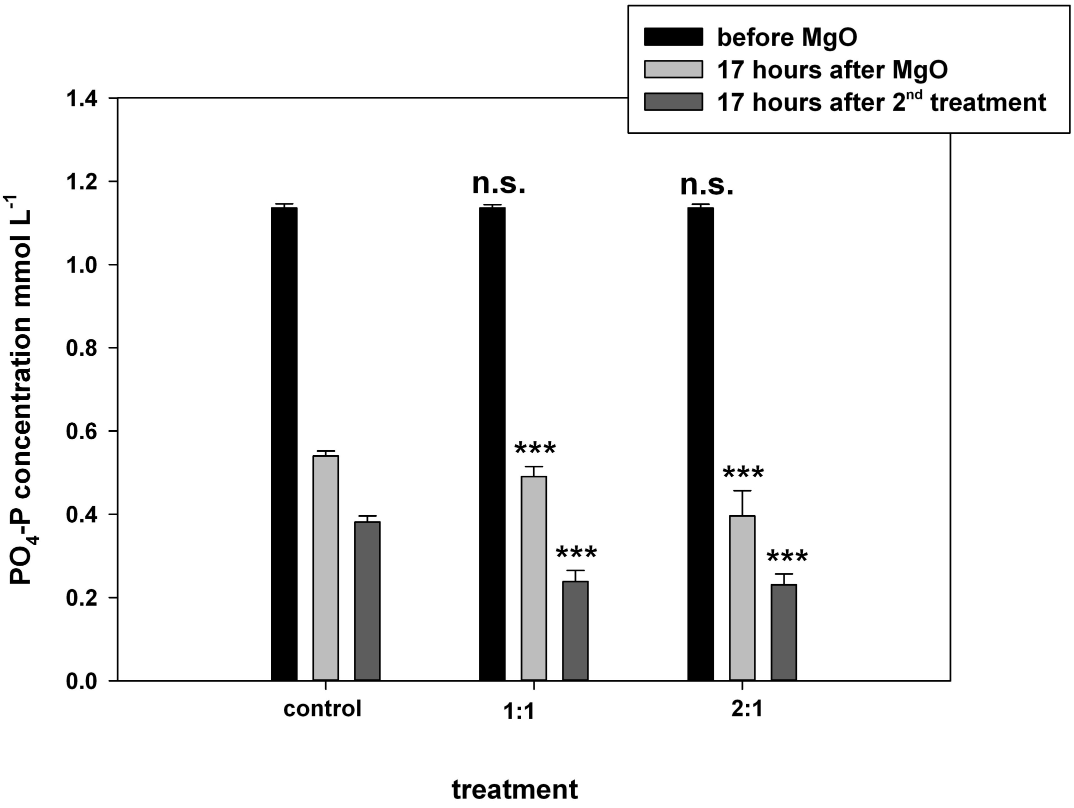


Fig. II-17: PO_4-P concentrations in untreated pig slurry before and 17 hours after the addition of MgO in molar Mg:P ratios of 1:1 and 2:1. MgO was also added a second time to remove the remaining PO_4-P. The control samples did not receive MgO but were shaken simultaneously with the samples for 1 hour. Asterisks denote the statistical significance between the control sample and the corresponding MgO treated samples (n.s. not significant, * $p \leq 0.05$, ** $p \leq 0.01$, *** $p \leq 0.001$).

The PO_4-P concentration in the control samples decreased significantly ($p \leq 0.001$) after each treatment step. Shaking decreased the PO_4-P concentration through spontaneous struvite precipitation by 52% and by further 14% after the 2nd treatment, resulting in an overall PO_4-P removal of 66% in the control samples. Adding MgO in a molar Mg:P ratio of 1:1 and 2:1 decreased the PO_4-P concentration in total by 80%, showing no difference between the two molar Mg:P ratios. Remarkable is the fact that the PO_4-P concentration in the control sample was reduced to almost the same extent without MgO addition compared to the samples receiving MgO after the first treatment. Both reductions were highly significant ($p \leq 0.001$) for all three treatments control, 1:1 and 2:1.

Digestate samples

Usually, during the biogas process, the pH of the material in the biogas plant is increased by +0.5 to +2 units caused by the transformation of CO_3^{2-} and 2 H^+ to CO_2 and H_2O. Yet another reason is the formation of ammonium carbonate ($(NH_4)_2CO_3$) (Möller and Müller, 2012). The decrease in the concentration of dissolved PO_4-P as well as in the concentration of Ca^{2+} and Mg^{2+} ions before and after digestion is attributed to the spontaneous precipitation of phosphates (struvite, $MgKPO_4$, $CoNH_4PO_4$, $NiNH_4PO_4$, $CoKPO_4$), which is enhanced by the substantial increase of the digestate pH shifting the chemical equilibrium towards the transformation of HPO_4^{2-} to PO_4^{3-}. Further, during the process of anaerobic digestion, dissolved PO_4-P is partially associated with suspended solids, reducing the PO_4-P concentration further. Many ionic species like K^+, Ca^{2+}, CO_2^{3-} might influence struvite formation by reactions with its component ions (Le Corre et al., 2009). Spontaneous precipitation results in a low concentration of Ca^{2+}, Mg^{2+} and inorganic P in the digestate. Möller and Müller (2012) describe further, that P losses are small (< 10%) during anaerobic digestion and the higher losses might be attributed to spontaneous precipitation processes. The precipitated nutrients will be retained in the digesters.

This precipitation processes, induced by the elevated pH in the biogas plant, explain the huge difference between the PO_4-P concentration of the raw swine slurry entering the biogas plant and the by almost 2/3 reduced PO_4-P concentration in the effluent. The remaining PO_4-P in the liquid digestate can be precipitated (Figs. II-18 and II-19). Digestate 1 is the effluent of biogas plant 1. The effluent of biogas plant 3 was digested twice.

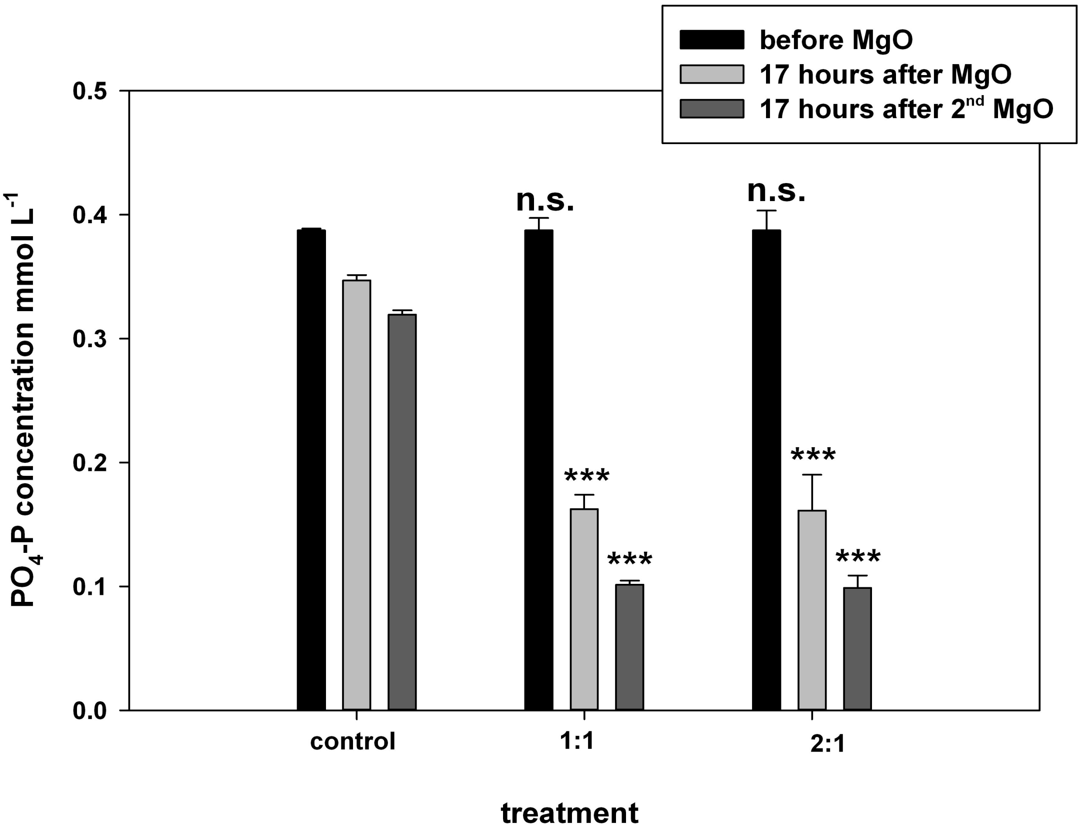


Fig. II-18: PO_4-P concentrations in digestate 1 before and 17 hours after the addition of MgO in molar Mg:P ratios of 1:1 and 2:1. MgO was also added a second time to remove the remaining PO_4-P. The control samples did not receive MgO but were shaken simultaneously with the samples for 1 hour. Asterisks denote the statistical significance between the control sample and the corresponding MgO treated samples (n.s. not significant, * $p \leq 0.05$, ** $p \leq 0.01$, *** $p \leq 0.001$).

The initial PO_4-P concentration in digestate 1 was 0.39 mmol L^{-1} and decreased in the control samples after shaking by 10%. Adding MgO to the digestate samples reduced the PO_4-P concentration by 58%. There was no difference in the removal efficiencies of the two molar Mg:P ratios of 1:1 or 2:1. The second addition of MgO reduced the PO_4-P concentration in the samples by further 16% within both treatments and resulted in an overall PO_4-P reduction of 74%. The remaining digestate had a PO_4-P concentration of 0.1 mmol L^{-1} or 9.5 mg L^{-1}. For this digestate sample, the addition of an excess quantity of MgO (molar Mg:P ratio of 2:1) did not result in higher PO_4-P removal. Both declines (17 hours after the treatment and 17 hours after the 2nd treatment) in the control sample as well as in the samples receiving MgO were highly significant ($p \leq 0.001$).

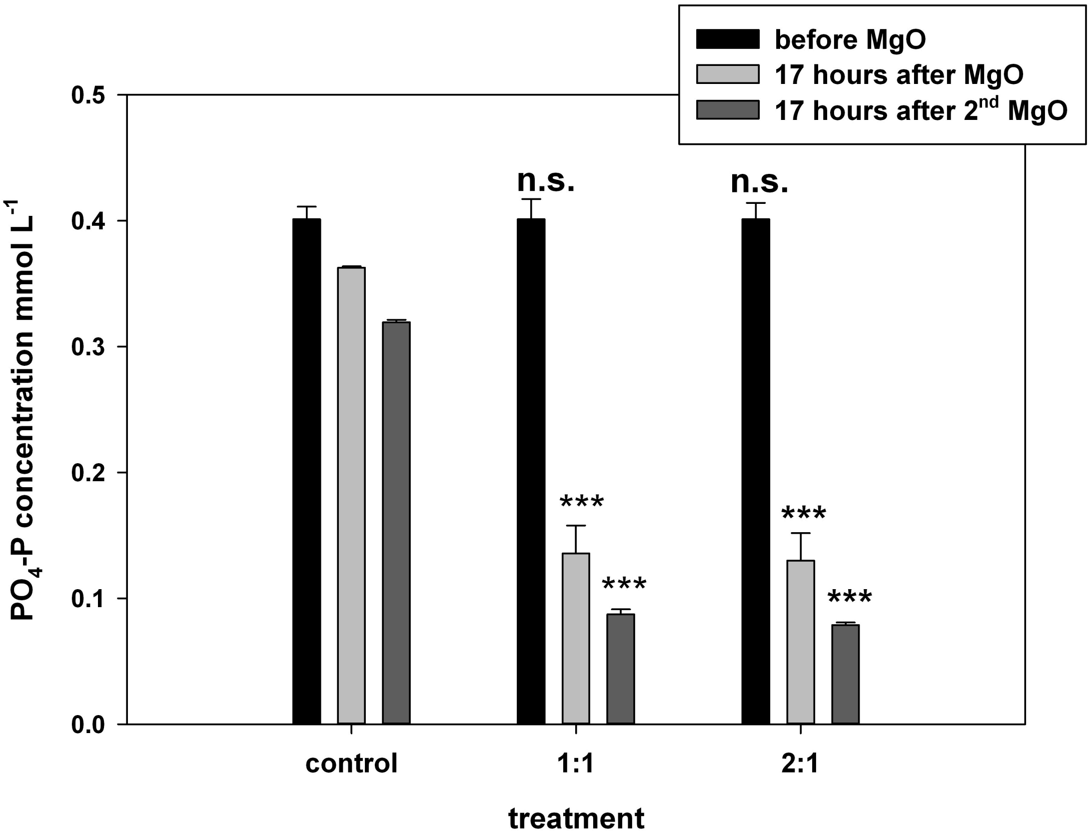


Fig. II-19: PO_4-P concentrations in digestate 3 (digested twice) before and after the addition of MgO in molar Mg:P ratios of 1:1 and 2:1. MgO was also added a second time to remove the remaining PO_4-P. The control samples did not receive MgO but were shaken simultaneously with the samples for 1 hour. Asterisks denote the statistical significance between the control sample and the corresponding MgO treated samples (n.s. not significant, * $p \leq 0.05$, ** $p \leq 0.01$, *** $p \leq 0.001$).

Initial PO_4-P concentration in this double digested sample was 0.4 mmol L^{-1} (38 mg L^{-1}) and therewith almost the same as the initial concentration of the digestate of biogas plant 1. This confirms that phosphate losses were low during anaerobic digestion (< 10%), as described by Möller and Müller (2012). The PO_4-P concentration in the control samples was, as well as in digestate 1 (Fig. II-18), reduced by 10%. The addition of MgO resulted in similar removal efficiencies of 66% for both molar Mg:P ratios of 1:1 and 2:1. The repeated MgO addition removed only slightly more PO_4-P, resulting in an overall PO_4-P reduction of 78% (molar Mg:P ratio 1:1) resp. 82% (molar Mg:P ratio 2:1). The decline from the initial PO_4-P concentration to the concentration after 17 hours and the further decline from 17 hours after treatment to 17 hours after 2nd treatment were highly significant ($p \leq 0.001$) for all three treatments control, 1:1 and 2:1.

After the anaerobic treatment, the effluent of the third biogas plant flowed into an open lagoon. There, it was treated aerobically in order to remove the remaining organic material and nitrogen. This intense aeration led to further spontaneous phosphate precipitation and thus a decrease in the PO_4-P concentration by 60%, from 0.4 mmol L^{-1} to 0.16 mmol L^{-1}. In order to test the PO_4-P removal and thus struvite precipitation potential of this aerobically treated effluent, samples were taken right before the effluent left the farm and flowed into the storage lagoon bordering a small river.

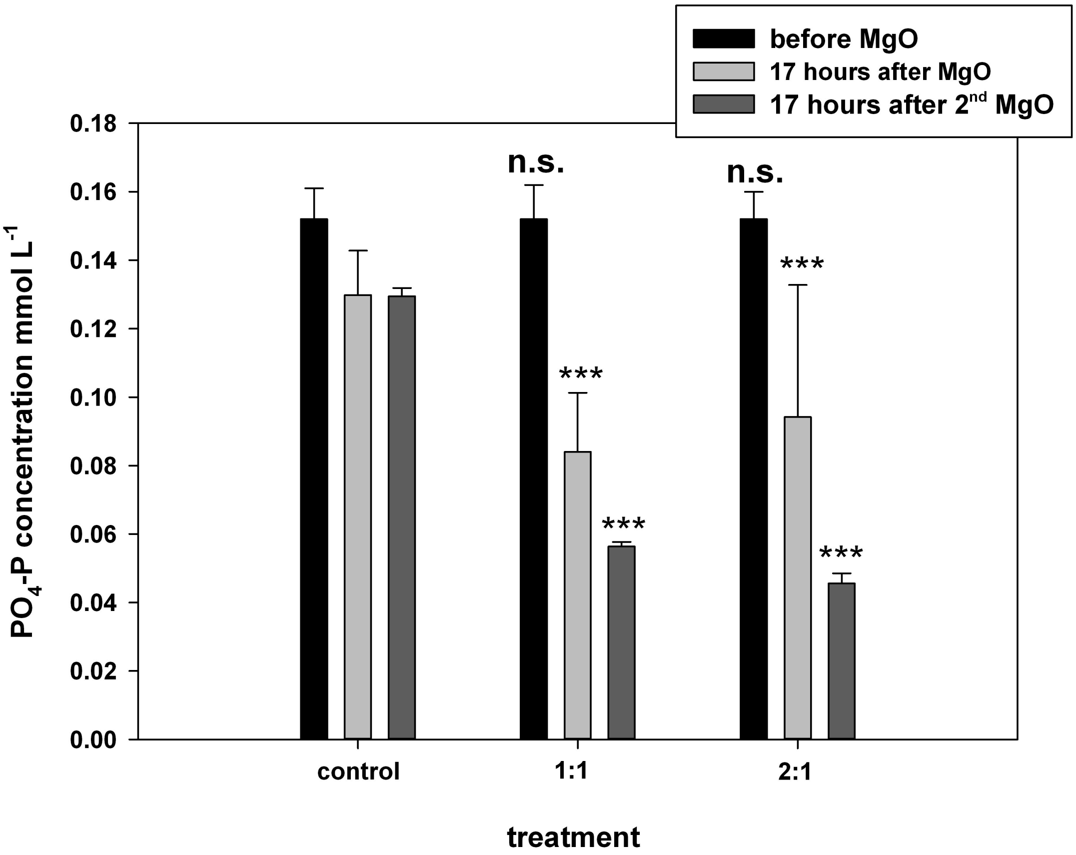


Fig. II-20: PO_4-P concentrations in the effluent leaving the farm before and after the addition of MgO in molar Mg:P ratios of 1:1 and 2:1. MgO was also added a second time to remove the remaining PO_4-P. The control samples did not receive MgO but were shaken simultaneously with the samples for 1 hour. Asterisks denote the statistical significance between the control sample and the corresponding MgO treated samples (n.s. not significant, * $p \leq 0.05$, ** $p \leq 0.01$, *** $p \leq 0.001$).

The PO_4-P concentration in the effluent leaving the farm decreased in the control samples by 10% after shaking and did not decrease further when shaken again. This can be explained by the fact that most of the easily precipitating PO_4-P might already have precipitated spontaneously during the digestion and the following aeration. Shaking of the samples could then remove only small quantities of the PO_4-P present. The first addition of MgO in a molar Mg:P ratio of 1:1 reduced the PO_4-P concentration to a greater extent than the addition of the Mg:P ratio of 2:1. However, by adding MgO a second time, the overall PO_4-P concentration was reduced by 70% in both treatments. The final concentration of the treated effluent after the second treatment was 0.05 mmol L^{-1}. The decline in the PO_4-P concentration after 17 hours in the control samples was highly significant ($p \leq 0.001$) whereas the further treatment did not result in a significant ($p > 0.05$) decrease in the PO_4-P concentration. The samples receiving MgO in a molar Mg:P ratio of 1:1 or 2:1 showed a highly significant ($p \leq 0.001$) decrease in the PO_4-P concentration after each treatment step.

General discussion

Struvite precipitation reduced the initial solute phosphate concentration in the different pig slurry and digestate samples from the Chinese pilot pig farm remarkably. In the untreated pig slurry, shaking of the control samples achieved an only slightly lower PO_4-P reduction (66%) compared to the samples where MgO was added (79%). This might be explained by the aeration during shaking where slurry with an optimum molar ratio of the free ions Mg^{2+}, NH_4^+ and PO_4^{3-} was produced and thus spontaneous struvite precipitation was induced. Suzuki et al. (2002) observed this effect as well when aerating raw swine wastewater, achieving 65% - 99% P removal merely through aeration. The considerable effect of shaking was lower (7% - 14%) in my control samples of the digestates. The addition of MgO reduced the PO_4-P concentration significantly in all digestate samples, achieving a total PO_4-P removal of 74% - 82%. However, there was almost no difference in PO_4-P removal between the two molar Mg:P ratios (1:1 and 2:1). A reason for the inefficacy of the elevated Mg:P ratio might be the binding of the additional magnesium to organic complexing agents (Burns et al., 2003). Further, some of the initially measured free PO_4^{3-} ions were, initiated by the shaking process, bound inorganically in crystalline form or adsorbed onto (organic) particles in the digestate and were thus not able to use the added Mg^{2+} ions to form struvite (Hjorth et al., 2010). The excess MgO precipitated at the bottom of the centrifuge tube without having any effect on PO_4-P removal. During the settling period of 17 hours, the struvite crystals sank down and accumulated in the centrifuge tube tip. When MgO was added again after 17 hours and shaken for 1 hour, some phosphate might be released from the organic complexes or get desorbed initiated by the excess supply of Mg^{2+} ions and the shifted ion balance, resulting in further marginal PO_4-P precipitation.

During the biogas process, the PO_4-P concentration decreased in the digestate by almost 2/3 due to spontaneous phosphate precipitation in the digester. Further, the PO_4-P concentration was reduced by 60% during the aerobic treatment on the farm, where turbulences favored spontaneous struvite precipitation.

The results obtained during the above mentioned experiments with PO_4-P removal efficiencies of 70% - 82% are in good accordance with reported ones from Maekawa (1995) and Nelson et al. (2000). The authors carried out struvite precipitation experiments in swine wastewaters by adding $MgCl_2$ and yielded PO_4-P removal efficiencies of 40% - 88% (Maekawa, 1995) and 62% - 95% (Nelson et al., 2000). The PO_4-P removal efficiencies vary over a broad range and might on the one hand be explained by the supplementation of PO_4-P through the addition of KH_2PO_4 (Maekawa, 1995), resulting not only in spontaneous struvite but also in the precipitation of other phosphate minerals. On the other hand, complexing agents like organic material bind Mg and thus decrease their availability for struvite precipitation, as described by Burns et al. (2001). The authors achieved also almost complete PO_4-P removal (91%) at pH 8.5 when using $MgCl_2$ in a molar Mg:P ratio of 1.6:1. However, their results obtained with wastewater with an initial pH value of pH 7.5 were 76% and thus in the same range as my above-mentioned results.

Burns et al. (2003), as well as Laridi et al. (2005), achieved PO_4-P removal efficiencies of 95% resp. 98% by adding $MgCl_2$ to swine wastes with an elevated pH (pH 8.5). Laridi et al. (2005) pretreated swine wastewater with a 32% ferric chloride ($FeCl_2$) solution. This reduced not only the suspended solid load but also a significant quantity of phosphorus through precipitation. However, the following precipitation step yielded an almost pure struvite product. The pre-treatment was described as a good method to remove the suspended solids, which hinder struvite formation, as observed in our experiments as well as in the ones from Nelson et al. (2000). But the crystallization of solid iron phosphate, e.g. $FePO_4$, increases metal complexes in the sludge, which then had to be treated and discharged properly.

Song et al. (2002b) eliminated the interference from organic and inorganic components in swine wastewaters by using a chemical solution containing the five main components for precipitation (N, P, Mg^{2+}, Ca^{2+} and CO_3^{2-}). Therewith, the authors obtained PO_4-P removal efficiencies of up to 97% with a slightly elevated molar Mg:P ratio and pH 9.5. At lower pH (pH 8), the PO_4-P removal efficiency increased by 20% when raising the molar Mg:P ratio from 1:1 to 2:1. For higher pH values, the authors observed no significant effect on removal efficiency with an excessive Mg dosage. This is contradictory to my results where pH was in the same range and a higher molar Mg:P ratio of 2:1 resulted in either the same or only slightly (1% - 2%) higher PO_4-P removal compared to a molar ratio of 1:1.

Beal et al. (1999) used MgO as precipitating agent in raw swine manure and digestate. Struvite formation was forced by heating the manure and digestate samples to 35°C, resulting in almost complete PO_4-P removal (92% resp. 98%). An increased substrate temperature enhances particle movement (Brownian motion) and thus the formation of struvite. However, a higher temperature favors ammonia volatilization, which thus decreases the availability for struvite precipitation and contributes to environmental N loads. Further, it is also creating additional costs, which will then increase the price for the recovered product (struvite). Burns et al. (2003) describe that struvite formation occurs spontaneously within the first 10 minutes after the addition of Mg^{2+}. So even if an increased temperature favored the particle movement, struvite crystallization will take place immediately when the swine wastewater/digestate is supersaturated with Mg^{2+} and PO_4^{3}.

The previously described results were obtained under laboratory conditions. In contrast to that, Suzuki et al. (2007) carried out struvite precipitation experiments in a demonstration crystallization reactor running continuously on a Japanese research farm for 3.5 years. Swine wastewater was screened (1.5 mm mesh) and then aerated by a moderate airflow to increase the pH by the release of CO_2 from below pH 7.5 to pH 8 (Eqs. II-2 and II-3, chapter 2.6). The dropwise addition of a 30% $MgCl_2$ solution achieved PO_4-P removal rates of 49%. Simple aeration reduced the PO_4-P concentration remarkably by 60% due to struvite precipitation. However, no reduction was observed in the PO_4-P concentration when swine wastewater was neither aerated nor MgO added (Suzuki et al., 2007). The results show that optimizing struvite precipitation in swine wastewater is difficult and broad ranges of PO_4-P removal efficiencies were published in literature. Burns et al. (2001) and Suzuki et al. (2002) achieved high PO_4-P removal efficiencies (> 90%) in laboratory scale experiments but when the authors adopted their technique on farm scale and operated it continuously, the PO_4-P removal efficiencies were 30% - 40% lower. A reason is the regularly changing composition of the swine wastewater, which is highly dependent on the animals' food and water consumption, and the volume of water used by the workers for washing the barn (Suzuki et al., 2002).

This challenge with a changing composition and thus varied PO_4-P concentrations of the untreated pig slurry as well as digestates was observed during the three research stays in Beijing as the operation of the biogas plant was changed regularly in order to adapt to the varying conditions and needs on the farm. The first experiments (chapter 4.3) were carried out with a PO_4-P concentration of the digestate of about 2 mmol L^{-1} as the compost plant was not working and almost all solid feces were fed into the biogas plant. The residence time in the biogas plant remained the same as before and solid feces were added in excess, resulting in an incomplete digestion and thus a low gas production and a much higher DM and nutrient content of the digestate, aggravating struvite precipitation. As during the following research stays the compost as well as the biogas plants were working properly and digestion time was long enough to digest the material completely, the experiments started with a much lower initial PO_4-P concentration of the digestate of 0.4 mmol L^{-1}.

4.5 Ultracentrifugation for removal of suspended solids

I observed differences in precipitation when the experiments were carried out in China or at INRES, Plant Nutrition in Bonn, Germany. Therefore, sample composition was analyzed and the main difference was found in the DM content, which was much lower (≤ 1.5%) in Chinese slurries and digestates samples. The high DM content and consequently the organic particles in the German slurry hindered PO_4-P precipitation by complexation of the available phosphate or magnesium. Therefore, these digestate samples were diluted to a DM content of 1%, centrifuged and treated as described in chapter 3.4.2. The supernatant was used for further experiments.

In order to remove the remaining, finely dispersed organic matter fraction and the suspended solids in the digestates, two possible techniques were tested: mechanical removal by ultracentrifugation and chemical oxidation of organic compounds by H_2O_2. Every pretreatment step (centrifugation, ultracentrifugation and exemplarily for one sample the subsequent addition of H_2O_2) reduced the initial PO_4-P concentration. This reduction is attributed to the removal of small to medium sized particles, which might lead to an overestimation of the PO_4-P concentration in the supernatant. Precipitation was carried out as described in chapter 3.4.2.

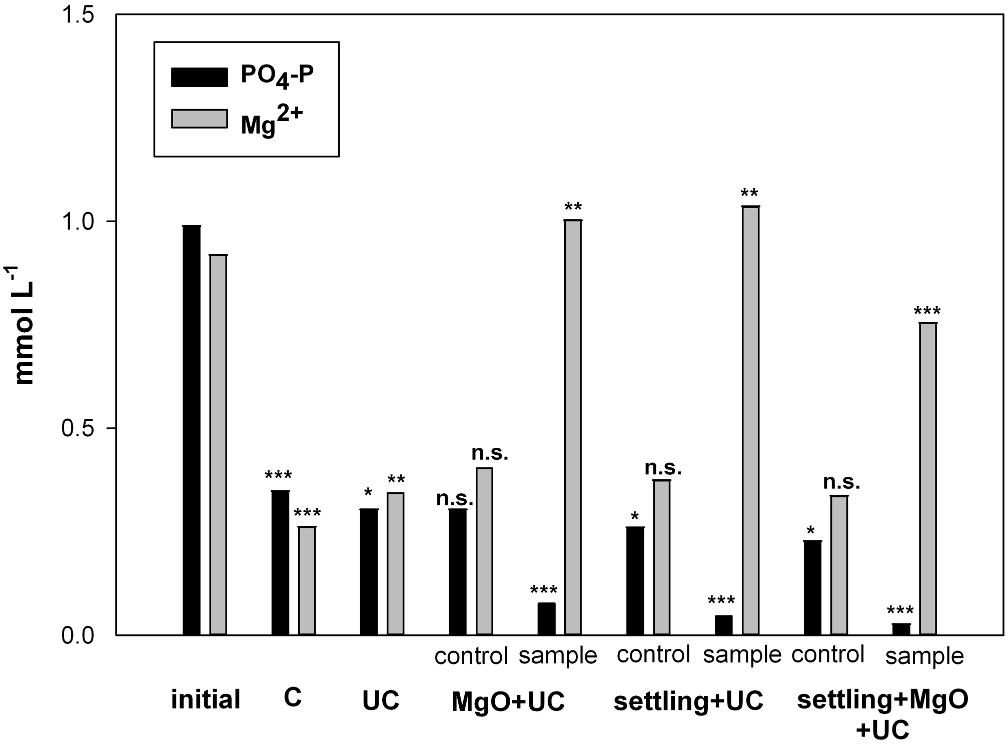


Fig. II-21: PO_4-P and Mg^{2+} concentrations in Chinese digestate from biogas plant 1 in mmol L^{-1} after each treatment step. Initial treatment illustrates the PO_4-P and Mg^{2+} concentrations in the samples before the treatment started. The samples were centrifuged for 2 hours at 30.000 g (C) and ultracentrifuged for 2 hours at r_{av} 125.000 g (UC). Afterwards, the samples were split into control samples (no MgO added) and samples, where MgO was added in a molar Mg:P ratio of 1:1. Control and treated samples were shaken for 1 hour and, 17 hours later, ultracentrifuged at r_{av} 125.000 g (MgO+UC). During the next step (settling+UC), the samples were not moved for 24 hours but thereafter ultracentrifuged at r_{av} 125.000 g. Then, MgO was added again in a molar Mg:P ratio of 1:1, shaken, and after 17 hours ultracentrifuged at r_{av} 125.000 g. Asterisks denote the statistical significance of the treatment compared to the previous treatment step. The MgO treated samples were compared with their corresponding control samples (n.s. not significant, * $p \leq 0.05$, ** $p \leq 0.01$, *** $p \leq 0.001$).

The initial PO_4-P and Mg^{2+} concentrations of this digestate sample were 1 mmol L^{-1} resp. 0.9 mmol L^{-1} and decreased significantly by 65% resp. 72% through centrifugation as organic material was removed. The following ultracentrifugation step reduced the PO_4-P concentration slightly further. At the same time, the Mg^{2+} concentration increased slightly, possibly through a release of Mg^{2+} from adsorbed suspended solids. Shaking did not reduce the PO_4-P concentration in the control samples significantly. The addition of MgO in a molar Mg:P ratio of 1:1 reduced the PO_4-P concentration, compared to the control sample, by 75%. Further struvite precipitated in the control and the MgO treated samples during the 24 hours settling period as well as after the repeated treatment (shaking for the control samples and MgO addition for the treated samples). In total, 91% of the PO_4-P present in the digestate samples could be precipitated when adding MgO in a molar Mg:P ratio of 1:1. In the control samples, the PO_4-P concentration decreased by 25% due to spontaneous struvite precipitation. I calculated, compared to the added quantity, an almost complete Mg^{2+} precipitation after the first and slightly lower precipitation after the second addition of MgO. At the same time, however, only 75% of the available PO_4-P in the samples was precipitated. Mg^{2+} was added in a molar Mg:P ratio of 1:1 and was thus theoretically enough to precipitate the available PO_4-P completely in form of struvite. However, as only 75% of the PO_4-P precipitated, almost 25% of the added Mg^{2+} might have formed soluble ion pairs with anions e.g. HCO_3^-, CO_3^{2-}, OH^- and SO_4^{2-} or being adsorbed to organic, suspended solids in the digestate, resulting in the formation of stable complexes and not being available for struvite formation. The second addition of MgO removed further 43% of the PO_4-P present in the sample. Here, too, almost half (47%) of the added Mg^{2+} did not precipitate as struvite but in other complexes. The following graph illustrates the results from the ultracentrifugation experiments with digestate 2, produced at the INRES, Plant Nutrition.

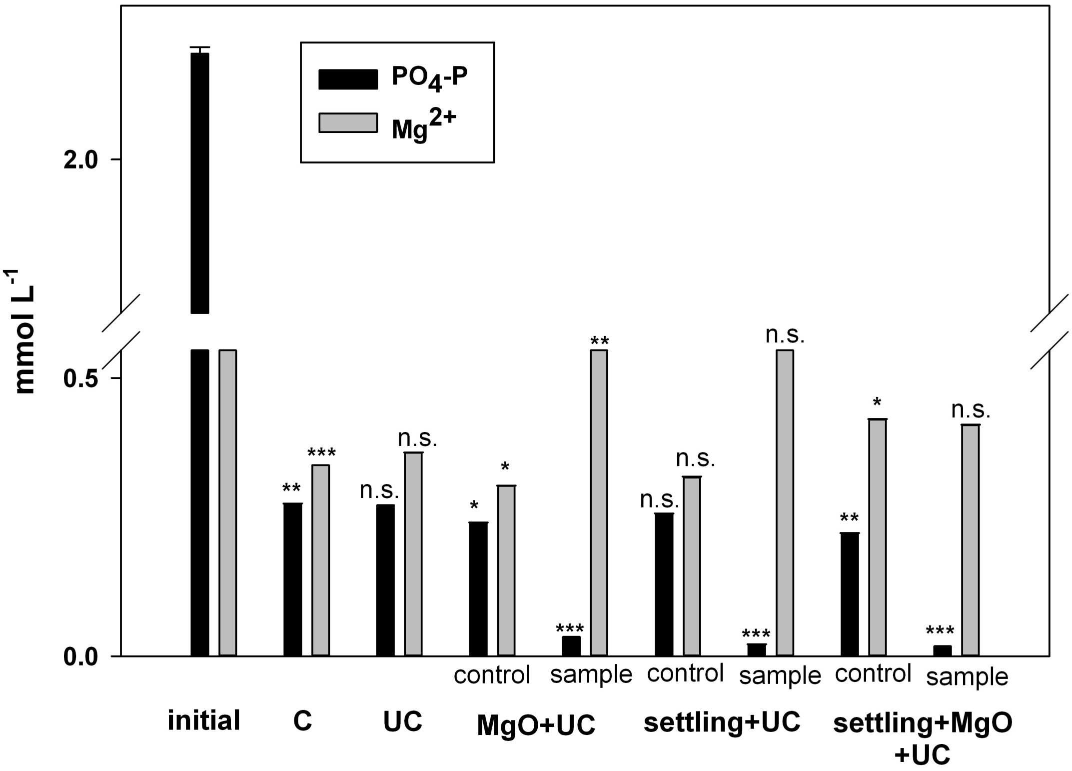


Fig. II-22: PO_4-P and Mg^{2+} concentrations in digestate 2 in mmol L^{-1} after each treatment step. Initial treatment illustrates the PO_4-P and Mg^{2+} concentrations in the samples before the treatment started. The samples were centrifuged for 2 hours at 30.000 g (C) and ultracentrifuged for 2 hours at r_{av} 125.000 g (UC). Afterwards, the samples were split into control samples (no MgO added) and samples, where MgO was added in a molar Mg:P ratio of 1:1. Control and treated samples were shaken for 1 hour and, 17 hours later, ultracentrifuged at r_{av} 125.000 g (MgO+UC). During the next step (settling+UC), the samples were not moved for 24 hours but thereafter ultracentrifuged at r_{av} 125.000 g. Then, MgO was added to the samples again in a molar Mg:P ratio of 1:1, shaken, and after 17 hours ultracentrifuged at r_{av} 125.000 g. Asterisks denote the statistical significance of the treatment compared to the previous treatment step. The MgO treated samples were compared with their corresponding control samples (n.s. not significant, * $p \leq 0.05$, ** $p \leq 0.01$, *** $p \leq 0.001$).

Centrifugation reduced the initial PO_4-P and Mg^{2+} concentrations in digestate 2 significantly by 88% resp. 56%. The following ultracentrifugation step did not reduce the concentrations further. In the control samples, the PO_4-P concentration decreased slightly through shaking. However, the addition of MgO reduced the PO_4-P concentration by 87%. The repeated treatment (shaking for the control samples and MgO addition for the treated samples) reduced the PO_4-P concentration only slightly further and might be explained by the fact that the concentration decreased already after the first addition of MgO by 87% (below 0.05 mmol L^{-1}

(4.75 mg L^{-1})). This made further precipitation difficult. In total, 93% of the PO_4-P present after the ultracentrifugation step precipitated as struvite.

For the chemical removal of organic material and suspended solids, digestate samples were treated with a 30% H_2O_2 solution. In order to check if H_2O_2 can remove additional quantities of PO_4-P compared to ultracentrifugation, samples from digestate 2 were additionally oxidized with H_2O_2.

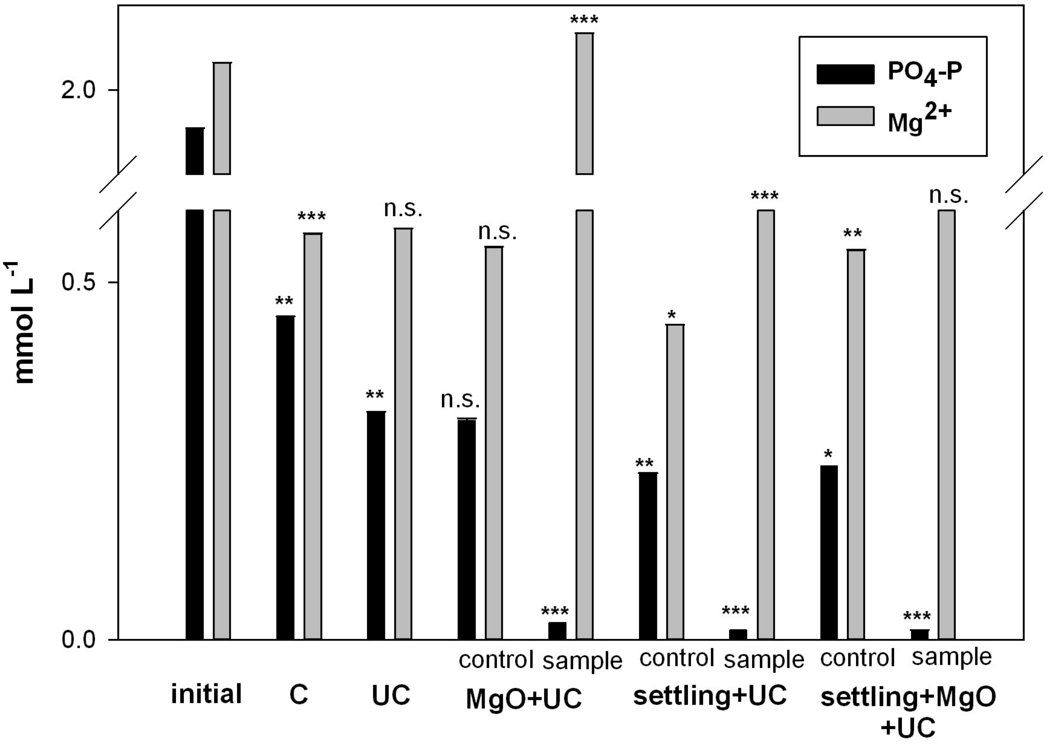


Fig. II-23: PO_4-P and Mg^{2+} concentrations in digestate 2 in mmol L^{-1} after each treatment step. Initial treatment illustrates the PO_4-P and Mg^{2+} concentrations in the samples after the pretreatment with a 30% H_2O_2 solution. The samples were centrifuged for 2 hours at 30.000 g (C) and ultracentrifuged for 2 hours at r_{av} 125.000 g (UC). Afterwards, the samples were split into control samples (no MgO added) and samples, where MgO was added in a molar Mg:P ratio of 1:1. Control and treated samples were shaken for 1 hour and, 17 hours later, ultracentrifuged at r_{av} 125.000 g (MgO+UC). During the next step (settling+UC), the samples were not moved for 24 hours but thereafter ultracentrifuged at r_{av} 125.000 g. Then, MgO was added to the samples again in a molar Mg:P ratio of 1:1, shaken, and after 17 hours ultracentrifuged at r_{av} 125.000 g. Asterisks denote the statistical significance of the treatment compared to the previous treatment step. The MgO treated samples were compared with their corresponding control samples (n.s. not significant, * $p \leq 0.05$, ** $p \leq 0.01$, *** $p \leq 0.001$).

The pretreatment with H_2O_2 reduced the initial PO_4-P concentration in the digestate samples. A possible reason might be that different ions (e.g. PO_4-P) were released during oxidation of the organic material, thus altering ion activities. This might have created conditions that favored the formation of ion pairs resulting in a spontaneous struvite precipitation. The centrifugation step decreased, as well as in the other digestates described above, the initial PO_4-P and Mg^{2+} concentrations significantly by 70% resp. 75%. Ultracentrifugation decreased the PO_4-P concentration significantly by further 9% whereas the Mg^{2+} concentration increased even slightly. The following treatment did not change the PO_4-P concentrations further as the PO_4-P decreased almost completely after the first addition of MgO. The 24 hours settling time removed further small amounts of the PO_4-P present.

General discussion

Centrifugation removed organic matter and bigger sized particles and thus 65% - 88% of the initial PO_4-P and 56% - 75% of the Mg^{2+} in the different digestate samples. The following ultracentrifugation step removed then the finely suspended solids. However, their influence seemed to be low as the PO_4-P concentration decreased only slightly (0% - 9%). Shaking of the control samples yielded a total PO_4-P reduction of 20% - 25% due to spontaneous struvite precipitation. Adding MgO to the samples resulted in a PO_4-P removal of 74% for the Chinese digestate and 92% for the H_2O_2 pretreated samples. The following settling period, where no MgO was added and the samples were not moved, removed further 3% - 10% of the PO_4-P. This was attributed to slowly settling struvite crystals, which formed and grew after MgO was added but were then too small to be removed during the previous ultracentrifugation step. Further PO_4-P was removed in the Chinese digestate 1 (Fig. II-21) after the repeated addition of MgO (Mg:P ratio 1:1), whereas it had no effect on the other two digestate samples. In total, 91% - 96% of the PO_4-P present after ultracentrifugation could be precipitated as struvite. For the overall PO_4-P removal, it was more efficient when the samples were not disturbed for 24 hours so that struvite could be formed and settle down than adding MgO a second time. Thus, the results support the assumption that organic particles and suspended solids prevent struvite precipitation by complexing added Mg^{2+} and/or the available PO_4-P.
Particle size distribution in slurry is an important aspect, as only particles above a certain size will sediment. If particle mass density is similar to the mass density of water, the particles will not settle at all. Further, in slurry and digestate, viscosity

plays also an important role as it might slow down sedimentation. This aspect is described by Stokes' law, an equation where the dynamic viscosity, the radius of the object, the particle's settling velocity and the frictional force, also known as Stokes' drag, acting on the interface between the fluid and the particle, are included. Anaerobic digestion reduces the concentration of DM and particle size in the digestate. Massé et al. (2005) observed, that particles < 10 µm account for 64% of DM in raw slurry and increases to 84% of DM in anaerobically digested slurry. The conditions in the biogas digester- high temperature and stirring- facilitate microbial degradation of larger particles, resulting in relatively small particles with slowly degradable material.

In my previously described experiments, separation was achieved through sedimentation and was chosen due to the low costs and the simple technology. The conical shape of the centrifuge tubes facilitated sampling as the struvite crystals and particles accumulated in the tip. The separation efficiency of DM increased with an increasing DM content of the slurry. This might be explained by the continuous movement, which enhanced the attachment of small particles to larger particles and thus improving the settling of small particles (Hjorth et al., 2010). However, the precipitation velocity of a solid particle being separated from the liquid phase depends on the size. The small particles have a laminar flow and thus result in the slowest settling velocity (Hjorth et al., 2010). The Chinese digestate (Fig. II-21) had an average DM content of ≤ 1.5%. In this DM range, settling was described as unhindered and should have been completed within 1 hour (Ndegwa et al., 2001). Initially, the samples of digestate 2 (Fig. II-22) had a DM content of 3.5% and were, before starting the experiment, diluted to 1%. For diluted slurries with 0.5% DM and 1% DM, Ndegwa et al. (2001) observed a slower, retarded settling presumably as at this low DM fewer of the fine particles can co-precipitate with the larger, fast-settling particles. Increasing the gravitational force by centrifugation reduced on the one hand the settling time for the struvite crystals. On the other hand, the organic particles in the digestate were removed, too, which facilitated struvite formation. Further, the additional ultracentrifugation removed a large quantity of suspended solids, leaving an almost clear digestate solution and thus facilitating struvite precipitation.

4.6 Oxidation with H_2O_2 for removal of suspended solids

For the chemical oxidation of organic material and suspended solids, the untreated pig slurry, as well as the digestates, were treated with a 30% H_2O_2 solution. When H_2O_2 came in contact with slurry or digestate, CO_2 was generated and bubbled out of the digestate with an intense foam production. This lasted until all organic material was digested. The resulting CO_3^{2-} reacted with the available Ca^{2+} in the digestate, formed $CaCO_3$ and precipitated.

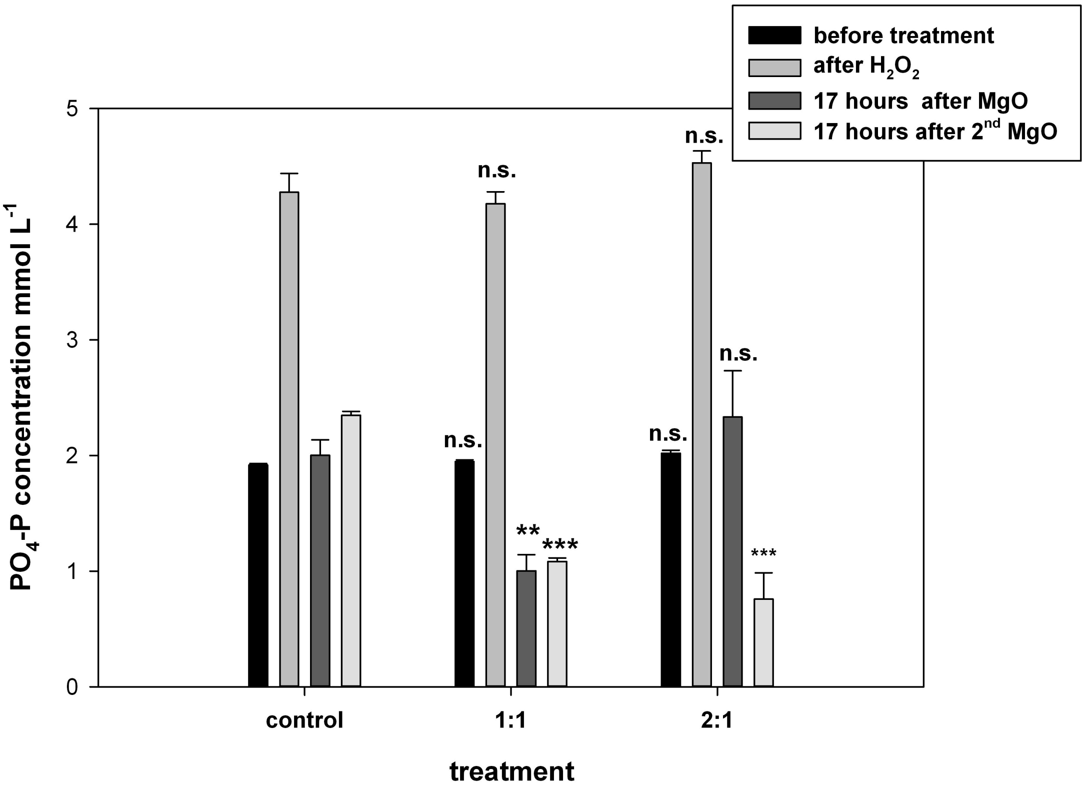


Fig. II-24: PO_4-P concentrations in untreated pig slurry (mmol L^{-1}). The graph shows the initial concentration, the concentration after the treatment with 30% H_2O_2, followed by first and second addition of MgO in a molar Mg:P ratio of 1:1 and 2:1. Molar Mg:P ratios refer to the PO_4-P concentration after the treatment with H_2O_2. The control samples did not receive MgO. Asterisks denote the statistical significance of the results compared to the control samples (n.s. not significant, * $p \leq 0.05$, ** $p \leq 0.01$, *** $p \leq 0.001$).

The PO_4-P concentration increased considerably from 1.9 mmol L^{-1} to 4.3 mmol L^{-1} when H_2O_2 was added to the untreated pig slurry. This is attributed to the oxidation of organic material and the associated release of solute phosphate. Spontaneous struvite precipitation decreased the PO_4-P concentration in the control samples by 53% after shaking. However, the PO_4-P concentration increased significantly after shaking the control samples again. A reason might be a delayed oxidation reaction that was induced by the shaking process and thus releasing additional PO_4-P. Another reason might be a further release of CO_2, which thus increased pH and facilitated struvite precipitation. The addition of MgO (Mg:P ratio 1:1) reduced the PO_4-P concentration, compared to the control samples, significantly by 76%. However, the addition of MgO in a molar ratio of 2:1 resulted in a lower PO_4-P removal (48%). The second addition of MgO decreased only the PO_4-P concentration in the 2:1 treated samples (83%). Final concentration of the treated digestate was 0.9 mmol L^{-1}.

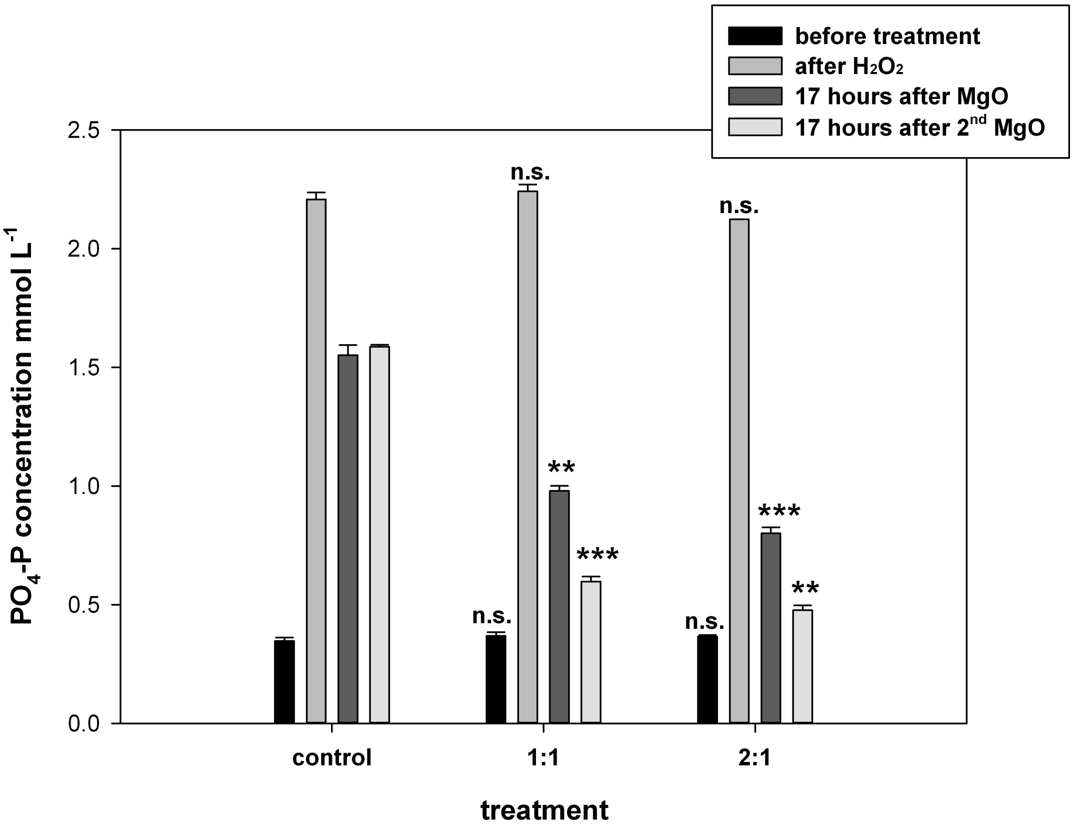


Fig. II-25: PO_4-P concentrations in digestate from biogas plant 1 (mmol L^{-1}). The graph illustrates the initial concentration, the concentration after the treatment with 30% H_2O_2, followed by first and second addition of MgO in a molar Mg:P ratio of 1:1 and 2:1. Molar Mg:P ratios refer to the PO_4-P concentration after the treatment with H_2O_2.The control samples did not receive MgO. Asterisks denote the statistical significance of the results compared to the control sample (n.s. not significant, * $p \leq 0.05$, ** $p \leq 0.01$, *** $p \leq 0.001$).

The PO_4-P concentration increased from initially 0.36 mmol L^{-1} to 2.2 mmol L^{-1} after the treatment with H_2O_2. Shaking decreased the PO_4-P concentration in the control samples by 30% and did not decrease further when the samples were shaken again.

The PO_4-P concentration decreased by 56% after MgO was added in the ratio 1:1 and even further (62%) with the ratio 2:1. The second addition of MgO decreased the PO_4-P concentration further, resulting in a total PO_4-P removal of 73% (1:1) resp. 78% (2:1). After the treatments, the digestate had a PO_4-P concentration of 0.88 mmol L^{-1}. These results are identical to the ones obtained with digestate from biogas plant 2 and will thus not be shown.

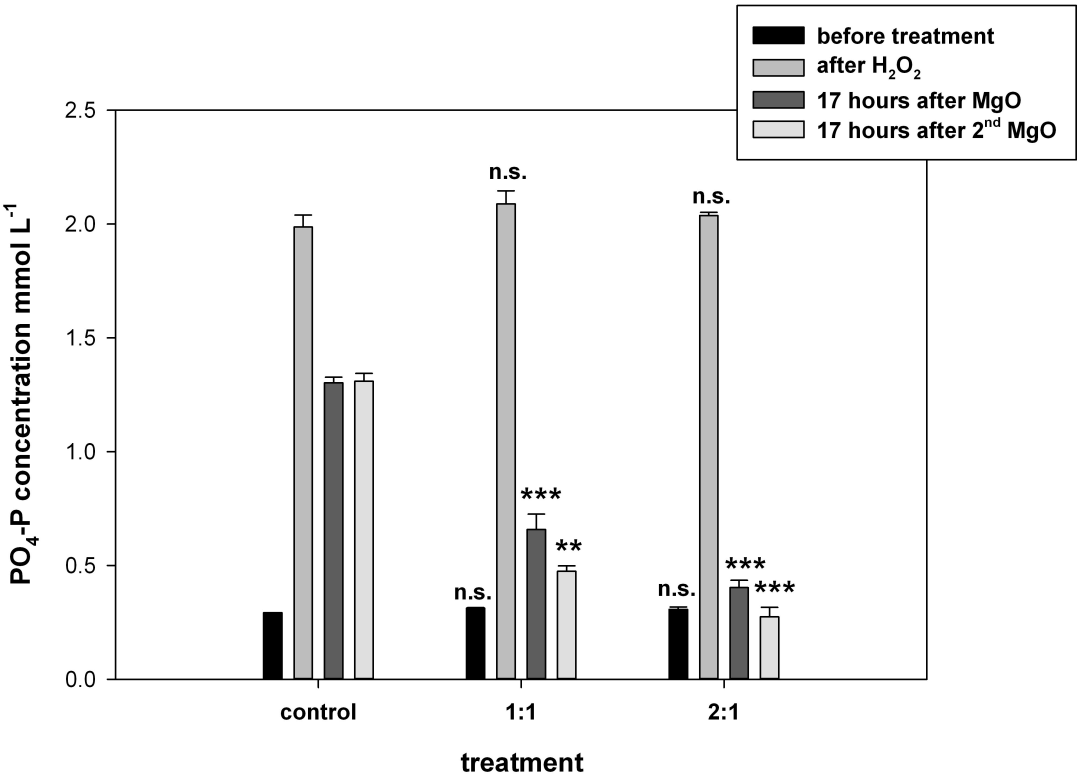


Fig. II-26: PO_4-P concentration in digestate from biogas plant 3 (digested twice, mmol L^{-1}). The graph shows the initial concentration, the concentration after the treatment with 30% H_2O_2, followed by first and second addition of MgO in a molar Mg:P ratio of 1:1 and 2:1. Molar Mg:P ratios refer to the PO_4-P concentration after the treatment with H_2O_2.The control sample did not receive MgO. Asterisks denote the statistical significance compared with the control sample (n.s. not significant, * $p \leq 0.05$, ** $p \leq 0.01$, *** $p \leq 0.001$).

The treatment with H_2O_2 increased the initial PO_4-P concentration from 0.3 mmol L^{-1} to 2 mmol L^{-1}. Even if the initial PO_4-P concentration was slightly lower compared to digestate 1, identical concentrations were achieved after the organic material was oxidized. Shaking decreased the PO_4-P concentration in the control samples (34%). However, it was not reduced further when the samples were shaken again. The PO_4-P concentration in the samples receiving MgO (molar Mg:P ratio of

1:1) decreased remarkably after the first addition (69%), and only slightly further (8%) when MgO was added again. Adding MgO in the molar ratio of 2:1 removed 80% with the first MgO addition and further 7% with the second. In this sample, the elevated MgO ratio affected the PO_4-P reduction.

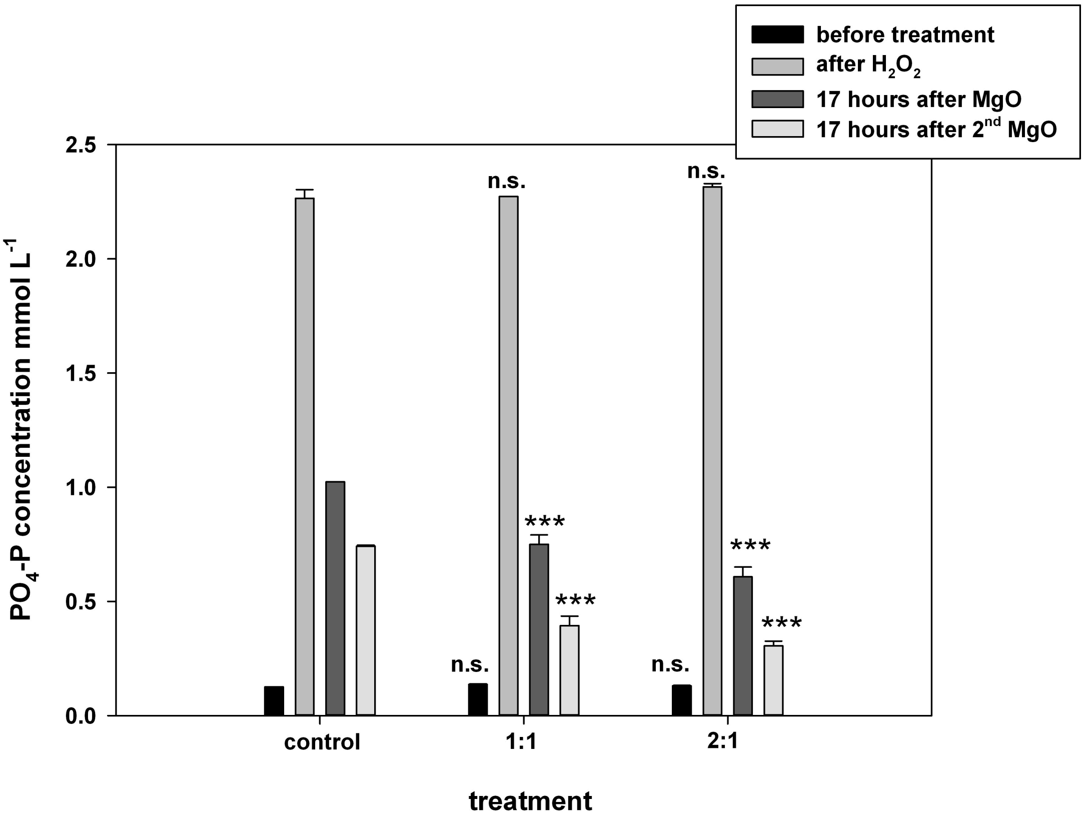


Fig. II-27: PO_4-P concentration in the effluent leaving the farm (mmol L^{-1}). The graph illustrates the initial concentration, the concentration after the treatment with 30% H_2O_2, followed by first and second addition of MgO in a molar Mg:P ratio of 1:1 and 2:1. Molar Mg:P ratios refer to the PO_4-P concentration after the treatment with H_2O_2.The control sample did not receive MgO. Asterisks denote the statistical significance compared with the control sample (n.s. not significant, * $p \le 0.05$, ** $p \le 0.01$, *** $p \le 0.001$).

This sample had the lowest initial PO_4-P concentration (0.13 mmol L^{-1}) but showed the highest ability to release solute phosphate through oxidation. This resulted in an increased PO_4-P concentration of 2.3 mmol L^{-1}. Shaking of the control samples removed in total 67% of the PO_4-P present. The addition of MgO (1:1) achieved a PO_4-P removal of 67% and, when added a second time, further 16% so that in total 83% PO_4-P were removed. The addition of MgO at an increased molar Mg:P ratio of 2:1 removed a slightly higher proportion of PO_4-P (87%) and was thus more efficient than the Mg:P ratio 1:1.

General discussion

Oxidizing the slurry and digestate samples increased the PO_4-P concentrations considerably as the majority of P in animal slurries can be found in the particle fraction, where 70% of the P is adsorbed to particles or is forming parts of complexes. Only 30% of the P is dissolved in the liquid phase (Hjorth et al., 2010). The PO_4-P concentrations decreased significantly during the different treatment steps on the pilot farm, reducing the solute PO_4-P from initially 2 mmol L^{-1} in the undigested slurry to 0.13 mmol L^{-1} when leaving the farm. Treating the samples with H_2O_2 resulted in an abrupt release of large amounts of dissolved P, which became dissolved from complexes in slurry and digestates. These releases were moderate for the untreated pig slurry as the PO_4-P concentration doubled after the H_2O_2 treatment. PO_4-P releases were considerably high for the digestates. However, surprisingly, the highest increase in the PO_4-P concentration after oxidation was achieved in the effluent leaving the farm. This effluent was digested twice and afterwards aerated for further removal of organic components and nitrogen. Oxidation increased the PO_4-P concentration 17 times compared to the initial concentration, indicating that there was still a huge quantity of P bound to organic material ("hidden P"). If the amount of P contained in the farm effluent exceeds the nutrient uptake in well fertilized soils, this P contributes to P losses through surface runoff and eutrophication.

Spontaneous struvite precipitation reduced the PO_4-P concentration in the oxidized control samples after shaking by about 30% for the digestates and almost 55% for the untreated pig slurry and the aerobically treated effluent. Further, the oxidation with H_2O_2 increased the pH of the samples, which thus facilitated struvite precipitation. The addition of MgO resulted in an overall decrease in the PO_4-P concentrations by 56% - 87%. However, the PO_4-P removal efficiencies were, except for the undigested pig slurry, significantly higher (4% - 12%) with an increased molar Mg:P ratio (2:1). In these cases, a calculation on cost effectiveness for the usage of a doubled quantity of MgO has to be carried out and might be justifiable if the gained struvite can be sold at a reasonable price.

4.7 Analysis and composition of the precipitate

In general, particle formation is referred to as nucleation or induction (Burns et al., 2003). Homogenous nucleation occurs when the phosphorus precipitate is the nucleus (Parsons, 2001). When other suitable nuclei are present, like e.g. sand grains, struvite formation is heterogeneous. Batch experiments with nutrient solutions showed that struvite particle size increased from 0.1 to 3.0 mm when the reaction time increased from 1 to 180 minutes (Stratful et al., 2001). Hence, a bigger particle size enhances the recovery of the precipitated material. In my experiments with slurry and digestate, where organic matter and suspended solids were present, the reaction time was 17 hours and thus enough for struvite formation and crystal growth.

A visible quantity of a precipitate (Fig. II-28) formed at the bottom of the vessels after the respective treatments. All precipitates were collected and dried at 50°C, as higher temperatures will lead to struvite instability and transformation to dittmarite ($MgNH_4PO_4 * H_2O$) due to the evaporation of water (Sarkar, 1991). After the drying process, the precipitates had a greyish-brown discoloration originating from the organic C still present in the samples.

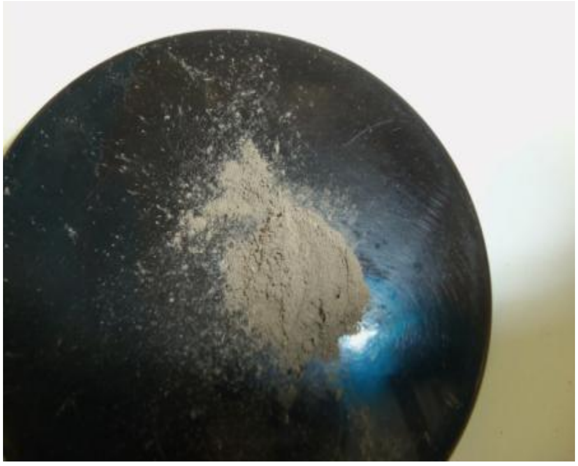


Fig. II-28: Struvite precipitate after drying at 50°C

Afterwards, the precipitates were analyzed by X-ray diffractometry. For the two untreated slurry samples (Figs. II-29 and II-30), five main mineral components were identified. The purity of the minerals was not quantified and the quantity of the remaining precipitate varied between the samples. The following charts show the results from X-ray diffractometry in undigested slurry, digestate samples and samples treated with H_2O_2.

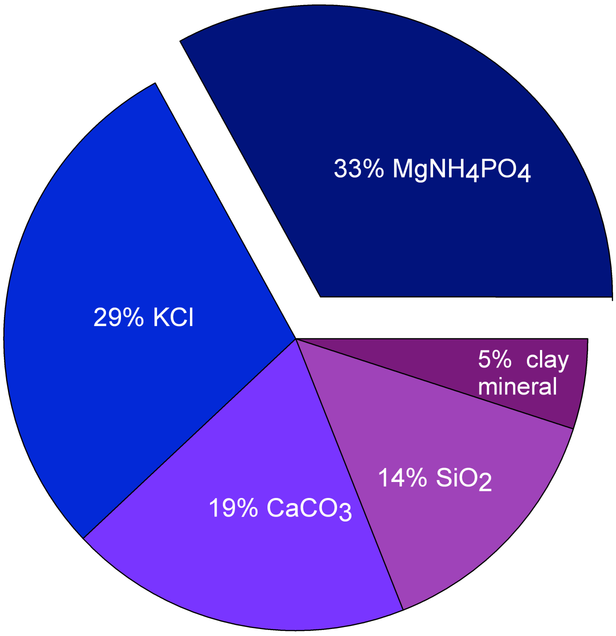


Fig. II-29: Composition (in %) of the precipitate in the control sample without MgO in undigested slurry, analyzed by X-ray diffractometry.

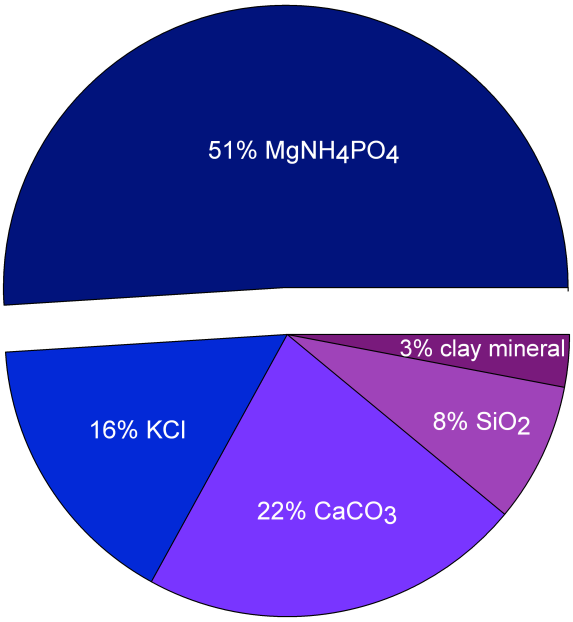


Fig. II-30: Composition (in %) of the precipitate with MgO added at a molar Mg:P ratio of 2:1 in undigested slurry, analyzed by X-ray diffractometry.

The mineral composition of the two undigested pig slurry precipitates varied considerably. The two main differences in the samples illustrated in Figs. II-29 and II-30 could be observed in the quantities of struvite and KCl. 33% of the precipitate in the control sample and 51% in the MgO added sample were identified as struvite. This difference can clearly be attributed to the added MgO, which induced a higher struvite precipitation. Further, the quantity of KCl varied remarkably with 29% in the control sample and 16% in the MgO added sample. The percentage of $CaCO_3$, SiO_2 and smectite, an Mg-rich clay mineral, varied only slightly in the two samples.

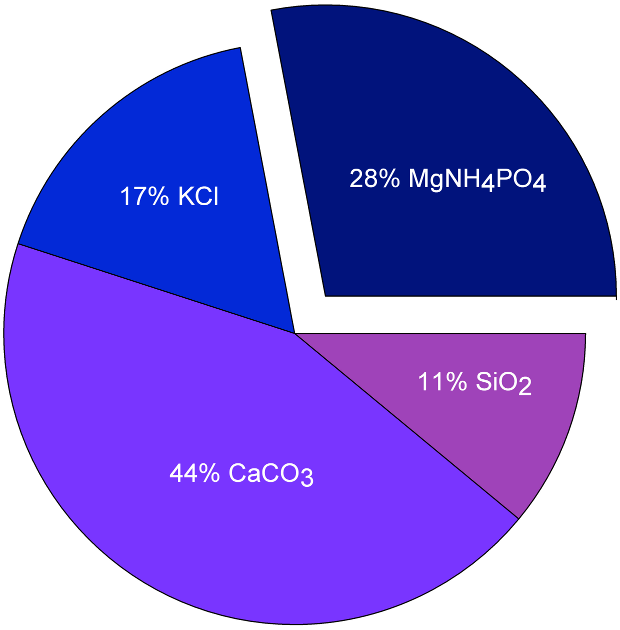


Fig. II-31: Composition (in %) of the precipitate in the control sample without MgO in digestate, analyzed by X-ray diffractometry.

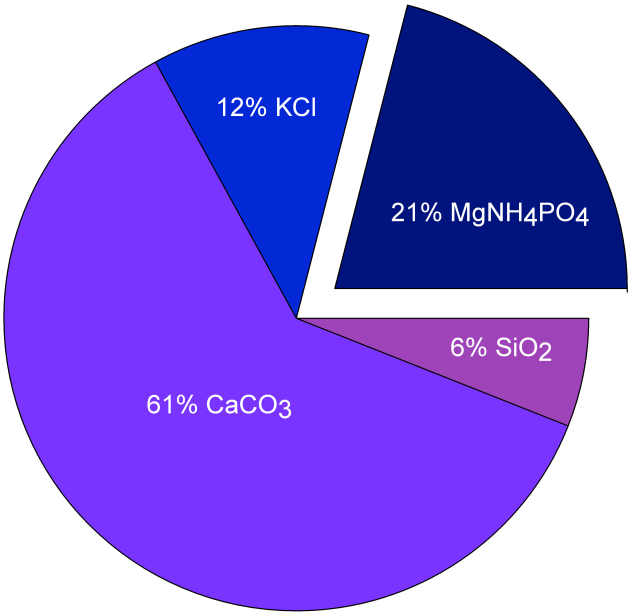


Fig. II-32: Composition (in %) of the precipitate with MgO added at a molar Mg:P ratio of 2:1 in digestate, analyzed by X-ray diffractometry.

The two precipitates obtained after the treatment of digestate samples varied also in their mineral composition. The share of the obtained struvite was higher (28%) in the control sample than in the MgO treated sample (21%). The amount of KCl was only slightly higher in the control sample. The biggest difference was observed in the $CaCO_3$ content, which was considerably higher in the MgO added sample. SiO_2 was almost doubled compared to the control sample.

A remarkable decrease of 30% in the struvite fraction could be observed when comparing Figs. II-30 and II-32. This can be explained by the influence of the biogas process during which some of the nutrients partially crystallized out as phosphates and carbonates due to an elevated pH. This was already described above in chapter 4.4 when comparing the initial PO_4-P concentration of the slurry/digestate and was also described by Marcato et al. (2008), who observed a significant precipitation of Ca (44%) and Mg (32.5%) during the biogas process. The presence of SiO_2 in the precipitates indicates the existence of sand that was brought into the system by wind blowing dust or dirt into the slurry retention pond before entering the biogas plant. Further, some of the effluents from the pig houses were channeled away in unhitched drains, carrying away soil particles and bringing them also into the retention pond. This might explain the presence of SiO_2 and the Mg-rich clay mineral (smectite) in the undigested samples.

In my experiments with Chinese pig slurry and digestate, similar precipitate composition was obtained as described by Shepherd et al. (2009) during struvite precipitation in pig slurry from two facilities in Iowa, USA. The authors did not find any KCl in their precipitate samples. This contradicts my findings with moderate percentages of KCl (12% - 29%) and can be attributed to the different feeding practices on the farm. Soybean contains high concentrations of K^+ (Hjorth et al., 2010) and is a basic component in the pig diet on the Chinese farm (Mendoza-Huaitalla et al., 2011). The high proportion of KCl in the precipitate might thus be explained by the supplementation of nutrients to the regular pig diet (basic soybean meal). However, about 90% of the supplemented K^+ in the pig fodder ratios is excreted- mainly in urine, as it is highly soluble, but also in feces (Burton and Turner, 2003; Mendoza-Huaitalla et al., 2010). Excretion led to K contents in manures from fattening pigs of 13 g kg^{-1} (dry basis) and were slightly lower compared to results from pig manure composition of other studies in China (16.50 g kg^{-1} or 17.24 g kg^{-1}), but much higher compared to studies from Belgium (4.96 g kg^{-1}), Denmark (3.20 g kg^{-1}) or Canada (1.52 g kg^{-1}). Mendoza-Huaitalla (2010) explained this great variability with differences in the husbandry management systems among the countries (e.g. gan qing fen: collecting the dry manure management in China), the use of local feedstuff like vegetables e.g. carrots and higher pig ratios.

The high calcium content, precipitated as $CaCO_3$, may result from the high proportion of Ca in the feed of mainly farrowing sows as Ca is related to milk production. Excess amounts of Ca were either excreted by the sows or washed away with feed particles, ending up in the wastewater stream flowing into the biogas plant. Schuchardt et al. (2011) calculated that about 20% of the excreted Ca was found in the urine and 80% in the feces. This explains the difference in the moderate percentage of $CaCO_3$ in untreated slurry and the higher percentage in digestate as for the biogas process additional feces and thus more Ca was added. However, besides excretion, the Ca content in the drinking/washing water might also play an important role. The main water source in the pig farm is groundwater, distributed from a well of 30 m - 40 m depth (Mendoza-Huaitalla, pers. communication, 2012). Unfortunately, there are no data on the drinking/washing water quality available but the Ca concentration might be high and thus increase the concentration in the retention pond and the biogas plant.

The precipitate of the control sample pretreated with H_2O_2 (Fig. II-33) revealed that the two main components were KCl and $CaCO_3$, both accounting for around 40%, respectively. The share of SiO_2 is with 20% considerable and highest compared to Figs. II-29 to II-34. In contrast to the other precipitates, no phosphate, neither in form of struvite nor in form of other phosphate minerals, was precipitated. This is astonishing, as the PO_4-P concentration increased after the pretreatment with H_2O_2 due to the release of organically bound P and decreased remarkably after shaking the samples (Chapter 4.6.). The PO_4-P must have been precipitated, but it was likely arranged in an amorphous form, which cannot be identified by X-ray diffractometry. The mineral structure and thus the composition of the precipitates was determined exemplarily for the above mentioned samples. Afterwards, all samples were decomposed by acid digestion (with HNO_3) and analyzed on their nutrient contents (Mg, P, K, Ca).

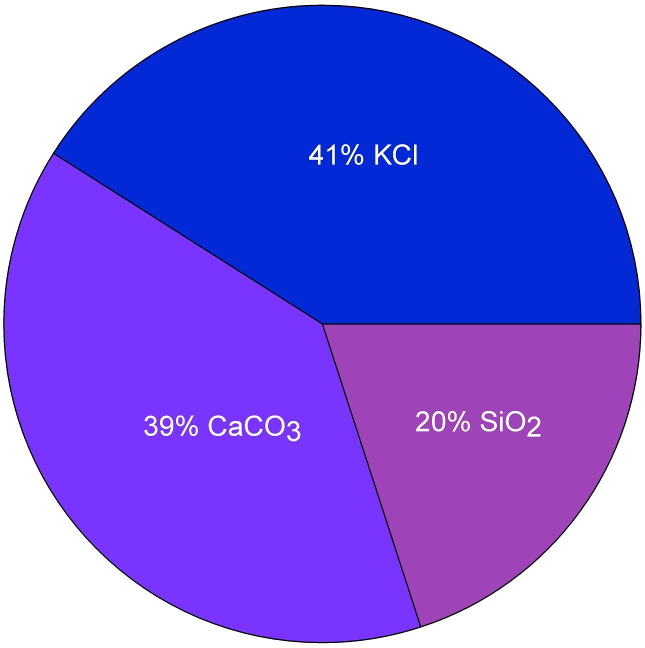


Fig. II-33: Composition (in %) of the precipitate in the control sample without MgO in undigested slurry, pretreated with H_2O_2 and analyzed by X-ray diffractometry.

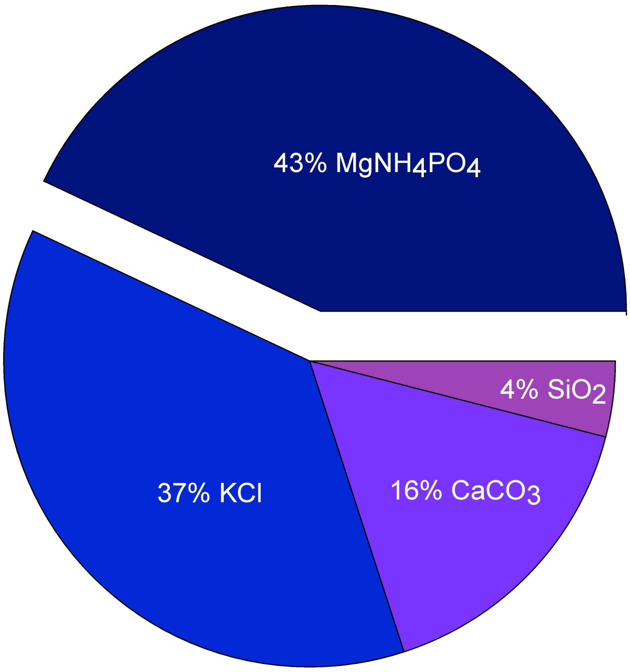


Fig. II-34: Composition (in %) of the precipitate with MgO added at a molar Mg:P ratio of 2:1 from undigested slurry samples, pretreated with H_2O_2 and analyzed by X-ray diffractometry.

Based on the obtained concentrations, the molar ratios of $Mg^{2+}:PO_4^{3-}:K^{+}:Ca^{2+}$ were calculated and shown in table II-1. Results were normalized to Mg^{2+}, which was set to 1.

Tab. II-1: Molar ratios of the nutrients Mg, P, K, Ca in the resulting precipitate samples from undigested slurry, digestate and the effluent leaving the farm. Results were normalized to Mg^{2+}, which was set to 1.

Sample type	Molar ratio		Sample type	Molar ratio	
	$Mg^{2+}:PO_4^{3-}$	$K^+:Ca^{2+}$		$Mg^{2+}:PO_4^{3-}$	$K^+:Ca^{2+}$
Undigested slurry:			**Biogas plant 2:**		
Mg:P 1:1	1 : 1.3	0.8 : 1.9	Mg:P 1:1	1 : 1.5	0.7 : 3.2
Effluent leaving farm			**Biogas plant 3:**		
			Control	1 : 1.4	1.8 :1.4
Mg:P 2:1	1 : 0.4	9.3 : 2.8	Mg:P 1:1	1 : 1.2	3.9 : 2.2
			Mg:P 2:1	1 : 1.4	0.9 : 1.6

The acid digestion step used for the decomposition of the dried precipitate, led, as well as drying the samples in the oven, to degassing of the ammonium present in the struvite. Thereby, the ammonium concentration could not be measured and the molar ratio calculated.

The molar ratio of $Mg^{2+}:PO_4^{3-}$ of the precipitates was in the range of 1:1.2 - 1:1.5 whereas the molar ratio of pure struvite is 1:1. However, dependent on the (pre)treatment, the PO_4-P precipitated not only as struvite but also as component in other phosphates or even in amorphous form. Hence, the formed precipitate was enriched with phosphorus resulting from the formation of other phosphate containing compounds that may have been formed but have not been identified. Thus, I was able to recover phosphorus but only in part as struvite. All samples contained large amounts of Ca^{2+} in the form of $CaCO_3$. This can, if applied as fertilizer to slightly acidic soils, help to increase soil pH and thus reduce the need for liming.

5. Conclusion

Pig slurry and digestate are valuable resources of phosphorus. Experiments with slurry and digestate samples from the pilot pig farm in the sub-urban area of Beijing showed that phosphate could be regained through struvite ($MgNH_4PO_4$) precipitation, and therewith confirmed my first hypothesis.

After the addition of MgO, almost 80% of the solute PO_4-P could be precipitated as struvite. Although anaerobic digestion should have favored precipitation conditions, I did not observe higher PO_4-P removal in digestate samples, which was thus inconsistent with my second hypothesis.

The third hypothesis states that struvite precipitation is influenced by slurry/digestate components and characteristics and was confirmed in my experiments. A changed pH did not reveal significant differences in PO_4-P removal efficiencies, it was rather the molar Mg:P ratio and the repeated addition of MgO that influenced struvite precipitation. The organic matter and suspended solids present in the samples influenced struvite precipitation. The chemical oxidation with H_2O_2 released formerly bound phosphate so that the repeated addition of MgO resulted in high PO_4-P removal efficiencies of 67% - 87%. The PO_4-P concentration of the effluent leaving the farm increased considerably after oxidation, indicating that there was still a huge quantity of P bound to organic material (“hidden P”). This “hidden P” might contribute to P losses through surface runoff and eutrophication if the amount of P contained in the farm effluent exceeds the nutrient uptake in well fertilized soils.

III. Nitrogen recovery

1. Introduction

Intensive agriculture and animal husbandry create large amounts of wastewater containing nutrients like nitrogen (N) and phosphorus (P). This causes, especially in agricultural areas with high animal densities, the problem of storage and treatment of large slurry quantities. In Germany, slurry application is regulated by the Düngeverordnung (DüV), which defines the dispersal period and the permitted spreading areas. According to DüV (2008), the legitimate amount for total nitrogen applied with slurry is 170 kg N ha^{-1}. However, excess or inappropriate slurry application (e.g. in winter) might lead to nutrient leaching and relocation to deeper soil horizons or ground- and surface waters. Ammonium (NH_4^+) in slurry and nitrate (NO_3^-), formed after oxidation in soil, can thus lead to eutrophication of water bodies like algal bloom or fish killing (Søndergaard and Jeppesen, 2007). However, the high nitrogen concentrations do not only harm aquatic organisms but also mammals. In their intestinal tract, high nitrate concentrations in the drinking water can be reduced to nitrite (NO_2^-) and thus causing cyanosis in newborns and babies. Further, nitrite might also form nitrosamines, which are carcinogenic and harm the elderly (Wolff and Wassermann, 1972). In order to avoid threats to human and animal health, the German threshold value according to the drinking water directive is 50 mg NO_3^- L^{-1} (TrinkwV, 2001).

Nitrogen is the main nutrient limiting the amount of slurry that can be applied to agricultural fields. Ammonium-nitrogen (NH_4-N) is the fraction of manure that is most readily available to plants. However, it is also the portion most easily lost via volatilization and most affected by field management and environmental conditions (Meisinger and Jokela, 2000). In general, slurry application on agricultural fields is always accompanied by nutrient losses through surface run off and gaseous losses like mainly soluble nitrogen compounds (e.g. NH_3) and unpleasant odor. Therefore, application methods injecting slurry directly into the soil should be favored (Misselbrook et al., 1996; Jokela and Meisinger, 2008).

Based on the high nitrogen content in slurry and the application constraints, nutrient recovery methods can play an important role in manure management. Further, these methods could allow higher slurry spreading rates, particularly, as agriculture is intensified in developing and emerging countries and the prices for raw fertilizer materials are rising. Therefore, it is necessary to develop chemical and physical processes to extract the nutrients and redistribute them from areas with high animal farming densities to areas with nutrient shortages. However, slurry redistribution is limited by transportation and spreading costs due to the relatively low nutrient and the relatively high water content. Volume reducing treatments such as vacuum evaporation might favor the economical feasibility. However, if no cheap source of thermal energy is available, this pretreatment (e.g. evaporation) will cause additional costs and will thus be the main limiting factor (Bonmatí and Flotats, 2003b). Another strategy for a better nutrient management in areas with a structural nitrogen surplus is the nitrogen removal and subsequent recovery. The recovered product can then be returned into the agricultural system and thus close the nitrogen cycle and simultaneously save energy by avoiding the production of new N-containing fertilizers (Bonmatí and Flotats, 2003b).

On the pilot farm, the anaerobic digestion process is followed by an aerobic process, which reduces the nutrient overload in wastewater and thus minimizing the eutrophication potential of animal wastes. This work focused on the development and implementation of a simple ammonia stripping technology, which can transform the nutrients into a concentrated and thus transportable and economical attractive form.

The problem of organic waste management and thus the excess application of animal manures in Chinese agriculture was described by Ju et al. (2005), who focused on the “utilization and management of organic wastes in Chinese agriculture”. The authors describe that the industrialization in China came along with a shifted consumption behavior, resulting in a more and more intensified animal production. That means that animal production shifted, especially in peri-urban areas, from small, individual household scale production to a large-scale production. This shift led more and more to a specification and thus a “decoupling” of plant production from animal production, resulting in nutrient accumulation and environmental pollution in those areas. The authors advocate for a recoupling of the two production systems- animal and crop production- as the therewith accompanied use of animal wastes as fertilizers for plant production can lead to better soil fertility and help to reduce the pollution from animal husbandry. In 2001, the State Environmental Protection Administration (SEPA) launched, according to the authors Ju et al. (2005), a compulsory decree for waste treatment from animal production plants in the Beijing area. Since then, livestock farms have to treat their wastes in anaerobic and aerobic digesters. The combination of both processes has several advantages like degradation of persistent toxic substances (e.g. halogenated hydrocarbons), sanitation of the waste (Ju et al., 2005; Quan et al., 2010), preventing volatile organic compound emissions, controlling odors, better nutrient mineralization and energy recovery through methane production (Bonmatí and Flotats, 2003b). Furthermore, the anaerobic process can reduce the chemical oxygen demand (COD) and total P concentration (Bonmatí and Flotats, 2003b). The national discharge standards of pollutants for livestock and poultry define that NH_3-N and total P must be lower than 80 mg L^{-1} and 8.0 mg L^{-1}, respectively (Quan et al., 2010).

Coal is the main source for ammonia fertilizer production in China, whereas the rest of the world uses natural gas since the early 1960s. For many years, fertilizer production was subsidized in China. Thus, the producers benefited from lower prices (30% - 50%) in electricity and natural gas (Kahrl et al., 2010) compared to other industrial producers, resulting in fertilizer prices below world market prices. Nowadays, Chinas government started to reduce the subsidies and to restructure the fertilizer industry, shifting the subsidies from producers to farmers (Kahrl et al., 2010). Further, strict export tariffs are also now levied on fertilizers and the expansion of the fertilizer industry is reduced in order to overcome the threat of creating a long-term problem of surplus capacity (Crugroup, 2013). An interesting aspect when taking the fertilizer-derived nitrogen flows into consideration is, that in China in 2008, the amount of fertilizer N lost to the atmosphere through volatilization was larger than the total amount of N fertilizer consumed in all of Africa (Kahrl et al., 2010).

2. State of the art

During the last 30 years, different technologies for nitrogen removal of various kinds of wastewaters were investigated. A major finding describes that it is often easier and less expensive to remove nitrogen in the form of ammonia from wastewater than converting it to nitrate-nitrogen before removing it (Culp et al., 1978). Thus, three main stripping technologies were established:

(i) (direct) aeration
(ii) air stripping
(iii) water-sparged aerocyclone reactor

These three approaches vary in their technological requirements as well as in their ammonia removal efficiencies. The “aeration process” is a general term and can be divided into air stripping, describing the process of gas removal from water, and aeration, where oxygen is transferred into water. The tendency of a component to evaporate from the liquid into the gas phase at equilibrium is described by Henry’s law. The ratio of the equilibrium concentration of a specific component in the liquid to its concentration in the air is called Henry’s Law constant and described by the following equation:

$$p = k_{H,pc} * c_1 \qquad \text{(Eq. III-1)}$$

where p is the partial pressure of the solute in the gas above the solution, c_1 is the concentration of the solute and $k_{H,pc}$ is the Henry’s law constant; a constant with the dimension of pressure divided by concentration. The constant is further a measure for the gas absorbing capacity of a solution and illustrates that the gas concentration in a liquid is directly proportional to the partial pressure above the liquid. The higher the Henry’s Law constant, the higher the tendency of a compound to volatilize.

For the process of aeration, gas transfer efficiency depends almost completely on the contact area of the laminar layer between air and water. If the contact area between liquid and gaseous phase is increased, the transfer of volatile components into the gas phase is enhanced. Increasing the airflow rate in a stripping column or creating low-pressure above the liquid can achieve an increased contact area. Matter-Müller et al. (1981) showed, that Henry's Law constant of ammonia is small, and thus hardly volatile.

2.1 Stripping technologies

(i) Direct aeration (Fig. III-1) is the simplest technology with the easiest setup. Air is forced from the base via a flexible tube into the reactor containing wastewater. Volatile ammonia is then released into the air and transported out into the ambient atmosphere. However, this technique focuses only on the ammonia removal from wastewater but not on ammonia recovery. The main advantages of this technique are the simple design of the stripping column and its simple, inexpensive process (Liao et al., 1995).

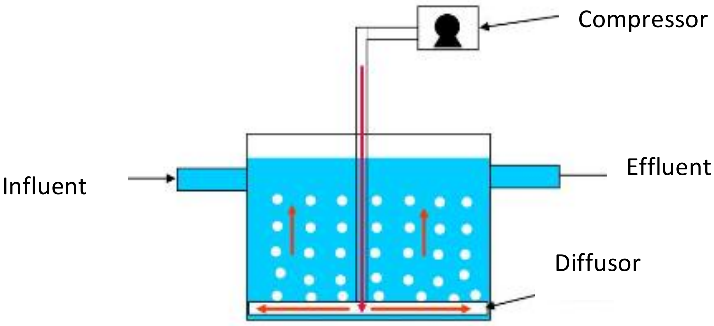


Fig. III-1: Schematic drawing of an air stripping device. Air is entering the system from the bottom. (http://iaspub.epa.gov/tdb/pages/treatment/treatment Overview.do?treatmentProcessId=-346223903 2012/12/04)

(ii) Air stripping (Fig. III-2) is the most commonly used technique for ammonia removal. A prerequisite is the specialized stripping tower that is responsible for the, compared to aeration, higher construction costs. But the overall costs are still relatively low and by using the simple equipment, high ammonia removal rates are obtained (Ozturk et al., 2003). The main component is a stripping column filled with surface increasing materials like ceramic rings, hence offering a larger mass transfer area. Wastewater enters the system from the top of the column and trickles down the filling material. Air is blown in a countercurrent flow from the bottom of the column into the wastewater. Volatile compounds like ammonia pass into the airflow and are then transported via a gas outlet at the top into an acid trap (mainly H_2SO_4) forming ammonium salts. The weak spot in this system originates from the packing material. Due to chemical reactions between CO_2 in the air and metal ions in the wastewater, scaling and fouling on the packing material occurred (Djebbar and Naraitz, 1998). Air stripping in combination with absorption was examined in different waste types by several authors: urea fertilizer plant wastes (Minocha and Prabhakar, 1988), dewatered sewage sludge (Janus and van der Roest, 1997; Thorndahl, 1992); landfill leachate (Cheung et al., 1997; Kabdasli et al., 2000); condensates from a sugar beet factory (Schiweck and Nähle, 1990; González and García, 1996) and pig slurry (Liao et al., 1995; Bonmatí and Flotats, 2003a).

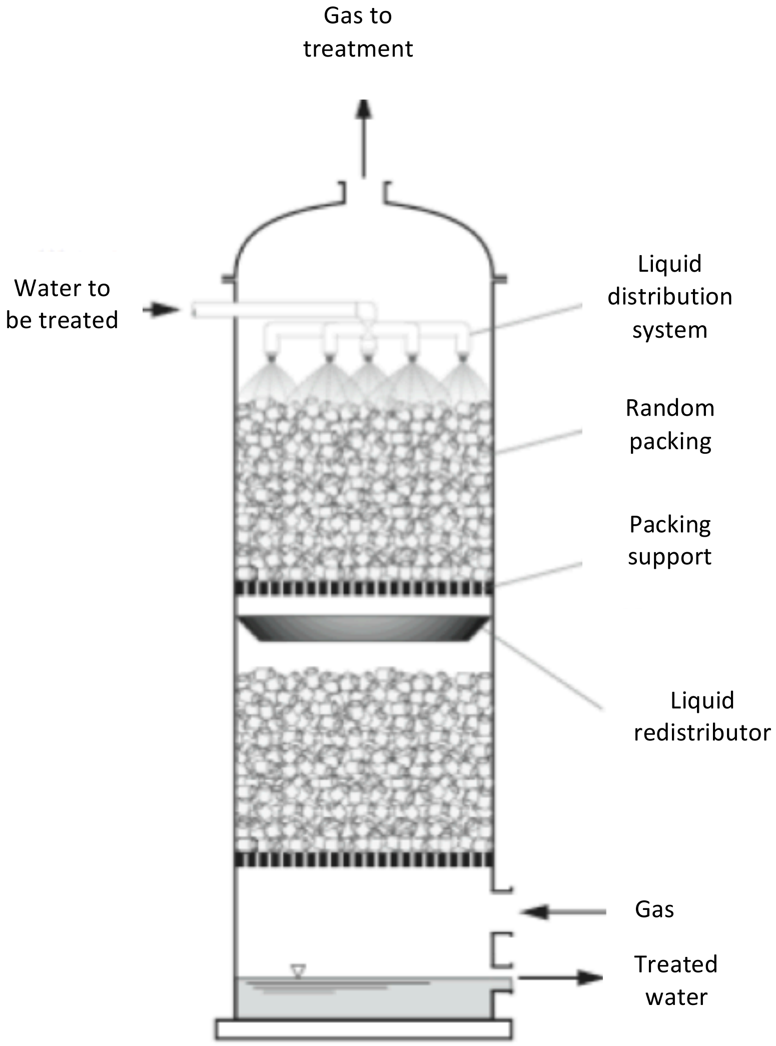


Fig. III-2: Scheme of a packed air stripping tower (Crittenden et al., 2005).

(iii) The water-sparged aerocyclone reactor (WSA) (Fig. III-3) is a technical improvement of the air stripping column. Design and operating mode is similar to the air stripper (Fig. III-2). However, the WSA column does not contain any packing material for surface enlargement. It consists of two vertical tubes in the center and a cyclone header at the top. The wastewater is sprinkled from the inner tube through pores towards the centerline of the WSA, thus increasing the surface area of the wastewater by forming droplets and distributing them evenly. In the reactor, the sprayed droplets encounter compressed air, which is fed into the aerocyclone from the top and forming a rotating airflow field, thus creating a large gas-liquid contact area that favors ammonia stripping. The treated wastewater is collected in a tank at the bottom and recirculates whilst the air and ammonia leave the aerocyclone at the top.

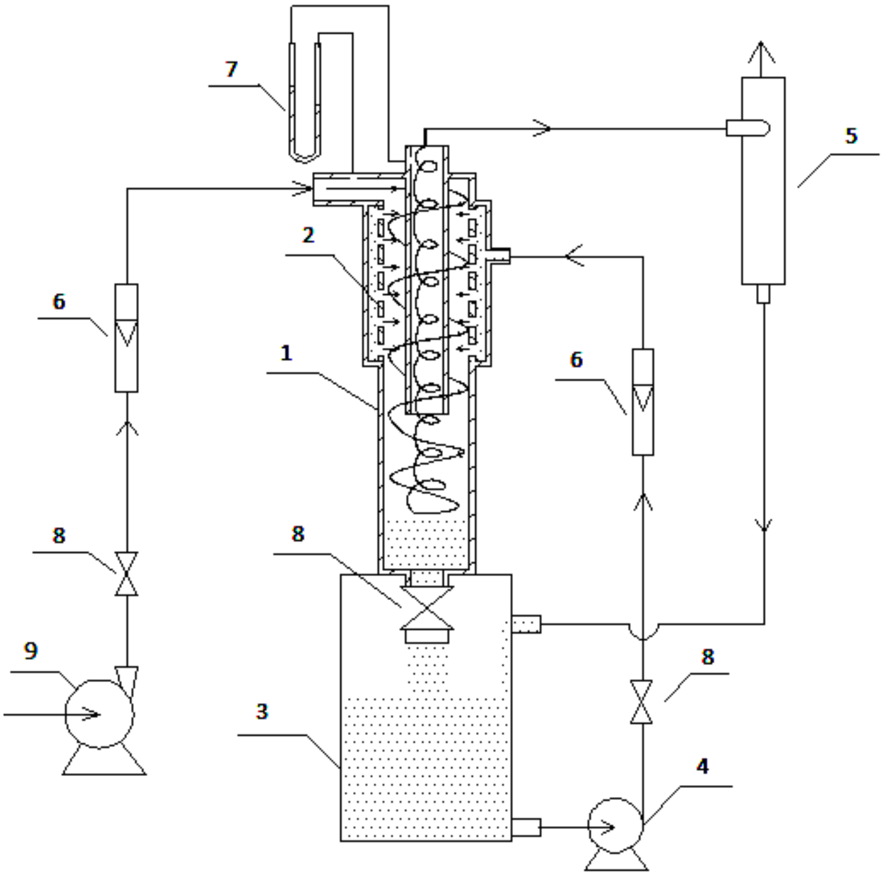


Fig. III-3: Flow diagram and experimental setup of a WSA. 1. Water-sparged aerocyclone, 2. Porous section/concentric tubes, 3. water tank, 4. circulating pump, 5. Gas-liquid separator, 6. Rotameters, 7. U-type manometers, 8. Valves, 9. Air pump (Quan et al., 2011).

2.2 Main processes in ammonia stripping

The two main processes influencing ammonia removal are

- concentration gradient
- diffusion

The main driving force in the ammonia stripping process is the concentration gradient between the highly concentrated ammonia source (e.g. slurry or digestate) and the ammonia free sink. The ammonia molecules in the source aim to balance the different concentrations in order to achieve equilibrium. However, the concentration gradient is influenced by pH and temperature. A changing pH changes the proportion of available molecules (e.g. NH_3 and the protonated NH_4^+ as described below) and thus providing an increased proportion of molecules for balancing the concentrations. Temperature is also playing an important role as a higher temperature leads to a faster molecular movement (enhanced Brownian motion) and thus a faster equilibrium between the two concentrations.

Molecular adjustment is achieved through diffusion. The driving force of diffusion is the local concentration gradient, where different concentrations can be equalized completely without interfering forces from outside within a certain time period. If temperature is higher, molecules move faster, change their direction more often and thus leading to a faster diffusion. However, the mass of the diffusing particles is also important. Heavy molecules have a lower velocity, thus interacting mainly with the direct environment therewith diffusing more slowly than small, light molecules. Diffusion is fastest in a gas, as molecules can travel respectable distances before they collide with neighboring molecules. In a liquid, diffusion is slower, because molecules remain slightly tied to each other when they move.

In my system, diffusion was a slow process as after some time the molecular concentration above the liquid was increased. This decelerated the molecular flow out of the liquid and thus the overall flow. Diffusion velocity is increased when the concentration gradient is high and thus the difference of the two concentrations.

Diffusion can also be enhanced by changing towards a turbulent transport through the creation of air movement and turbulences. The air movement causes a faster molecular movement above the liquid and thus a faster re-establishment of the concentration gradient and an overall faster equilibrium between the two liquids.

2.3 Dissociation balance between ammonia and ammonium dependent on pH and temperature

Ammonia (NH_3), a water-soluble gas, can be stripped out of nitrogen containing liquids. In an aqueous solution, ammonia is in equilibrium with its protonated form ammonium (NH_4^+), corresponding to the following dissociation equations:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \qquad \text{(Eq. III-2)}$$

$$NH_4^+ \leftrightarrow NH_3 + H^+ \qquad \text{(Eq. III-3)}$$

Dissociation is a process, where a chemical compound splits into two or more molecules, atoms or ions. Usually, the process is reversible and the reaction is as fast as the corresponding back reaction. For a general reaction

$$aA + bB \leftrightarrow yY + zZ \qquad \text{(Eq. III-4)}$$

the law of mass action is: $\frac{c^y(Y) \times c^z\,(Z)}{c^a\,(A) \times c^b(B)} = K$ (Eq. III-5)

with the equilibrium constant K.

The equilibrium constant K* of Eq. III-3 can be expressed reciprocally as:

$$K^* = \frac{c\,NH_4^+}{c\,NH_3 + c\,H^+} = K^*\,(T) \qquad \text{(Eq. III-6)}$$

Equation III-6 illustrates the correlation of K* as a function of temperature. The ratio of molecular NH_3 to protonated NH_4^+, or the chemical equilibrium, will thus be determined by pH and temperature. This is also demonstrated in Fig. III-4. Whilst low temperatures increase the proportion of NH_4^+, high temperature and a high pH shifts the equilibrium towards the molecular NH_3. In order to maximize the amount of strippable ammonia, an increase in pH and/or raise in temperature is thus necessary.

Apart from the above-mentioned Eqs. III-2 and III-3, focusing on the dissociation equilibrium in the liquid, there is another thermodynamic equilibrium, the ammonia gas/liquid equilibrium, which plays also a crucial role in ammonia stripping. The dependency of temperature and pH on free ammonia can be calculated according to the following equation (Bonmatí and Flotats, 2003a):

$$NH_3 = \frac{[NH_3+NH_4^+]}{1+\frac{[H^+]}{K_a}} = \frac{[NH_3+NH_4^+]}{1+10^{pKa-pH}} \qquad \text{(Eq. III-7)}$$

where NH_3 is the free ammonia concentration, $[NH_3+NH_4^+]$ is the total ammonia concentration, $[H^+]$ is the hydrogen ion concentration and K_a is the acid ionization constant for ammonia (5.7×10^{-10}). The temperature dependency of pK_a, the logarithmic constant (equal to – log10 K_a), can be described as follows:

$$pK_a = 4 \times 10^{-8} \times T^3 + 9 \times 10^{-5} \times T^2 - 0.0356 \times T + 10.072 \qquad \text{(Eq. III-8)}$$

where T is the absolute temperature in K. This equation was derived through polynomial regression by Bonmatí and Flotats (2003a) using data from Lide (1993). Equations III-6 and III-7 indicate that the free ammonia fraction is higher when temperature and pH are higher (Bonmatí and Flotats, 2003a). This will then contribute to a higher amount of strippable ammonia (Fig. III-4).

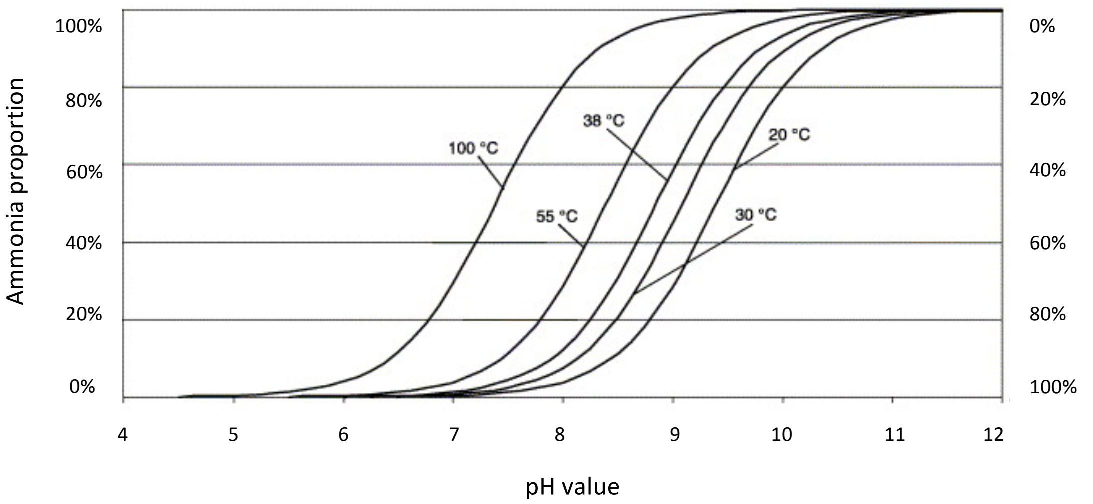


Fig. III-4: Dissociation balance between ammonia and ammonium dependent on pH and on temperature (Fricke et al., 2007).

According to the law of thermodynamics, gas molecules move faster with an increased temperature, which thus enhances the proportion of volatile NH_3 and increases the reaction velocity. Fig. III-4 illustrates the proportion of NH_4^+ to NH_3 as a function of pH and temperature. A lower pH reduces NH_3 volatility by shifting its dissociation reaction towards the ionic NH_4^+. Hence, it is necessary to increase pH or temperature for a higher proportion of (strippable) NH_3 as described subsequently:

to achieve a proportion of 80% NH_3 at 20°C, a raise in pH above pH 10 is necessary, or for the same effect at pH = 9 an increase in temperature to at least 55°C is needed.

In general, a rise in temperature by 10°C frequently causes a 2 - 4 fold shift in molecular diffusion of NH_3 as a reason of a faster molecular movement. In addition, a rise in temperature promotes further desorption of NH_3 from water because of the increasing dissolution, leading to an accelerated mass transfer rate and liquid-gas distribution ratio (Değermenci et al., 2012). As a result, a lower temperature comes along with a drop in vapor pressure and a shift in solubility of $NH_{3,}$ reducing the concentration of protonated NH_4^+ (Marttinen et al., 2002).

In my stripping experiments with rotating discs, the substrate entered the system with pH 8.3 and an ambient temperature of 15°C - 20°C, so the proportion of NH_3 to NH_4^+ was low. After running the experiments, dissociation equilibrium shifted due to the removal of NH_3 further into the direction of NH_4^+. After some time, no further strippable NH_3 was available and only NH_4^+ was left in the substrate. The NH_3 concentration did not decrease further over time and the removal efficiency curve reached saturation.

2.4 Main findings in ammonia stripping

Budzianowski and Koziol (2005) carried out ammonia stripping experiments in the presence of CO_2 with an aqueous ammonia solution in order to establish a phase equilibrium model. The authors used air stripping where the ammonia and the CO_2 solution were fed from the top and humidified air entered the system from the bottom. For an enhanced or complete ammonia stripping, a high air load (air/gas flow rate), a high pH value (pH 10 - pH 11) and higher temperatures (which decreased the gas solubility) were required. During their stripping experiment, the pH decreased because of ammonia desorption from the solution and the subsequent interaction with CO_2. Thus, not only ammonia adsorption but also the simultaneous desorption must be considered. When ammonia stripping experiments were carried out with animal wastewaters, scaling and fouling was observed on the ceramic rings and described by Quan et al. (2009). The authors focused on the calculation of absorption/desorption fluxes and coefficients in order to compare them with their model. Therefore, they did not mention any numerical values, which might be compared with the results obtained in my work. Furthermore, my system is a closed system whereas the system from Budzianowski and Koziol (2005) (as most of the stripping columns) is an open, circulating system.

Bonmatí and Flotats (2003a) carried out air stripping experiments with fresh and anaerobically treated pig slurry. In the fresh material, the ammonia nitrogen concentration decreased during air stripping experiments over time. The authors observed further lower ammonia removal rates in fresh pig slurry due to a fall in pH, shifting the dissociation equilibrium towards the proportion of NH_4-N and thus towards a reduced ammonia volatility. In digested pig slurry, removal efficiencies above 96% could be obtained. The authors concluded further, that it is possible to completely remove ammonia without pH modification. This was in accordance with Collivignarelli et al. (1998), who reported experiments performed with an old landfill leachate showing that it was possible to achieve high ammonia removal efficiencies without addition of lime when temperature was maintained between 60°C - 70°C.

Quan et al. (2009) examined a further, more technical stage of ammonia stripping by using a water-sparged aerocyclone reactor (WSAR, Fig. III-3). Stripping substrate was a calcium hydroxide $Ca(OH)_2$ solution spiked with different ammonia concentrations. pH was adjusted to pH 11 - pH 12, where ammonium nitrogen is almost completely converted into molecular ammonia in aqueous solutions (Fig. III-4, chapter 2.3). The authors concluded, that mass transfer coefficients are almost constant. Therefore, in theory, in every open system controlled by diffusion through a gas film, stripping efficiency is independent of the concentration of the volatile substance.

2.5 Measures optimizing the stripping process

The cost intensive factors in ammonia stripping are, besides the acquisition costs of the stripping column, the price for energy to increase the stripping temperature and the chemicals used for pH adjustment. Excess energy e.g. waste heat from other processes like biogas production might be used to heat up the stripping device, and thus the liquid temperature, shifting the dissociation equilibrium towards ammonia and thus reducing the chemicals needed for a pH increase (Rautenbach et al., 1995).

Ammonia stripping can be optimized further, besides adjusting pH and temperature, by changing the following parameters:

- surface area
- air flow

2.5.1 Surface area

A higher surface area enhances the interface between liquid and gaseous phase and thus facilitates the NH_3 transformation into the gas phase. In conventional stripping systems, surface enlargement is either obtained by packing the stripping columns with different amounts/kinds of filling materials with diverse surface compositions, by elongated stripping columns or by spraying the substrate into the airstream.

2.5.2 Airflow rate

An elevated airflow rate improves the contact area between the liquid substrate and the air, thus leading to a faster NH_3 transfer and volatilization rate. Various authors described this correlation between airflow rate and stripping efficiency (Liao et al., 1995; Yoon et al., 2008; Quan et al., 2010). Liao et al. (1995), achieved e.g. with an accelerated airflow almost complete ammonia removal by simultaneously reducing the stripping time.

Based on the above mentioned problem of nutrient overload in wastewaters from animal husbandry and the actual state of the art concerning nitrogen removal, I established two hypotheses:

I. **It is possible to remove ammonia from anaerobically treated pig slurry (and simultaneously produce ammonium sulfate as fertilizer) by using the experimental, low technology setup of rotating discs.**

II. **A change in the parameters like rotation speed and temperature influence ammonia stripping and thus the NH_4-N removal efficiency in the rotating disc system most.**

3. Materials and Methods

3.1 General facts

The ammonia stripping experiments were carried out at INRES- Division Plant Nutrition, University of Bonn, Germany.

Digestate characteristics

Due to the small volume of the digestate samples resulting from laboratory anaerobic digestion experiments and the need of large quantities for the ammonia stripping experiments, digestate was collected from a nearby biogas plant (Bruno Leenen, Kalenborn, Germany). The composition of the biogas effluent was as follows: 66% processed food leftovers from canteen kitchens and fat, 33% recirculate liquid which was mixed with 50% pig and cattle manure. Due to the high share of food leftovers, the digestate had a very viscous and hydrophobic texture. Initial pH value was about 8.3 and conductivity of the samples was 34.2 mS cm^{-1}. DM content was 2.78%, ODM 14.43% and TKN 4.4 g L^{-1}.

3.2 Experimental setup

The stripping device was built according to the scheme in Fig. III-5 and is illustrated in Figs. III-6 and III-7.

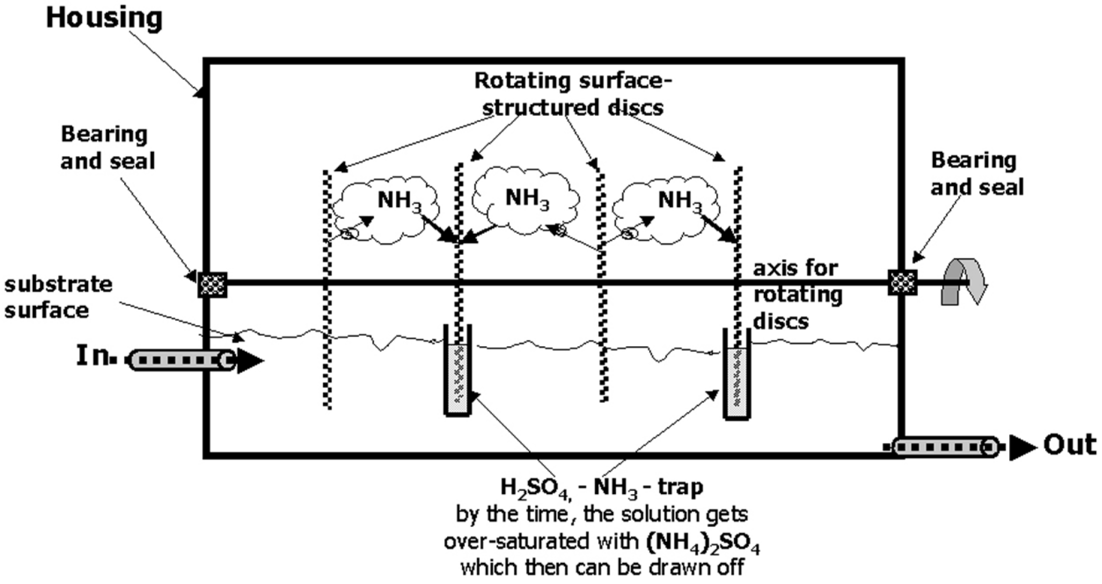
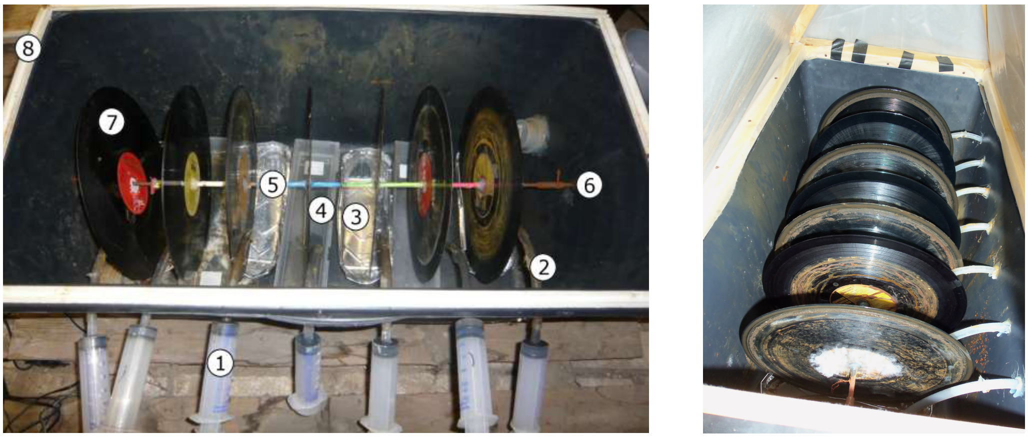


Fig. III-5: Scheme of the ammonia stripping device with rotating discs (simplified schematic drawing - not to scale; *not shown*: motor and gear) (Project Proposal).



Figs. III-6 and III-7: Ammonia stripping machine with rotating discs (detailed view). 1: syringe for sampling from the outside, 2: silicone tube dipping into container, 3: container with substrate (digestate/NH_4HCO_3), 4: container with H_2SO_4, 5: shaft, 6: fixed bearing, 7: rotating disc, 8: sealing

The stripping system was based in a 90 L tank (Fassbender Tenten, 1209011). The discs used for surface enlargement were conventional records (Vinyl, Ø 30 cm) fixed with hot glue on a shaft, which was driven by an adjustable motor (MODELCRAFT RB350600-0A101R, Conrad Electronics). The discs dipped into a container filled either with substrate (NH_4HCO_3 or digestate) or acid (H_2SO_4) (Fig. III-6) using the rotational speed to build a thin layer on the surface, thus allowing ammonia to volatilize. NH_3 volatilized, left the slurry and was attracted to the nearby rotating disc. The disc was covered with a thin layer of H_2SO_4 where the NH_3 was trapped. Afterwards, NH_3 was dissolved again as NH_4^+ and was released into the H_2SO_4-solution container changing the solution into ammonium sulfate ($(NH_4)_2SO_4$).

In order to adjust the experimental setup to various experimental needs, the shaft could be loaded with a higher number of discs to increase the surface area. The first containers for digestate and H_2SO_4 were made of steel. Due to the coexistence of acidic and alkaline environmental conditions in the tank, the containers corroded after the first experiments and had to be replaced by aluminum containers for digestate and acid-resistant polypropylene (rothoKunststoff AG) containers. Two stripping device were built and run simultaneously in order to repeat the experiments and to handle the varying setups.

Each stripping device was covered with a lid to prevent gaseous losses. Initially, the lid consisted of a triangular wooden construction covered with plastic foil (perfecta Bauplane, pe-ld, 45 µm). After some fumigation losses through the foil were recognized, the coverage was changed into chipboard, which completely covered the tank. Two different rotational speeds (10 rpm and 44 rpm), adjustable by the motor, were used to increase the airflow and to enhance stripping. Several test runs with ammonium hydrogen carbonate (NH_4HCO_3) as substrate were conducted to check functionality, stability and permanency of the stripping devices.

During the first experiments, the stripping devices were positioned in a wooden carport, which had an open front but was closed at three sides. After realizing that stripping efficiency was influenced by temperature fluctuations during day and night and the turbulences created by wind, the stripping devices were relocated to a room in the basement of a building where temperature remained constant.

3.3 Ammonium determination

Ammonium nitrogen (NH_4-N) was determined in untreated pig slurry samples as well as in digestate before and after the phosphate precipitation process in order to see concentration changes and to identify precipitation ratios. The *Berthelot reaction* (indophenol method) was used for NH_4-N determination. In China, the method was carried out and reagents were prepared according to the “Chinese Standard Methodology Reference Book”. The samples were mixed with salicylic acid ($C_6H_4(OH)COOH$), sodium hypochlorite (NaClO), sodium hydroxide (NaOH), potassium sodium tartrate ($C_4H_4KNaO_6$) and nitroprussid ($Na_2[Fe(CN)_5NO] \times 2\ H_2O$) and were shaken thoroughly until all components were dissolved. After a reaction time of 1 hour, the samples were transferred into a rectangular shaped cuvette (10 mm) and analyzed photometrical at 697 nm (Uv-vis Spectrophotometer 756, Laipade Science Instruments, Shanghai, China).

However, the samples from the stripping experiment in Germany were analyzed using a test kit from Merck (Merck Spectroquant Ammonium-Test, 2 - 75 mg L^{-1} NH_4-N and 5 - 150 mg L^{-1} NH_4-N, Darmstadt, Germany). The samples were prepared according to the manual. 5 ml of reagent NH_4-1 (mixture of the above mentioned liquid organic and inorganic compounds) were transferred to a test tube, there, depending on the measuring range, 0.1 or 0.2 ml of the sample was added.

After that, 1 micro spoon of reagent NH_4-2 (nitroprussid) was added and shaken manually until dissolved. Reaction time was 15 minutes. The samples were filled in a cuvette (Hellma precision cuvette, 6030-0G, 10 mm) and measured photometrical at 697 nm (WTW, PhotoLab S12, Weilheim, Germany).

As sample size increased and ammonium determination using the test kit was not feasible in an appropriate time, the samples were measured in a continuous flow analyzer (Bran+Luebbe GmbH, Autoanalyzer 3, Norderstedt, Germany). For sample preparation, the samples were diluted 10.000 times in order to reach a measuring range between 0 - 0.5 mg L^{-1} NH_4-N. A tray containing the samples (Bran+ Luebbe, compact sampler) was inserted into the auto sampler and analysis was started. According to Merck manual (2009), the reaction is as follows: in an alkaline environment NH_4^+/NH_3 reacts, assisted by nitroprussid ($Na_2[Fe(CN)_5NO] \times 2\ H_2O$) as a catalyst, with hypochlorite-ions to monochloramine (NH_2Cl). Monochloramine reacts with a substituted phenol and forms an indophenol-derivate (*indosalicylate*). This leads to a green-blue coloration that can be measured photometrically at 660 nm - 697 nm.

3.4 Experiments

During the first pilot tests, where ammonium hydrogen carbonate (NH_4HCO_3) was used as substrate, gaseous losses during filling were observed. Therefore, in all following experiments, the H_2SO_4 containers were filled before the digestate was brought into the system. In order to control the influence of the concentration gradient on stripping behavior and velocity, a container was filled with 0.5 L digestate and placed next to one filled with 0.5 L H_2SO_4. No disc was rotating in this system. Further experiments were carried out where only one disc rotated through the acid container. The same experiment was repeated with the disc rotating in the digestate. Both results were compared in terms of velocity and efficiency.

The shaft was loaded with a doubled number of rotating discs in order to compare the influence of an enhanced surface area on stripping velocity. For a surface area of 0.14 m^2, one disc was positioned on the shaft. 0.28 m^2 surface area was achieved with two discs, where one rotated through the substrate whereas the other one through H_2SO_4. A further increase in surface area to 0.57 m^2 was achieved by doubling the number of discs again, resulting in two discs rotating through substrate and two through H_2SO_4. Each disc rotated through a single basin containing either 0.5 L of substrate (NH_4HCO_3/digestate) or 0.5 L of H_2SO_4. The attempt to increase the surface area by doubling the number of rotating discs again, failed, as the space in the tank was limited. Therefore, only seven discs could be squeezed into the tank, resulting unintentionally in an unequal substrate:H_2SO_4 ratio of 4:3 containers. This increased the substrate:acid ratio in favor of the digestate. The resulting surface area was 1 m^2.

3.5 Sampling

Samples (substrate as well as acid) were taken without removing the lid to avoid gaseous losses. With fixed syringes at the outside of the tank (Fig. III-6), 10 mL - 15 mL of a sample of each container was taken via a silicone tube, that was dipping permanently into the material. Afterwards, the sample was filled directly into 50 mL polyethylene bottles. During sampling, ambient and sample temperatures were determined with an insertion thermometer (Carl Roth GmbH & Co. KG, TFA®). On average, samples were taken twice a day. However, in some experiments sampling was carried out every hour to illustrate exemplarily the process of ammonia stripping. After sampling, they were stored at +4°C until measurement. Samples from a stripping device taken at the same point of time were used for mean value calculation and illustrated in a graph.

pH and conductivity (WTW, pH 330) were measured before, in the middle and at the end of the experiment. To avoid any turbidity during the photometrical analysis, digestate samples were diluted and filtered (Macherey-Nagel MN 261 G ¼ Ø150 mm) with a diaphragm pump (vacuumbrand GmbH & Co., Typ CVC 24).

3.6 Calculation of the ammonia stripping efficiency and recovery rate

In order to compare the different stripping efficiencies obtained in our experiments more easily, the following calculation (Eq. III-9) was used.

Ammonia removal efficiency η is, according to the measured results, defined as:

$$\eta\ (\%) = \left(\frac{C_{in} - C_t}{C_{in}}\right) \times 100 \qquad \text{(Eq. III-9)}$$

where C_{in} is the initial NH_4-N concentration and C_t the NH_4-N concentration at any time t.

NH_4-N_{total} is the recovery rate, calculated as the sum of the NH_4-N concentration in the remaining substrate and the NH_4-N concentration in the acid trap. Calculation was as follows:

$$NH_4 - N_{total}(\%) = \left(100 - NH_4 - N_{substrate}\right) + NH_4 - N_{acid} \qquad \text{(Eq. III-10)}$$

3.7 Calculation of the disc holding capacity (DHC)

The disc holding capacity (DHC) is the amount of substrate that stuck on the disc when rotating once through substrate. Substrate containers were weighed before and after treatment and the values were referred to the wetted surface area. Calculation was as follows:

$$DHC\ (g\ cm^{-2}) = \frac{(amount\ before\ rotation\ (g) - amount\ after\ rotating\ once\ (g)}{surface\ area\ disc\ (cm^2) \times wetted\ area\ (\%)} \qquad \text{(Eq. III-11)}$$

4. Results

This chapter illustrates and evaluates the ammonia stripping results. It starts with a short overview on the main findings obtained during the pilot experiments, where some basic parameters like functionality, optimum H_2SO_4 concentration in the acid trap and leak tightness were determined. Afterwards, the different results of the experiments carried out with digestate will be shown.

4.1 Pilot tests with ammonium hydrogen carbonate (NH_4HCO_3) solution

Determination of the optimum acid strength (H_2SO_4) in the acid trap

Feasibility and functionality of the stripping system was evaluated with pilot tests using an aqueous NH_4HCO_3-solution. These pilot tests were also used to determine the optimum strength of the H_2SO_4-solution in the acid trap. Therefore, three different H_2SO_4-solutions with concentrations of 0.5 mol L^{-1}, 1 mol L^{-1} and 2.83 mol L^{-1} were used in two experimental setups. All tests were run in parallel with differing surface areas to check the best ammonia stripping performances and the highest removal efficiencies. Each container was filled with either 0.5 L H_2SO_4 or 0.5 L NH_4HCO_3. The NH_4-N concentration in the NH_4HCO_3-solution was the same for all setups (2.23 mol L^{-1}). Efficiency η (%) was calculated according to Eq. III-9. The following graph illustrates the stripping behavior of the NH_4HCO_3-solution in the presence of 0.5 mol L^{-1}, 1 mol L^{-1} and 2.83 mol L^{-1} H_2SO_4 (Fig. III-8).

The experiments with a surface area of 0.57 m^2 were carried out by two discs rotating through containers filled with acid and two with substrate. The same experiments were conducted with a reduced surface area of 0.28 m^2, where only one disc rotated through acid and one through substrate. During the first day, ammonia removal efficiency was the same for all experimental setups except the one with 0.57 m^2 surface area and 2.83 mol L^{-1} H_2SO_4. The three curves diverged after 1.5 days (36 hours) when 50% of the NH_4-N was removed. The experiments with 0.28 m^2 surface area were most efficient as within 2 days 85% of the ammonia was removed. However, with an attenuated H_2SO_4 of 1 mol L^{-1} the NH_4-N removal was slow-going but constantly and thus in the end slightly more efficient.

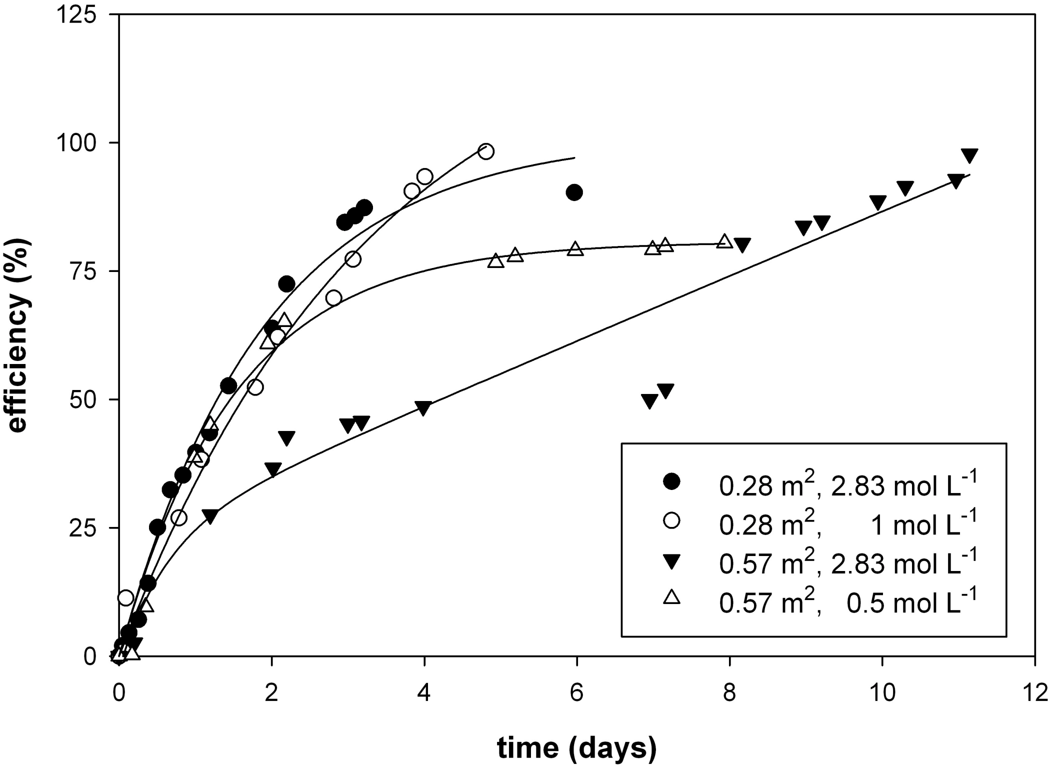


Fig. III-8: Ammonia removal efficiency (%) over time using two different surface areas (0.28 m^2 and 0.57 m^2). Concentrations of the H_2SO_4-solutions were 0.5 mol L^{-1}, 1 mol L^{-1} and 2.83 mol L^{-1}. The used substrate was a 2.23 mol L^{-1} NH_4HCO_3-solution.

This curve (0.28 m^2) did not reach asymptotic behavior during the experimental period, showing that there was always strippable ammonia available until the end of the experiment. After the curves reached their maximum, NH_4-N was not reduced further. In the experiments with a higher surface area but lower acid concentration (0.5 mol L^{-1} H_2SO_4), NH_4-N removal started similar to the other experiments with lower surface area but slowed down after 2.1 days (50 hours) when 65% NH_4-N were removed and leveled off at day 4 with a total removal efficiency of 75%. The differences in surface area seem to compensate for the different acid concentrations (one experiment having a higher surface area but lower acid concentration and the other one a lower surface area but higher acid concentration). This leads to similar stripping behavior and efficiency until 50% NH_4-N is removed. Afterwards, the traction of the strong acid was higher and more NH_4-N was removed.

The results from the experiment with 0.57 m^2 surface area and 2.83 mol L^{-1} H_2SO_4 differed from my expectations. Normally, one would either expect a similar removal behavior as observed with the other three experiments or even a faster stripping process and thus NH_4-N removal efficiency as surface area and acid concentration were enhanced. However, the removal efficiency was lower and the overall stripping process less efficient, achieving a 50% NH_4-N removal after 4 days (96 hours) and 97% removal after 11 days. This almost linear stripping curve might be explained by the lid, which was constructed in a triangular shape and could be opened. Repeated visual checks, however, led to substantial NH_3 losses (see also Fig. III-9). For this reason, I decided to neglect this result and to focus only on the other three experiments. Influences by temperature variations could be neglected as the average temperature was 19.9°C - 20.9°C for the experiment with 1 mol L^{-1} H_2SO_4 and 22.12°C - 24.4 °C for 2.83 mol L^{-1} H_2SO_4. At the end of the experiments with the highly concentrated H_2SO_4, I observed the formation of ammonium salts in the acid trap and on the rotating discs.

Best and fastest stripping efficiency was observed with 2.83 mol L^{-1} H_2SO_4 but removal efficiency was only slightly higher compared to 1 mol L^{-1} H_2SO_4. As there was no detailed information available from other authors (except Bonmatí and Flotats (2003a) who used “a strong acid solution”) concerning the optimum acid concentration, the decision was made based on economic considerations and 1 mol L^{-1} H_2SO_4 was used in the acid sink for all following experiments.

The most important parameter for a successful stripping process is the capability of the sulfuric acid to absorb the NH_3 molecules. This requires a closer look at the ratio of available protons (H^+) to the amount of binding ammonia (NH_3). It seems that the acid strength influenced the process more, the lower the proton:ammonia ratio was. Lowest stripping efficiency was observed with 0.5 mol L^{-1} H_2SO_4. Thus, the corresponding molar H^+:NH_3 ratio was 1:2.23. With 1 mol L^{-1} H_2SO_4, the stripping process was slightly faster and the stripping more efficient. The related molar H^+:NH_3 ratio was 1:1.12. Highest efficiency was observed with an acid concentration of 2.83 mol L^{-1} (corresponding molar H^+:NH_3 ratio was 1:0.4). In order to get an efficient and almost complete stripping process, the ratio between a proton and an ammonia molecule should at least be 1:1. With this ratio it is ensured that each ammonia molecule can find a proton to bind to.

The pilot tests were carried out using a 2.23 mol L^{-1} NH_4HCO_3-solution, representing a 10 times elevated NH_4-N concentration compared to the later used digestate. As further experiments were carried out with digestate or NH_4HCO_3 with similar NH_4-N concentrations (0.2 mol L^{-1}), the molar ratio of H^+:NH_3 provided by 1 mol L^{-1} H_2SO_4 is 1:0.11 and this, theoretically, allows complete ammonia recovery.

4.2 Ammonia removal rates

Table III-1 compares the theoretical ammonia removal rates with the measured NH_4-N concentrations in the remaining substrate during the experiments. At a lower molar H^+:NH_3 ratio, the measured removal rates are in good accordance with the theoretically calculated ones. However, at higher molar H^+:NH_3 ratios, the measured removal rates are nearly double as high as the theoretically determined ones. As samples were always taken from the remaining substrate in the container, a reduction in the NH_4-N concentration does not necessarily represent the stripped NH_3, which was simultaneously trapped in the acid. A reason for this discrepancy could rather be the experimental location and design. The stripping device in the wooden carport was exposed to temperature fluctuations and wind, thus possibly leading to partially gaseous NH_3 losses from the system through a not tightly closed sealing or the lid built of plastic foil.

Tab. III-1: Theoretical and real ammonia removal (%) dependent on the proton (H^+) : ammonia (NH_3) ratio

Ratio H^+ : NH_3	Removal (theoretical) (%)	Removal (measured) (%)
1 : 2.23	45	81
1 : 1.12	89	98
1 : 0.4	100	90

4.3 Ammonia recovery

4.3.1 Ammonia recovery using NH_4HCO_3-solution

Based on the assumption of evaporation losses in the system and the supporting results described above in Tab. III-1, further ammonia recovery tests were carried out. Therefore, samples were not only taken and analyzed from the substrate but simultaneously also from the acid containers. In the following, results are illustrated exemplarily for experiments carried out with a NH_4HCO_3-solution and a surface area of 1 m^2 (Fig. III-9).

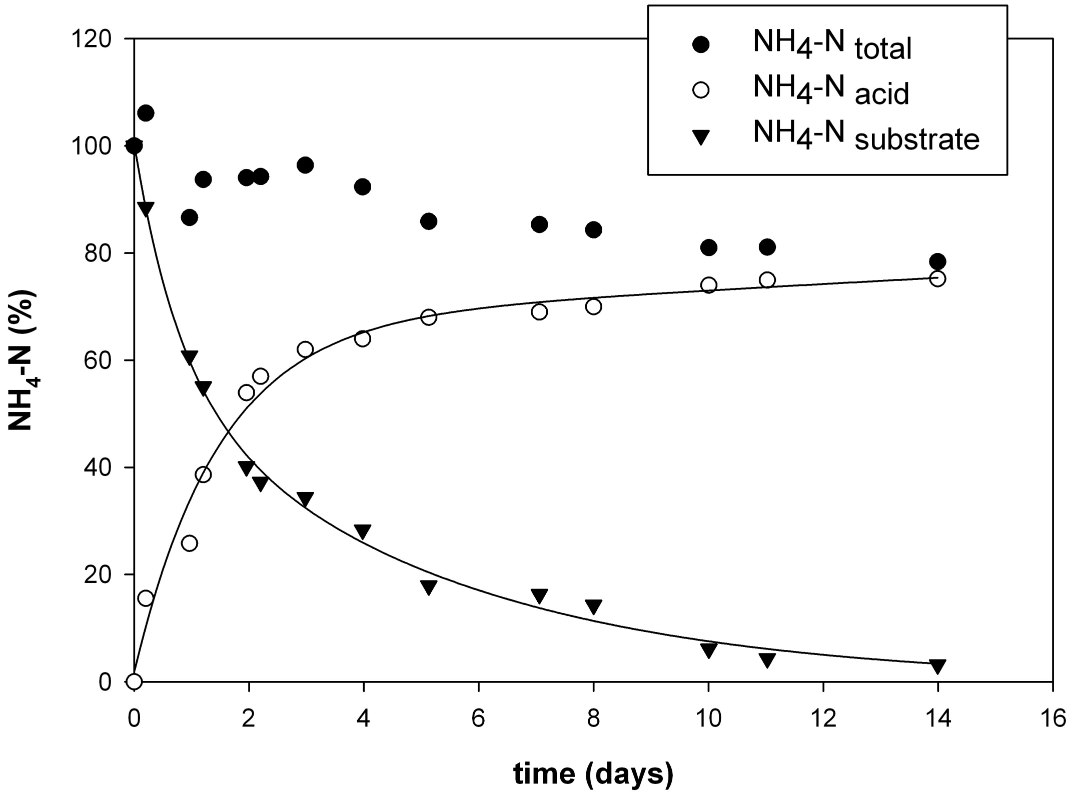


Fig. III-9: NH_4-N removal (in %) over time using a surface area of 1 m^2 and NH_4HCO_3 as substrate. The NH_4-N concentrations were measured in the substrate and the corresponding acid trap. The sum of both is illustrated as NH_4-N_{total}.

I observed a fast NH_4-N removal (58%) in the substrate within the first 2 days with further, slower removal (97%) during the following 12 days. However, in the samples taken simultaneously from the acid trap, only 53% of the NH_4-N could be detected at day 2 and around 75% at day 14. The NH_4-N_{total}, representing the sum of NH_4-N in the remaining substrate and the acid, illustrates the discrepancy between the two concentrations. Ideally, both values should sum up to a recovery of 100%. After 2 days, the NH_4-N_{total} is 94%, which is, taking variations in measurement and sampling into account, still an acceptable rate. During the further procedure, however, the NH_4-N_{total} concentration decreased constantly down to 78%, thus supporting the assumption of gaseous losses through the lid, which was built of plastic foil. In order to prevent further gaseous losses, the rubber seal at the top of the tank was renewed and the lid was changed to chipboard.

4.3.2 Ammonia recovery using digestate

Ammonia recovery experiments with digestate were carried out after changing the lid in the experimental setup from plastic foil to chipboard. Figures III-10 and III-11 show exemplarily the ammonia recovery results for digestate carried out with 1 m^2 and 0.57 m^2 surface area.

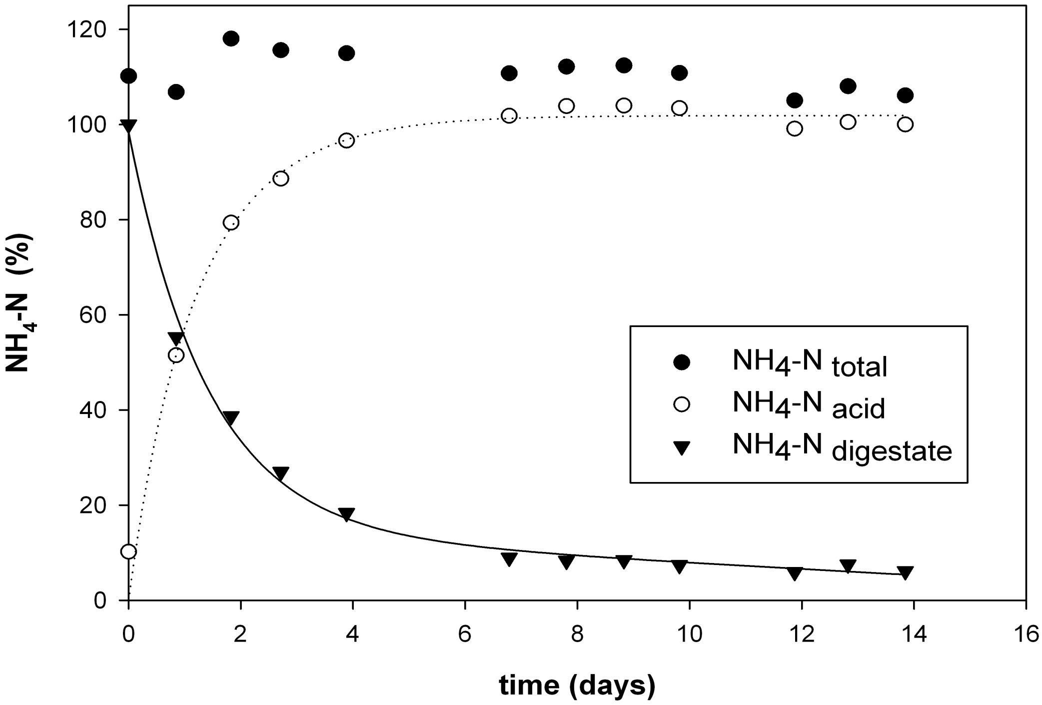


Fig.III-10: NH$_4$-N (in %) over time using a surface area of 1 m^2 and digestate. The NH$_4$-N concentrations were measured in the substrate and the corresponding acid trap. The sum of both is shown as NH$_4$-N$_{total}$.

The graphs show the NH$_4$-N recovery in digestate, in acid and summed up as NH$_4$-N$_{total}$ during the stripping process with 1 m^2 (Fig. III-10) and 0.57 m^2 (Fig. III-11) surface area. The NH$_4$-N concentrations decreased exponentially in the digestates whereas, at the same time, inversely, the concentrations in the acid increased. For 1 m^2 surface area, 50% NH$_4$-N removal was obtained after 1.1 days, whilst at the same time 60% NH$_4$-N were detected in the acid trap. When the experiment was stopped after 14 days, the NH$_4$-N concentration in the remaining digestate was rather low (6%). NH$_4$-N$_{total}$ values varied between 106% and 115%, implying that not only the free available NH$_4$-N was stripped off the digestate. It rather seems that additionally various other forms of available NH_4-N were released due to microbial processes (e.g. protein degradation), which could then be stripped. This additional NH_4-N release can be seen more clearly in Fig. III-11.

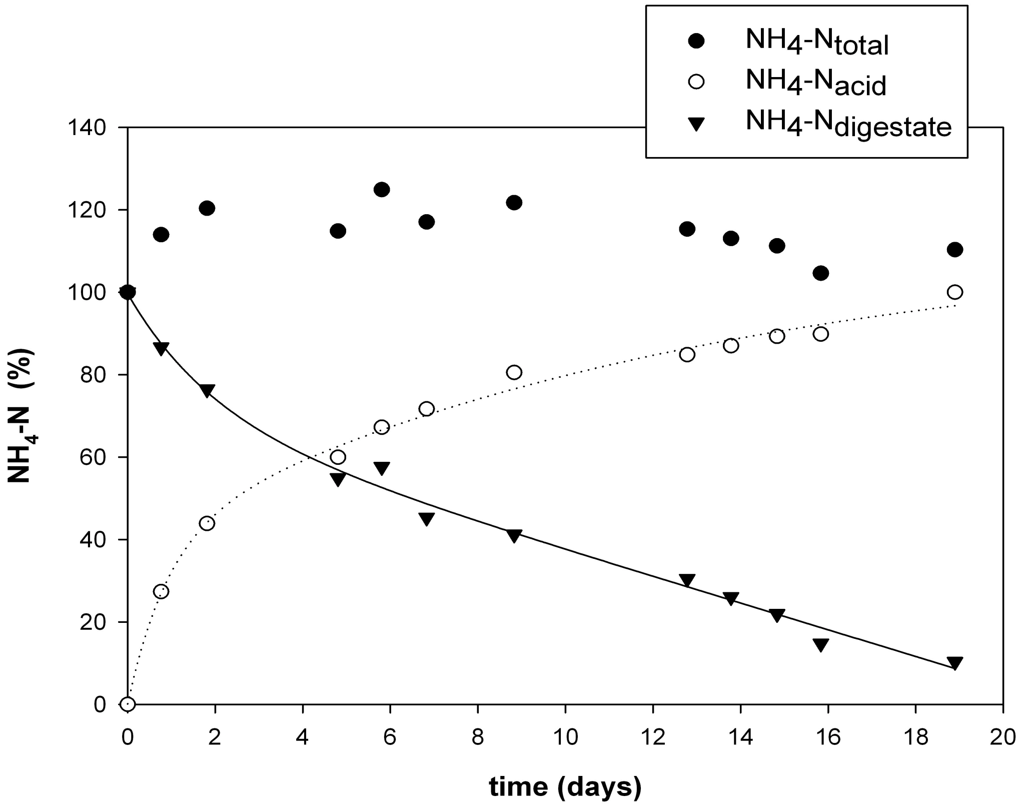


Fig. III-11: NH_4-N (in %) over time using a surface area of 0.57 m^2 and digestate. The NH_4-N concentrations were measured in the substrate and the corresponding acid trap. The sum of both is shown as NH_4-N_{total}.

After 6.1 days, the NH_4-N concentration decreased in the digestate by 50%. However, in parallel, 50% NH_4-N was already recovered in the acid after 3.2 days. The NH_4-N_{total} concentrations varied between 115% and 120%, showing that some additional NH_4-N was released from the digestate and contributed to apparently higher overall stripping efficiencies. The variation in NH_4-N_{total} was highest during the first week and decreased slightly at the end.

Figures III-10 and III-11 show clearly, that changing the lid construction could stop the previously observed gaseous losses. Furthermore, when using digestate as substrate, various other forms of NH_4-N will be released. Thus, apparently the overall stripping efficiency is increased whereas in fact, the quantity of additionally released NH_3 is higher and the real stripping efficiency is lower.

4.4 The influence of a varied surface area

The main factor influencing ammonia stripping efficiency and velocity from wastewaters is the available surface area. A higher surface area available for the stripping process is accompanied by a faster ammonia volatilization as e.g. higher process efficiency is achieved with packed stripping columns (Djebbar and Narbaitz, 1998). As my system did not use a packed stripping column but rotating discs for surface enlargement, this was the only parameter, which could be varied to proof this effect. The influence of a modified surface area on stripping speed and efficiency was tested with both substrates- NH_4HCO_3 and digestate- in order to evaluate differences due to the substrate composition. I expected a faster and more efficient stripping process at an increased surface area.

4.4.1 The influence of a varied surface area on ammonia stripping when using NH_4HCO_3

The NH_4-N concentration in the NH_4HCO_3-solution was adjusted to 0.20 mol L^{-1} in order to equal the NH_4-N concentration in the digestate. This enables a comparison between the substrate with and the one without organic material. The NH_4-N concentration for the experiments with 0.28 m^2 and 0.57 m^2 surface area was 0.34 mol L^{-1}. The H_2SO_4 concentration in the acid trap was 1 mol L^{-1} for all experiments. Efficiency was calculated according to Eq. III-9.

Ammonia stripping with 0.14 m^2 available surface area was executed by one disc rotating through the acid container (Fig.III-12). The substrate container in the system was not stirred, confining ammonia volatilization exclusively to the open, exposed surface area (0.041 m^2) above the container. The stripping behavior followed a saturation curve where, within the first two days, stripping efficiency increased exponentially to 32% and decreased afterwards. After 7 days, when 55% NH_4-N removal efficiency was obtained, the experiment reached some kind of steady state and no further stripping occurred.

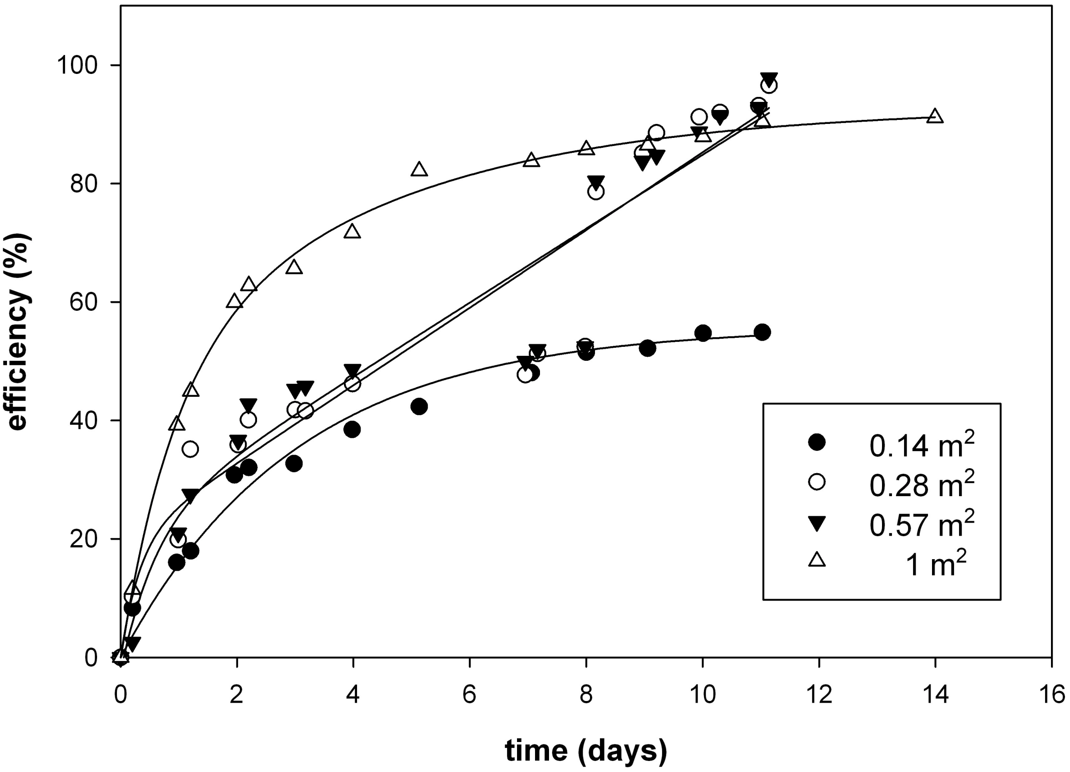


Fig. III-12: Ammonia removal efficiency (in %) over time using different surface areas (0.14 m^2, 0.28 m^2, 0.57 m^2 and 1 m^2) and a NH_4HCO_3-solution.

By doubling the surface area to 0.28 m^2 (one disc rotating through the acid and one through the substrate), we expected a faster and more efficient stripping process. Average temperature was 20.7°C during the experimental period. After two days, ammonia removal efficiency was slightly higher (36%) compared to the experiment above with one disc rotating through acid. If the surface area was again doubled to 0.57 m^2 and 2 discs rotated through acid and 2 through substrate, the NH_4-N removal efficiency was again slightly higher (37% after 2 days, 48% after 3.9 days) than with 0.28 m^2 surface area. These two experiments were carried out in parallel under a carport with an open front. Thus, they were partially exposed to changing weather conditions like wind and temperature fluctuations (21.1°C during daytime, 8.5°C during night), which largely influenced ammonia stripping. In the end, 97% of the NH_4-N present could be removed within 11 days.

Fastest ammonia removal was observed with the highest surface area of 1 m^2 with 7 rotating discs (3 through acid and 4 through substrate). This experiment was carried out in parallel to the one with 0.14 m^2 surface area. Average sample temperature was 19.4°C (22.1°C in the beginning, 17.1°C at the end). NH_4-N removal was fast in the beginning, achieving 50% removal in 1.45 days (34.8 hours) and 61% in two days. Then, similar to the other curves, the curve run flattened slightly and removal slowed down. During the next 12 days, further 30% NH_4-N were removed from the substrate. In contrast to the other experiments, I did not observe any stagnation. Due to a lack of time, these pre-experiments could not be repeated.

The differences in stripping behavior might not exclusively be explained by the different surface area but rather by the distinctive volume ratios of substrate and acid. All experiments showed similar behavior with fast, exponential NH_4-N reduction in the beginning until the second day when the curves started to bend and removal efficiency slowed down. The slope of the four curves was steepest for the highest and lowest for the smallest surface area. The three setups (0.14 m^2, 0.28 m^2 and 0.57 m^2) had an even number of containers filled with H_2SO_4 and substrate, whereas the experimental setup for 1 m^2 surface area differed. Due to a lack of space in the stripping tank, the shaft could only be loaded (if loaded completely) with an odd number of discs. So four discs rotated through containers filled with substrate and three through those with acid, shifting the substrate:acid ratio from 1:1 towards 1:0.75. This excess of substrate in the system might lead to a higher amount of volatilizable NH_3, increasing the concentration in the surrounding air and thus leading to higher and faster absorption and dissolution rates in the sink.

Additionally, each container filled with acid was flanked by one filled with slurry. Thus, ammonia could easily be trapped on both sides of the disc rotating through the acid and hence enhance total NH_3 removal. Remarkably is also the only slightly (2%) higher NH_4-N removal efficiency for 0.57 m^2 compared to 0.28 m^2 surface area. Normally, one would expect that with a doubled surface area only half of the stripping time would be needed. However, these results show that surface area is not the limiting factor, but rather the absorption capacity of the sink. Even though the H^+:NH_3 ratio is 1:0.11 and this, theoretically, would allow complete ammonia trapping, the sink could not bind all available NH_3.

An improvement could be an increased surface area through specially designed discs, which thus favors the absorption of ammonia.

4.4.2 The influence of a varied surface area on ammonia stripping when using digestate

By completing the pre-tests with NH_4HCO_3 as substrate, functionality and reliability of the stripping device was proven. All components of the device were cleaned carefully and dried for several days to assure that neither substrate nor acid residues remained. The substrate was then changed from the aqueous NH_4HCO_3-solution to the highly viscous and hydrophobic textured digestate. Initial NH_4-N concentration in the digestate was about 3.5 g L^{-1} (0.18 mol NH_4-N L^{-1}) and thus slightly lower than the concentration in the NH_4HCO_3-solution (0.20 mol NH_4-N L^{-1}). Figure III-13 illustrates the results of the stripping experiments with differing surface areas (0.14 m^2, 0.28 m^2, 0.57m^2 and 1 m^2), digestate and 1 M H_2SO_4 in the acid trap.

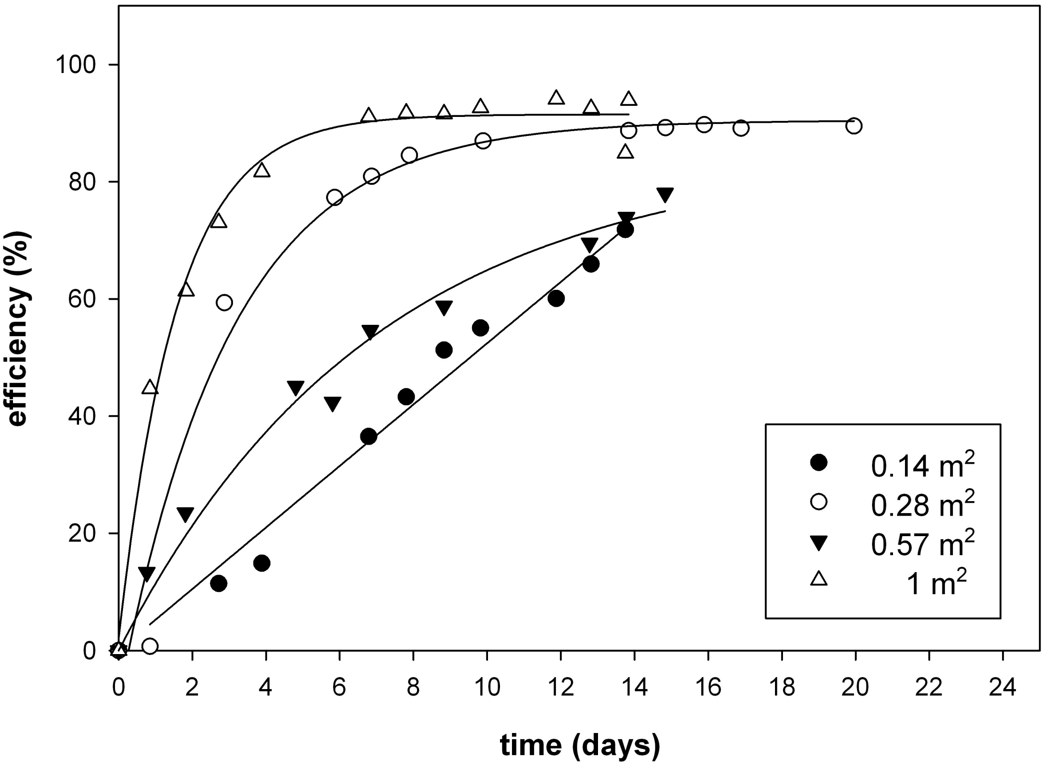


Fig. III-13: Ammonia removal efficiency (%) over time using different surface areas (0.14 m^2, 0.28 m^2, 0.57 m^2 and 1 m^2) and digestate.

With the lowest surface area (0.14 m^2, one disc rotating through acid), 15% of the NH_4-N was removed within 4 days, increasing almost linear to 50% within 8.5 days. When the experiment was stopped after two weeks, 71% of the NH_4-N was removed from digestate. The approximating curve displays an almost linear stripping behavior. According to the stripping theory where concentration gradient and diffusion are the main driving forces, linear behavior is unlikely to occur. It rather seems that the experiment was stopped too early. With an extended running time, the curve might have reached a maximum and leveled off as illustrated in the other experiments. Apart from that, during the first 2 days (43 hours) after starting the experiment, the calculation of the removal efficiency resulted in a negative value as the NH_4-N concentration increased by 3% - 5%. This was probably caused by an additional release from digestate through microbial processes (chapter 4.3.2). The experiment with 0.28 m^2 surface area removed 60% NH_4-N within 2.8 days and further 17% during the next 3 days. After that, the curve showed asymptotic behavior; indicating that almost all strippable ammonia was removed. Further small amounts were removed, reaching a maximum removal efficiency of 87% within 10 days. Then, ammonia stripping slowed down and only marginal amounts were removed until the end of the experiment.

An interesting but unexpected behavior was observed when doubling the number of discs rotating through acid and digestate again to 0.57 m^2. Then, the overall NH_4-N removal was less efficient compared to 0.28 m^2 surface area as after 2 days, 24% of the NH_4-N and after 6 days 50% were removed. The curve increased exponentially until day 13, removing 74% NH_4-N. However, the experiment was, just as the one with 0.14 m^2 surface area, also stopped too early so the change to saturation could only be assumed. As the ratio of rotating discs in digestate and acid were the same for both experiments, one would either expect a similar trend for 0.28 m^2 and 0.57 m^2 surface area as it was observed with NH_4HCO_3 (Fig. III-12) or, what is even more plausible, a faster stripping for 0.57 m^2 as double the amount of digestate was in the system, thus holding potentially twice the amount of strippable ammonia. Additionally, with more rotating discs, the air movement in the stripping system was slightly higher and this might contribute to a faster and more efficient stripping process, which should result in a curve in-between the ones from 0.28 m^2 and 1 m^2 surface area.

Since this stripping behavior could not be explained from a chemical point of view, some other, environmental or setting factors might have influenced the process. The number of discs on the shaft was adapted to the respective experimental setup before each run, thus changing the distance between the discs for the 0.57 m^2 surface area experiment. Accidentally, this distance might have been bigger for 0.57 m^2 than for 0.28 m^2 and thus slowing down the NH_3 diffusion into the acid trap. This is the most probable explanation of the stripping behavior for 0.57 m^2 surface area as it was almost the same with 0.28 m^2 surface area for NH_4HCO_3 but much slower for digestate. With the highest surface area of 1 m^2, 50% NH_4-N was removed from digestate within 1.3 days (30 hours) and 84% within 4 days. The removal efficiency increased afterwards only slightly up to 90% during the next 3 days and stagnated until day 14, when the experiment was stopped. Both curves, 1 m^2 and 0.28 m^2, increased almost linear in the first five days. The slope of the curve with 1 m^2 surface area is steeper than with 0.28 m^2, as stripping efficiency is higher in the beginning attributed to the higher surface area. When the curves reached their turning point, they changed into saturation and NH_4-N did not decrease further as it was removed almost completely. The slopes for 0.14 m^2 and 0.57 m^2 surface area were smoother, so I could not observe 80% NH_4-N removal during the experimental period.

4.5 Comparing the ammonia removal efficiencies of digestate and NH_4HCO_3

The ammonia removal efficiencies from the experiments with NH_4HCO_3 and digestate are directly compared in Fig. III-14.

Stripping behavior was slightly faster and thus ammonia removal more efficient in digestate than in NH_4HCO_3-solution when using a surface area of 1 m^2. Within the first days, microbial activity might have facilitated and enhanced NH_3 volatilization, thus leading to a slightly faster NH_4-N removal. Further, as ammonia stripping is pH dependent (chapter 2.3), the slightly higher pH in the digestate (pH 8.3) compared to NH_4HCO_3 (pH 8.0) might also have contributed to a faster NH_4-N removal. 44% NH_4-N removal was achieved within 20 hours in digestate and 28 hours in the NH_4HCO_3-solution.

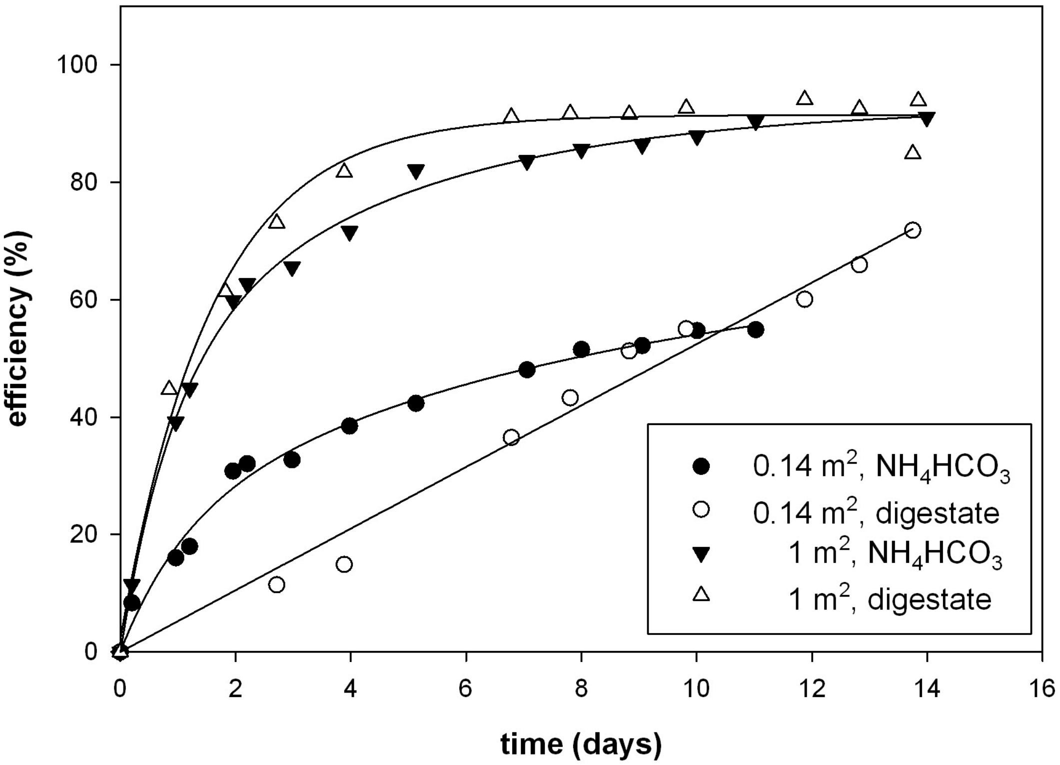


Fig. III-14: Comparing the ammonia removal efficiencies (in %) over time with surface areas of 0.14 m^2 and 1 m^2 when using digestate and NH_4HCO_3.

The NH_4-N removal increased over the next days, removing 83% NH_4-N in digestate within 3.8 days, whereas it took 7 days for NH_4HCO_3. Although the slope of the curve for the NH_4HCO_3-solution decreased after 2 days, NH_4-N removal continued, resulting in 91% removal efficiency after 11 days. For digestate, the slope was steeper, achieving 90% NH_4-N removal efficiency after 6 days. Then, NH_4-N decreased only marginal until the end of the experimental period at day 14. For the experiments with 0.14 m^2 surface area, stripping behavior varied considerably for digestate and the NH_4HCO_3-solution. The NH_4-N concentration in the digestate increased due to microbial activity during the first 3 days, thus resulting in negative removal efficiency. Simultaneously, the NH_4-N decreased already in the NH_4HCO_3-solution, resulting in 31% NH_4-N removal in two days. Thus, NH_4-N removal was faster in the NH_4HCO_3-solution than in digestate, where removal was more or less linear. At day ten, the two curves crossed each other when around 54% NH_4-N were removed. The curve for the NH_4HCO_3-solution approached saturation, whereas the curve for digestate still increased. When the experiments were stopped, 28% NH_4-N resp. 45% NH_4-N was left in digestate and NH_4HCO_3.

Ammonia stripping was more efficient with digestate than with the NH_4HCO_3-solution, as microbial activity enhanced ammonia volatilization. The organic material did not seem to influence the stripping behavior directly. However, it might have slightly increased the mount of digestate sticking on the discs, thereby increasing surface area and NH_3 volatilization.

4.6 Disc holding and disc adsorption capacity

I observed a different degree of wear on the rotating discs after the first experiments with digestate when changing the setup of the stripping devices (positioning more or fewer discs on the shaft). As texture and distribution behavior on the disc were completely different for the three substrates digestate, H_2SO_4 and NH_4HCO_3, tests on adsorption capacity were carried out. Therefore, one disc was run successively through water (as a reference media) and through the three used substrates. Thereafter, the wetted surface (in %) was measured. After each run, the disc was rinsed with deionized water and completely dried with paper towels. The disc rotated then once with a velocity of 10 rounds per minute (rpm) through pure water and 50% of the disc surface was wetted. For aqueous H_2SO_4 and NH_4HCO_3, surface wetting was slightly lower with around 40%. The “wetting process” started from the outer edge dipping into the substrate. The liquid trickled then slowly into the direction of the disc center. In fact, the grooves on the disc should have favored the trickling to the center, but even for water and the aqueous substrates it did not work well and the discs were never completely wetted. On each side of the disc, the liquid covered around 12 cm - 15 cm from the outer edge. For the digestate, which had a viscous and hydrophobic texture, disc coverage was even worse. Only about 25% (5 cm - 10 cm of the outer edge) of the disc was covered with digestate, thus limiting surface area extension and NH_3 volatilization.

In order to determine the factor limiting volatilization most (spreading the substrate on the disc or adsorbing it from the container), the disc holding capacity (DHC) for the three used substrates was determined as described in chapter 3.7. The

DHC is the amount of substrate that stuck on the disc when rotating once through substrate.

The results are to be seen in Tab. III-2. The highly viscous texture and the organic material in the digestate led to a higher adsorption on the discs' outer area. The calculated DHC was almost 8 times higher for the disc rotating through digestate than those rotating through aqueous substrates. However, the advantage of a higher adsorption on the disc and thus DHC did not contribute much to the overall surface area increase as the viscous texture made trickling difficult. Further, during the experimental period, the organic components in the digestate deposited on the outer 2 cm – 5 cm of the disc. There, they started to build a small barrier, which thus complicated trickling, and surface area enlargement even more.

In order to test the influence of a faster rotating disc on DHC, adsorption and trickling ability, the rotating speed was increased from 10 rpm to 44 rpm and 80 rpm.

Tab. III-2: Disc holding capacity (DHC) for the used substrates under different disc rotating speeds.

	DHC ($mg\ cm^{-2}$)		**% increase from**	**DHC ($mg\ cm^{-2}$)**	**% increase from**
Substrate	**10 rpm**	**44 rpm**	**10 – 44 rpm**	**80 rpm**	**10 – 80 rpm**
H_2O	2.23	2.76	23.8%	4.01	79.8%
H_2SO_4	2.79	4.10	46.9%	4.89	75.3%
NH_4HCO_3	2.97	4.10	38.0%	4.62	55.5%
Digestate	25.69	29.88	16.3%	34.90	35.8%

By accelerating the rotating speed fourfold, DHC increased remarkably for all substances, ranging from 16% for digestate up to 47% for H_2SO_4. If rotation velocity was increased further, from 44 rpm to 80 rpm, DHC increased by almost 20% for digestate and 30% for H_2SO_4. So the H_2SO_4 dispersion was influenced most by the raised velocity. The higher disc velocity came along with an increased wetted disc and thus enlarged surface area, which led to an enhanced NH_3 volatilization. Ideally, all further experiments should have been carried out with the higher velocities. However, the higher rotating speed came along with the spreading of substrate droplets on the device wall and the formation of small puddles besides the substrate containers, which led to overall liquid losses. In order to avoid these losses, the experiments were either carried out with a disc velocity of 10 rpm or 44 rpm.

4.7 Ammonia removal efficiencies with different disc rotation velocities

In order to induce a higher air flow in my stripping system, I raised the rotational speed of the discs. I expected that enhanced turbulences created around the rotating discs would speed-up ammonia transfer by an increased diffusion into the gas phase. In my experiments, the rotational speed was increased four times from 10 rpm to 44 rpm. An attempt with a velocity of 80 rpm and 106 rpm was not pursued further as the faster disc rotation caused spillage of the substrate. Fig. III-15 shows the different stripping efficiencies for 0.14 m^2 surface area, where also the position of the rotating disc was compared. The results with an increased rotating speed for 0.28 m^2 and 0.57 m^2 surface area are shown in Fig. III-16.

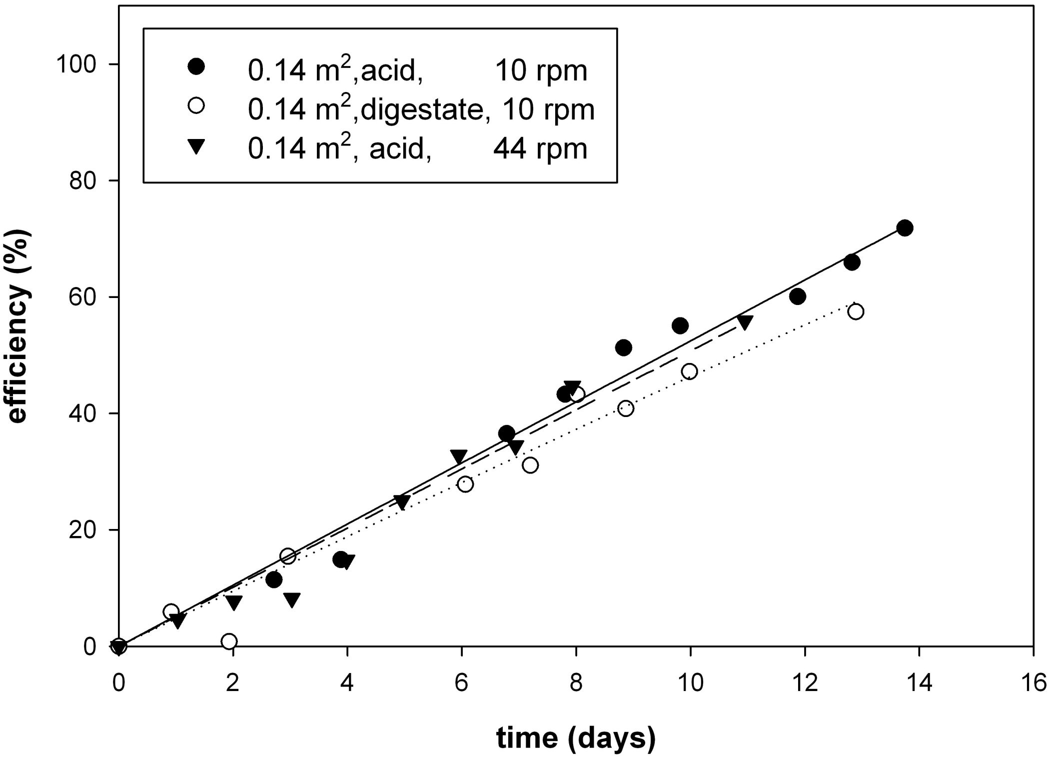


Fig. III-15: Ammonia removal efficiencies (in %) over time for one disc (0.14 m^2 surface area) rotating either in digestate or in acid. Further, ammonia removal efficiency (in %) with an increased disc velocity is also shown.

In both experiments with one disc rotating through either digestate or acid, I observed a low NH_4-N removal efficiency during the first four days (below 15%). Afterwards, the efficiency increased and 55% of the NH_4-N was removed within seven days. The fourfold higher disc rotating velocity did not influence stripping behavior and efficiency. A reason for the generally low stripping efficiency was likely that turbulences, which were created by the rotating disc, were still too low for mixing the air thoroughly and thereby increasing stripping efficiency. Another, more plausible explanation is the unchanged surface area of the digestate container, to which the NH_3 volatilization out of the digestate was still confined to. Even if the rotational speed of the discs rotating through acid and therewith simultaneously the available adsorption surface on the disc was increased, NH_3 volatilization speed did not change. This indicates, that for this setup, the volatilization out of the digestate was the limiting factor and not the absorbing capacity of the acid sink.

The ammonia removal efficiency of the disc rotating with 10 rpm through digestate was slightly lower than when rotating with 10 rpm through acid. So even if more NH_3 evaporated out of the digestate due to the rotating disc and thus surface enlargement, the uptake rate of the not stirred sink was lower as surface area was small.

The effect of an increased disc velocity for higher surface areas (0.28 m^2 and 0.57 m^2) is illustrated in Fig. III-16. For both surface areas, the experiments with an elevated rotational speed came along with a higher NH_4-N removal and thus stripping efficiency. For 0.28 m^2 surface area and 44 rpm, 80% removal efficiency was obtained after four days, whereas it took almost seven days to achieve the same efficiency for 10 rpm. The shapes of the curves are similar, with a steeper slope for the faster rotating discs. This can also be seen for the doubled surface area, where 56% efficiency is obtained after 8 days compared to 3.8 days (less than half). Due to time shortage, the experiment with a higher velocity was stopped after 8 days when 70% efficiency was obtained. At this point, ammonia removal started to level off.

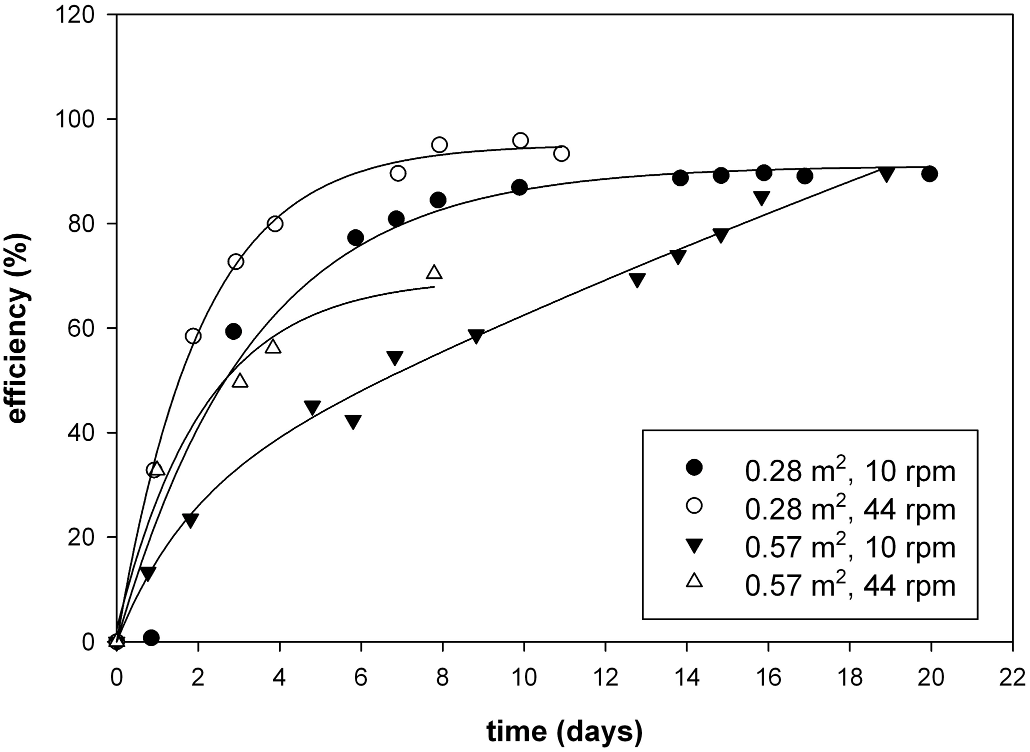


Fig. III-16: Ammonia removal efficiencies (in %) over time with different surface areas (0.28 m^2 and 0.57 m^2), low (10 rpm) and increased disc velocities (44 rpm).

At 10 rpm, ammonia stripping rates were lower but increased almost linearly up to 90% and did not reach asymptotic behavior during the experimental period.

4.8 The influence of temperature changes on ammonia removal efficiency

The transition of NH_4-N to NH_3 and *vice versa* is temperature as well as pH dependent. According to the law of thermodynamics, with an increased temperature, gas molecular movement is faster and thus leading to a higher proportion of volatile NH_3 and a higher reaction velocity (chapter 2.3, Fig. III-4).

However, raising the temperature by about 7°C by running the device in a greenhouse at an average temperature of 22°C, did not improve removal efficiencies as expected. At 15°C, even more NH_3 could be stripped (Fig. III-17). In the experiments with a surface area of 1 m^2, 50% NH_4-N removal efficiency was obtained 1.3 days faster when running at 15°C compared to 22°C. A similar result of a 1.1 day faster removal was achieved with 0.28 m^2 surface area at 15°C.

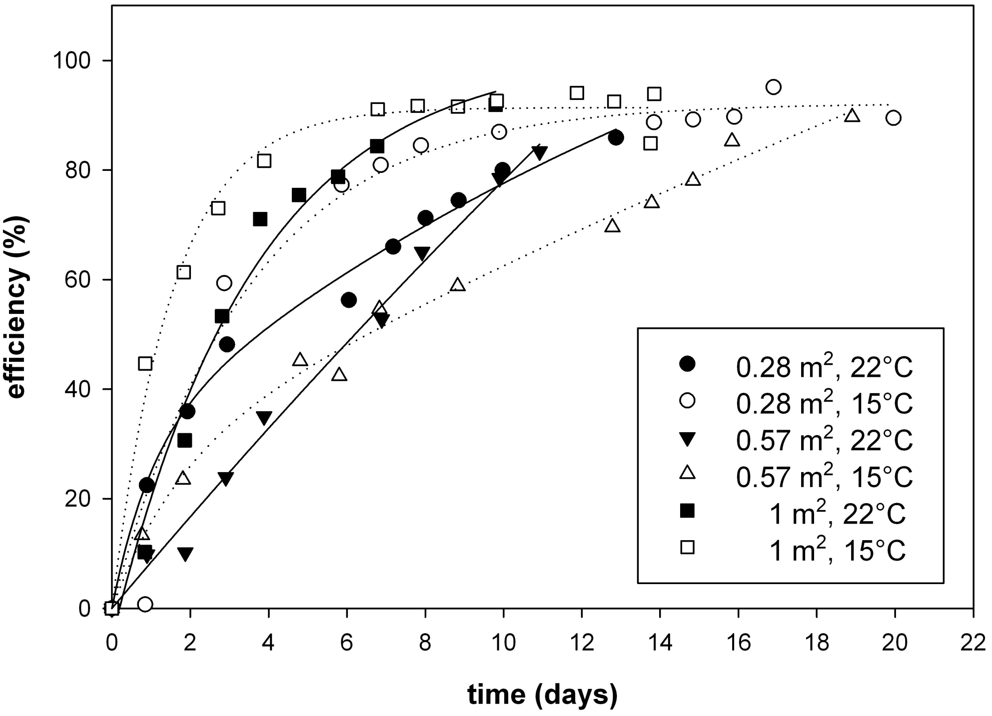


Fig. III-17: Ammonia removal efficiencies (in %) over time with varying surface areas (0.28 m^2, 0.57 m^2 and 1 m^2) and temperatures (15°C and 22°C).

In both experiments, the curves increased faster and reached saturation earlier than at higher temperatures. Only the experiment with a surface area of 0.57 m^2 achieved, after a slow beginning, a higher stripping efficiency with the elevated temperature. The intercept and the slope of the curve from the experiment carried out at 22°C was steeper, resulting in a removal efficiency of 83% after almost 11 days. When the experiment was carried out at 15°C, it took four more days to achieve the same efficiency. These results are conflictive with the above mentioned law of thermodynamics, as I would expect an enhanced ammonia volatilization due to a faster molecular movement. An explanation for the lower stripping efficiency might be the moderate temperature increase of only 7°C.

4.9 Difficulties during experimental realization and suggestions for improvement

Variations in stripping efficiencies, which could neither be explained by differences in the surface area nor by the surrounding environment, were analyzed based on the influence of the disc position in the system. Therefore, the NH_4-N removal efficiency of each single disc was analyzed (Fig. III-18). Fig. III-18 shows, that ammonia stripping was faster if acid and digestate discs were alternating, whereas it took almost twice the time to obtain similar NH_3 removal when only one acid disc was neighboring a digestate disc.

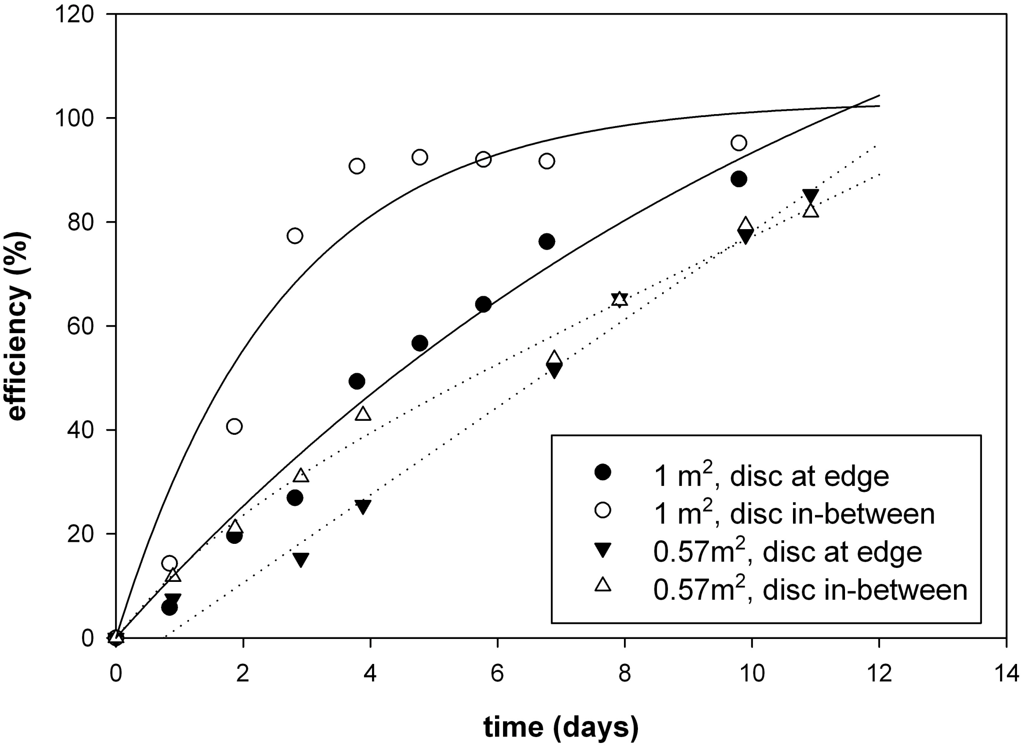


Fig. III-18: Ammonia removal efficiencies (in %) over time dependent on the disc position with two different surface areas (0.57 m^2 and 1 m^2). Disc in-between: the disc rotating through digestate was flanked on both sides by discs rotating through acid. Disc at edge: the disc rotating through digestate was flanked by only one disc rotating through acid.

This difference was remarkable in the experiment with 1 m^2 surface area, where 50% NH_4-N was removed within 2 days when the digestate disc was flanked by two acid discs, whereas it took nearly double the time (3.8 days) for the same efficiency when the digestate disc was flanked by only one acid disc. So the system with rotating discs will work best if the spacing between the discs is as small as possible and if acid trap and digestate discs are alternating as the stripping is largely dependent on diffusion. As diffusion is a rather slow process, the system could be speeded up if more turbulence would enhance the transfer of NH_3 from the digestate to the acid traps.

The above mentioned ammonia stripping experiments were not carried out under optimal conditions and the setup could be adapted to obtain better overall stripping efficiencies. The parameters comprise mainly the construction of the stripping device (higher surface, more surface roughness of the discs, increase of turbulence) and the optimum substrate conditions (pH value and temperature).

The discs should be fixed permanently on at least 4 exchangeable shafts in order to guarantee a constant distance between the rotating discs, thereby enabling a better comparison of the results and efficiencies of the stripping process. It would also be beneficial to use more than 7 discs and position them closer to each other to enhance diffusion. For time saving reasons, it would be helpful to run more than two devices in parallel.

One of the main challenging tasks was the changing number of containers filled with digestate. This varying number of containers brought different amounts of digestate and thus strippable NH_3 into the system, changing the digestate:acid ratio. Therefore, it would have been much better to have constantly the same amount of digestate in the system e.g. by filling the whole tank in the beginning with digestate and fixing some acid containers on the side walls. So, irrespective of the number of rotating discs, during the whole experimental period there would always be the same amount of strippable ammonia in the system. Further, the installation of a small fan in the tank can promote air turbulences within the system, which would then contribute to a faster stripping process. These turbulences could increase the overall mass transfer ratio as observed by Quan et al. (2009) during their stripping experiments using columns with an enhanced air flow.

For a better stripping process, it is also necessary to increase the pH of the digestate. The addition of e.g. NaOH increases the initial pH from 8 to 10 and obtain a proportion of 80% NH_3 at 20°C. If pH is increased further (pH 11), nearly all of the nitrogen present would be in form of NH_3 (Fig. III-4). In my experiments, I did not increase the pH as I wanted to study the stripping ability of the device at initial digestate conditions. It was planned to execute the ammonia stripping experiments before and after phosphate precipitation. Due to time shortage, the precipitation experiments after the stripping process could not be carried out and thus not compared. Further, I expected that with an increased pH the conditions for a spontaneous phosphate precipitation were enhanced and thus would lead to an even more viscous digestate with phosphate crystals. Nevertheless, for a fast and efficient stripping process it is absolutely necessary to increase the pH in order to have a high proportion of strippable ammonia available.

An increased temperature can also shift the equilibrium from NH_4^+ towards strippable NH_3 and thus decrease the amount of chemicals (NaOH, $Ca(OH)_2$) necessary for pH adjustment. Therefore it would be necessary to increase the temperature in the digestate and the surrounding environment not only by 7°C but by 30°C or 50°C. Without changing the pH, an increase to 55°C would have resulted in a proportion of 50% NH_4^+ to 50% NH_3 and this would have enhanced and accelerated the stripping efficiency. Temperature could have been increased more, if the measurement of the device would have been smaller in order to fit into a climate chamber, where temperature and humidity could be regulated and controlled. This would guarantee a constant temperature.

As the experiment was also carried out in order to establish a stripping device on the pilot pig farm in China, where no additional heating, except sunlight, is available, the temperature increase to 40°C would be the maximum. In this case, pH increase would be the most suitable measure to enhance stripping.

For a further enhanced stripping and a professional operation, the contribution of process engineers would be necessary. Due to the coexistence of acidic and alkaline environmental conditions in the tank, the containers and other metal parts corroded after some experiments and had to be replaced by aluminum or acid-proof plastic containers. The coverage of the device should also be made of non gas-permeable materials in order to avoid gaseous losses. Specially designed and constructed discs with sharpened grooves might also contribute to an enhanced stripping efficiency due to a higher surface area.

4.10 Financial benefit of the fertilizer production

The financial benefit of the recovered product is not only dependent on the construction and acquisition costs of the rotating disc system, which would be rather high as for professional use the 900 discs with Ø 2 m, as well as the containers, had to be made of stainless steel but also on the operating costs. Running the system with high rotating speed for at least 4 days to remove about 90% of the NH_4-N present will consume electricity. Further, the use of an appropriate quantity of acid present in the acid trap containers will increase the operation costs as well as the mechanical parts, which are prone to deterioration and had to be maintained regularly.

Tab. III-3: Actual sales prices for different fertilizers in China and Germany (€ kg^{-1}). Data for Chinese fertilizers from Ban Hongqin and Roelcke, May 2013 (pers. communication).

	China	Germany
Urea fertilizer	0.25 € (2 ¥)	0.42 €
DAP (di-ammonium phosphate) with 18% N and 20% P	0.47 € (3.8 ¥)	0.49 €
NPK (15/15/15, Cl)	0.37 € (3 ¥)	0.40 €
NPK (15/15/15, S)	0.41 € (3.3¥)	0.40 €

The sales prices paid by farmers for the different fertilizers are quite similar in China and Germany. The only difference can be seen in the costs for urea fertilizer in China, which are only half compared to Germany.

5 Discussion

The two main factors for an enhanced stripping efficiency described in literature are surface area enlargement and airflow (rate).

With my approach of the rotating disc system, the surface area could be varied and different NH_4-N removal efficiencies obtained. The system removed 80% NH_4-N within 80 hours (3.3 days) and 90% within 150 hours (6.2 days) with a surface area of 1 m^2 and the initial digestate pH 8.3. With this, ammonia removal was faster using my rotating disc system with 1 m^2 surface area than ammonia stripping carried out with swine wastewater by Liao et al. (1995). The authors achieved 80% ammonia removal in > 250 hours with direct aeration and an initial pH of pH 9.3. However, my system removed the same quantity 170 hours (7.1 days) faster. When I used fewer rotating discs and thus a smaller surface area of 0.28 m^2, 80% ammonia removal was obtained after 6.5 days, which is still almost 4 days faster than the results obtained by Liao et al. (1995) with direct aeration. However, by increasing the pH from 9.3 to pH 12 by adding lime, the authors obtained 90% ammonia removal within 100 hours (4.1 days), which was then almost 2 days faster than my system. Consequently, at lower pH values, the rotating disc system was more efficient (to some extent considerably) in ammonia removal than the direct aeration carried out by Liao et al. (1995). A disadvantage of the aeration method used by the authors is also the loss of ammonia as the transporting air carries the volatilized ammonia out of the digestate and out of the stripping system. In my closed, rotating disc system, ammonia was not lost to the surrounding environment but was rather trapped in the acid and formed simultaneously a valuable fertilizer. However, the rotating disc system is, due to the mechanical parts e.g. engine and shaft more fragile and needs more maintenance than the simple aeration technique.

Liao et al. (1995) achieved their best stripping result with 90% ammonia removal in 7 hours after changing from the simple direct aeration setup to stripping towers filled with plastic rings for surface enlargement and countercurrent flows of swine wastewater with pH 11.5 and air. When the authors used swine manure with initial pH 9.5, they achieved 91% ammonia removal in 55 hours (2.3 days), which was

2.7 times faster compared to the best results with the rotating disc system with a surface area of 1 m^2 and 6 times faster when using 0.28 m^2 surface area.

In the experiments from Liao et al. (1995) surface area was, in contrast to pH and air flow rates, not changed. A higher airflow entering from the bottom into the column led to a faster release of volatile NH_3 from the swine wastewater into the air and thus to a faster overall ammonia reduction.

In my stripping system, I had, except for light turbulences created in straight distance to the rotating discs, no real airflow. An attempt to increase these slight turbulences was carried out by raising the rotating speed of the discs (chapter 4.7), which then induced a higher ammonia release from digestate. However, due to the construction, the disc velocity could only be increased four-fold (from 10 rpm to 44 rpm). This acceleration reduced the required stripping time for a 50% ammonia removal by almost half (0.28 m^2 surface area: 2.6 days using 10 rpm and 1.4 days using 44 rpm). For 0.57 m^2 surface area, the effect of an increased disc velocity for 50% removal was even more clear as 5.9 days using 10 rpm and 2.5 days using 44 rpm were needed. However, this acceleration was not enough to achieve the same stripping efficiencies in the same time as Liao et al. (1995) when using air stripping.

The experiments with a slightly increased temperature (7°C) yielded lower NH_4-N removal as the experiments with lower temperature. This was in accordance with data described by Liao et al. (1995) who had also only a marginal rise in temperature in their liquid influent, ranging from 6°C - 13°C vs. 16°C - 22°C. The authors did not observe a significant temperature effect on ammonia removal above pH 10.5, e.g.: results for pH 11.5 at 13°C are similar to those of pH 11.5 and pH 10.5 at 20°C. This is quite clear, as at around pH 10, the proportion of NH_3 to NH_4-N is almost 100% (Fig. III- 4).

Marttinen et al. (2002) observed, in contrast to Liao et al. (1995), a 16% higher stripping efficiency at initial pH 7.5 when raising the temperature in substrates from landfill leachate from 10°C to 20°C. The authors used an air stripper and by increasing the pH to pH = 11, stripping efficiency went up from 64% at 6°C to 89% at 20°C. Yoon et al. (2008) observed a six fold higher stripping efficiency by raising the temperature from 20°C to 50°C. This is in good accordance to

Değermenci et al. (2012), who observed a reduction in stripping time from 58 hours to 8.3 hours by increasing the temperature from 20°C to 50°C. Bonmatí and Flotats (2003a) observed complete removal from an ammonia solution when using an air stripping column. The authors observed that pH was an important factor influencing ammonia stripping. When pH was increased from pH 7.5 to pH 11.5 the time needed for complete ammonia stripping decreased from 5 to 3 hours. For digestate, they observed 60% removal efficiency after 2 hours at an initial pH of pH 8.5. When pH was increased to pH 9.5 and 11.5 the same efficiency was achieved in 1 hour. Ammonia removal through air stripping is clearly more efficient as our system with rotating discs where, even with an increased disc velocity, still 1.4 days were necessary to remove 50% NH_3.

Değermenci et al. (2012) used a stripping column to remove ammonia from an ammonia solution. Within 9 minutes, they achieved a removal efficiency of 50% with an elevated pH (pH = 11). After 50 minutes almost complete ammonia removal was achieved. This is considerably faster and thus efficient, compared to my results using the NH_4HCO_3-solution where 50% ammonia removal was achieved after 1 day with a surface area of 1 m^2.

However, the financial benefit, when selling the regained nutrients to a similar price as conventionally produced fertilizer, would be small and thus the incentive to build and operate devices for nutrient recovery. So the Chinese decision makers should not only focus on the revenues but rather on the environmental aspect as N and P could be removed and exported, thus reducing the threat for the environment in the vicinity of large animal farms. Further, as fertilizer production relies considerably on coal and China is facing severe air pollution, this shift could not only contribute locally but also countrywide to a better air and thus environmental quality.

6. Conclusion

Large amounts of wastewater created in animal husbandry and the following excessive disposals on agricultural fields contribute to environmental and thus particularly water and air pollution. Several experiments proved my first hypothesis, as it was possible to remove large quantities of ammonia from anaerobically treated slurry. Simultaneously, the NH_3 stripping experiments produced an ammonium sulfate solution, which could further be used as liquid mineral fertilizer. The rotating disc systems achieved, dependent on the available surface area, 70% - 80% NH_4-N removal in digestate within 3 - 4 days and almost complete removal (90%) within 10 - 13 days. Ammonia stripping was most efficient when the experiments were carried out with the maximum available surface area of 1 m^2. However, ammonia stripping in my rotating disc system takes longer than in conventional, already available systems.

The second hypothesis that parameters like rotation speed and temperature influence ammonia stripping most has also been proven. A four-fold increase in the rotation speed decreased the stripping time remarkably and in some experiments even by almost half. The increase in temperature was too small to improve the conditions for ammonia volatilization, resulting in an even lower NH_4-N removal efficiency in these experiments. Organic material in the digestate did not influence the stripping process directly as NH_4-N removal was even higher compared to the ones obtained in pre-experiments with an aqueous NH_4HCO_3-solution. However, digestate enhanced the grip on the discs and thus might have increased the surface area and facilitated ammonia volatilization. One might envisage as well redesigning the system in that there is a continuous flow of digestate and eventually acid over the discs to provide more constant stripping conditions and reduce the need for large surface areas.

IV. General conclusion

Large amounts of wastewater created in animal husbandry and its excessive disposal on agricultural fields or into water bodies contribute substantially to environmental, and more precisely, to water and air pollution in the pilot region.

Important outcomes of the experiments are: i) the successful recovery of phosphate through struvite ($MgNH_4PO_4$) precipitation in pig slurry and digestate and ii) the identification of the most relevant parameters influencing phosphate precipitation; iii) the successful construction and performance of a low-budget and low-technology ammonia stripping device, which reduced the NH_4-N remarkably in digestate, and iv) the identification of parameters influencing ammonia stripping. i) The solute phosphate (PO_4-P) could almost completely (about 80%) be regained through struvite precipitation in untreated pig slurry as well as in digestate by adding MgO. For the untreated pig slurry samples, simple aeration was enough to precipitate more than half of the PO_4-P. However, aeration will promote ammonia volatilization and thus contribute to indirect greenhouse gas emissions.

ii) A changed pH did not reveal significant differences in PO_4-P removal efficiencies. In contrast, the molar Mg:P ratio and the repeated addition of MgO influenced struvite precipitation most. Nevertheless, the biogas process reduced the overall PO_4-P concentration by 2/3 as phosphate precipitated spontaneously due to an increased pH in the digester (Möller and Müller, 2012). The final aerobic treatment on the farm led to further spontaneous struvite precipitation and thus a reduction of the PO_4-P concentration.

Ultracentrifugation revealed that a significant fraction of P is bound to organic or hardly crystallized slowly settling compounds. Organic matter and suspended solids influenced struvite precipitation most, which makes a pretreatment necessary. The chemical oxidation of the organic matter resulted in an intense foam production, during which NH_3 volatilized but released also formerly bound phosphate from the digestate samples. Even if struvite precipitation was enhanced, this oxidation step could not be carried out on the pilot farm. Besides the H_2O_2, antifoaming agents need to be added to the slurry or digestate and will thus create not only additional costs but also influence the wastewater composition. Although the PO_4-P concentration of the effluent leaving the farm was rather low, these samples showed the highest effect on oxidation, indicating that there was still a huge quantity of P fixed to organic material. If the Chinese farmers irrigate their fields with this wastewater, they will fertilize their fields in an uncontrolled manner and thus unintentionally over-fertilize their land. This contributes to P losses through surface runoff and eutrophication of surface water.

This is an important finding and should be kept in mind as the implementation of the Renewable Energy Resources Law 2010 (Roelcke et al., in preparation), which subsidies the construction of biogas plants, might lead to an augmented anaerobically treatment of animal wastes in this region, resulting in large quantities of wastewaters still high in phosphate. Further, Heimann et al. (in preparation) and Ostermann (personal communication) analyzed soil samples and found in one of their sampled agricultural field, which did not receive any manure but was regularly and exclusively irrigated with stream water, a reduced pH in the topsoil of pH 5.9. This reduction was attributed to the high ammonium content in the digestate and thus the irrigation water, which led to acidification due to the release of protons during plant uptake (Ostermann, personal communication).

For the practical implementation of a cheap and efficient phosphate removal system on the pilot farm, I would suggest a struvite precipitation treatment step before the untreated pig slurry enters the biogas process. The biogas process and thus gas production will not be influenced by the treatment, as P is not a limiting factor for gas production (Möller and Müller, 2012). Further, as P might also precipitate spontaneously in the digester, it is necessary to remove it before digestion. Additionally, the analysis of the precipitate composition showed that almost 50% of the precipitate consisted of struvite, which could then be exported from the pilot farm as valuable fertilizer. As the precipitate consisted further of $CaCO_3$, it can thus simultaneously be used for liming and increasing soil pH.

iii) The successful implementation and performance of the ammonia stripping device consisting of rotating discs reduced the NH_4-N concentration in the digestate remarkably. With the maximum available surface area of 1 m^2, 85% of the NH_4-N could be removed within 4 days and almost complete within 10 - 13 days. Although ammonia stripping using the rotating disc system worked, it took longer than conventional, already available techniques like air stripping or stripping using the water-sparged aerocyclone reactor. Further, if the rotating disc system is adapted directly without changes to the requirements on the pilot pig farm with 100 m^3 slurry (or even more) produced per day, around 890 discs with a diameter of 2 m would be needed (445 discs, each, for digestate and for acid). However, it is not feasible to install a device with rotating discs on the farm, as space is limited. The conventional available systems are not only expensive; they also need good maintenance and adjustment, which might not be guaranteed on small-scale farms.

The best and most efficient step for ammonia stripping would be after the biogas process. Then, the excess ammonia could be stripped and for economic reasons, the aeration treatment of the remaining wastewater could be saved.

Currently, the price of the recycled N-fertilizer gained from the rotating disc system cannot compete with conventional fertilizers produced in large fertilizer production plants in China. Conventional fertilizer prices range from 2 ¥ (0.25 €) for urea fertilizer to 3.8 ¥ (0.47 €) for DAP (di-ammonium phosphate). However, Chinese decision makers should not only focus on the revenues of the nutrient recovery system but rather on the environmental aspect as N and P could be removed and exported, thus reducing the threat for the environment in the vicinity of large animal farms. Further, as fertilizer production relies considerably on coal and China is facing severe air pollution, this shift could contribute not only to locally but also countrywide to a better air and thus environmental quality.

As population is still increasing and thus the demand for meat is still high, environmental pollution due to animal husbandry will also play an important role in the future.

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