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**Nutrient recovery from human urine:  
Treatment options and reuse potential**

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## Summary

A “No Mix” sanitation system was installed in a dormitory at the University of CanTho in South Vietnam, with the objective of recycling nutrients from source separated wastewater. The “Yellow Water” treatment plant was assessed for its efficiency in recovering phosphorus and nitrogen from human urine. The pilot plant achieved phosphorus removal efficiencies of 98% with both diluted and undiluted urine. Phosphorus was recovered in the form of struvite, a solid mineral fertilizer with heavy metal concentrations below the German Fertilizer Regulation’s threshold limits. About 110 g of struvite could be generated after one treatment cycle, during which 50 L of urine were processed. Nitrogen removal by air stripping showed best results when circulating the urine for 3 h through the stripping column at a high flow rate (80 L h<sup>-1</sup>). With these settings, more than 90% of the nitrogen could be removed from the urine, and virtually 100% of this nitrogen could be recovered in the form of liquid ammonium sulfate. In future, treatment costs could be further reduced by making use of the solar energy that is available during daytime in South Vietnam.

In a second experiment, a pilot scale evaporation technology was operated in Vietnam for recovering nitrogen and phosphorus from human urine by solar still for use as fertilizer. After 26 days of sun exposure, 360 g of solid fertilizer material was recovered from 50 L undiluted urine. This urine-derived fertilizer was mainly composed of sodium chloride, and had phosphorus and nitrogen contents of almost 2%. When tested with maize and ryegrass, the urine fertilizer led to biomass yields and phosphorus and nitrogen uptake rates comparable to those induced by a commercial mineral fertilizer. Urine acidification with sulfuric or phosphoric acid prior treatment reduced nitrogen losses, improved the nutrient content of the generated fertilizers and induced higher yields and nitrogen and phosphorus uptake rates than the commercial mineral fertilizer. However, acidification is not recommended in developing countries due to additional costs and handling risks. The fate of micropollutants and the possibility of separating sodium chloride from other beneficial nutrients require further investigation.

Finally, six urine-derived struvite fertilizers generated by innovative precipitation technologies were assessed for their quality and their effectiveness as phosphorus sources for crops. Struvite purity was influenced by drying techniques and magnesium dosage. In a pot trial, the urine fertilizers led to biomass yields and phosphorus uptake rates comparable to or higher than those induced by a commercial mineral fertilizer. Heavy metal concentrations were below the threshold limits specified by the German Fertilizer and Sewage Sludge Regulations. The computed loading rates of heavy metals to agricultural land were also below the threshold limits decreed by the Federal Soil Protection Act. Urine-derived struvite contributed less to heavy metal inputs to farmland than other recycling products or commercial mineral and organic fertilizers. When combined with other soil conditioners, urine-derived struvite is an efficient fertilizer which covers the magnesium and more than half of the phosphorus demand of crops.

## Zusammenfassung

Ein "No Mix" Sanitärsystem wurde in einem Wohnheim an der Universität Can Tho in Vietnam mit der Zielsetzung installiert, die Nährstoffe aus den getrennt erfassten Abwasserströmen wiederzugewinnen. Zunächst wurde die Effizienz der Phosphor- und Stickstoffrückgewinnung einer Gelbwasseraufbereitungsanlage bewertet. Die Pilotanlage erreichte eine Phosphoreliminierung von 98% in verdünntem und unverdünntem Urin. Phosphor wurde als Struvit – ein bewährter Mehrkomponentendünger – zurückgewonnen, dessen Schwermetallgehalte unter den Grenzwerten der deutschen Düngemittelverordnung liegen. Etwa 110 g Struvit konnten durch die Behandlung von 50 L Urin gebildet werden. Der Wirkungsgrad der Strippung war am höchsten, als der Urin für 3 Stunden bei hoher Fließgeschwindigkeit ( $80 \text{ L h}^{-1}$ ) durch die Strippkolonne zirkuliert wurde. Mit diesem Verfahren wurden über 90% des Stickstoffes ausgestrippt, von denen wiederum fast 100% als flüssiges Ammoniumsulfat zurückgewonnen wurden. Die Betriebskosten könnten zukünftig gesenkt werden, wenn man Sonnenenergie nutzen würde, die in Vietnam tagsüber stets verfügbar ist.

In einem zweiten Versuch wurde eine Pilotanlage basierend auf Verdampfungstechnologie betrieben, um aus Urin Stickstoff und Phosphor zur Nutzung als Düngemittel zu gewinnen. Nach 26 Tagen Sonneneinwirkung wurden 360 g Feststoffe aus 50 L unverdünntem Urin zurückgewonnen. Der Urindünger bestand hauptsächlich aus Natriumchlorid und hatte Phosphor- und Stickstoffkonzentrationen von circa 2%. Versuche mit Mais und Weidelgras haben gezeigt, dass der Urindünger ähnliche Ertrags-, Stickstoff- und Phosphorwirkungen induzierte wie ein herkömmlicher Mineraldünger. Durch das Ansäuern des Urins mit Phosphor- oder Schwefelsäure vor der Behandlung konnten Stickstoffverluste reduziert, die Nährstoffgehalte des Düngers verbessert, und die Ertrags-, Stickstoff- und Phosphorwirkungen verbessert werden. Allerdings ist die Verwendung von Säure in Entwicklungsländern nicht zu empfehlen, da sie zusätzliche Kosten und Risiken birgt. Weiterer Forschungsbedarf besteht hinsichtlich des Verbleibes von Mikroverunreinigungen, sowie der Möglichkeit einer Trennung von Natriumchlorid und den nützlicheren Pflanzennährstoffen.

Schließlich wurden sechs Fällungsprodukte aus neuartigen Sanitärsystemen auf ihre Düngewirkung untersucht. Die Reinheit war abhängig von Trocknungsmethode und Magnesium-Dosierung. Im Topfversuch induzierten die Urindünger ähnliche oder höhere Ertrags-, Stickstoff- und Phosphorwirkungen wie ein herkömmlicher Mineraldünger. Die Schwermetallgehalte lagen unterhalb der Grenzwerte der deutschen Düngemittel- und Klärschlammverordnung. Die berechneten Frachten von Schwermetallen befanden sich ebenfalls unterhalb der Grenzwerte der Bundes-Bodenschutzverordnung. Urindünger tragen also bei der Ausbringung weniger zu den Schwermetallfrachten bei als andere Recyclingprodukte oder herkömmliche mineralische und organische Dünger. Wenn man Urindünger mit anderen Bodenverbesserern kombiniert, sind sie effiziente Düngemittel, die den Magnesiumbedarf und mehr als die Hälfte des Phosphorbedarfes von Pflanzen decken.

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## List of abbreviations

DM	dry matter
ICP-OES	inductively coupled plasma-optical emission spectroscopy
MAP	magnesium ammonium phosphate, struvite
NEQ	nutrient equivalent
TKN	total Kjeldahl nitrogen
XRD	X-ray diffraction spectroscopy

## General introduction

Historical farming systems relied on natural levels of soil nutrients and the natural biogeochemical cycle. The loss of soil fertility caused by agriculture was countered by applying organic fertilizing agents such as farmyard manure, animal and plant refuse, household waste or so-called fossil manures (e.g. lime, chalk, sea shells) (Fussell, 1962). The use of human excreta as an agricultural fertilizer was common practice in East Asia for many centuries, and is still widespread in countries like Japan, China and Vietnam (Drangert, 1998; Jensen, 2005). In Victorian London, night-soil men collected the “night soil” from overflowing cesspools and sold the human waste to farmers outside the city walls (Johnson, 2006). This practice was abandoned in Europe during the Industrial Revolution as cities expanded and the distances, loads and transportation costs to agricultural land increased. Hence, filth was no longer turned to food, and sewage - now considered to be injurious to human health - was to be discarded in the cheapest and most effective way (Goddard, 1996). With the introduction of water closets, human waste was directly disposed of into water bodies instead of being returned to the soil (Cordell, 2009), and the increased dilution rendered the valuable fertilizing components of sewage practically worthless (Goddard, 1996).

The “Sanitation Revolution” was followed by the “Green Revolution”, which saw the development of high-yielding cultivars, the invention of the Haber-Bosch process, large scale phosphate rock mining, and the use of pesticides, herbicides and hydrocarbon energy to feed a rapidly growing world population. Yet, this progress in technology, public health and food production had a profound impact on the global phosphorus cycle (Ashley et al., 2011). Since the mid-1900s, the inputs of phosphorus to the biosphere have quadrupled (Falkowski et al., 2000). Phosphorus now moves in a linear direction from mines to lakes and oceans (Ashley et al. 2011), thus creating the ironic situation of having both too much and too little (Elser and Bennett, 2011). Excess phosphorus in waterways and coastal zones leads to eutrophication and algal blooms, and is therefore regarded as pollutant. On the other hand, phosphorus is a non-renewable resource and existing reserves could be depleted within the next 50 to 100 years (Cordell et al., 2009). Phosphorus has become the focus of intense geopolitical interest as most of the commercially viable reserves are controlled by Morocco/Western Sahara and China (Rosemarin, 2004). With a World Food Price Index shooting up dramatically in 2008 and reaching an all-time high in February 2011 (FAO, 2011), the food riots witnessed in 2008 and the famines ravaging the Horn of Africa were probably just a taste of things to come. Indeed, the world population is forecast to exceed 9.3 billion people by 2050 (UN, 2011), with a growing middle-class switching to more meat- and dairy-based diets, and an increasing conversion of food crops to biofuel in view of oil scarcity and climate change.

Given that phosphorus cannot be substituted by alternative resources, it is apparent that a new revolution is needed (Ashley et al., 2011): Phosphorus must be captured and moved from where there

is too much to where there is too little (Elser and Bennett, 2011). So far, the key drivers for phosphorus recovery from wastewater sludge were to prevent the pollutant from entering waterways and the spreading of biosolids on agricultural land. Cordell et al. (2011) presume that the future will see new drivers: they believe that the quality of the recovered phosphorus and its efficiency as a fertilizer will take over pollution prevention.

In fact, the world has been using the same type of toilet for 200 years now. Countries that can afford the flush toilet may experience benefits in human health and economic development from this wasteful technology, which uses drinkable water to carry away urine and feces for treatment by expensive and energy-intensive technologies (Grant et al., 2012). Challenged though by its ageing infrastructure and new pressures such as climate change or increasing regulatory requirements, the sanitation industry is at a turning point and needs reengineering (Mitchell et al., 2011). In developing countries on the other hand, over 780 million people still lack access to improved sources of drinking water and 2.5 billion people – about 37 % of the world population – have no access to improved sanitation (UNICEF and WHO, 2012). They urgently need affordable infrastructures and sustainable sanitation solutions.

Especially since the adoption of the United Nations Millennium Development Goals in 2000 (one of the targets was to halve, by 2015, the proportion of the population without access to safe drinking water and basic sanitation), new ways of collecting and treating human waste were conceived. Scientists have devised so-called ecological sanitation (ecosan) technologies, which can convert urine and feces into fertilizer, clean water and energy. A promising concept is the “No Mix” or separation toilet, of which the bowl has two openings to separate urine and feces. The benefits of using source-separating toilets are manifold. They save up to 80 % of the water used for toilet flushing – this represents 30 % of the average daily water use of a Western European (Larsen et al., 2001). Also, human urine contributes to less than 1 % of the composition of municipal wastewater whilst adding more than 50 % of the phosphorus and more than 75 % of the nitrogen load (Larsen and Gujer, 1996). Collecting the so-called “yellow water” fraction (i.e. human urine) separately as a concentrated solution free of fecal pathogens greatly facilitates treatment for nutrient recovery.

More recently, a number of pilot projects were launched to assess the acceptance and the performance of No Mix sanitation systems. Urine separation and the related impacts on conventional municipal wastewater treatment systems were described by Larsen and Gujer (1996) and Wilsenach and van Loosdrecht (2003). Udert et al. (2003b,c,d) gave insight into urine-collecting systems and their affinity for blockages, while Maurer et al. (2006) reviewed the existing process engineering options available for treating collected urine (e.g. evaporation, reverse osmosis, nitrification, precipitation, ammonia stripping, electrodialysis, nanofiltration, advanced oxidation). The crystallization of struvite in urine was thoroughly investigated at laboratory scale (Ganrot et al., 2007a; Lind et al., 2000; Ronteltap et al., 2007a, 2010; Tilley et al., 2008a,b; Wilsenach et al., 2007) and to a

lesser extent at pilot scale (Etter et al., 2011). In terms of nutrient recycling, pot and field experiments were performed using stored urine (Kirchmann and Pettersson, 1995; Heinonen-Tanski et al., 2007; Simons, 2008), whereas Ganrot et al. (2007b, 2008) and Simons (2008) tested the plant availability of urine-derived solids in climate chamber and greenhouse trials.

The detailed analysis of several removal and recovery technologies showed that decentralized sanitation systems are extremely flexible and can therefore be adapted to satisfy the needs in industrialized, emerging and developing countries (Lienert and Larsen, 2007). In industrialized countries, increasing public health and environmental concerns call for treatment methods which improve the sustainability of existing wastewater treatment systems by polishing effluents that were – before the identification of emerging contaminants – believed to be clean. Yet, many of these technologies cannot be implemented in developing countries as they are often chemically, energetically and operationally intensive and require high levels of financial input and engineering expertise (Shannon et al., 2008). As for parts of the developing world, people have used human manure for centuries to fertilize crops so that they often have no aversion to handling excrements. Low-tech ecological sanitation options could be especially beneficial in areas close to agricultural zones, where water and electricity provision are scarce, and no sewage networks exist.

As mentioned already, the No Mix technology is at an early stage of exploration with many processes and equipment having only been evaluated at laboratory scale. At the moment, the lack of data and the small amount of practical experience using ecological sanitation facilities impede the implementation and commercialization of the different ecological sanitation components. The research presented in this study aims at filling some of these knowledge gaps by focusing on the implementation of pilot scale technologies in a developing country (Vietnam), and by exploring the practical aspects of nutrient recovery. Given that the fertilizer value of the recovered phosphorus for use in food production is likely to be the most important future driver for recovering and reusing nutrients from wastewater (Cordell et al., 2011) this study also focuses on the agronomic aspects of phosphorus recycling from human urine.

In Chapter I, a Yellow Water Treatment module is presented. It consists of a two-step chemical-physical process in a precipitation reactor followed by a stripping and an absorption column. These processes generate magnesium ammonium phosphate (MAP or struvite, solid form) and ammonium sulfate (liquid form), two products which can be reused as fertilizers. The overall aim of this case study was to evaluate the performance of processes and equipment under environmental conditions as they prevail in the Mekong Delta in South Vietnam. Chapter II describes the attempt of implementing a pilot scale evaporation technology for treating human urine at the University of Can Tho in South Vietnam. The design of this pilot plant is very simple and it was manufactured with materials available from local hardware suppliers to keep operational and investment costs low. Operation did not require any engineering expertise and treatment was achieved by means of solar

radiation. The fitness-for-purpose of this technology was assessed, and the generated products were analyzed for their composition and fertilizer value. Finally, Chapter III looks at a selection of urine-derived struvite fertilizers generated by several precipitation technologies. The urine fertilizers were assessed for their composition and their effectiveness as phosphorus sources for plants. The yields they induced were assessed in a greenhouse pot experiment and compared to those produced by a commercial mineral fertilizer. A computer model was used to weigh the environmental impacts (i.e. nutrient and heavy metal loading rates) of applying urine-derived struvite to agricultural land against those caused by other recycling products derived from wastewater treatment, by commercial mineral and organic fertilizer and by directly applying human urine.

**Nitrogen and phosphorus recovery from human urine by struvite  
precipitation and air stripping in Vietnam**

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## 1. Introduction

Phosphorus is an essential element for all living organisms: phosphate is a component of DNA, RNA, and ATP and has an essential role in cellular metabolism. On a terrestrial basis, phosphorus is the eleventh most abundant element in the earth's crust and largely confined to thick and widespread sedimentary beds, some of which are exploited for fertilizer production and industrial use (Krauskopf and Bird, 1995). Even though phosphorus appears to be rather abundant, the occurrence of exploitable deposits in terms of quality and accessibility is limited to few places. A small number of countries like Morocco and Western Sahara, China, the United States, and South Africa control more than 70% of the global phosphate reserves, which will last about 100 years at current consumption rates ([http://minerals.usgs.gov/minerals/pubs/commodity/phosphate\\_rock](http://minerals.usgs.gov/minerals/pubs/commodity/phosphate_rock)). Yet, consumption is likely to grow with the accelerated population expansion and, as with any finite resource, the level of impurities and the extraction or processing costs will increase as the reserves become depleted. Phosphorus may well turn out to be the geostrategic resource of the future, especially because there is no substitute for it in living organisms and in agriculture (Gilbert, 2009).

Phosphorus enters the food chain after being taken up by plants, and is discharged to wastewater treatment works after excretion from the human body. Conventional centralized wastewater treatment systems, as they have been implemented in developed countries, eliminate such nutrients and can therefore be characterized as “end-of-pipe” solutions. They consume large amounts of freshwater and require an increased expenditure of funds in order to cover the costs of compliance with increasing regulatory requirements and the modification or maintenance of existing assets (Larsen et al., 2001). The alternative concept of “source control” may be an innovative way of promoting the sustainability of wastewater management, especially in developing countries where vast systems of sewer infrastructure have not yet been established. The so-called “No Mix” technology aims at collecting the various wastewater streams separately at source and treating them individually with the objective of recovering valuable nutrients and reusing the clarified water. A “Decentralized Sanitation and Reuse” pilot system, which integrates source separation of individual wastewater flows with ground-breaking technologies for specific treatment of the different wastewater streams, was installed on the premises of the University of Can Tho in South Vietnam.

This paper focuses on the separate collection and treatment of human urine. The so-called “Yellow Water” fraction accounts for only around 1% of all municipal wastewater, but contains most of the nutrients (more than 75% of the total N load and around 45% of the total P load) (Wilsenach and van Loosdrecht, 2003). Urine-collecting systems and their affinity for blockages, caused by the precipitation of inorganic compounds in pipes and storage tanks, were studied thoroughly by Udert et al. (2003b,c,d). Whereas a lot of research has been performed in understanding the precipitation thermodynamics of struvite and the major influencing parameters (e.g., magnesium dosage, mixing

rate, and pH) at laboratory scale (Ganrot et al., 2007a; Lind et al., 2000; Ronteltap et al., 2007, 2010; Tilley et al., 2008a,b; Wilsenach et al., 2007), our work focuses rather on the implementation of urine treatment technologies at pilot scale and explores the practical aspects of nutrient recovery. The Yellow Water Treatment module presented in this study consists of a two-step chemical–physical process in a precipitation reactor followed by a stripping and an absorption column. These processes generate magnesium ammonium phosphate (MAP or struvite, solid form) and ammonium sulfate (liquid form), two products which can be reused as fertilizers. The overall aim of this case study was to evaluate the performance of processes and equipment under environmental conditions as they prevail in the Mekong Delta in South Vietnam.

The specific objectives of this study were to assess:

- the efficiency of phosphorus removal from diluted and undiluted urine by struvite precipitation,
- the efficiency of phosphorus recovery in the form of struvite,
- the quality of the generated struvite,
- the efficiency of nitrogen removal from undiluted urine by air stripping,
- the efficiency of nitrogen recovery by acid absorption.

## **2. Materials and methods**

### ***2.1. Urine, reagents and stock solutions***

A No Mix sanitation system was installed in a dormitory at the University of Can Tho in South Vietnam. The dormitory accommodated 100 male students in ten rooms with bathroom. Each of the ten bathrooms was equipped with one waterless urinal and one No Mix toilet, which operates with only small amounts of flushing water for urine (manufacturer: Gustavsberg, Sweden). The urine was discharged via two separate pipe networks (urinals, toilets) into one common storage tank located behind the dormitory. Diluted urine (mixture of urine from waterless urinals and No Mix toilets which use small amounts of flushing water, dilution factor of around 3) originated from this storage tank at the test site. Undiluted urine was collected from 100 male students living in a neighboring dormitory, who directly urinated into plastic bottles. Undiluted urine was stored in a large plastic tank. In both cases, the urine was completely hydrolyzed and had a pH value of 9.1 and 9.6 for undiluted and diluted urine, respectively. The urine was pumped into the precipitation reactor by using a submersible pump. Sodium hydroxide (NaOH, 50%) and sulfuric acid solutions (H<sub>2</sub>SO<sub>4</sub>, 1:10 vol.) were prepared

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by using NaOH pellets and H<sub>2</sub>SO<sub>4</sub> (96-98%) obtained from MERCK. Magnesium oxide (MgO) was also obtained from MERCK.

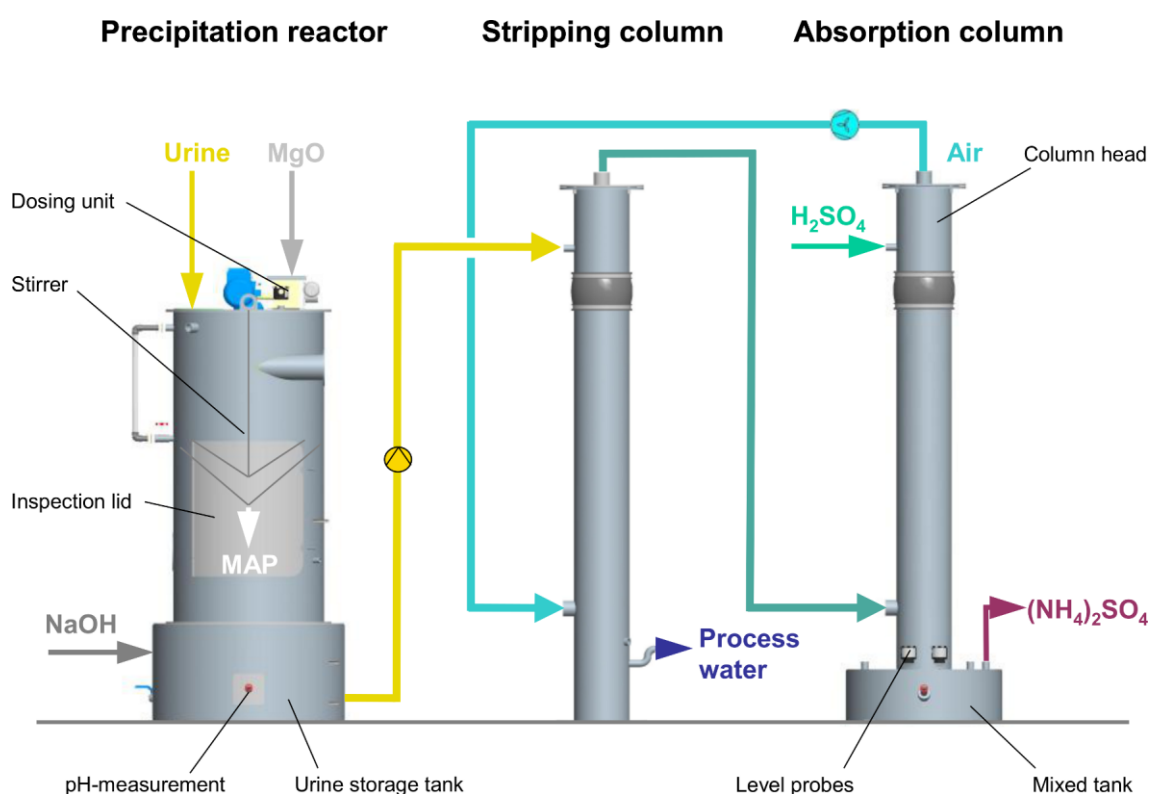
## ***2.2. Struvite precipitation***

In the precipitation reactor, MgO was dosed with a Mg/P molar ratio of 1.5:1 to a volume of 50 L of stored urine in order to initiate struvite precipitation. The mixture was stirred for 30 min, followed by a 3 h sedimentation phase during which the struvite particles were left to settle down. The phosphorus-depleted supernatant was then transferred to a separate holding tank (the so-called conditioning tank) via an overflow valve, whereas the precipitate was collected in a filter bag made of synthetic fabric. The filter bag was dried for 48 h at 105°C and the generated amount of struvite was determined by weighing. Precipitation experiments with a 3 h sedimentation phase were performed with undiluted urine (nine replications). A second series of experiments with sedimentation times of 3, 2, and 1 h (two replications, respectively) was performed with diluted urine. Additionally, the precipitation process was simulated on bench-scale by using a jar tester and Imhoff cones. Three glass beakers were filled with 1 L of diluted urine. MgO was dosed with a Mg/P molar ratio of 1.5:1 to two of the samples. The third sample did not receive any MgO and acted as a control. The samples were stirred for 30 min by means of a jar tester. After 30 min, the samples were transferred into 3 Imhoff cones, and the settleable solids (mL L<sup>-1</sup>) were recorded at various intervals for 3 h. Phosphorus concentrations of the raw urine and of the supernatant in the Imhoff cones were measured before magnesium addition and after 3 h of sedimentation, respectively.

## ***2.3. Ammonia stripping and absorption***

In the conditioning tank, optimum conditions (prevalence of nitrogen in the form of NH<sub>3</sub>) were created for the stripping process: The temperature was raised to 40°C by means of an integrated heating unit, and the pH was increased to 10 by adding sodium hydroxide solution (NaOH, 50%) to the phosphorus-depleted urine. The conditioned urine was then pumped to the top end of the stripping column, through which it was flowing in counter-current with an air stream generated by a compressor. The ammonia passed from the liquid to the gas phase, and the ammonia-enriched air was carried to the base of the absorption column. Inside this second column, the air came in contact with a sulfuric acid solution (1:10 vol.), which absorbed the ammonia from the gas phase in order to produce a liquid fertilizer in the form of ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>). Both the stripping and the absorption columns were filled with plastic media (Raschig rings), thus aiding the transfer of nitrogen from the liquid to the gas phase, and vice versa. The air was circulated in a closed loop through both columns in order to maximize ammonia recovery. The nitrogen- and phosphorus-depleted waste stream occurring at the base of the stripping column was discharged into a septic tank. The stripping and absorption stages were performed with undiluted urine only. The capacity of the stripping feed pump ranged from

10 to 90 L h<sup>-1</sup>. Experiments were performed at both high (80 L h<sup>-1</sup>) and low (10 L h<sup>-1</sup>) flow rates (two replications for each flow rate), whereas the acid flow through the absorption column and the air flow rate were kept constant (55 L h<sup>-1</sup> and 130 m<sup>3</sup> h<sup>-1</sup>, respectively; acid volume of 20 L H<sub>2</sub>SO<sub>4</sub>, 1:10 vol.). One series of measurements (two replications) was performed by circulating the urine (i.e. the so-called waste stream) for 3.5 h through the stripping column at high flow rate (80 L h<sup>-1</sup>). Energy consumption was computed by taking readings from an electricity meter. An illustration of the precipitation reactor, the stripping column and the absorption column is given in Fig. 1.



**Fig. 1.** The Yellow Water Treatment Module: a two-step chemical-physical process consisting of a precipitation reactor followed by stripping and absorption columns.

#### 2.4. Sample collection and analysis

Samples were collected before and after each stage of treatment (i.e., raw urine, urine post-precipitation, conditioned urine or feed to stripping, urine post-stripping or waste stream, sulfuric acid before and after absorption) in order to assess the efficiency of the different processes. The samples were transferred into glass bottles and stored in the fridge at Can Tho University. All samples were analyzed for phosphates with Hach-Lange test cuvettes (LCK350), and for total Kjeldahl nitrogen (TKN) by using the Kjeldahl method. A composite sample of the precipitates generated from undiluted urine was analyzed at the University of Bonn (Germany) for its crystal structure by X-ray diffraction spectroscopy (XRD), and for its elemental composition (trace elements, micro- and

macroelements) by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Data is generally expressed as the observed mean, followed by its standard error ( $\pm$ SE).

### 3. Results

#### 3.1. Struvite precipitation

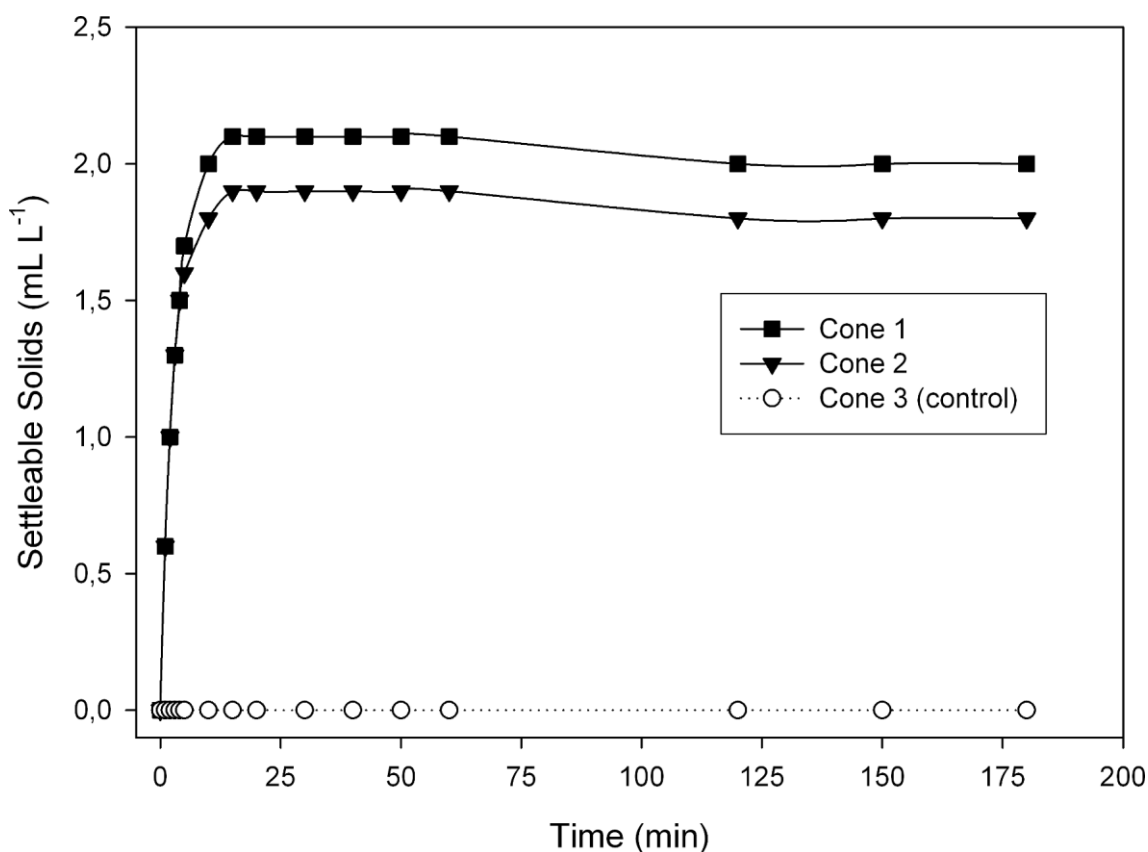
During the stage of precipitation, the concentrations of soluble orthophosphates in undiluted urine decreased on average from  $311 \pm 9$  mg PO<sub>4</sub>-P L<sup>-1</sup> to  $5 \pm 0.4$  mg PO<sub>4</sub>-P L<sup>-1</sup>. This corresponds to a PO<sub>4</sub>-P-removal efficiency of 98%. With an average starting load of  $16 \pm 0.4$  g PO<sub>4</sub>-P contained in 50 L of undiluted urine,  $112 \pm 10$  g of struvite could be generated. For diluted urine, phosphate concentrations decreased from  $111 \pm 1$  mg PO<sub>4</sub>-P L<sup>-1</sup> to  $2 \pm 0.2$  mg PO<sub>4</sub>-P L<sup>-1</sup>; thus again achieving a PO<sub>4</sub>-P-removal efficiency of 98%. From diluted urine, only  $32 \pm 2$  g of struvite could be generated from a starting load of  $6 \pm 0.1$  g PO<sub>4</sub>-P. Decreasing the sedimentation time from 3 to 1 h did not have a significant impact on phosphate removal efficiencies, as shown in Table 1.

**Table 1.** Phosphate removal efficiency (%) from diluted urine by struvite precipitation in the precipitation reactor after 1, 2 and 3 h of sedimentation.

Sedimentation time (h)	1	2	3
PO <sub>4</sub> -P urine input (mg L <sup>-1</sup> )	$109 \pm 1.0$	$112 \pm 0.3$	$112 \pm 4.0$
PO <sub>4</sub> -P urine output (mg L <sup>-1</sup> )	$3 \pm 0.0$	$2 \pm 0.3$	$2 \pm 0.3$
PO <sub>4</sub> -P removal efficiency (%)	$97 \pm 0.0$	$98 \pm 0.2$	$98 \pm 0.2$

These findings were confirmed by bench-scale experiments in which the precipitation reactor was replaced by a jar tester (stirring) and Imhoff cones (sedimentation). PO<sub>4</sub>-P concentrations decreased from 82 to 6 mg L<sup>-1</sup>, which corresponds to 93% of PO<sub>4</sub>-P removal. Virtually all of the particles had settled down after less than 30 min of sedimentation (Fig. 2).

It turned out to be difficult to recover the precipitate from the filter bag: between 10 and 30 g of struvite remained trapped within the fibers of the relatively thick filter material. Such losses were insignificant when performing the experiments with undiluted urine. In this case, about 81% of the generated struvite could be recovered. However, when using diluted urine, less than 10% of the precipitate could be recovered. Electricity consumption during the stage of precipitation was low (<1 kWh).



**Fig. 2.** Settleability of struvite particles in Imhoff Cones after 30 min stirring by jar tester (cones 1 and 2: MgO dosage; cone 3: no MgO dosage, control).

X-ray diffraction spectroscopy analysis revealed that 85% of the crystalline solids (96.8% of the sample was crystalline) were composed of struvite ( $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ). The remaining 15% were identified as dittmarite ( $\text{NH}_4\text{MgPO}_4 \cdot \text{H}_2\text{O}$ ). The results of the elemental analysis are presented in Table 2.

### 3.2. Ammonia stripping and absorption

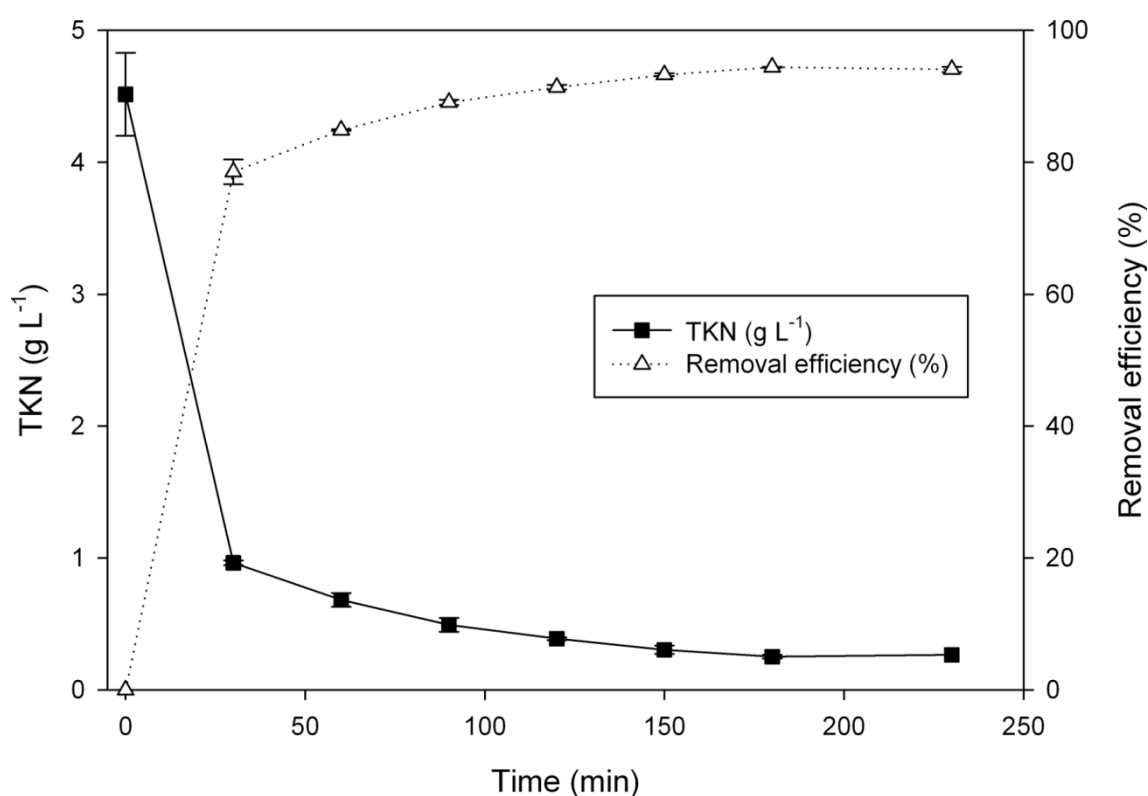
Given the high buffer capacity of urine, 1 L of NaOH (50%) was required per 50 L batch of urine to raise the pH from 9 to 10. The heating unit had to be switched on for about 15 min in order to reach a temperature of 40°C after a period of 30 min (ambient temperature: 30°C).

At the lower flow rate (10 L h<sup>-1</sup>), average nitrogen removal efficiencies of 91% could be achieved during the stripping process. The duration of treatment required for such an efficient nitrogen removal was around 5 h, with an electricity consumption of 9-10 kWh. At high flow rates (80 L h<sup>-1</sup>), the stripping process was completed after 45 min with lower nitrogen removal rates ranging between 60 and 73%. The energy consumption was lower at only 2-3 kWh. When circulating the urine for 3.5 h

through the stripping column at high flow rate, the nitrogen removal efficiency increased to 94% and the energy consumption ranged between 4 and 6 kWh. Figure 3 demonstrates that, during recirculation mode, 80% of the nitrogen was removed after only 30 min of air stripping. After 3 h of stripping, the N-removal efficiency had reached 94%. This corresponds to a decrease of TKN concentrations from  $4515 \pm 315$  to  $266 \pm 0$  mg L<sup>-1</sup>.

**Table 2.** Concentrations of macroelements (mg g<sup>-1</sup>) and micro- and trace-elements (µg g<sup>-1</sup> DM) in struvite precipitated from undiluted human urine (composite sample; As, Cd, Co, Cr, Hg, Li, Mo, Nb, Ni, Pb, Se, Sn V: below detection limit of ICP-OES).

Macroelements	(mg g <sup>-1</sup> DM)	Micro- and trace-elements	(µg g <sup>-1</sup> DM)
Ca	16	Al	410
K	2.71	As	<15
Mg	104	B	13.4
Na	8.98	Ba	9.74
P	126	Cd	<0.2
S	1.35	Co	<0.3
N	53	Cr	<0.2
		Cu	178
		Fe	44.3
		Hg	<4.2
		Li	<1.0
		Mn	4.14
		Mo	<1.0
		Nb	<0.3
		Ni	<0.8
		Pb	<0.9
		Se	<15
		Si	86.8
		Sn	<1.4
		Sr	30.6
		V	<0.1
		Zn	90.2



**Fig. 3.** Nitrogen removal rates ( $\text{g TKN L}^{-1}$ ) and efficiency of ammonia stripping (%) during recirculation mode at high flow rate ( $80 \text{ L h}^{-1}$ ). Error bars represent the standard error ( $n = 2$ ).

Nitrogen recovery during the absorption stage was least efficient at high flow rate (N-recovery of 28 and 46%). However, the recirculation of urine at high flow rate led to a complete recovery of the previously stripped ammonia in the form of ammonium sulfate. A summary of the process parameters and the nutrient removal and recovery efficiencies is presented in Table 3.

**Table 3.** Process design parameters and nutrient removal and recovery efficiencies (%) for the stages of stripping and absorption.

Flow rate urine feed	( $\text{L h}^{-1}$ )	10	80	80, recirculation
Process time	(min)	300	45	230
Energy consumption	(kWh)	9-10	2-3	4-6
N-removal efficiency	(%)	91	60-73	94
Absorption efficiency	(%)	76	28-46	100



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## 4. Discussion

### 4.1. Struvite precipitation

The precipitation of struvite is a highly efficient treatment method for recovering phosphorus from human urine. For both diluted and undiluted urine, PO<sub>4</sub>-P-removal rates of 98% could be achieved in the precipitation reactor. The cost-efficiency of the treatment process was highest when running the plant with undiluted urine. In this case, larger quantities of precipitate were generated with each treatment cycle and the amount of material remaining trapped in the filter fabric was negligible. Jar tests have revealed that the sedimentation time can be reduced from 3 to 1 h since the struvite particles are settling relatively fast.

X-ray diffraction spectroscopy results have shown that 15% of the sample dried at 105°C was composed of dittmarite, which is a dehydration product of struvite. Sarkar (1991) and Bhuiyan et al. (2008) found that crystalline struvite is thermally stable up to a temperature of 55°C. From this temperature, and depending on the rate of heating, it can give off NH<sub>3</sub> and H<sub>2</sub>O molecules. The weight loss is complete when the temperature reaches 250°C. Similarly, dittmarite can rehydrate to struvite at room temperature by absorbing water molecules. Bridger et al. (1962) suggest that, in terms of solubility in ammonium citrate solution, the phosphate availability of struvite is higher than that of dittmarite. In order to prevent the loss of water molecules from the crystal structure, the recovered struvite particles should be air-dried or dried at a temperature lower than 55°C. On the other hand, the monohydrate has a higher phosphorus content than struvite (19.9% vs. 12.6%, respectively) and could therefore be more profitable from the fertilizer transportation point of view. In any case, either product can easily be generated by simply using different temperature settings when drying the urine-derived particles: <55°C for obtaining struvite and >250°C for dittmarite.

The struvite generated by the precipitation process contains all major nutrient elements required for plant growth (N, P, S, K, Ca, and Mg) and the micronutrients boron, copper, iron, manganese, and zinc. Additional beneficial elements detected in the struvite sample were sodium, aluminum, silicon, and potentially strontium. The threshold values for As, Pb, Cd, Cr, Ni, Hg, Tl and Zn assigned by the German Fertilizer Regulations (2008) and the German Sewage Sludge Regulations (1992) are presented in Table 4. The concentrations of all analyzed contaminants are well below these threshold limits, except for mercury (the detection limit of mercury as measured by ICP-OES is 4.2 mg g<sup>-1</sup> – it can therefore not be deduced whether the threshold limit of 1 mg g<sup>-1</sup> has been exceeded or not!). Our findings are in agreement with those of Ronteltap et al. (2007b), who have studied the behavior of heavy metals during struvite precipitation in source-separated urine. They found that only a fraction of the already low amounts of heavy metals in urine are incorporated in struvite particles. They also showed that during struvite precipitation, more than 98% of the hormones and pharmaceuticals remained in solution. It can therefore be concluded that urine-derived struvite is a

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sound fertilizer, by means of which insignificant amounts of hazardous substances are introduced into the environment. Since the micropollutants are not incorporated in the struvite, they will remain in the waste stream together with organic compounds and salts other than N, P, and Mg. Hence, the waste stream of the pilot plant cannot directly be discharged into the environment, but requires further treatment.

The agronomic effectiveness of struvite recovered from wastewater treatment processes has been evaluated in a number of greenhouse or growth-chamber tests (e.g., perennial ryegrass, spring wheat, white lupin plant, and rye seeds) and was found to be similar to, or to outperform the commercial mineral phosphate fertilizers that were used as a reference (Gonzalez-Ponce and de Sa Garcia Lopez, 2007, 2008; Johnston and Richards, 2003; Massey et al., 2009; Plaza et al., 2007; Römer, 2006). When compared to superphosphate, a wastewater-derived struvite was more efficient in increasing yield and supplying P to lettuce, which was probably related to its higher magnesium content and the synergistic effect of Mg on P uptake (Gonzalez-Ponce et al., 2009). Simons (2008) has shown that struvite precipitated from urine produced yield and phosphate uptake values comparable to those induced by superphosphate when tested with ryegrass and red clover.

As shown in Table 2, struvite is a phosphorus-based mineral fertilizer, containing smaller amounts of nitrogen, potassium, magnesium, and calcium. Assuming that  $26.4 \text{ kg P ha}^{-1} \text{ a}^{-1}$  are required to maintain soil fertility on a long-term basis (2007), around 200 kg of struvite need to be applied per ha to satisfy this P-demand. The application of 200 kg of struvite would also cover 7% of N, <1% of K, 2% of Ca, 1% of S, and 10% of Mg demand, and add  $37 \text{ g Cu ha}^{-1}$  and  $19 \text{ g Zn ha}^{-1}$  to the soil. The threshold limits for heavy metal inputs given by the German Federal Soil Protection Act (1999) are  $360 \text{ g Cu ha}^{-1} \text{ a}^{-1}$  for Cu and  $1200 \text{ g Zn ha}^{-1} \text{ a}^{-1}$  for Zn. Thus, struvite application would only contribute 10% of the allowed Cu inputs, and 1.6% of the allowed Zn inputs.

#### ***4.2. Ammonia stripping and absorption***

Gas stripping is a process that is commonly used for wastewater treatment. It is applied for removing volatile organic compounds from wastewater (Kutzer et al., 1995) as well as ammonia from industrial effluent (Gonzalez Benito and Garcia Cubero, 1996; Saracco and Genon, 1994) and from swine manure (Bonmati and Flotats, 2003; Liao et al., 1995). Only few studies have been performed with human urine: Basakcildan-Kabakci et al. (2007) and Behrendt et al. (2002) have recovered ammonia from human urine by stripping and absorption at laboratory scale. At pilot scale in Vietnam, the processes of N-stripping and ammonia recovery were more efficient at the lower urine flow rate than at high flow rates. However, at low flow rate, the duration of urine treatment and the energy consumption were highest. A cost-effective compromise was achieved by circulating the urine through the stripping column at a high flow rate. A similar trend was observed for the absorption process:

chemical absorption was higher at low flow rate. When circulating the urine through the stripping column, the recovery of ammonia by the sulfuric acid was complete.

**Table 4.** Heavy metal concentrations ( $\mu\text{g g}^{-1}$  DM) of urine-derived struvite as compared to the threshold values ( $\mu\text{g g}^{-1}$  DM) given by the German Fertilizer Regulations (DüMV, 2008) and the German Sewage Sludge Regulations (AbfKlärV, 1992).

Element	Struvite ( $\mu\text{g g}^{-1}$ DM)	DüMV ( $\mu\text{g g}^{-1}$ DM)	AbfKlärV ( $\mu\text{g g}^{-1}$ DM)
As	<15	40	-
Pb	<0.9	150	900
Cd	<0.2	50	10
Cr	<0.2	50 mg kg <sup>-1</sup> P <sub>2</sub> O <sub>5</sub>	-
Cr (total)	<0.2	-	900
Cr VI	Not analyzed	2	-
Ni	<0.8	80	200
Hg	<4.2	1	8
Tl	Not analyzed	1	-
Zn	90.2	-	2500

An overall balance summarizing the expenditures and the products that are generated by the Yellow Water Treatment module in order to produce 1 kg of solid or liquid fertilizer (under the conditions as they were encountered in South Vietnam) is presented in Table 5. This worked example is based on the following assumptions:

- use of 50 L of undiluted urine per batch (urine feed for precipitation: average PO<sub>4</sub>-P concentration of 310 mg L<sup>-1</sup>, urine feed for stripping: average TKN concentration of 4.5 g L<sup>-1</sup>),
- Mg/P dosage, molar ratio of 1.5:1,
- duration of stirring: 30 min, followed by 3 h of sedimentation,
- phosphate removal efficiency of the precipitation process: 98%,
- addition of 1 L NaOH (50%) per batch in order to increase the pH to 10,
- operation of the heating unit for 15 min per batch in order to reach a temperature of 40°C,
- recirculation of the urine for 3.5 h through the stripping column at a flow rate of 80 L h<sup>-1</sup>,
- absorption process operated with a volume of 20 L of sulfuric acid (10 vol%),
- stripping efficiency: 94%, absorption efficiency: 100%.

**Table 5.** Expenditures and products (P as struvite, N as ammonium sulfate) generated by the Yellow Water Treatment module under the conditions encountered in the Mekong Delta, Vietnam.

Expenditure	P (1 kg, as struvite)	N (1 kg, as ammonium sulfate)
MgO (kg)	2.33	None
NaOH pellets (kg)	None	2.35
H <sub>2</sub> SO <sub>4</sub> (96-98%) (L)	None	9.40
Number of treatment cycles	70.76	4.70
Duration of treatment (h)	247.62	16.45
Energy (kWh)	≤70.76	18.8-28.2

Treatment costs could be reduced by making use of the solar energy that is available during daytime in South Vietnam. The piping could be directly exposed to the sun in order to increase the temperature of the urine, which has a positive impact on the stripping process. Alternatively, photovoltaic cells could be used to generate the power that is required for heating and pumping.

## 5. Concluding remarks

In this paper, the efficiencies of phosphorus and nitrogen removal and recovery by struvite precipitation and air stripping were investigated. The results suggest that struvite precipitation is a highly efficient method for removing phosphorus from diluted and undiluted urine. In both cases, PO<sub>4</sub>-P-removal efficiencies of 98% could be achieved. Phosphorus recovery was most efficient with undiluted urine because larger amounts of particles were generated with each treatment cycle, and the amount of material remaining trapped in the filter material was negligible. The generated precipitates were to 85% composed of struvite. The remaining 15% were identified as dittmarite, which is a dehydration product of struvite. Some of the struvite crystals had probably lost water molecules when they were dried at 105°C. This can be avoided by drying urine-derived struvite at temperatures <55°C. All measured heavy metal concentrations were below the threshold values given by the German Fertilizer Regulations and the German Sewage Sludge Regulations. Nitrogen removal rates were higher when pumping the urine at a low flow rate through the stripping column, leading to high energy consumption and long duration of treatment. A cost-efficient alternative was to circulate the urine through the stripping column at a high flow rate. Chemical absorption of nitrogen was higher when pumping the urine at a low flow rate through the stripping column. When urine was circulated through the stripping column, ammonia absorption was complete.

## **Acknowledgments**

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**Solar thermal evaporation of human urine for nitrogen and  
phosphorus recovery in Vietnam**

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## 1. Introduction

The separate collection, storage and treatment of human urine were addressed by numerous studies conducted since the mid 1990s, with particular interest in nutrient removal and recovery technologies. Urine separation and the related impacts on conventional municipal wastewater treatment systems were described by Larsen and Gujer (1996) and Wilsenach and van Loosdrecht (2003). Udert et al. (2003a,b,c) gave insight into urine-collecting systems and their affinity for blockages, while Maurer et al. (2006) reviewed the existing process engineering options available for treating collected urine (e.g. evaporation, reverse osmosis, nitrification, precipitation, ammonia stripping, electrodialysis, nanofiltration, advanced oxidation). The crystallization of struvite in urine was thoroughly investigated at laboratory scale (Ganrot et al., 2007a; Lind et al., 2000; Ronteltap et al., 2007, 2010; Tilley et al., 2008a,b; Wilsenach et al., 2007). In terms of nutrient recycling, pot and field experiments were performed using stored urine (Heinonen-Tanski et al., 2007; Kirchmann and Pettersson, 1995; Simons, 2008), whereas Ganrot et al. (2007b, 2008) and Simons (2008) tested the plant availability of urine-derived solids in climate chamber and greenhouse trials.

Yet, the treatment methods described above are chemically, energetically and operationally intensive and were first of all developed for improving the sustainability of existing wastewater treatment systems in industrialized regions by polishing effluents that were – before the identification of emerging contaminants – believed to be clean (Shannon et al., 2008). Implementing these complex technologies in developing countries, which are probably most affected by increasing demand and costs of commercially available fertilizers, and besides most likely to accept urine-derived fertilizer products owing to a traditional usage (Phuc et al., 2006), is therefore virtually impossible. However, urine treatment prior to application is recommended (Pronk and Koné, 2009): the nutrient concentration of human urine is rather low as opposed to the large storage capacities that are required for collection and transport. The high pH may lead to ammonia emissions and odor problems during storage, transport and spreading unless expensive distribution systems are used (Udert et al., 2006), and the impact of pharmaceutical and hormone input into agricultural land is not fully understood yet (Lucas and Jones, 2009; Winker et al., 2010).

Of the technical options evaluated by Maurer et al. (2006), evaporation is deemed to be most suitable for areas close to agricultural zones with insufficient or unreliable electricity provision (Pronk and Koné, 2009). Operational and investment costs can be kept low by constructing simple reactors with materials available from local hardware suppliers. These can then be operated by local workforce, who need not be highly educated or have much expertise. Solar radiation, an abundant resource in most regions of the developing world, can be used as energy source. A waste stream, which would need further treatment or even transfer to full-scale wastewater treatment, is not required when using drying techniques.

This paper presents the attempt of implementing a pilot scale evaporation technology for treating human urine at the University of Can Tho in South Vietnam. The overall aim of this study was to evaluate the robustness of the technology with special focus on nutrient recovery from human urine.

The specific objectives of this study were to:

- assess the performance of the solar still (photoreactor) under environmental conditions as they prevail in the Mekong Delta in South Vietnam by monitoring a selection of relevant process parameters during operation (temperatures, volumes, pH, electric conductivity, nitrogen and phosphorus concentrations),
- assess the impact of pH on nitrogen losses and nutrient concentrations by acidifying urine prior to treatment,
- characterize the urine-derived fertilizer products,
- estimate the agronomic effectiveness of the urine-derived fertilizer products in a greenhouse pot experiment.

## **2. Materials and methods**

### ***2.1. Nutrient sources***

Urine was collected from a No Mix sanitation system installed in a dormitory at the University of Can Tho in South Vietnam, which has previously been described by Antonini et al. (2011, c.f. Chapter I). The dormitory accommodated 100 male students in 10 rooms with bathroom. Each of the 10 bathrooms was equipped with one No Mix toilet and one waterless urinal (manufacturer: Gustavsberg, Sweden). The urine was discharged via two separate pipe networks (urinals, toilets) into one common storage tank located behind the dormitory. Diluted urine (mixture from waterless urinals and No Mix toilets, diluted with small amounts of flushing water from toilets) originated from this storage tank at the test site. Undiluted urine was collected from 100 male students living in a neighboring dormitory, who directly urinated into plastic bottles. Undiluted urine was stored in a large plastic tank. Both diluted and undiluted urine were completely hydrolyzed.

### ***2.2. Nutrient recovery by solar still***

50 L of undiluted urine was fed into a solar still – a pilot system constructed entirely of resources that were available at local hardware dealers. The photoreactor, which had a surface area of 2 m<sup>2</sup>, was made of concrete covered with black tiles (base) and mirrors (sidewalls), and was protected



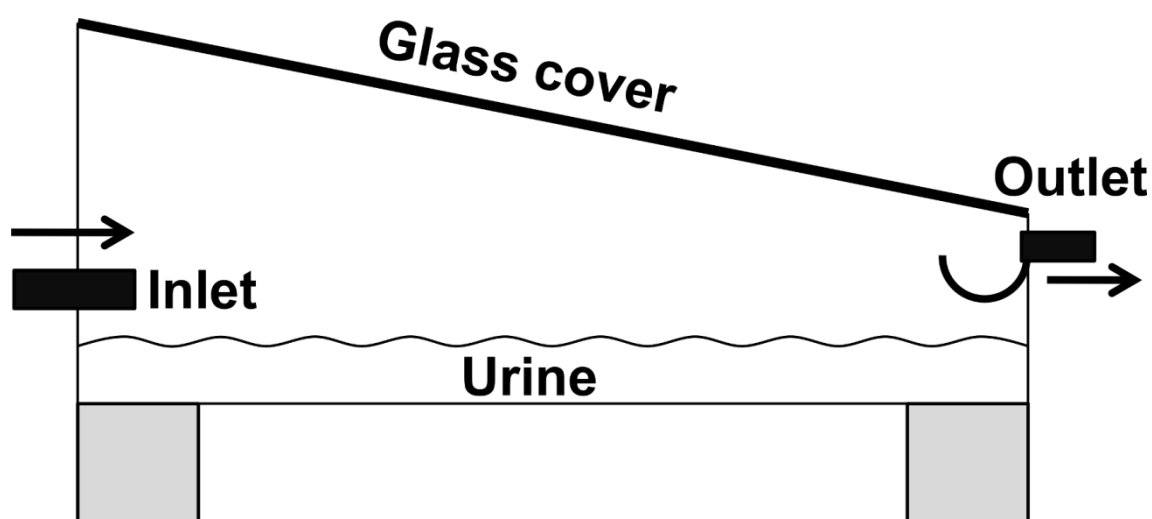
by a glass cover sloping at approximately  $11^\circ$  (see Fig. 1). The temperature of the urine increased by means of convection and the greenhouse effect, both caused by transmission of the solar radiation. The glass cover was cooled by the wind, thus causing the vapor inside the still to condense and to form small droplets at the underside of the cover. Under the influence of gravity, these droplets ran down the underside of the glass cover into a drainage pipe, and were evacuated from the unit by gravity flow. The solar still was set up in an open space in order to allow for maximum exposure to direct sunlight. Tinytag Plus 2 data loggers (Gemini Data Loggers Ltd., Chichester, United Kingdom) were used for measuring temperatures at ten minute intervals inside the solar still, and ambient temperatures in the shade near the solar still. After a treatment period of 26 days, the liquid fraction had evaporated completely and the generated solids (referred to as SOL) were recovered and weighed. During the first 2 weeks of treatment (from day 1 until day 16), urine samples were taken on a regular basis by means of a syringe and a plastic pipe that was introduced into the solar still via the drainage pipe. After day 16, the urine level was too low for sample collection. Urine samples were analyzed for total phosphate, total nitrogen, pH and electric conductivity. The condensate was collected by connecting the drainage pipe to a plastic jerry can, which was emptied on a regular basis. The volume of generated condensate was determined by using a measuring cylinder. Total nitrogen and pH of the condensate were also measured. Immediately after collection, all samples were transferred into a cool box and taken to the University of Can Tho for analysis. The samples were analyzed for total phosphate by using Hach-Lange LCK350 cuvette tests, for total nitrogen using the Kjeldahl method and for pH and electric conductivity using the WTW MultiLine P4 SET universal meter.

A second experiment was performed using acidified urine with the aim of assessing the impact of pH on nitrogen losses, and the nutrient content of the final products respectively. The pH of two batches of diluted urine (mixture from waterless urinals and NoMix toilets) was lowered by adding either sulfuric acid ( $\text{H}_2\text{SO}_4$ , 96%, approximate rate of addition: 27.76 mL  $\text{H}_2\text{SO}_4$  per liter of diluted urine) or phosphoric acid ( $\text{H}_3\text{PO}_4$ , 89%, approximate rate of addition: 31.46 mL  $\text{H}_3\text{PO}_4$  per liter of diluted urine) until pH values of 4 were reached. In both cases, 20 L of this acidified urine was fed into the solar still. After 20 days of treatment, the liquid fraction had evaporated completely and the generated solids (referred to as SOL-S and SOL-P) were recovered. For this experiment, no urine or condensate samples were collected during treatment – only the final products were analyzed for their nutrient content.

### ***2.3. Fertilizer characterization***

The three urine-derived fertilizer products (i.e. SOL, SOL-S, SOL-P), which were recovered from the solar still in Vietnam, were analyzed for their composition at the University of Bonn in Germany. The total phosphorus concentration of the fertilizer samples was determined photometrically using the molybdenum blue method and an Eppendorf ECOM 6122 photometer after pressure

digestion in nitric acid. Total nitrogen and sulfur were measured by EURO elemental analyzer (EURO EA 3000 series). The crystal structure of SOL and SOL-P was measured by X-ray diffraction spectroscopy (SOL-S could not be examined as there was not enough material available for analysis). Phosphorus of SOL and of the reference fertilizer REF-P was extracted by mixing 10 g of sample with 500 mL of distilled water, and 5 g of sample with 500 mL of citric acid (2%) (VDLUFA, 1995). The mixtures were placed on a rotary shaker at 40 rpm for 30 min. The samples were then filtered, and the phosphorus concentration of the filtrate was measured with an Eppendorf ECOM 6122 photometer (molybdenum blue method) for water-soluble P and, for the citric acid extracts, MERCK Spectroquant phosphate tests (vanadomolybdophosphoric acid method) and a WTW PhotoLab S12 photometer were used.



**Fig. 1.** Cross-section of the solar still used for nutrient recovery from human urine by solar thermal evaporation: Urine is fed into the basin via an inlet valve. The solar radiation that is transmitted through the transparent glass cover creates a greenhouse effect, which in turn causes the urine to heat to a temperature higher than that of the cover. The water vapor in contact with the glass cover condenses and runs down into a drainage pipe to form the condensate that is evacuated from the photoreactor via an outlet pipe.

#### **2.4. Greenhouse experiment**

All three materials were assessed for their agronomic effectiveness in a greenhouse trial performed at the University of Bonn (Germany). A short description of the three fertilizers, which were tested in the greenhouse pot experiment, is given in Table 1.

**Table 1.** Description of the urine-derived fertilizer products evaluated in the greenhouse pot experiment in Germany.

Material	Source of material	P (%)	N (%)	S (%)
SOL	Solids recovered from the solar evaporation of 50 L undiluted urine	1.87	1.84	3.24
SOL-P	Solids recovered from the solar evaporation of 20 L diluted urine mixed with phosphoric acid	17.55	8.33	1.04
SOL-S	Solids recovered from the solar evaporation of 20 L diluted urine mixed with sulfuric acid	5.25	5.46	4.67
REF-P	Mineral phosphorus fertilizer purchased from Landgard eG (Remagen)	8.22	0.16	12.51

The greenhouse evaluation was carried out using a local P-deficient soil (“Meckenheim” subsoil, 2.11 mg P<sub>2</sub>O<sub>5</sub> available per 100 g of soil), and ryegrass (*Lolium multiflorum italicum*) or maize (*Zea mays* L.) as test crops. All test materials were thoroughly mixed with 6 kg of air-dried, 2-mm-sieved soil and 3 kg of sand in Kick-Brauckmann pots at rates equivalent to 24 mg P per kg soil, based on the total P content of the materials received. Before sowing the seeds, basal nutrients (micronutrient mixture) were mixed with the soil, according to the concentrations presented in Table 2. Nitrogen was added in the form of ammonium nitrate, such as to achieve a uniform nitrogen content of 1530 mg per pot by taking into account the amounts of N already added with the test substrates. A common mineral phosphorus fertilizer (REF-P) was purchased from Landgard eG (Remagen, Germany) and used as a reference. A control treatment which received no phosphorus was incorporated (BLANK). The total number of treatments was 10, and these were replicated 4 times in a randomized block design, leading to a total number of 40 pots. This experimental set-up was conceived to isolate phosphorus as the only growth-limiting nutrient. Ryegrass was seeded at a rate of 1.8 g per pot, and 4 maize seeds were placed in every pot. The pots were irrigated on a daily basis with distilled water such as to maintain a level of 70% of soil water holding capacity. The ryegrass was harvested at 27, 40, 58 and 82 days after sowing. The maize was harvested at 82 days after sowing. Micronutrients and nitrogen were reapplied to both crops after every grass harvest (i.e. after 27, 40, 58 and 82 days) in order to prevent nutrient deficiencies other than those induced by phosphorus. The samples were dried at 65°C and weighed before and after drying. The dry biomass was ground by using a disk mill for ryegrass and a rotary mill for maize, and further processed by dry-ashing in a muffle furnace and digestion in hydrochloric acid. The phosphorus concentration of the biomass was measured photometrically using the molybdenum blue method and an Eppendorf ECOM 6122 photometer. The nitrogen concentration of the biomass was analyzed by using the elemental analyzer (EURO EA 3000 series).

**Table 2.** Amounts of macro- and micronutrients (mg nutrient pot<sup>-1</sup>) applied to each treatment in the greenhouse pot experiment. Micronutrients and nitrogen (as NH<sub>4</sub>NO<sub>3</sub>) were reapplied to both crops after every grass harvest (i.e. after 27, 40, 58 and 82 days) in order to prevent nutrient deficiencies other than those induced by phosphorus.

Nutrient	mg nutrient pot <sup>-1</sup>	Form of supply
P	220	Test material
N	1530	Test material, NH <sub>4</sub> NO <sub>3</sub>
K	1800	K <sub>2</sub> SO <sub>4</sub> <sup>a</sup>
Mg	400	MgSO <sub>4</sub> 7H <sub>2</sub> O <sup>a</sup>
Fe	100	FeSO <sub>4</sub> 7H <sub>2</sub> O <sup>a</sup>
Cu	20	CuSO <sub>4</sub> 5H <sub>2</sub> O <sup>a</sup>
Mn	20	MnSO <sub>4</sub> H <sub>2</sub> O <sup>a</sup>
Zn	20	ZnSO <sub>4</sub> 7H <sub>2</sub> O <sup>a</sup>
B	5	H <sub>3</sub> BO <sub>3</sub>
Co	5	Co(NO <sub>3</sub> ) <sub>2</sub> 6H <sub>2</sub> O
Mo	5	(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> 4H <sub>2</sub> O

<sup>a</sup> The total amount of sulfur added by the use of these chemical compounds was 2093 mg S pot<sup>-1</sup>.

## 2.5. Data analysis

Phosphorus and nitrogen uptake into shoots were calculated on a pot basis by multiplying the dry matter yield by the respective phosphorus and nitrogen content of the biomass. Cumulative shoot dry matter yield and nutrient uptake were calculated by combining the data of the 4 harvests. Data is generally expressed as the observed mean, followed by its standard error ( $\pm$ SE). Statistical analysis (one-way ANOVA, followed by Scheffé post-hoc test at  $\alpha=0.05$ ) was performed by using SPSS Statistics 17.0 for Windows. The Scheffé method was selected because it is very conservative and controls the familywise error rate for all possible contrasts. Different lowercase letters (Figs. 4 and 5) indicate statistically significant differences according to the Scheffé test at the 0.05 level.

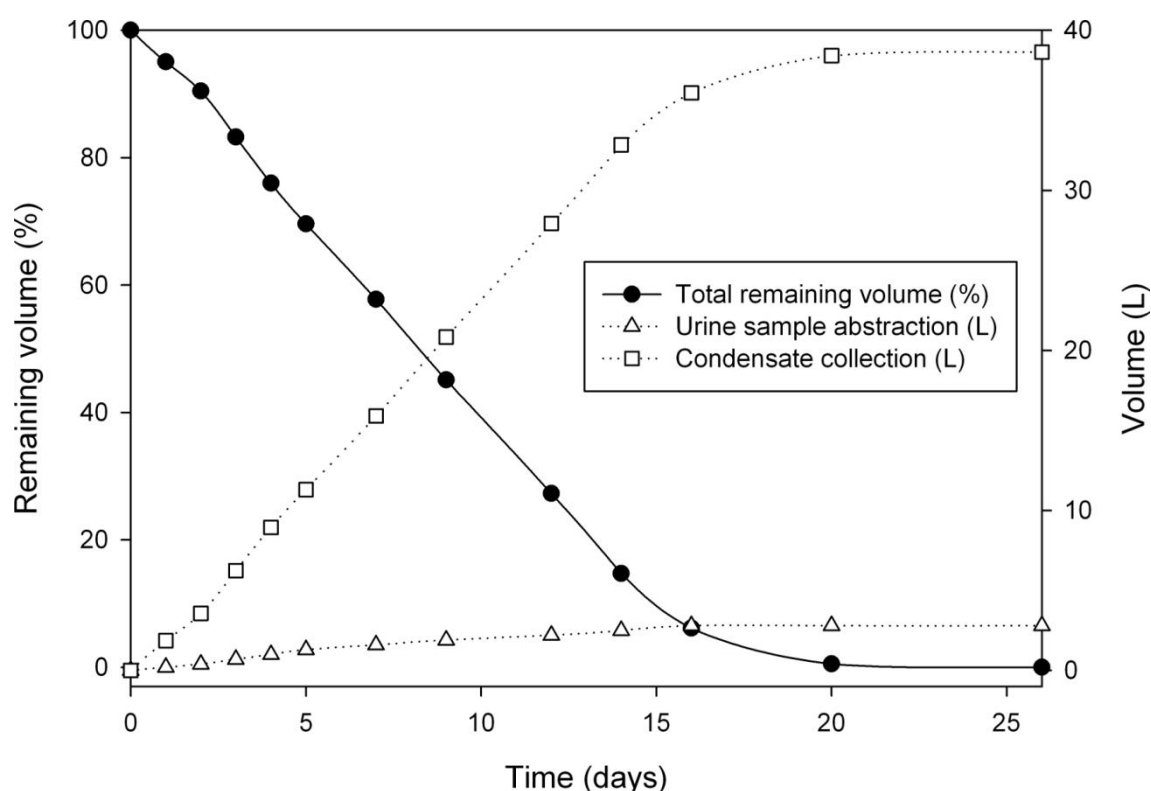
## 3. Results

### 3.1. Nutrient recovery by solar still

Temperatures inside the solar still reached peaks of around 60°C at midday. Throughout the treatment period, temperature maxima inside the photoreactor ranged from 45°C to 62°C. At nighttime, the temperatures went down to around 25°C, thus being similar to the ambient temperatures

measured outside the reactor. On average, the maximum temperatures recorded inside the solar still at noon were 20°C higher than the maximum ambient temperatures, which ranged from 30°C to 40°C.

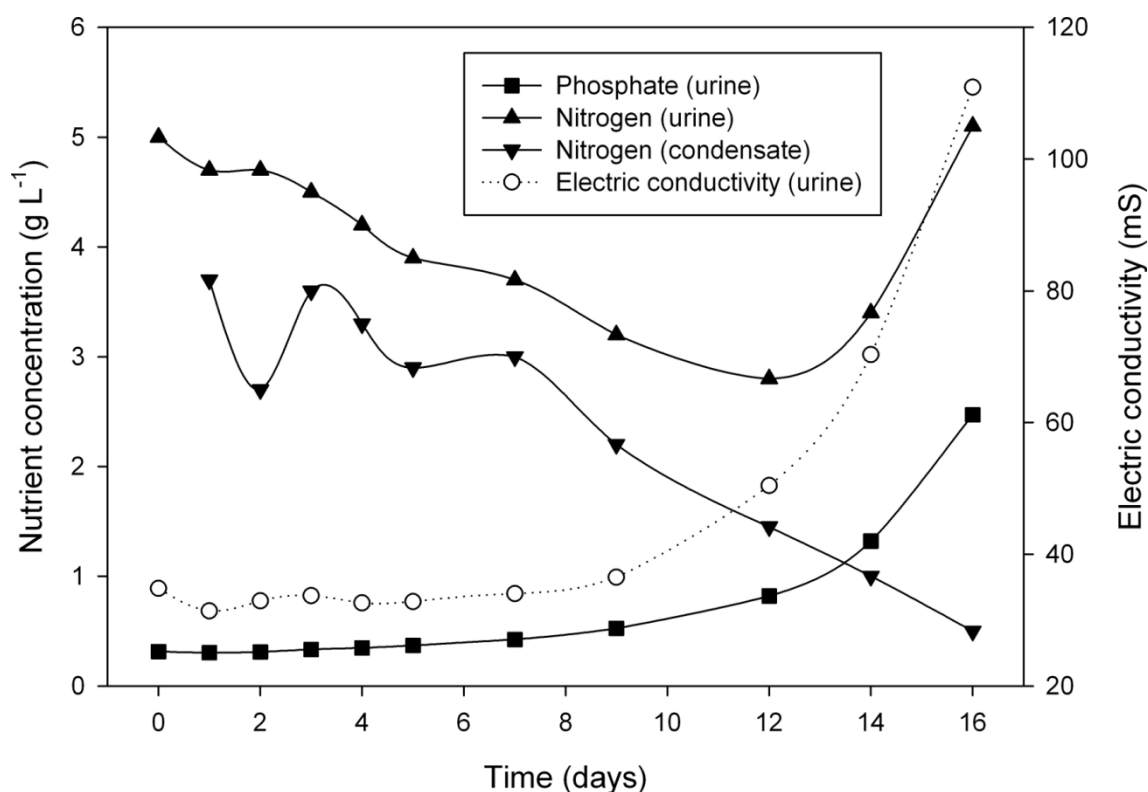
During treatment, a total volume of 2.80 L of urine samples were removed from the solar still for analytical purposes. The total volume of condensate collected in the jerry can added up to 38.64 L, which means that a loss of 8.56 L (17%) of the liquid fraction needs to be accounted for. The rates of urine removal and condensate generation, as well as the total “hypothetical” volume (i.e. corrected for losses) of urine remaining in the solar still at any point of treatment, are presented in Fig. 2.



**Fig. 2.** Volume reduction of 50 L undiluted human urine by solar thermal evaporation. Total volume (% , corrected for gaseous losses) remaining in the solar still at any point of treatment, in function of urine sample abstraction (L, cumulative) and condensate collection (L, cumulative) in the jerry can.

The concentration of total phosphate increased gradually throughout the 26 days of treatment. As shown in Fig. 3, the urine that was fed into the unit initially had a phosphate concentration of 0.3 g L<sup>-1</sup>, whereas the last urine sample taken on day 16 had a concentration of 2.5 g L<sup>-1</sup>. The urine nitrogen concentration by contrast first decreased from 5.0 g L<sup>-1</sup> to 2.8 g L<sup>-1</sup> (day 12), then rose again up to 5.1 g L<sup>-1</sup> on day 16. The nitrogen concentrations, which were recorded for the condensate samples decreased from 3.7 g L<sup>-1</sup> down to 0.5 g L<sup>-1</sup> on day 16. The electric conductivity showed a pattern which was very similar to that of the total phosphate concentration: the conductivity gradually increased from 31.40 mS on day 1, and reached 110.90 mS on day 16. It was therewith directly

correlated to the phosphate concentration (correlation coefficient of 0.995). The pH measurements didn't show a particular trend. The pH of the urine samples varied from 9.3 to 9.7. The pH of the condensate was slightly higher with values lying between 9.6 and 10.0. After complete evaporation of the liquid fraction, about 360 g of solid material (SOL) could be recovered from the solar still.



**Fig. 3.** Electric conductivity (mS) and nutrient concentrations (g L<sup>-1</sup>) measured in urine and condensate (nitrogen only) during the first two weeks of solar thermal evaporation by solar still (no data for days 16 to 26 because the urine level in the reactor was too low for sample collection).

### 3.2. Fertilizer characterization

The results presented above showed that from the 250 g of nitrogen, which were fed into the solar still at the beginning of the trial, almost 32% were lost with the condensate in the form of dissolved ammonia/ammonium. The recovered solids (SOL, see Table 1) had a rather low nitrogen concentration of 1.84%, when compared to those that had been mixed with sulfuric or phosphoric acid prior treatment. SOL-P (derived from urine acidified with phosphoric acid) had a nitrogen-content of 8.33% and for SOL-S, which was derived from urine mixed with sulfuric acid, a nitrogen concentration of 5.46% was recorded. The addition of acid not only led to an increase of nitrogen in SOL-P and SOL-S – their phosphorus concentrations were also much higher. SOL-P and SOL-S had

phosphorus concentrations of 17.55% and 5.25% respectively (as opposed to 1.87% for SOL), and SOL-S also had a higher sulfur concentration of 4.67% (as opposed to 3.24% for SOL).

Analysis by X-ray diffraction spectroscopy showed that almost 90% of the SOL sample was composed of ordinary sodium chloride (see Table 3). SOL-P on the other hand was, through the addition of phosphoric acid, to 87% composed of ammonium dihydrogen phosphate (biphosammite). The remaining 13% were identified as sodium chloride. There is no data available for SOL-S as there was not enough material available for analysis.

Solubility tests revealed that the phosphorus content of SOL was soluble to 95% in citric acid and to 84% soluble in water. REF-P was characterized by a P-solubility of 74% (of total P) in water and 90% (of total P) in citric acid. There is no data available for SOL-S and SOL-P as there was not enough material available for analysis.

**Table 3.** Crystal structure of two urine-derived fertilizer products (SOL, SOL-P) identified by X-ray diffraction spectroscopy, in percent (no data available for SOL-S).

Mineral	Chemical formula	SOL <sup>a</sup>	SOL-P <sup>b</sup>
Sodium chloride	NaCl	90%	13%
Aphthitalite	NaK <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub>	6%	0%
Niter	KNO <sub>3</sub>	4%	0%
Biphosammite	NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	0%	87%
Crystalline portion of the sample		96%	98%

<sup>a</sup> SOL was derived from 50 L undiluted urine, of which 2.8 L were abstracted for sample analysis.

<sup>b</sup> SOL-P was derived from 20 L diluted urine mixed with phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, 89%, approximate rate of addition: 31.46 mL H<sub>3</sub>PO<sub>4</sub> per liter of diluted urine). No sample abstraction.

### 3.3. Greenhouse experiment

#### 3.3.1. Yield and nutrient uptake by ryegrass

The dry matter yield of ryegrass was significantly higher for all test substrates than for the blank control treatment, which had received no phosphorus fertilization at all (see Fig. 4a). SOL-S and SOL-P induced the best results (total dry matter yields of 39.70±2.09 g pot<sup>-1</sup> and 34.65±2.29 g pot<sup>-1</sup> respectively), with SOL-S significantly exceeding the yield of REF-P (dry matter yield of 28.54±1.31 g pot<sup>-1</sup>). SOL was the only test material that caused a dry matter yield slightly lower than that of REF-P (26.65±1.00 g pot<sup>-1</sup>). A similar trend was observed for phosphorus and nitrogen uptake by ryegrass. As shown in Fig. 4b and c, plants treated with SOL-S and SOL-P were, after a growth period of 82 days, capable of taking up more nitrogen and phosphorus from the soil than those treated with SOL or

with the reference fertilizer REF-P. Phosphorus uptake for SOL-P and SOL-S was  $126.31 \pm 18.28$  mg P pot<sup>-1</sup> and  $157.06 \pm 15.13$  mg P pot<sup>-1</sup> respectively, as compared to the  $63.50 \pm 0.38$  mg P pot<sup>-1</sup> of SOL. In the case of nitrogen, the uptake for SOL-P and SOL-S reached  $1.81 \pm 0.14$  g N pot<sup>-1</sup> and  $1.90 \pm 0.07$  g N pot<sup>-1</sup> respectively. For SOL, a nitrogen uptake of  $1.34 \pm 0.05$  g N pot<sup>-1</sup> was recorded. For both nitrogen and phosphorus, the nutrient uptake of SOL differed insignificantly from that of the reference fertilizer REF-P.

### 3.3.2. Yield and nutrient uptake by maize

The dry matter yield of maize as affected by the test materials is shown in Fig. 5a. After 82 days of growth, maize plants treated with SOL-S and SOL-P yielded the highest amounts of dry matter ( $92.57 \pm 3.03$  g pot<sup>-1</sup> and  $79.82 \pm 13.46$  g pot<sup>-1</sup> respectively). SOL and REF-P induced much lower dry matter yields ( $30.89 \pm 2.47$  g pot<sup>-1</sup> and  $35.52 \pm 1.98$  g pot<sup>-1</sup>), which did not differ significantly from the blank control treatment ( $16.10 \pm 3.13$  g pot<sup>-1</sup>). As for phosphorus uptake, again the highest values were noted for SOL-S and SOL-P ( $120.25 \pm 4.82$  mg P pot<sup>-1</sup> and  $105.78 \pm 19.82$  mg P pot<sup>-1</sup>). Fig. 5b demonstrates that the fertilizers REF-P and SOL, with phosphorus uptake values of  $44.36 \pm 2.18$  mg P pot<sup>-1</sup> and  $42.28 \pm 5.00$  mg P pot<sup>-1</sup>, were not significantly different from the blank control treatment ( $19.85 \pm 3.19$  mg P pot<sup>-1</sup>). Fig. 5c reveals an identical trend for nitrogen uptake: SOL-S and SOL-P performed best with  $1.28 \pm 0.07$  g N pot<sup>-1</sup> and  $1.19 \pm 0.19$  g N pot<sup>-1</sup>. Again, SOL ( $0.55 \pm 0.05$  g N pot<sup>-1</sup>) and REF-P ( $0.58 \pm 0.03$  g N pot<sup>-1</sup>) differed not significantly from the blank control variable ( $0.34 \pm 0.06$  g N pot<sup>-1</sup>).

## 4. Discussion

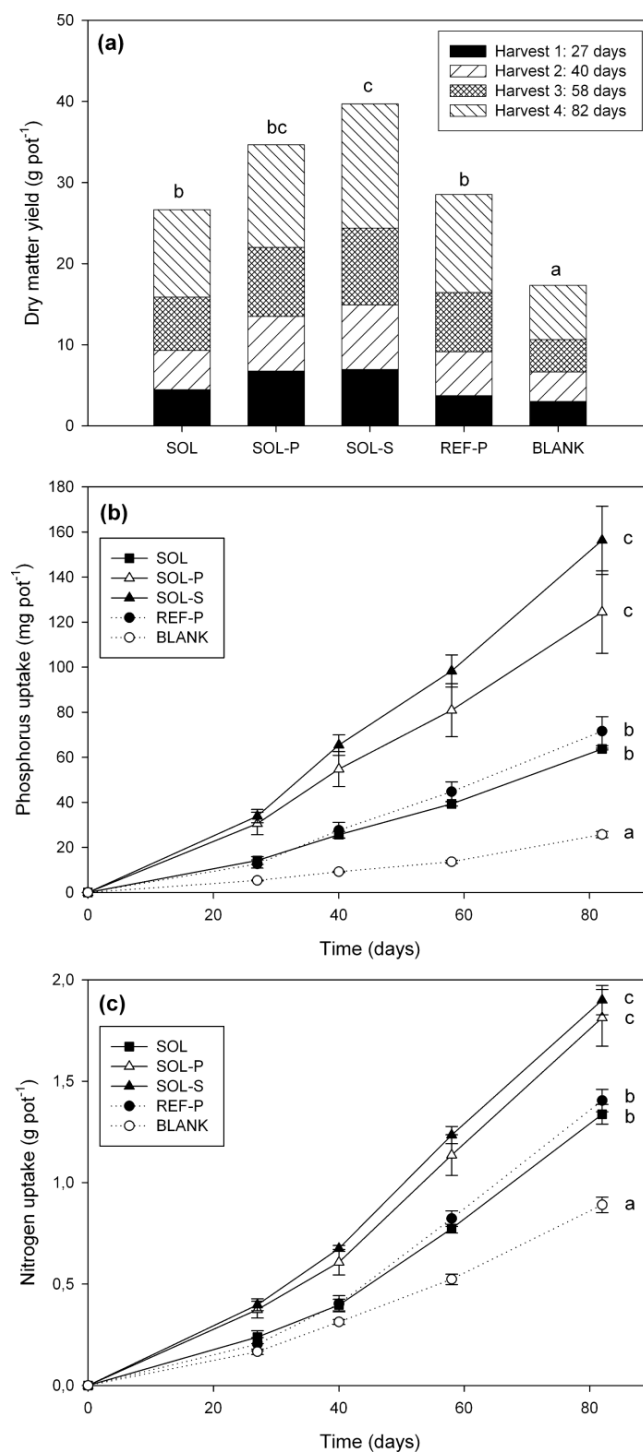
### 4.1. Nutrient recovery by solar still

Data has shown that the solar thermal distillation of human urine by means of solar still was very practicable with few resources and little expertise. With a surface area of 2 m<sup>2</sup>, it took only 26 days of treatment in order to reach the complete evaporation of the liquid fraction from 50 L of undiluted urine. This corresponds to a rate of almost 1 L m<sup>-2</sup> day<sup>-1</sup>. 8.56 L of the urine could not be recovered in the form of condensate. This loss of 17% of the liquid fraction was probably due to poor insulation of the pilot system, and could easily be improved for future experiments. Treatment was achieved by mere exposure to sunlight, and therefore no complex technologies, no qualified workforce and no cost-intensive energy sources were required to operate the system.

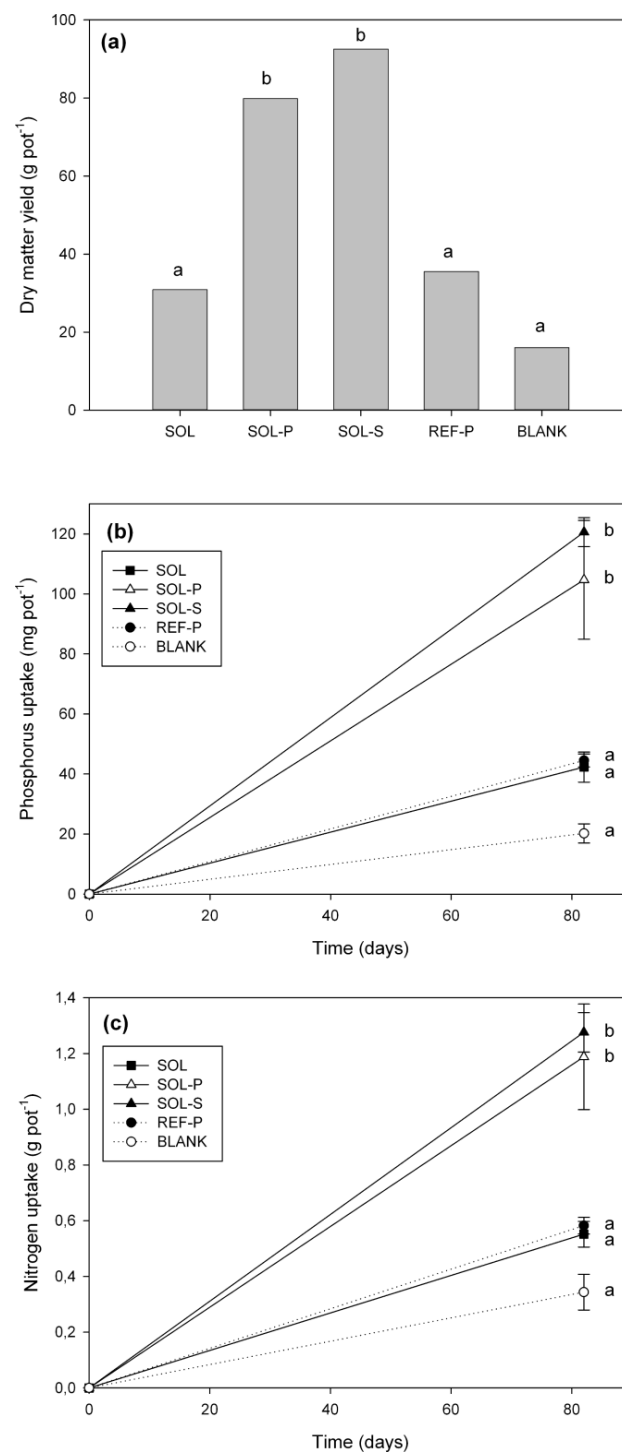
It was possible to concentrate nutrients – this was suggested by an increase of the electric conductivity in the urine samples, and confirmed by an increase of total phosphate concentrations by a factor of 8 within the first 2 weeks of treatment. When considering the final fertilizer product (SOL),



nitrogen concentrations had increased from 0.50% in the collected urine to 1.84% in the recovered solids, and phosphate concentrations rose from 0.03% in the collected urine to 1.87% in the recovered solids, thus representing increases by a factor of 3.68 and 62.33 respectively. Unlike for phosphorus, the nitrogen concentrations were not directly correlated to the electric conductivity as up to 32% of the nitrogen had escaped the solar still with the condensate. Indeed, treatment at high pH and high temperatures promote the prevalence of nitrogen in the form of volatile ammonia, making this a considerable drawback of the evaporation method. It was shown that, by acidification of the urine with phosphoric or sulfuric acid, the nitrogen content of the final products SOL-P (acidified with phosphoric acid) and SOL-S (acidified with sulfuric acid) was much higher (almost three times for SOL-S and 4.5 times for SOL-P) than that of SOL. The disadvantage of urine acidification, however, is the high buffering capacity of urine. It strongly increases during urine storage due to urea hydrolysis and makes acid addition for preventing ammonia volatilization not viable (Udert et al., 2006). Hellstrom et al. (1999) have demonstrated that adding acid directly to the collection tank in order to prevent the decomposition of urea during storage was much more economical. They found that only 60 meq of sulfuric acid was needed per liter of undiluted urine to keep the pH below 4 for more than 250 days, as opposed to 600-650 meq of acid that were required per liter of undiluted urine to reach the same pH after complete hydrolysis of urea. However, in full scale systems with long pipes, urease-active bacteria are ubiquitous and most of the urea will be hydrolyzed before reaching the storage tank (Udert et al., 2003b). In theory, the nitrogen, which was lost with the condensate, could be reclaimed by adding a further treatment stage for processing the condensate, a procedure known as gas stripping. High pH and high temperatures are optimum conditions for gas stripping as nitrogen is prevalent in the form of volatile ammonia. By increasing the surface area of the condensate (e.g. by means of stirring or trickling through packing material), the ammonia passes from the liquid to the gas phase. If the ammonia-enriched air is brought in contact with a sulfuric acid solution, the ammonia is absorbed from the gas phase and forms ammonium sulfate, which can be used as a liquid fertilizer (DüMV, 2008). Ammonia stripping is a process that has been successfully tested with a number of waste streams such as landfill leachate (Cheung et al., 1997), industrial effluent (Gonzalez Benito and Garcia Cubero, 1996; Saracco and Genon, 1994), swine manure (Bonmati and Flotats, 2003; Liao et al., 1995; Zhang and Jahng, 2010), and anaerobic digester effluent (Gustin and Marinsek-Logar, 2011; Lei et al., 2007; Quan et al., 2010). Only few laboratory-scale experiments were performed on nitrogen removal from human urine by stripping and absorption (Basakcilaran-Kabakci et al., 2007; Behrendt et al., 2002). Even though the addition of acids such as phosphoric or sulfuric acid prior to solar evaporation may enhance the nutrient value of the recovered fertilizer, this practice is not recommended in developing countries due to high costs, logistics and risks of handling concentrated acid solutions (Pronk and Koné, 2009). The same arguments are valid with acid usage for preventing urine hydrolysis during storage and for the stripping/absorption process.



**Fig.4.** Dry matter yield (g pot<sup>-1</sup>) and phosphorus (mg pot<sup>-1</sup>) and nitrogen (g pot<sup>-1</sup>) uptake by ryegrass as affected by sources (SOL: solids derived from the solar evaporation of 50 L undiluted urine; SOL-P: same as SOL except 20 L diluted urine mixed with phosphoric acid; SOL-S: same as SOL except 20 L diluted urine mixed with sulfuric acid; REF-P: commercial mineral fertilizer; BLANK: no phosphorus fertilization). Error bars indicate standard errors. Different lowercase letters indicate statistically significant differences according to the Scheffé test at the 0.05 level.



**Fig.5.** Dry matter yield (g pot<sup>-1</sup>) and phosphorus (mg pot<sup>-1</sup>) and nitrogen (g pot<sup>-1</sup>) uptake by maize as affected by sources (SOL: solids derived from the solar evaporation of 50 L undiluted urine; SOL-P: same as SOL except 20 L diluted urine mixed with phosphoric acid; SOL-S: same as SOL except 20 L diluted urine mixed with sulfuric acid; REF-P: commercial mineral fertilizer; BLANK: no phosphorus fertilization). Error bars indicate standard errors. Different lowercase letters indicate statistically significant differences according to the Scheffé test at the 0.05 level.

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#### **4.2. Fertilizer characterization**

Although it was possible to concentrate the essential plant nutrients nitrogen and phosphorus in a solid fertilizer material, X-ray diffraction spectroscopy has shown that these were not the only elements to accumulate. The micronutrients sodium and chloride, for example, which are only required in trace amounts for plant growth, made up 90% of the SOL fertilizer. Kirchmann and Pettersson (1995) reported sodium and chloride concentrations in stored urine of almost  $1 \text{ g L}^{-1}$  and  $2.5 \text{ g L}^{-1}$  respectively. Taking into account that in this study, the non-volatile nutrient phosphorus was concentrated by a factor of 62, a comparable increase in magnitude of sodium and chloride may be possible. The same could be true for other trace elements or heavy metals which, in large concentrations, may induce stress or even be toxic to plants. The sodium chloride content of SOL-P was, at only 13%, much lower than the one recorded for SOL. This can be explained by the facts that only 20 L of diluted urine was used for producing SOL-P (as opposed to 50 L undiluted urine in the case of SOL), and that this urine was further diluted by the addition of phosphoric acid. Additional measurements showed that the phosphorus content of SOL was highly water-soluble. A similar behavior has to be assumed for the sodium chloride contents of SOL. Regular application of fertilizers with high salt content may eventually lead to an excessive accumulation of water-soluble salts in the soil. Soil salinisation will have a negative impact on soil fertility and consequently affect agricultural productivity.

The advantage of direct exposure to sunlight is the fact that urine is irradiated with ultraviolet radiation and infrared heat, which are known to be effective in the degradation of micropollutants and the hygienization of water. The SODIS (solar water disinfection) method (<http://www.sodis.ch>, last accessed on 05/09/2011), which involves the storage and solar exposure of raw water in transparent containers (plastic bottles), for example was developed for decontaminating drinking water in developing countries with hot climates (McGuigan et al., 1999). Joyce et al. (1996) found that the heating effect of equatorial sunlight could induce complete inactivation of fecal bacteria even in high-turbidity water when temperatures exceeded  $55^{\circ}\text{C}$ . The SODIS technology was successfully tested for inactivating the vegetative cells of a range of emerging waterborne diarrheal pathogens, and its limitation was identified to be the survival of spore forming microbial species (Boyle et al., 2008; Lonnen et al., 2005). Research has also been carried out in the photodegradation of persistent organic pollutants (e.g. alkanes, aliphatic alcohols, carboxylic acids, alkenes, aromatics, polymers, surfactants, herbicides, pesticides and dyes) in water solution in combination with photocatalysts such as titanium dioxide, hydrogen peroxide, Photo-Fenton and ozone (Alfano et al., 2000; Bahnemann, 2004; Blanco-Galvez et al., 2007; Ollis et al., 1991; Robert and Malato, 2002). Andreozzi et al. (2003), Buser et al. (1998), and Doll and Frimmel (2003) referred to solar photodegradation as a means of natural degradation for pharmaceuticals in surface waters. As a result, it can be assumed that the greater part of the pathogens and micropollutants that might be present in the collected urine are likely to be

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degraded by the end of treatment, and that the drying technology may be suitable for generating a hygienically safe fertilizer. Photodegradation can be further promoted when using UV-transmitting glazing.

### ***4.3. Greenhouse experiment***

The data gathered during the greenhouse trial revealed that none of the test materials inhibited plant growth. SOL could not quite compete with the reference fertilizer REF-P with both test crops ryegrass and maize. This was probably related to the high sodium chloride content of SOL. Although SOL didn't inhibit plant growth, it may be recommended to apply it in limited quantities only in order to avoid soil salinisation problems. Another option would be to test the fertilizer efficiency of SOL with cash crop halophytes, which are able to accumulate or secrete salts such as sodium and chloride. *Salicornia europaea* (samphire, eaten raw or steamed as a side dish to fish) and *Limonium gmelinii* for example have been used as test crops for recycling sodium chloride from human urine in bioregenerative life support systems (Balnokin et al., 2010; Tikhomirova et al., 2011).

SOL-P and SOL-S, which were derived from acidified urine, had higher agricultural productivities than REF-P and SOL. The explanation for the improved agricultural effectiveness of SOL-P and SOL-S could be the fact that, through the addition of phosphoric and sulfuric acid respectively, the organic compounds contained in the stored urine were completely mineralized and therefore better available for utilization by the test crops. This would explain why no crystalline phosphate minerals were detected in the SOL sample although this fertilizer was to almost 2% composed of phosphorus. Possibly, the phosphate was still bound in organic molecules which were not detected by X-ray diffraction spectroscopy. Nevertheless, the organic phosphate must have been plant-available to some extent since the crops fertilized with SOL performed similar to the ones that were treated with the commercial mineral fertilizer REF-P. Furthermore, solubility tests proved that the P-content of SOL was highly water soluble and therewith available for plant uptake.

## **5. Conclusions**

In this paper, the feasibility of implementing a pilot scale evaporation technology for treating human urine at the University of Can Tho in South Vietnam was investigated. The results showed that it was possible to concentrate the nutrients derived from 50 L of undiluted human urine in 360 g of solid fertilizer material after 26 days of mere exposure to direct sunlight. Investment and operational costs were low as the photoreactor was characterized by a simple design with low maintenance and operational efforts, and entirely constructed of materials available at local hardware suppliers. No energy source other than solar radiation was required. Nitrogen losses could potentially be minimized

by acidifying the urine prior to treatment, or by absorbing the gaseous ammonia in sulfuric acid during treatment. However, this practice is not recommended in developing countries because of additional costs and handling risks. Although the fertilizer derived from undiluted urine had a high sodium chloride content, its agronomic efficiency was comparable to that of the commercial mineral fertilizer used as a reference. Since this study has focused on nitrogen and phosphorus recovery only, it would be interesting to understand the behavior of other nutrients during solar thermal evaporation in order to determine whether the nutrients that are beneficial for plant growth can be separated from the salts being detrimental for crop production. Previous studies made by others suggest that solar radiation may be an appropriate hygienization method that could, even when used with human urine, potentially produce a safe fertilizer by degrading pathogens and micropollutants. This hypothesis and the mechanisms of solar disinfection in a colored and turbid medium such as human urine require further investigation.

## **Acknowledgments**

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**Greenhouse evaluation and environmental impact assessment of different  
urine-derived struvite fertilizers as phosphorus sources for plants**

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## 1. Introduction

Excess phosphorus in waterways and coastal zones leads to eutrophication and algal blooms, and is therefore regarded as pollutant. Nonetheless, phosphorus is also a scarce, non-renewable resource and existing reserves could be depleted within the next 50-100 years (Cordell et al., 2009). Given that phosphorus cannot be substituted by alternative resources, it is apparent that a “new revolution” is needed (Ashley et al., 2011). Phosphorus must be captured and moved from where there is too much to where there is too little (Elser and Bennett, 2011). So far, the key drivers for phosphorus recovery from wastewater sludge were to prevent the pollutant from entering waterways and the spreading of sewage sludge on agricultural land. Cordell et al. (2011) presume that the future will see new drivers: they believe that the quality of the recovered phosphorus and its efficiency as a fertilizer will take over pollution prevention. Fact is that the sanitation industry, challenged by its ageing infrastructure and new pressures such as climate change or increasing regulatory requirements, is at a turning point (Mitchell et al., 2011) and stakeholders have seized the opportunity for trialing and introducing more sustainable decentralized sanitation systems.

By now, many different treatment options exist for processing source-separated urine (Maurer et al., 2006), of which struvite precipitation has been comprehensively studied at laboratory scale (Ganrot et al., 2007a; Lind et al., 2000; Ronteltap et al., 2007, 2010; Tilley et al., 2008a,b; Wilsenach et al., 2007) and to a lesser extent at pilot scale (Antonini et al., 2011, c.f. Chapter I; Etter et al., 2011). This paper focuses on the agronomic aspects of phosphorus recycling from human urine. A selection of urine-derived struvite fertilizers generated by innovative precipitation technologies was assessed for their composition and their effectiveness as phosphorus sources for plants. The yields they induced were assessed in a greenhouse pot experiment and compared to those produced by a commercial mineral fertilizer. A computer model was used to weigh the environmental impacts (i.e. nutrient and heavy metal loading rates) of applying urine-derived struvite to agricultural land against those caused by other recycling products derived from wastewater treatment, by commercial mineral and organic fertilizers and by directly applying human urine.

## 2. Materials and methods

### 2.1. Phosphorus sources

All MAP fertilizers tested in this study were derived from human urine (MAP: magnesium ammonium phosphate). A summary of the origin and the major characteristics of each urine-derived fertilizer are presented in Table 1. MAP-1: was collected from a plastic storage tank connected to a waterless urinal at the University of Bonn (Germany). After approximately 2 months of urine



collection, the storage tank was disconnected from the No Mix system and emptied. The sludge from the bottom of the storage tank was collected and dried at 40°C. MAP-2: was derived from undiluted urine collected from 100 male students at the University of Can Tho in South Vietnam. The students urinated directly into plastic bottles, and the undiluted urine was stored in a large plastic tank. Urine was batch-fed into the precipitation reactor of the “DeSa/R” (Decentralized Sanitation and Reuse) pilot system, which was developed by Huber SE (Berching, Germany) and described in more detail by Antonini et al. (2011, c.f. Chapter I). Magnesium oxide was added with a Mg:P molar ratio of 1.5:1 in order to initiate struvite precipitation. The mixture was stirred for 30 min, followed by a 3 h sedimentation phase during which the struvite particles were left to settle down. The phosphorus-depleted supernatant was removed via an overflow valve, whereas the precipitate was collected in a filter bag made of synthetic fabric. The filter bag was dried for 48 h at 105°C. MAP-3: was derived from a No Mix sanitation system installed at the premises of Huber SE in Berching, Germany (Paris et al., 2007). Urine from No Mix toilets and waterless urinals installed in the office building was collected in an underground storage tank and batch-fed into the precipitation reactor of the “DeSa/R” pilot system. The procedure for treating the stored urine was similar to the one described for MAP-2: Magnesium oxide was added with a Mg:P molar ratio of >1.5:1 (the exact ratio was not provided), the mixture was stirred for 30 min and the struvite particles were left to settle down for 3 h after which the phosphorus-depleted supernatant was removed via an overflow valve. The precipitate was collected in a filter bag and dried at ambient temperature. MAP-4: was recovered by the so-called “NuReBas” (nutrient recovery with bag filtration systems) process developed at RWTH Aachen University, Institute for Environmental Engineering – ISA, Germany (Gethke et al., 2007). Urine from waterless urinals and urine-diversion toilets was collected at GIZ (Deutsche Gesellschaft für Internationale Zusammenarbeit GmbH) Building 1 in Eschborn, Germany. Urine was batch-fed into the collection tank of the “NuReBas” precipitation reactor and circulated for 2 h through a filter bag containing the amount of magnesium oxide necessary to achieve a Mg:P ratio of 2:1. The precipitates were dried at ambient temperature. MAP-5 and MAP-6: were derived from undiluted urine collected by means of a waterless urinal at the University of Bonn, Germany. Urine was fed into a stirred batch reactor and magnesium oxide was added with a Mg:P molar ratio of 1.5:1. The mixer was operated for 30 min, followed by a 3 h sedimentation phase allowing the struvite particles to settle down. The phosphorus-depleted supernatant was drained from the reactor, and the precipitate was collected in a filter bag. The material recovered from the filter bag was split into two sub-samples of which one was dried at 40 °C and the other at 200°C. These materials are referred to as MAP-5 and MAP-6, respectively. The high drying temperature was chosen to remove part of the six water molecules from the struvite (MAP, hexahydrate) crystal structure. The aim was to produce two chemically different MAP fertilizers in order to assess whether the presence or absence of water molecules would have an impact on the agronomic efficiency.

**Table 1.** Description of the urine-derived test materials evaluated in the greenhouse pot experiments: origin, Mg:P molar ratio adopted for magnesium oxide dosage, temperature (°C) at which the precipitates were dried and total phosphorus content (%) of the test materials as determined by ICP-OES (n.a.: not applicable).

Test material	Origin	Mg:P dosage	T (°C)	P (%)
MAP-1	Sediment from a storage tank connected to a waterless urinal (University of Bonn, Germany)	n.a.	40	11.4
MAP-2 <sup>a</sup>	Struvite precipitation from undiluted urine by MgO addition (University of Can Tho, Vietnam)	1.5:1	105	12.6
MAP-3	Struvite precipitation from diluted urine by MgO addition (Huber SE, Berching, Germany)	>1.5:1	ambient	9.7
MAP-4	Struvite precipitation from undiluted urine by circulation through a filter bag containing MgO (RWTH Aachen University – ISA, Germany)	2:1	ambient	7.2
MAP-5	Struvite precipitation from undiluted urine by MgO addition (University of Bonn, Germany)	1.5:1	40	11.0
MAP-6	Struvite precipitation from undiluted urine by MgO addition (University of Bonn, Germany)	1.5:1	200	18.0
REF-A/B	Cederan phosphate fertilizer	n.a.	n.a.	8.9

<sup>a</sup> Source: Antonini et al. (2011).

## 2.2. Fertilizer characterization

All test materials were ground in a porcelain mortar and passed through a 0.49 mm sieve for homogenization. Samples were analyzed for their crystal structure by X-ray diffraction (XRD) spectroscopy and for their elemental composition (trace elements, micro- and macro-elements except nitrogen) by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Nitrogen was determined using the Eurovector Elemental Analyzer. The XRD and ICP-OES results for MAP-2 were derived from Antonini et al. (2011, please refer to Chapter I).

Phosphorus solubility was determined by mixing 10 g of sample with 500 mL of distilled water, and 5 g of sample with 500 mL of citric acid (2%) (VDLUFA, 1995). The mixtures were placed on a rotary shaker at 40 rpm for 30 min. The samples were then filtered using Macherey-Nagel filter papers (MN 640 m, average retention capacity 4-12 µm). The phosphorus concentration of the filtrate was measured with an Eppendorf ECOM 6122 photometer (molybdenum blue method) for water-soluble P. For the citric acid extracts, MERCK Spectroquant phosphate tests (vanadomolybdo-phosphoric acid method) and a WTW PhotoLab S12 photometer were used.

### 2.3. Greenhouse experiments

The six phosphorus sources were assessed for their agronomic effectiveness in a greenhouse pot trial. Due to space constraints and availability of the test materials, two greenhouse experiments with identical set-ups were performed in two consecutive vegetative periods in Bonn (Germany). These two pot trials are referred to as “Experiment A” (test substrates: MAP-1, MAP-2, taking place from July to October 2008) and “Experiment B” (test substrates: MAP-3, MAP-4, MAP-5, MAP-6, taking place from July to October 2009). Both greenhouse experiments were carried out under local environmental conditions, meaning that there was no possibility to control climate factors such as light, temperature or humidity. A local P-deficient soil (“Meckenheim” subsoil, 9.2 mg total P kg<sup>-1</sup> soil) was used as growth medium, and Italian ryegrass (*Lolium multiflorum* Lam.) or maize (*Zea mays* L.) as test crops. All test materials were thoroughly mixed with 6 kg of air-dried, 2 mm-sieved soil and 3 kg of sand in double walled plant culture pots (Kick–Brauckmann pots by STOMA, Germany) at rates equivalent to 24.4 mg P kg<sup>-1</sup> of soil/sand mixture, based on the total P content of the materials received. Before sowing the seeds, basal nutrients (nutrient solution, applied using a dispenser) were mixed with the soil in accordance with the concentrations presented in Chapter II, Table 2 (this data was originally published in Chemosphere as Supplemental Material (SM), SM Section 1). Nitrogen was added in the form of ammonium nitrate, such as to achieve a uniform nitrogen content of 1530 mg per pot by taking into account the amounts of N already added with the test substrates. A common mineral phosphorus fertilizer (Cederan phosphate fertilizer, referred to as REF-A and REF-B for experiments A and B, respectively) was purchased from Landgard eG, Remagen (Germany) and used as a reference. A control treatment that received no phosphorus was incorporated (BLANK-A and BLANK-B for trial A and B, respectively). The total number of treatments was 8 for experiment A and 12 for experiment B. These were replicated four times in a randomized block design, leading to a total number of 32 pots in experiment A and 48 pots in experiment B. This experimental set-up was conceived to isolate phosphorus as the only growth-limiting nutrient.

Ryegrass was seeded at a rate of 1.8 g per pot and four maize seeds were placed in every pot. The pots were irrigated on a daily basis with distilled water such as to maintain a level of 70% of soil water holding capacity. This was achieved by watering every pot to a desired weight after having determined the weight of a pot holding 9 kg of soil/sand mixture saturated to 100% with water. The soil was wetted from below in order to prevent the leaching and accumulation of water-soluble nutrients at the bottom of the pots. In greenhouse experiment A, the ryegrass was harvested at 27, 40, 58 and 82 d after sowing. The maize was harvested at 82 d after sowing. As for experiment B, the ryegrass was harvested at 27, 49 and 76 d after sowing. The maize was harvested at 51 d after sowing. Micronutrients, potassium and nitrogen were reapplied to both crops after every grass harvest in order to prevent nutrient deficiencies other than those induced by phosphorus. The application rates were the same as those presented in SM Section 1, except for phosphorus which was not reapplied.

The harvested biomass was dried at 65°C and weighed before and after drying. The dry biomass was ground by using a disk mill for ryegrass and a rotary mill for maize. It was further processed by dry-ashing in a muffle furnace followed by digestion in hydrochloric acid. The phosphorus concentration of the biomass was measured photometrically using the molybdenum blue method and an Eppendorf ECOM 6122 photometer.

#### **2.4. Biomass data analysis**

Phosphorus uptake into shoots was calculated on a pot basis by multiplying the dry matter yield by the respective phosphorus content of the biomass. Phosphorus uptake was expressed as percentage of total phosphorus; the latter was assumed to be 275 mg P pot<sup>-1</sup> (i.e. 55 mg P supplied with 6 kg of Meckenheim subsoil, and 220 mg P added in the form of fertilizer). Cumulative shoot dry matter yield and phosphorus uptake were calculated by combining the data of the three or four ryegrass harvests. Data is generally expressed as the observed mean, followed by its standard error ( $\pm$ SE). Statistical analysis (one-way ANOVA, followed by the Scheffé post hoc test at  $\alpha = 0.05$ ) was performed by using SPSS Statistics 17.0 for Windows. Different lowercase letters (Figs. 1 and 2) indicate statistically significant differences according to the Scheffé test at the 0.05 level.

#### **2.5. Computer modeling and calculations**

The nutrient equivalents (NEQs) and heavy metal fluxes of each urine-derived struvite fertilizer were computed using a model developed by Hammer and Clemens (2007). The model assumes that adequate equivalents of seven nutrients are required to supply arable fields with sufficient fertilizer. One NEQ is defined as follows for a selection of six macro-nutrients and humic substances (in kg ha<sup>-1</sup> a<sup>-1</sup>): nitrogen, 170; phosphorus, 26.4; potassium, 132.8; calcium, 177.5; magnesium, 18; sulfur, 20; humic substances, 1500. For every fertilizer, one nutrient is responsible for limiting the amount that can be applied to arable land such as to avoid over-fertilization (defined by a NEQ equal to 1). The limiting nutrient defines the application rate per ha and thus the pollutant or heavy metal loading rates to agricultural land. The NEQ and heavy metal loading rates of the urine-derived struvite fertilizers assessed in this study were compared to those of the following recycling products and fertilizing agents taken from the literature: struvite derived from sewage sludge (MAP wastewater, Kern et al., 2008), sewage sludge obtained from a conventional aerobic activated sludge process followed by anaerobic digestion (Plaza et al., 2007), ashes from sewage sludge incineration (Franz, 2008), commercial superphosphate (Plaza et al., 2007), pig and cattle manure as well as human urine (Hammer and Clemens, 2007).

For sewage sludge ash and superphosphate, nitrogen concentrations were not published. It was assumed that these two fertilizers may at most contain traces of nitrogen and therefore concentrations of 0 mg N g<sup>-1</sup> were used as input data for calculating the NEQ and application rates. In

the case of sulfur, no data was published for struvite derived from sewage sludge, for superphosphate and sewage sludge. As struvite is, from a chemical point of view, mainly composed of magnesium, ammonium and phosphate, again a sulfur concentration of  $0 \text{ mg S g}^{-1}$  was used as input data for wastewater-derived struvite. The sulfur concentration of sewage sludge may vary strongly depending on the characteristics of the incoming wastewater and therefore it was refrained from assuming a typical sulfur concentration for sewage sludge. Instead, a concentration of  $0 \text{ mg S g}^{-1}$  was used as input data for sewage sludge although in reality this should be somewhat higher. In the case of superphosphate, however, it is widely accepted that this fertilizer has a sulfur content of minimum 11% (e.g. Food and Agriculture Organization of the United Nations specifications for commonly used fertilizers). Therefore, a concentration of  $110 \text{ mg S g}^{-1}$  was used as input data for computing the NEQ of superphosphate. Attention to these assumptions is drawn in the captions of the corresponding figures. In those cases where the measured concentrations of heavy metals were below the detection limit of the analytical method, the detection limit was used as input data for computing heavy metal application rates. The corresponding data is marked with an “\*” in the bar chart, meaning that this bar represents a worst case scenario. As for mercury, no data was published for superphosphate and sewage sludge. In this case, a concentration of  $0 \text{ } \mu\text{g Hg g}^{-1}$  was used as input data.

### 3. Results

#### 3.1. Fertilizer characterization

The results of the XRD analysis are presented in Table 2 (left). It was found that all test materials except MAP-6 were mainly composed of struvite. MAP-1 and MAP-5 were more or less pure struvite, whereas MAP-3 and MAP-4 contained traces of nesquehonite (type of magnesium carbonate, 11% and 26% respectively). Besides the 85% of struvite, MAP-2 was to 15% composed of the monohydrate dittmarite (MAP, monohydrate). MAP-6 was completely composed of dittmarite (100%).

Solubility tests revealed that the urine-derived fertilizers were, at 5% and less water-soluble phosphorus (of  $P_{\text{total}}$ ), almost not soluble in distilled water (see Table 2, right). Only the commercial mineral fertilizer used as reference (REF-A, REF-B) was characterized by a phosphorus fraction that was between 70% and 74% soluble in water. Concerning the solubility in citric acid, the phosphorus fraction of most test materials was almost completely (i.e. more than 96%) soluble. Only MAP-5, MAP-6 and the reference fertilizer (REF-A, REF-B) were characterized by a slightly lower solubility (89%, 87%, 90% and 86% of  $P_{\text{total}}$ , respectively).

The results of the elemental analysis (micro- and macro-nutrients) are presented in Table 3.

### 3.2. Yield and phosphorus uptake by ryegrass

In experiment A, the biomass yields induced by the urine fertilizers MAP-1 and MAP-2 significantly exceeded those recorded for the pots treated with the commercial mineral fertilizer REF-A and the control treatment where no phosphorus was added (Fig. 1, top). Thus, MAP-1 and MAP-2 led to dry matter yields of  $39\pm 1$  and  $38\pm 1$  g pot<sup>-1</sup> respectively, whereas REF-A only produced  $29\pm 1$  g pot<sup>-1</sup>. In experiment B, the biomass yields ranged from  $49\pm 3$  to  $53\pm 1$  g pot<sup>-1</sup>, and therewith did not significantly differ from the dry matter yield of  $49\pm 2$  g pot<sup>-1</sup> induced by the commercial mineral fertilizer REF-B. However, the urine fertilizers and the mineral fertilizer generated significantly higher biomass yields than the control treatment which had received no phosphorus fertilization at all (BLANK-B,  $26\pm 1$  g pot<sup>-1</sup>).

Fig. 1 (bottom) reveals that in terms of phosphorus uptake, again the urine fertilizers in experiment A significantly exceeded the performance of the commercial mineral fertilizer REF-A. Ryegrass treated with MAP-1 and MAP-2 took up  $53\pm 2$  and  $55\pm 3\%$  of the total phosphorus. Plants fertilized with the commercial mineral fertilizer REF-A took up significantly less phosphorus ( $26\pm 2\%$  of total P). In experiment B, ryegrass treated with the urine fertilizers took up between  $34\pm 2$  and  $39\pm 2\%$  of the total phosphorus. The phosphorus uptake recorded for the commercial mineral fertilizer REF-B ( $31\pm 1\%$ ) differed not significantly from the results observed for the urine fertilizers.

**Table 2.** Crystal structure (%) of the urine-derived fertilizers, as identified by X-ray diffraction spectroscopy (all samples were crystalline to more than 96%) and phosphorus solubility (in % of total phosphorus content) of the test fertilizers in distilled water and 2% citric acid solution (n.a.: not applicable).

Test material	Struvite (%) NH <sub>4</sub> MgPO <sub>4</sub> ·6H <sub>2</sub> O	Dittmarite (%) NH <sub>4</sub> MgPO <sub>4</sub> ·H <sub>2</sub> O	Nesquehonite (%) Mg(HCO <sub>3</sub> )(OH)·2H <sub>2</sub> O	Sylvite (%) KCl	P <sub>tot</sub> (%)	%P (of P <sub>tot</sub> ) water-soluble	%P (of P <sub>tot</sub> ) soluble in citric acid
MAP-1	98	0	0	2	11	4	100
MAP-2 <sup>a</sup>	85	15	0	0	13	2	99
MAP-3	89	0	11	0	10	<1	96
MAP-4	74	0	26	0	7	<1	100
MAP-5	100	0	0	0	11	<1	89
MAP-6	0	100	0	0	18	5	87
REF-A	n.a.	n.a.	n.a.	n.a.	9	74	90
REF-B	n.a.	n.a.	n.a.	n.a.	9	70	86

<sup>a</sup> Source (XRD data only): Antonini et al. (2011).

**Table 3.** Concentrations of macro-elements (mg DM g<sup>-1</sup>) and micro- and trace-elements (µg DM g<sup>-1</sup>) in urine-derived struvite fertilizers.

	MAP-1	MAP-2 <sup>a</sup>	MAP-3	MAP-4	MAP-5	MAP-6	REF-A/B
N (mg DM g <sup>-1</sup> )	45.2	53.3	42.9	29.3	55.6	60.0	1.6
P (mg DM g <sup>-1</sup> )	114	126	97	71	110	180	89
K (mg DM g <sup>-1</sup> )	15.1	2.7	2.6	2.1	2.6	3.6	13.8
S (mg DM g <sup>-1</sup> )	3.5	1.4	1.3	2.6	0.4	0.5	77.9
Mg (mg DM g <sup>-1</sup> )	65	104	101	145	97	157	2
Ca (mg DM g <sup>-1</sup> )	58	16	24	7	6	12	196
Na (mg DM g <sup>-1</sup> )	15.5	9.0	2.1	2.7	2.1	2.7	5.9
Al (µg DM g <sup>-1</sup> )	558	410	37	92	11	17	796
As (µg DM g <sup>-1</sup> )	<15.0	<15.0	<15.0	<15.0	<15.0	<15.0	<15.0
B (µg DM g <sup>-1</sup> )	14.6	13.4	4.0	3.1	1.8	2.5	22.6
Ba (µg DM g <sup>-1</sup> )	2.0	9.7	3.4	1.7	0.5	2.0	153.0
Cd (µg DM g <sup>-1</sup> )	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	11.5
Co (µg DM g <sup>-1</sup> )	1.7	<0.3	<0.3	<0.3	<0.3	<0.3	0.7
Cr (µg DM g <sup>-1</sup> )	<0.2	<0.2	<0.2	<0.2	<0.2	5.0	44.7
Cu (µg DM g <sup>-1</sup> )	3	178	528	83	6	14	17
Fe (µg DM g <sup>-1</sup> )	14	44	1050	454	56	148	759
Hg (µg DM g <sup>-1</sup> )	<4.2	<4.2	<4.2	<4.2	<4.2	<4.2	<4.2
Li (µg DM g <sup>-1</sup> )	2.1	<1.0	<1.0	1.4	<1.0	<1.0	<1.0
Mn (µg DM g <sup>-1</sup> )	3.3	4.1	6.6	92.3	<0.1	2.9	16.0
Mo (µg DM g <sup>-1</sup> )	1.5	<1.0	<1.0	<1.0	<1.0	<1.0	10.8
Nb (µg DM g <sup>-1</sup> )	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Ni (µg DM g <sup>-1</sup> )	<0.8	<0.8	2.3	<0.8	<0.8	1.6	24.8
Pb (µg DM g <sup>-1</sup> )	<0.9	<0.9	6.3	<0.9	<0.9	<0.9	1.8
Se (µg DM g <sup>-1</sup> )	<15.0	<15.0	<15.0	<15.0	<15.0	<15.0	<15.0
Si (µg DM g <sup>-1</sup> )	79	87	46	510	36	45	1970
Sn (µg DM g <sup>-1</sup> )	<1.4	<1.4	<1.4	<1.4	<1.4	<1.4	<1.4
Sr (µg DM g <sup>-1</sup> )	45	31	37	8	4	13	1170
V (µg DM g <sup>-1</sup> )	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	70.9
Zn (µg DM g <sup>-1</sup> )	36	90	142	87	7	17	278

<sup>a</sup> Source: Antonini et al. (2011).

### 3.3. Yield and phosphorus uptake by maize

As shown in Fig. 2 (top), the biomass yield induced by the urine fertilizers MAP-1 ( $78 \pm 12$  g pot<sup>-1</sup>) and MAP-2 ( $88 \pm 3$  g pot<sup>-1</sup>) in experiment A significantly exceeded the dry matter yield recorded for the maize plants treated with the commercial mineral fertilizer REF-A ( $36 \pm 2$  g pot<sup>-1</sup>) and the control treatment with no phosphorus fertilization ( $16 \pm 3$  g pot<sup>-1</sup>). In experiment B, the reference fertilizer REF-B induced the highest biomass yield ( $44 \pm 4$  g pot<sup>-1</sup>). The yields induced by the urine fertilizers were slightly lower: they ranged from  $31 \pm 2$  to  $38 \pm 2$  g pot<sup>-1</sup> and differed not significantly from the reference fertilizer REF-B. The trend observed for phosphorus uptake by maize is presented in Fig. 2 (bottom). Maize plants fertilized with MAP-1 and MAP-2 took up  $37 \pm 7$  and  $45 \pm 2\%$  of the total phosphorus. This significantly exceeded the  $16 \pm 1\%$  of total phosphorus that was taken up by the commercial mineral fertilizer REF-A. The amounts of phosphorus taken up by maize in experiment B were much lower: the values ranged from  $11 \pm 1$  to  $14 \pm 1\%$  of total phosphorus. This did not differ significantly from the amount of total phosphorus taken up by the maize plants treated with the commercial mineral fertilizer REF-B ( $15 \pm 1\%$ ). The blank control treatment, however, took up significantly less of the total phosphorus ( $2 \pm 0\%$ ).

### 3.4. NEQ and heavy metal fluxes

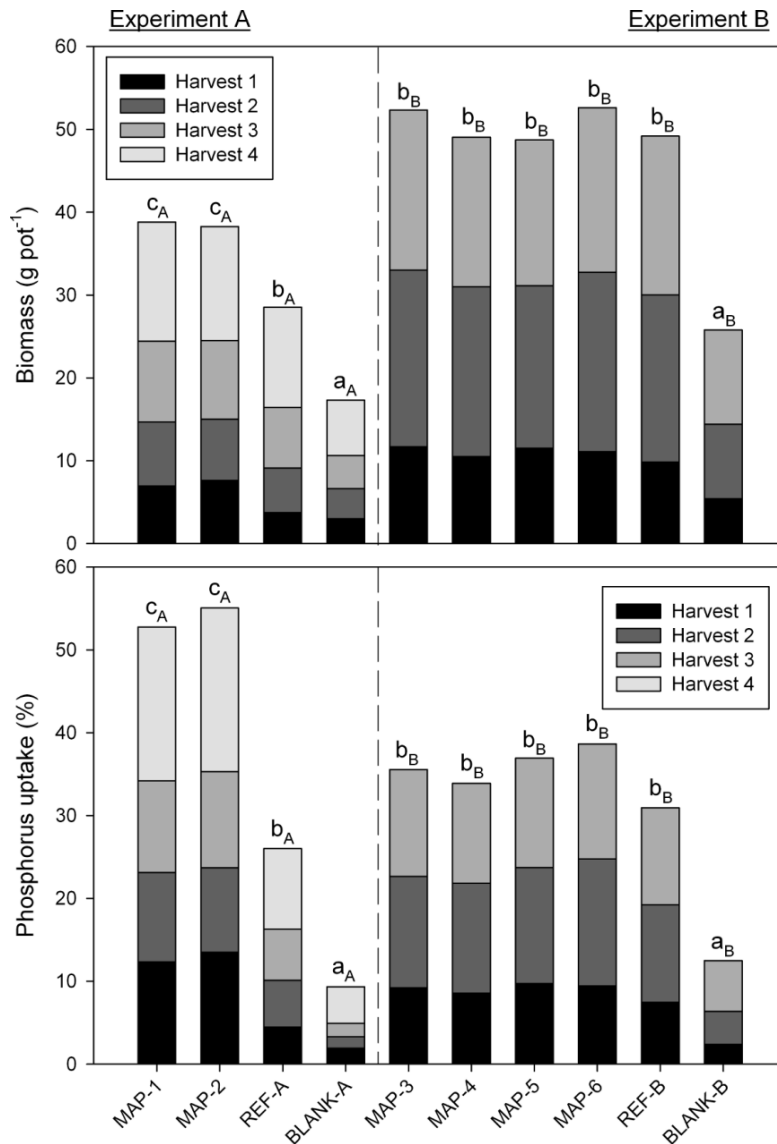
The urine fertilizers were compared to other recycling products derived from wastewater, to commercial mineral and organic fertilizers and to human urine in terms of their nutrient content (expressed as NEQ) and heavy metal contamination. Fig. 3 (top) shows the nutrients which controlled the application rate of the various fertilizers. The application rate of the struvite fertilizers was mainly limited by magnesium except for MAP-1, for which phosphorus was the limiting nutrient. Phosphorus was also the nutrient which controlled the application rate of sewage sludge, sewage sludge ash and pig manure whereas the spreading of cattle manure was limited by its humic substances content. The use of superphosphate and REF-A/B (reference fertilizer) was limited by sulfur. Urine application was limited by both sulfur and nitrogen.

The maximum application rates tolerated for each fertilizer are presented in Fig. 3 (bottom). The highest values were recorded for urine ( $18.52$  m<sup>3</sup> ha<sup>-1</sup> a<sup>-1</sup>), sewage sludge ( $3.57$  t DM ha<sup>-1</sup> a<sup>-1</sup>) and cattle and pig manure ( $2.00$  and  $1.20$  t DM ha<sup>-1</sup> a<sup>-1</sup> respectively). For all other fertilizers, the maximum application rates ranged from  $0.11$  and  $0.12$  t DM ha<sup>-1</sup> a<sup>-1</sup> (MAP-6 and MAP-4 respectively) to  $0.26$  t DM ha<sup>-1</sup> a<sup>-1</sup> (REF-A/B).

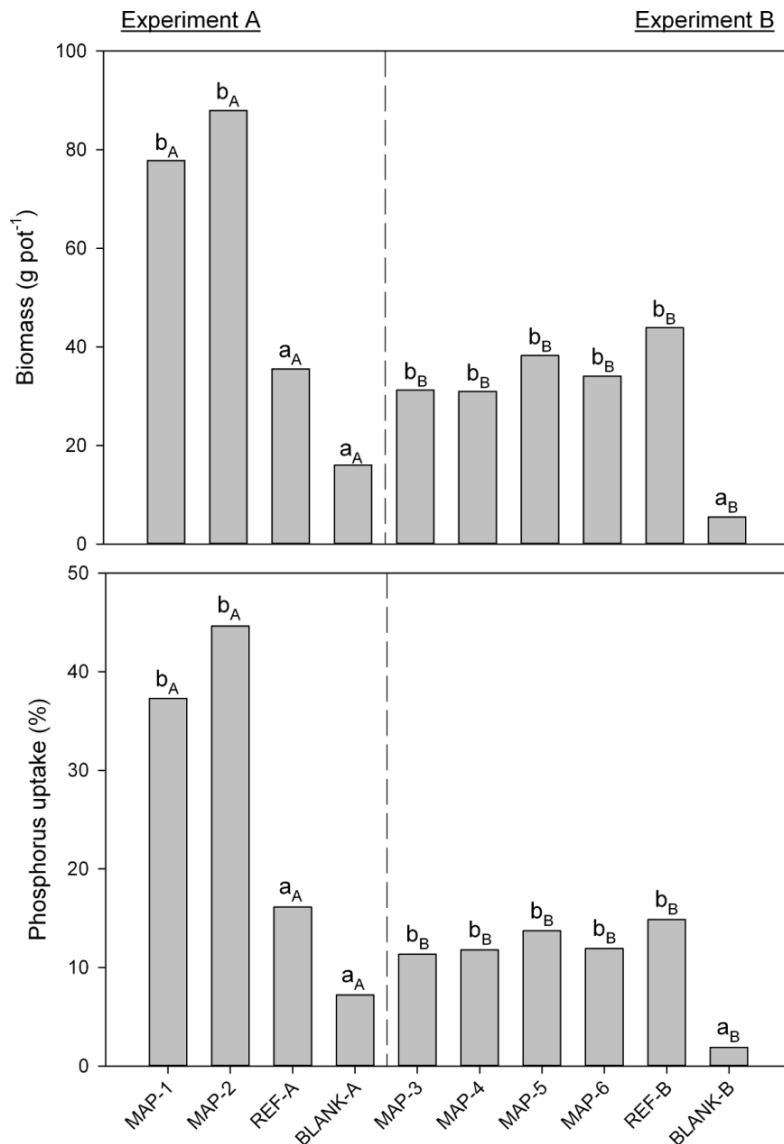
Table 4 shows the threshold values for heavy metal concentrations as specified by the German Fertilizer Regulations (DüMV, 2008) and the German Sewage Sludge Regulations (AbfKlärV, 1992) as well as the maximum annual loading rates to agricultural land according to the German Federal Soil Protection Act (BBodSchV, 1999) (please note that this data was originally published in Chemosphere as Supplemental Material (SM), SM Section 2). Except for possibly mercury, in the case of which the



detection limit of ICP-OES was higher than some of the threshold values, none of the urine-derived fertilizers exceeded the threshold concentrations given by the German Fertilizer and Sewage Sludge Regulations. Tl and Cr (VI) were not analyzed; therefore it is not possible to draw a conclusion for these two elements.



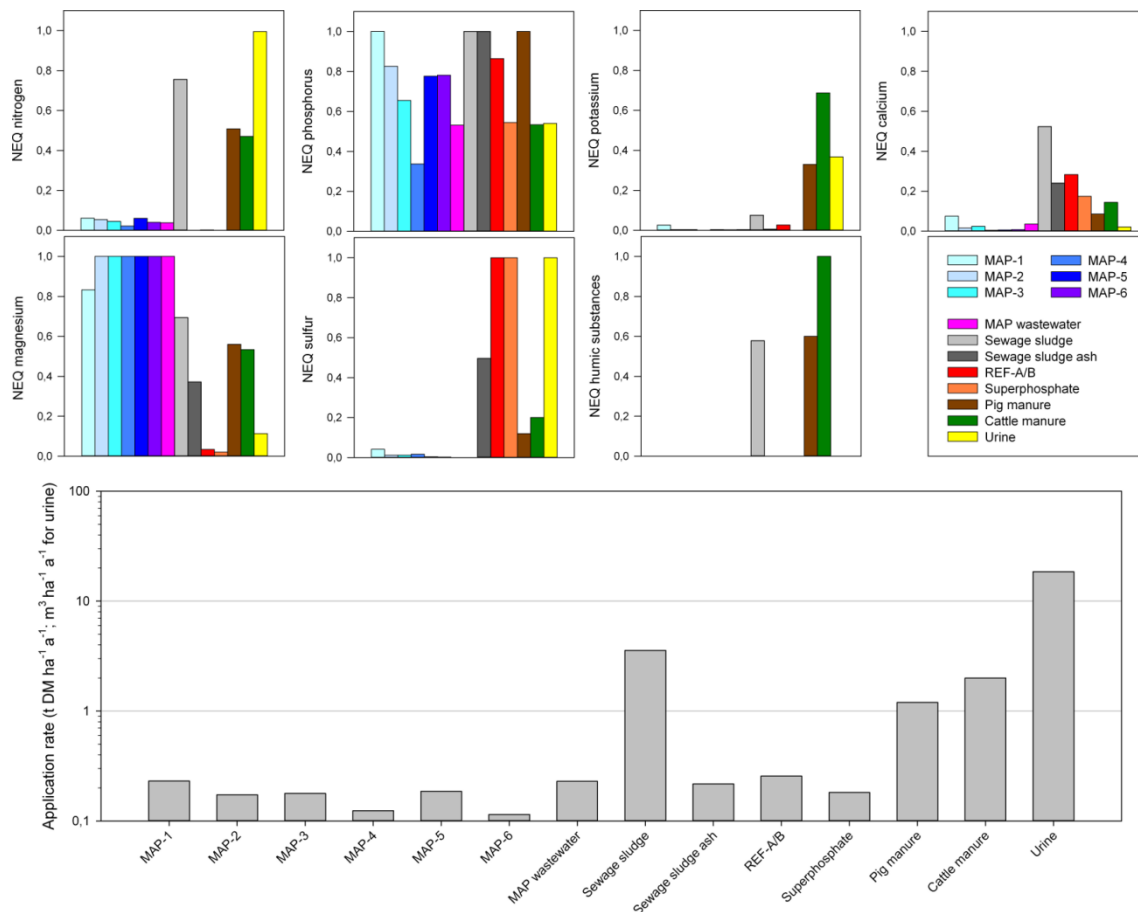
**Fig. 1.** Dry matter yield ( $\text{g pot}^{-1}$ ) and phosphorus uptake (%) by ryegrass as affected by sources. Experiment A harvested at 27, 40, 58 and 82 d after sowing. Experiment B harvested at 27, 49 and 76 d after sowing. Different lowercase letters indicate statistically significant differences according to the Scheffé test at the 0.05 level.



**Fig. 2.** Dry matter yield ( $\text{g pot}^{-1}$ ) and phosphorus uptake (%) by maize as affected by sources. Experiment A harvested at 82 d after sowing. Experiment B harvested at 51 d after sowing. Different lowercase letters indicate statistically significant differences according to the Scheffé test at the 0.05 level.

In terms of heavy metal loading rates, Fig. 4 demonstrates that all urine-derived struvite fertilizers were well below the threshold limits decreed by the Federal Soil Protection Act (BBodSchV, 1999). Except for mercury, the heavy metal loading rates computed for the six struvite fertilizers were much lower than those calculated for the other fertilizing agents. The application rate of mercury was probably over-estimated by the model as the relatively high detection limit of ICP-OES was used as input data. The loading rates ranged from 0.01 (sewage sludge ash) to 1.08  $\text{g Hg ha}^{-1}$

$a^{-1}$  (REF-A/B). The estimated cadmium loading rates ranged from  $0.02 \text{ g Cd ha}^{-1} a^{-1}$  for MAP-4 and MAP-6 up to  $2.95 \text{ g Cd ha}^{-1} a^{-1}$  for REF-A/B, and were therewith well below the regulatory limit of  $6 \text{ g Cd ha}^{-1} a^{-1}$ . For chromium, lead, nickel and zinc, the highest values were calculated for sewage sludge. In the case of zinc, the loading rate even exceeded the threshold limit of  $1200 \text{ g Zn ha}^{-1} a^{-1}$ . In general, liquid urine and the struvite fertilizers produced from urine contributed less to heavy metal accumulation in soils than sewage-derived fertilizers and the mineral and organic fertilizers.



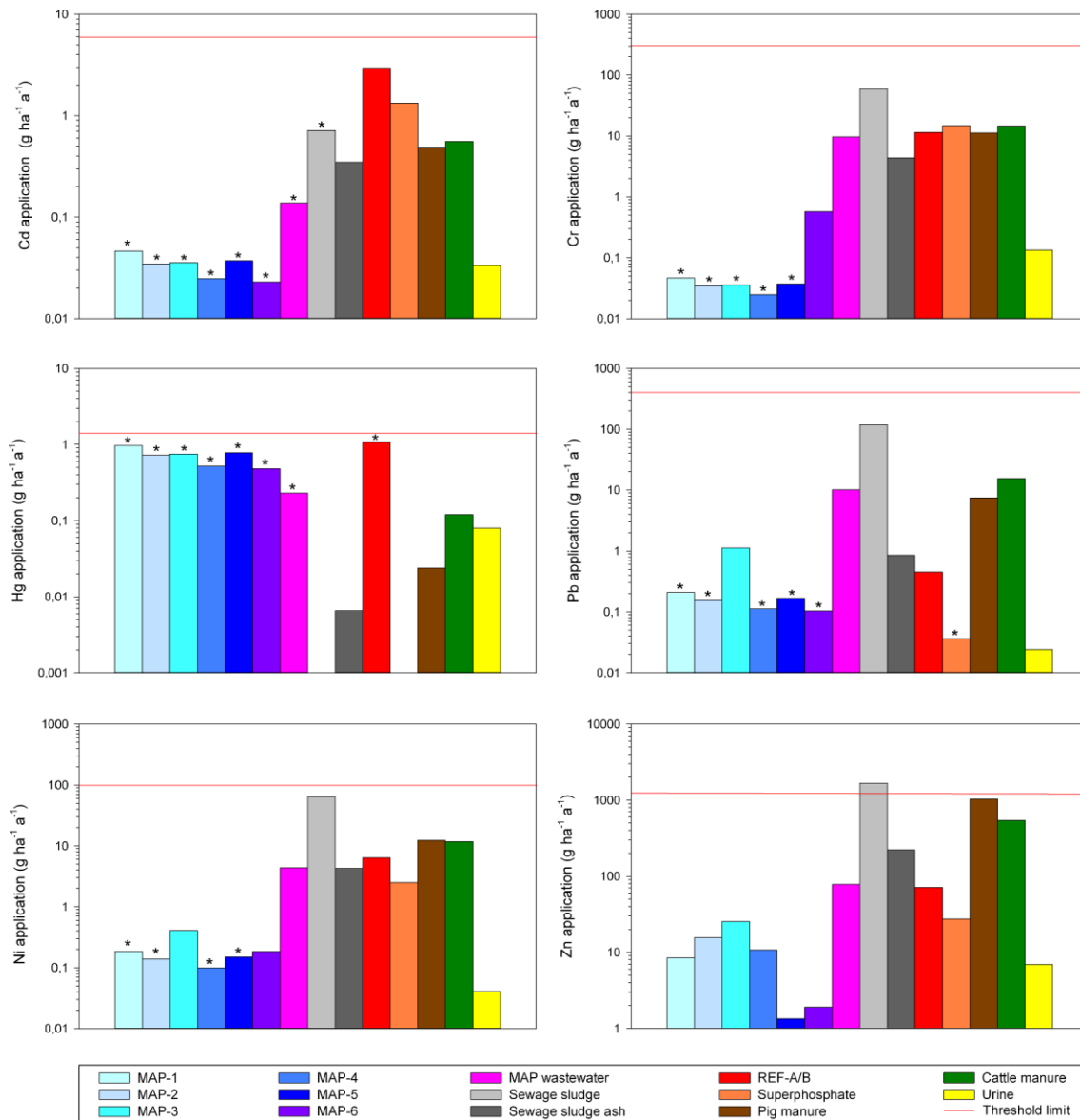
**Fig. 3.** Nutrient equivalents (NEQ) and maximum application rates ( $t \text{ DM ha}^{-1} a^{-1}$ , except for urine:  $m^3 \text{ ha}^{-1} a^{-1}$ ) of urine-derived struvite fertilizers, recycling products derived from wastewater treatment, commercial mineral and organic fertilizers and human urine. Limiting nutrients are characterized by a NEQ equal to one. Assumptions owing to lack of data: nitrogen concentrations for sewage sludge ash and superphosphate of  $0 \text{ mg N g}^{-1}$ . Sulfur concentrations for sewage sludge and struvite derived from sewage sludge of  $0 \text{ mg S g}^{-1}$ . Sulfur concentration of  $110 \text{ mg S g}^{-1}$  for superphosphate.

**Table 4.** Threshold values for heavy metal concentrations ( $\mu\text{g DM g}^{-1}$ ) in fertilizers and biosolids according to the German Fertilizer Regulations (DüMV, 2008) and the German Sewage Sludge Regulations (AbfKlärV, 1992), and threshold limits for heavy metal loading rates ( $\text{g ha}^{-1} \text{a}^{-1}$ ) according to the German Federal Soil Protection Act (BBodSchV, 1999).

Element	DüMV ( $\mu\text{g DM g}^{-1}$ )	AbfKlärV ( $\mu\text{g DM g}^{-1}$ )	BBodSchV ( $\text{g ha}^{-1} \text{a}^{-1}$ )
As	40	No threshold	No threshold
Pb	150	900	400
Cd	50 <sup>a</sup>	10	6
Cr	2 <sup>b</sup>	900	300
Ni	80	200	100
Hg	1	8	1.5
Tl	1	No threshold	No threshold
Zn	No threshold	2500	1200

<sup>a</sup> 50 mg  $\text{kg}^{-1}$   $\text{P}_2\text{O}_5$  for fertilizers with 5%  $\text{P}_2\text{O}_5$  or more (i.e. 2.2% P or more)

<sup>b</sup> Refers to Cr VI (not Cr total)



**Fig. 4.** Heavy metal fluxes ( $\text{g ha}^{-1} \text{a}^{-1}$ ) caused by applying the maximum rates of urine-derived struvite fertilizers, recycling products derived from wastewater treatment, commercial mineral and organic fertilizers, and human urine. There was no data available for estimating the fluxes of mercury caused by the application of sewage sludge and superphosphate. Bars marked with an (\*) represent a worst case scenario: heavy metal concentrations were below the detection limit, which was used for calculating application rates. Red lines represent threshold limits according to the German Federal Soil Protection Act (BBodSchV, 1999).

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## 4. Discussion

### 4.1. Fertilizer characterization

XRD results have shown that even urine sludge collected from the bottom of a NoMix storage tank (MAP-1) was to 98% composed of struvite. This observation is in agreement with the findings of Udert et al. (2003d), Tilley et al. (2008a) and Wohlsager et al. (2010) who reported a natural or spontaneous precipitation of struvite in stored urine, triggered by bacterial degradation of urea and the resulting increase of pH. Along with struvite, the minerals hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) and calcite ( $\text{CaCO}_3$ ) may precipitate, depending on the volumes of flush water used. Udert et al. (2003d) reported the occurrence of struvite in less diluted urine whilst calcite was found at high dilution factors. The precipitation of hydroxyapatite was observed over a wide range of dilution factors. The formation of different minerals can be explained by the fact that tap water provides extra amounts of magnesium and calcium, which are limiting factors for the incorporation of phosphorus into precipitates through spontaneous precipitation. Whilst magnesium and calcium are almost completely removed from solution during storage, the removal efficiencies for phosphorus range from 20% to 80%, depending on the urine dilution factor (Udert et al., 2003d; Tilley et al., 2008a; Wohlsager et al., 2010). The accumulation of heavy metals in urine sludge is low if not negligible given the already low amounts of heavy metals in urine (Ronteltap et al., 2007b; Wohlsager et al., 2010). Our measurements (Table 3) showed that the concentrations of heavy metals in urine sludge (MAP-1) were not substantially higher than those measured in struvite samples derived from the supernatant in the same collection tank (MAP-5 and MAP-6, although not the identical batch), or from collection tanks in general (MAP-2, MAP-3, MAP-4). In contrast, urine sludge was characterized by much higher calcium, potassium, sodium and sulfur concentrations than the other test materials. These are also valuable plant nutrients, and are not recovered by adding magnesium to the supernatant of stored urine in order to initiate struvite precipitation. It is therefore recommended to harvest the sludge from the bottom of urine storage tanks such as to maximize nutrient recovery from source-separated urine.

MAP-2 and MAP-6 were partially or totally composed of dittmarite. In the case of MAP-2, Antonini et al. (2011, c.f. Chapter I) assumed that a drying temperature of 105°C had been responsible for a partial degradation of the MAP hexahydrate (struvite) by loss of water molecules. Indeed, Sarkar (1991) and Bhuiyan et al. (2008) reported that struvite was stable up to a temperature of only 55°C. This theory was confirmed by splitting a struvite sample into two sub-samples and drying them at 40 and 200°C respectively. MAP-5, which had been dried at the lower temperature, was to 100% composed of struvite whereas the higher temperature led to a sample composed to 100% of dittmarite (MAP monohydrate, MAP-6). The loss of water molecules from MAP-6 was reflected by the fact that both micro- and macro-nutrients were more concentrated in this urine fertilizer than in MAP-5, except for the volatile nutrients nitrogen and sulfur (similar concentrations for MAP-5 and MAP-6). Overall,

it can be said that the drying of urine-derived struvite at high temperatures is an efficient method for increasing the phosphorus concentration in the final product. This could be important from a fertilizer storage and transportation point of view (i.e. price per unit of phosphorus).

All struvite fertilizers except MAP-1 were generated by adding magnesium to source-separated urine. MAP-2, MAP-5 and MAP-6 were produced by adding 1.5 mol magnesium per mol of phosphorus, while >1.5 mol (precise data was not available) and 2 mol of magnesium were added in order to yield MAP-3 and MAP-4, respectively. The higher magnesium dosage could account for the fact that these two urine fertilizers were not to 100% composed of struvite. In addition to struvite, they also contained a small percentage of nesquehonite ( $\text{Mg}(\text{HCO}_3)(\text{OH})\cdot 2\text{H}_2\text{O}$ , type of magnesium carbonate), and were characterized by higher Mg:P ratios measured in the final fertilizer product.

Although the composition of urine is dependent on the diet, no considerable difference in nutrient content was identified between MAP-2 (DeSa/R system in Vietnam) and MAP-3 (DeSa/R system in Germany). MAP-2 had a slightly lower calcium concentration than MAP-3, which probably reflects the low intake of dairy products in Vietnam. The sodium concentration, by contrast, was higher for MAP-2 than for MAP-3. Higher values of urinary sodium secretion may be reflected by the dietary practice in Asian countries of using soy sauce as seasoning (Brown et al., 2009). In terms of micro- and trace-elements, MAP-3 had much higher iron and copper concentrations, whereas MAP-2 was characterized by higher aluminum concentrations. These are most likely traces of contamination that can be related to alloys used for manufacturing the reactors of the DeSa/R system (Paris et al., 2007) or the piping system.

#### ***4.2. Greenhouse pot experiment***

In experiment A, the agronomic effectiveness (i.e. the induced biomass yield and phosphorus uptake) of the struvite fertilizers was significantly higher than that of the reference fertilizer. This observation is contradictory to the fact that the phosphorus content of the reference fertilizer was much more soluble – and therewith more available – than the one of the struvite fertilizers. The increased phosphorus uptake by ryegrass and maize plants treated with the less P-available struvite fertilizers could be related to the secretion mechanism of root exudates for mobilizing sparingly available phosphorus in the rhizosphere. Neumann and Römheld (2012) state that in some plant species, phosphorus deficiency may enhance the root secretion of organic acid anions (e.g. carboxylates such as oxalate, citrate, malonate and malate) and therewith increase the solubility of organic phosphorus forms by displacing phosphate anions from anion sorption sites on the soil matrix. In experiment A, the release of organic acid ions could have had an impact on soil pH and on the mobilization of other soil and/or fertilizer constituents. Furthermore, the struvite fertilizers were characterized by much higher magnesium concentrations than the reference fertilizer. The latter, however, contained much higher silicon and strontium concentrations than the urine fertilizers. It could well be the case that the

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extra magnesium improved plant growth, and/or that the high strontium concentrations induced phytotoxic effects. To prove this hypothesis, a more extensive experiment covering the uptake of all micro- and macro-nutrients would be necessary. It would also be recommended to perform a complete soil analysis before sowing and after harvesting the test crops, and to monitor the soil pH throughout the entire experiment. Leaching tests would be useful to determine the actual behavior of the phosphorus sources in the soil. Such a test could show whether the phosphorus released by the fertilizer is directly absorbed by the P-deficient soil and therefore not available to the plants. The greenhouse experiment revealed that the agronomic effectiveness of the magnesium ammonium phosphate fertilizers MAP-5 (hexahydrate) and MAP-6 (monohydrate) was not significantly affected by the presence or absence of water molecules within their crystal structure. This technique can be used to increase the phosphorus concentration in the final product in order to reduce storage and transportation costs per unit of phosphorus. Hence, we conclude that no additional thermal treatment is necessary after precipitating struvite from stored human urine.

#### ***4.3. NEQ and heavy metal fluxes***

Our calculations have shown that all urine-derived struvite fertilizers except for MAP-1 covered the magnesium demand of crops. For MAP-1, the computed NEQ for magnesium was 0.8 – which still covers most of the magnesium demand. MAP-1 covered the phosphorus demand of crops, as did sewage sludge, sewage sludge ash and pig manure. MAP-2, MAP-3, MAP-5 and MAP-6 all contained more than 0.5 phosphorus NEQ. Additional fertilizers must be applied in order to satisfy the nitrogen, potassium, calcium and sulfur requirements of crops.

Having taken into account the limiting nutrients, the highest possible fertilizer application rates were recorded for urine, sewage sludge and cattle and pig manure. The high water content of these four soil conditioners accounts for dilution of the nutrients and therefore it is possible to apply larger quantities of these more or less liquid fertilizers without causing over-fertilization.

As mentioned previously, the heavy metal concentrations in urine are low already and therefore the risk of incorporation into struvite particles is accordingly small. In fact, Ronteltap et al. (2007b) have provided evidence that struvite precipitation from human urine yields an environmentally safe product which is almost free from micro-pollutants. Their research showed that more than 98% of the hormones and pharmaceuticals remained in solution and that only a fraction of the already low amounts of heavy metals in urine are incorporated into struvite. Our research has confirmed that urine-derived struvite is a non-hazardous and efficient fertilizer which adds insignificant amounts of hazardous substances to the environment.



## 5. Conclusions

In this study, a selection of six urine-derived struvite fertilizers was assessed for their composition and their effectiveness as phosphorus sources for plants. We showed that the technology used for precipitating struvite from stored urine had no major impact on the composition of the final product. The only trend we observed was a positive correlation between magnesium dosing rates and magnesium concentration in the final product. The comparison of struvite produced from urine collected in Europe (Germany) and Asia (Vietnam) did not reveal a significant dietary effect. We recommend harvesting the sludge from urine storage tanks as it represents a supply of struvite which is produced by spontaneous precipitation. The test materials were evaluated in a greenhouse experiment. The urine fertilizers induced biomass yields and phosphorus uptakes similar or significantly higher than those generated by a commercial mineral fertilizer. Overall, it can therefore be concluded that urine-derived struvite is a valuable phosphorus source for plants. The model-based environmental impact assessment proved that urine-derived struvite is a hygienically safe fertilizer, which contributes less to heavy metal inputs to agricultural land than other recycling products or commercial mineral and organic fertilizers. When combined with other soil conditioners, urine-derived struvite is an efficient fertilizer and covers the magnesium and more than half of the phosphorus demand of crops.

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## Concluding remarks and outlook

In this thesis, two different pilot technologies for recovering nutrients from source-separated urine were presented. They were set up in the Mekong Delta area of South Vietnam to assess their suitability for implementation in developing countries, and more specifically in areas close to agricultural zones where water and electricity provision are scarce and no sewage network exists.

The Yellow Water Treatment module presented in Chapter I efficiently removed 98% of the  $\text{PO}_4\text{-P}$  load and, depending on the settings, up to 94% of the N load of undiluted urine. A greenhouse experiment showed that the recovered struvite induced significantly higher biomass yields and phosphorus uptake rates in ryegrass and maize than a commercial mineral fertilizer. Furthermore, all measured heavy metal concentrations were below the threshold values given by the German Fertilizer Regulations and the German Sewage Sludge Regulations. One drawback of this technology is the fact that it still generates a waste stream after having removed the nutrients nitrogen and phosphorus. This waste stream may contain micro-pollutants such as hormones and pharmaceutical residues, and must be discharged into a sewer or transported to a wastewater treatment works. Also, the use of hazardous chemicals such as sodium hydroxide and sulfuric acid is not recommended in developing countries due to additional costs and handling risks. Investment, operational and maintenance costs were high and the operation relied on competent engineering skills, a reliable energy supply and access to chemical substances. Given that the Yellow Water Treatment module produced a safe and efficient fertilizer, its operation in industrialized countries is absolutely recommended. Since the trend towards urban agriculture is becoming increasingly popular, this technology could one day be used in urban settings to collect the urine of the ever increasing number of city dwellers with the aim of closing nutrient cycles within city boundaries.

By means of operating the solar still presented in Chapter II, it was possible to convert the solids dissolved in 50 L undiluted human urine to 360 g of solid material by mere exposure to direct sunlight for 26 days. The photoreactor was constructed of materials available at local hardware dealers and the operation did not require much expertise or maintenance efforts. This evaporative technology did not generate a waste stream, thus meaning that all components of human urine were incorporated in the end product. Hence, this treatment method did not only recover nitrogen and phosphorus, but also significant amounts of salts such as sodium and chloride. This could lead to soil salinisation when applying the urine fertilizer repeatedly. After a single application to ryegrass and maize in a pot experiment, the agronomic efficiency of the urine-derived fertilizer was comparable to that of a commercial mineral fertilizer used as reference. Further research is required in order to determine whether solar radiation may be an appropriate hygienization method for degrading pathogens and micro-pollutants. The major drawback of this treatment option was the loss of almost one third of the urine nitrogen given the high pH and temperature during operation. It was shown that nitrogen losses

could be minimized by acidifying the urine prior to treatment, or by absorbing the gaseous ammonia in sulfuric acid after treatment. However, as mentioned earlier, this practice is not recommended in developing countries because of additional costs and handling risks.

In Chapter III, a selection of six urine-derived struvite fertilizers was assessed for their composition and their effectiveness as phosphorus sources for plants. A greenhouse experiment showed that urine-derived struvite is a valuable phosphorus source for plants, irrespective of the technology used to recover the magnesium ammonium phosphate fertilizer. Additionally, a model-based environmental impact assessment proved that urine-derived struvite is a hygienically safe fertilizer, which contributes less to heavy metal inputs to agricultural land than other recycling products or commercial mineral and organic fertilizers do. Since struvite only covers the magnesium and more than half of the phosphorus demand of crops, the application of additional fertilizers (e.g. nitrogen, potassium, sulfur, micro-nutrients) is necessary.

Overall, it can be concluded that new alternative sanitation systems can neither directly nor immediately replace the existing infrastructure in the western world. They could, however, be an option for remote or rural settlements that are not connected to a sewer system, or for ecological villages and National Parks. In Europe, waterless urinals are often installed in motorway service stations and during large public events such as music festivals. This is done primarily for saving water and energy costs, or as a consequence of lacking access to water and sewage networks. Unfortunately, the “Yellow Water” collected by these waterless urinals is not treated yet. Commercialization of the novel treatment technologies requires further research and development in order to automate and refine the treatment processes. In the developing world, ecological sanitation solutions could drastically improve the lives of people that are living in extreme poverty. In rural areas or urban slums for example, clean and affordable toilets that are operated without water and connection to a sewer system could largely improve people’s health. In this case, research should focus on stimulating the demand for safe sanitation, identifying the approaches that are accepted and work best under a given setting, while at the same time scaling up the most effective technologies.

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