Wood Ash as a Magnesium Source for Phosphorus Recovery from Source-Separated Urine

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ABSTRACT

Struvite precipitation is a simple technology for phosphorus recovery from source-separated urine. However, production costs can be high if expensive magnesium salts are used as precipitants. Therefore, waste products can be interesting alternatives to industrially-produced magnesium salts. We investigated the technical and financial feasibility of wood ash as a magnesium source in India. In batch experiments with source-separated urine, we could precipitate 99% of the phosphate with a magnesium dosage of 2.7 mol Mg mol P^{-1}. The availability of the magnesium from the wood ash used in our experiment was only about 50% but this could be increased by burning the wood at temperatures well above 600°C. Depending on the wood ash used, the precipitate can contain high concentrations of heavy metals. This could be problematic if the precipitate were used as fertilizer depending on the applicable fertilizer regulations. The financial study revealed that wood ash is considerably cheaper than industrially-produced magnesium sources and even cheaper than bittern. However, the solid precipitated with wood ash is not pure struvite. Due to the high calcite and the low phosphorus content (3%), the precipitate would be better used as a phosphorus-enhanced conditioner for acidic soils. The estimated fertilizer value of the precipitate was actually slightly lower than for wood ash, because 60% of the potassium dissolved into solution during precipitation and was not present in the final product. From a financial point of view and due to the high heavy metal content, wood ash is not a very suitable precipitant for struvite production. Phosphate precipitation from urine with wood ash can be useful if (1) a strong need for a soil conditioner that also contains phosphate exists, (2) potassium is abundant in the soil and (3) no other cheap precipitant, such as bittern or magnesium oxide, is available.

1. INTRODUCTION

Separating human urine at the source is an effective method of reducing nutrient loads in wastewaters and the subsequent treatment that they require (Larsen et al., 2001). Due to the high nutrient content, human urine can be used directly as a liquid fertilizer (Sridevi et al., 2009). However, factors such as the high transportation costs needed to move urine from urban areas to agricultural lands (Jönsson et al., 1998), social taboos and possible health risks associated with the direct application of urine to crops (Höglund et al., 2002) are drawbacks of direct urine application. Struvite precipitation is a simple and well-tested recovery method for phosphorus, the most important nutrient in urine besides nitrogen (Larsen and Gujer, 1996). By adding a magnesium source, struvite (magnesium ammonium phosphate hexahydrate, MAP, $MgNH_4PO_4 \cdot 6H_2O$) can easily be precipitated (Etter et al. 2011). If a pure magnesium salt is used, the struvite produced is virtually free of organic micropollutants and contains only small amounts of heavy metals (Ronteltap et al., 2007). Most of the pathogens, which might be precipitated with struvite, can be killed during drying at ambient temperatures (Decrey et al. 2011).

The chemical composition of source-separated ureolyzed urine is optimal for the recovery of struvite: the high pH value (in the range of 8 to 9) means that no base has to be added and the only compound missing for immediate struvite precipitation is magnesium (Udert et al., 2003a). Magnesium sources such as magnesium chloride ($MgCl_2 \cdot 6H_2O$), magnesium sulfate ($MgSO_4 \cdot 7H_2O$) and magnesium oxide (periclase, MgO) are typical sources used for struvite precipitation from wastewater (Demirer et al., 2005). However, the costs for industrially produced magnesium salts are high. An alternative can be magnesium-containing waste products such as bittern (Etter et al., 2011).

Wood ash is another interesting low-cost magnesium source. A similar product, fly ash from coal combustion, has been shown to be effective for the removal of phosphate from wastewaters (Kuziemska, 1980; Cheung and Venkitachalam, 2000). Fly ash contains compounds like alumina, silica, ferric oxide, calcium oxide, magnesium oxide and carbon (Ahmaruzzaman, 2010). Phosphate removal from wastewaters by fly ash was found to be dominated by hydroxylapatite precipitation (Johansson and Gustafsson, 2000). Wood ash is used directly in agriculture as a soil conditioner: it can be used to abate soil acidification and to fertilize agricultural and forest lands (Demeyer et al., 2001). To our

***Table 1** Comparison of the measured wood ash properties and literature values.*

	Our study		Olanders and Steenari (1995) [1]	Etiegni and Campbell (1991) [2]	Etiegni et al. (1991a) [3]
	Average	St.dev.			
	[g·kg^{-1}]	[g·kg^{-1}]	[g·kg^{-1}]	[g·kg^{-1}]	[g·kg^{-1}]
Calcium	274	9	226	187	303
Potassium	74.6	3.0	47.4	111	40.9
Magnesium	34.2	1.1	15.8	59.7	22.6
Manganese	19.3	1.2	-	10.5	6.68
Phosphate	16.6	1.5	-	17.0	14.4
Sulfate-S	12.3	3.9	-	-	4.56
Aluminum	10.8	0.6	20.8	10.4	23.0
Iron	6.09	0.57	23.7	8.80	19.9
Sodium	5.16	0.59	6.2	2.96	3.8
Zinc	2.67	0.16	2.7	2.68	0.709
Chromium	1.29	0.13	-	0.052	0.0805
Copper	1.05	0.11	-	0.345	0.148
Lead	0.596	0.023	-	0.051	0.133
Nickel	0.049	0.005	-	0.059	0.0430
Cadmium	0.028	0.003	0.06	<0.002	0.0153
Nitrogen	< 0.7	-	-	-	0.6

[1] Coniferous wood, 60% bark/40% wood chips, burnt at 500°C

[2] Lodgepole pine sawdust burnt at 538°C

[3] Wood chips, wood residue, bark. Furnace temperature not given.

knowledge, there is no scientific literature regarding the use of wood ash to remove phosphate from wastewater.

The goal of this research was to determine first, if wood ash could be used as a source of magnesium in the precipitation of phosphate from source-separated urine and second, to determine if it was a financially feasible replacement for more conventional magnesium sources. To address the first question, we conducted two experiments: A dissolution experiment was conducted to determine the properties of the urine solution as wood ash dissolved in the absence of phosphorus. In a subsequent precipitation experiment, wood ash was dosed into urine to determine the properties of the resultant precipitates. For the financial feasibility, we calculated the costs for wood ash and other magnesium sources available in India, such as bittern, MgO, MgCl$_2$·6H$_2$O and MgSO$_4$·7H$_2$O and compared them with the hypothetical financial value of struvite which was calculated based on current fertilizer prices in India.

2. MATERIALS AND METHODS

2.1. Wood ash

The wood ash used was collected from a residential fireplace in Switzerland. All visible unburned carbon particles were removed before use. To determine the chemical composition, various amounts of wood ash (25.5 mg, 32.3 mg, 50 mg, 52.5 mg, 100.3 mg, 113.7 mg) were digested in a mixture of 2 mL 65% nitrous acid, 1 mL 35% hydrogen peroxide and 47

mL distilled water and microwaved for 30 minutes and then analyzed using a wet chemical method (see 2.7 Wet chemical analysis). The chemical composition of the wood ash is given in Table 1. Average and standard deviation values were calculated from 5 measurements except for sulfate, where only 2 measurements were available.

2.2. Urine

Fully ureolyzed stored urine with a pH value of around 8.8 (Table 2) was collected from a storage tank that receives urine from men's NoMix toilets and waterless urinals in the Eawag main building (Forum Chriesbach) in Dübendorf, Switzerland. Phosphate-depleted urine was prepared by

***Table 2** Measured urine composition*

	Phosphate depleted ureolyzed urine [mg·L^{-1}]	Ureolyzed Urine [mg·L^{-1}]
Total phosphate-P	4.88	187
Magnesium	48.6	1.77
Total ammonia-N	2510	2720
Chloride	3000	2980
Sulfate	576	709
Calcium	23.6	17.7
Potassium	1350	1330
Sodium	1730	1670
pH [-]	8.51	8.77
El. conductivity [mS·cm^{-1}]	25.8	25.0

Table 3 *Overview of equations added to the basic PHREEQC database "wateq4f.dat". The data were taken from other PHREEQC databases or from the literature.*

Mineral	Equation	logK	Source
Struvite	$MgNH_4PO_4 \cdot 6H_2O$ (s) $\leftrightarrow$ $Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O$	-13.15	Taylor et al. (1963)
Potassium struvite	$MgKPO_4 \cdot 6H_2O$ (s) $\leftrightarrow$ $Mg^{2+} + K^+ + PO_4^{3-} + 6H_2O$	-10.62	Taylor et al. (1963)
Magnesium oxide (periclase)	MgO (s) $+ 2H^+ \leftrightarrow$ $Mg^{2+} + H_2O$	21.5841	minteq.v4.dat
Lime	CaO (s) $+ 2H^+ \leftrightarrow$ $Ca^{2+} + H_2O$	32.797	minteq.dat
Fairchildite	$K_2Ca(CO_3)_2$ (s) $\leftrightarrow$ $2 K^+ + Ca^{2+} + 2 CO_3^{2-}$	-8.0	unvalidated calculation (see text)
Acetate	several complexation and acid-base equations	-	minteq.dat

precipitating struvite with $MgCl_2 \cdot 6H_2O$. After dosing the magnesium source at a magnesium to phosphorus ratio of 1.1 mol Mg·mol P^{-1}, the urine was mixed for 15 minutes using a magnetic stirrer and then left overnight to react. The next day, the precipitated struvite was removed with coffee filters.

2.3. Reactor setup

A one-liter, double-walled glass reactor was used for both, the dissolution and the precipitation experiments. The solution was stirred magnetically to form a small vortex. The temperature of the solution was kept constant at 25±1 °C. The experiment time started when the wood ash was added to the urine solution.

2.4. Thermal stability measurements

The thermal stability of the solid residues of a spiked nitrified urine sample, a commercial ammonium nitrate fertilizer (27 % nitrogen, Landor, Birsfelden, Switzerland) and pure ammonium nitrate (Catalogue number 1.01188.1000, pro analysi, Merck, Darmstadt, Germany) was compared with differential scanning colorimetry (DSC). The measurements were carried out on a HP DSC827e (Mettler Toledo, Greifensee, Switzerland) under argon atmosphere at ambient pressure. The temperature range was 25 - 500 °C and the heating rate 4 °C·min^{-1}. To homogenize the samples, the dry solids were milled and sieved. The diameter of the final particles was smaller than 100 μm. About 1 mg of these particles was placed in gold coated crucibles (M20, Swissi, Basel, Switzerland) and compacted with a closing force of at least 4 kN. The measured power curves were integrated with the integral tangential method implemented in the STARe Software Version 8.10 (Mettler Toledo, Greifensee, Switzerland).

2.5. Precipitation experiment

The wood ash dosage was calculated based on literature values. We assumed that both magnesium and calcium reacted with phosphate in urine. According to Udert et al. (2003b) magnesium and calcium precipitate in source-sepa-

rated urine as struvite ($MgNH_4PO_4 \cdot 6H_2O$) and octacalcium phosphate ($Ca_8H_2(PO_4)_6 \cdot 5H_2O$). Values for the water-soluble fraction of magnesium (8.4 gMg·kgTSS^{-1}) and calcium (14.5 gCa·kgTSS^{-1}) in wood ash were taken from Khanna et al. (1994). Assuming a phosphate concentration of 190 mgP·L^{-1} and targeting a molar ratio of 1.5 mol (Mg+Ca)·mol P^{-1}, 11.4 g of wood ash was dosed in the experiments. The precipitation experiment lasted for 4 hours and the sampling interval was 30 minutes.

2.6. Sample preparation

Samples were immediately filtered with 0.45 μm filter cartridges (Macherey-Nagel, Düren, Germany). Approximately 4 mL of the sample were added to a prepared vial filled with 7.5 mL of 0.1 mol·L^{-1} HNO$_3$ and 2.5 mL of ultra pure water. The exact amount of the added sample was determined by comparing the weight of the vials before and after sample addition. All samples were stored at 4°C prior to analysis.

2.7. Wet chemical analysis

Ammonia was analyzed photometrically with flow injection analysis (Application Note 5520, FOSS, Hillerød, Denmark). Phosphate, chloride and sulfate were determined with ion chromatography (IC 881 Compact IC pro, Metrohm, Zofingen, Switzerland). All cations except for ammonium were analyzed with an inductively coupled plasma-optical emission spectrometer (ICP-OES, Ciros, Spectro Analytical Instruments, Kleve, Germany). The standard deviation of the wet chemical measurements was 5% or lower. Temperature, pH, and electrical conductivity were measured with electrodes (WTW, Weilheim, Germany).

2.8. X-ray diffractometry

X-ray diffraction analysis of the wood ash and the precipitate from the precipitation experiment was done with an X'Pert PRO diffractometer (PANalytical B.V., Almelo, The Netherlands) using Cu Kα radiation (45 kV and 40 mA). The minerals were identified with the software HighScorePlus 2.2 provided by PANalytical.

2.9. Computer simulations

The computer program PHREEQC Interactive (Version 2.15.0, Parkhurst and Appelo 1999) was used to calculate the theoretical concentrations in thermodynamic equilibrium between dissolved compounds and mineral phases. We used the database "wateq4f.dat" included in the PHREEQC package and extended the database with equilibrium constants for acetate complexation, the acid dissociation constant for acetic acid, and solubility constants for some relevant minerals (Table 3). Since we did not find any constant for the solubility product of fairchildite, we estimated the constant from enthalpy and entropy data given by Navrotsky et al. (1997). The calculation is given in the supplementary information. The resulting constant logK = -8.0 is not validated, but it confirms the general observation that fairchildite is highly soluble (Milton and Axelrod, 1947). Solid-solution equilibria were considered for the following minerals: anhydrite ($CaSO_4$), aragonite ($CaCO_3$), brucite ($Mg(OH)_2$), calcite ($CaCO_3$), epsomite ($MgSO_4 \cdot 7H_2O$), fairchildite

Table 4 *Retail prices of common fertilizers in the Indian state Tamil Nadu in September 2011. All prices from Agrisnet (2011) except magnesium sulfate (authors' own market survey)*

Type of fertilizers used for analysis	Retail price		Number of samples
	Average	St.dev.	
	[INR·kg^{-1}]	[INR·kg^{-1}]	[-]
N:P:K (10:26:26)	12.40	1.1	3
N:P:K (12:32:16)	11.60	2.2	4
N:P:K (14:28:14)	13.30	-	1
N:P:K (14:35:14)	13.50	-	1
N:P:K (15:15:15)	9.10	-	1
N:P:K (16:16:16)	7.40	-	1
N:P (20:20:0)	10.40	1.0	5
N:P (28:28:0)	14.44	-	1
N:P:S (20:20:0:13)	9.3	1.3	8
Monoammonium phosphate	10.4	-	1
Diammonium phosphate	13.4	1.5	7
Ammonium Sulfate	9.1	-	1
Magnesium Sulfate	10.6	-	1
Triple superphosphate	8.4	-	1
Muriate of Potash	6.0	1.2	7

($K_2Ca(CO_3)_2$), gypsum ($CaSO_4·2H_2O$), halite (NaCl), hydroxylapatite ($Ca_5(PO_4)_3OH$), lime (CaO), mirabilite ($Na_2SO_4·10H_2O$), nahcolite ($NaHCO_3$), natron ($Na_2CO_3·10H_2O$), nesquehonite ($MgCO_3·3H_2O$), periclase (MgO), portlandite ($Ca(OH)_2$), potassium struvite ($MgKPO_4·6H_2O$), struvite ($MgNH_4PO_4·6H_2O$), thenardite ($Na_2CO_3·H_2O$), thermonatrite ($Na_2CO_3·H_2O$), trona ($NaHCO_3.Na_2CO_3·2H_2O$). Nesquehonite was chosen as the only magnesium carbonate because it was found to precipitate in source-separated urine at elevated pH values (Hug and Udert, 2011).

2.10. Financial Analysis

In order to assess the financial feasibility of struvite production in India, we collected prices for various fertilizers in the state of Tamil Nadu in September 2011 (Table 4). Urea was not included, because its price is fixed by the Indian government. The financial value of nitrogen, phosphorus, potassium, magnesium and sulfur was estimated by linear regression, using the method of Tilley et al. (2009) and shown in Equation 1. All prices are expressed in the national currency, Indian Rupees (INR). In September 2011, 100 INR were approximately 1.50 EUR.

$$\text{Retail Price} = FV_N·i_N + FV_P·i_P + FV_K·i_K + FV_{Mg}·i_{Mg} + FV_S·i_S$$
$$[\text{INR·kg}^{-1}]$$
$$\text{Equation 1}$$

where i_X [kg$_X$·kg^{-1}] is the content of the nutrient in the fertilizer and FV_X [INR·kg$_X^{-1}$] is the fitted financial value of the respective nutrient. To calculate the financial value of struvite as a fertilizer, we used the constants FV_X and multiplied them with the nutrient concentrations of struvite, which are 57 g$_N$·kg$_{struvite}^{-1}$, 12.6 g$_P$·kg$_{struvite}^{-1}$ and 99 g$_{Mg}$·kg$_{struvite}^{-1}$.

In a second step, we calculated the input costs for producing struvite based on the market prices of different magnesium sources in India and the average transportation cost from the place of their availability (see Table 10). In the transport calculation we used a typical price for short distance transport (500 INR to transport 1000 kg over 50 km on a mini-truck). We also used this value to calculate the cost per kilometer for distances longer than 50 km, which is a conservative approach, because long distance transport usually has a lower per km price. A 50 km distance was assumed for short distance transport and 2000 km as the maximum distance of any place in India from the sea. The magnesium content and the product price used in Table 10 were given by the supplier Advance Inorganics, New Delhi (July 2011). We assumed that bittern and wood ash would be provided for free, because they are waste products.

The dosage ratios for magnesium chloride and magnesium sulfate (1.1 mol Mg mol P^{-1}) were chosen in accordance with Etter et al. (2011). The magnesium oxide dosage (1.5 mol Mg mol P^{-1}) was based on Antonini et al. (2009). The magnesium content of bittern and wood ash was measured in our laboratory. The bittern was provided by the Jakhau Salt Company (India). The dosage ratios for bittern (1.1 mol Mg mol P^{-1}) and wood ash (1.9 mol Mg mol P^{-1}) were assumed based on Etter et al. (2011) and our own work, respectively. We have not included the costs for reactor operation in this analysis, because they can vary significantly depending on the type and operation of the reactor used. In Nepal, raw magnesite rock that was calcined on-site was found to be an inexpensive magnesium source (Etter et al., 2011); however, since its feasibility strongly depends on local availability, it was not included in our analysis.

The financial value for wood ash and ureolyzed urine was based on the compositions given in Table 1 and Table 3, respectively. We assumed that the ureolyzed urine had a density of 1 kg·L^{-1}. The composition of the precipitate was taken from the PHREEQC simulations (Table 7).

3. RESULTS

3.1. Release of magnesium, calcium and potassium from wood ash

Figure 1 depicts the concentrations of magnesium, calcium and phosphate during the dissolution and the precipitation experiments. The concentration of ammonium, sodium, chloride and sulfate are not shown, because they changed by less than 15% in both experiments.
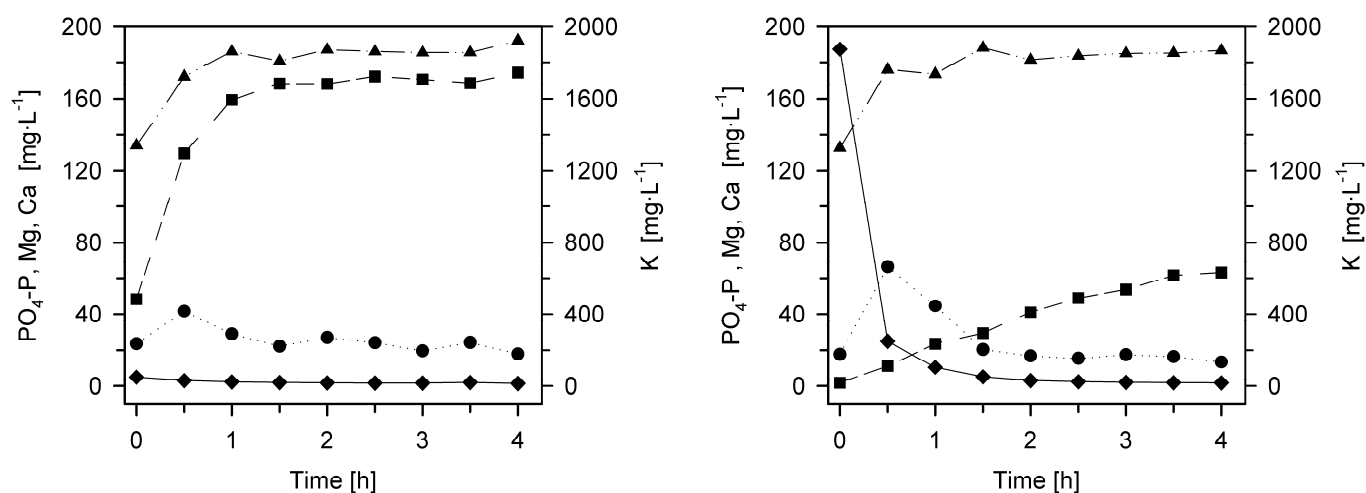
Figure 1 *Concentrations of phosphate (♦), magnesium (■), calcium (●) and potassium (▲) during dissolution of wood ash in phosphate-depleted, ureolyzed urine (left) and untreated ureolyzed urine (right).*

3.1.1. pH value

In both experiments, the pH increased significantly. In the dissolution experiment, the pH increased from 8.51 to 9.17 after the wood ash had been added. In the precipitation experiment, the initial pH value was higher (8.77), but the final pH value was in a similar range as in the dissolution experiment (9.21).

3.1.2. Phosphate

The urine in the dissolution experiment contained a small amount of phosphate (4.88 $mgP \cdot L^{-1}$), and this amount was further reduced to 1.39 $mgP \cdot L^{-1}$. In the precipitation experiment, 87% of the initial phosphate (187 $mgP \cdot L^{-1}$) was removed after 0.5 h; after 1.5 h, 97% was removed and the final removal was 99% after 4 hours.

3.1.3. Magnesium

In the dissolution experiment, the magnesium concentration

Table 5 *Major mineral compounds in wood ash and the recovered solids after precipitation. The order of minerals reflects their abundance.*

Wood ash		Solids after precipitation	
Name	Formula	Name	Formula
Calcite	$CaCO_3$	Calcite	$CaCO_3$
Quartz	SiO_2	Quartz	SiO_2
Lime	CaO	Struvite	$MgNH_4PO_4\ 6\ H_2O$
Periclase	MgO	Magnesian calcite	$(Mg_{0.129}Ca_{0.871})CO_3$
Bassanite	$CaSO_4 \cdot 0.5H_2O$		
Fairchildite	$K_2Ca(CO_3)_2$		

increased from 48.5 $mg \cdot L^{-1}$ to 174 $mg \cdot L^{-1}$. This increase cor-

responded to 32 % of the initial magnesium content in wood ash. In the precipitation experiment, the dissolved magnesium concentration increased steadily from an initial concentration of 1.77 $mg \cdot L^{-1}$ to a final concentration of 63.1 $mg \cdot L^{-1}$. This increase accounted for 16% of the wood ash magnesium. Assuming that phosphate precipitated as struvite, 37% of the magnesium in wood ash was used up for struvite precipitation. Dissolved and precipitated magnesium accounted for 53 % of the magnesium in wood ash. The total magnesium release from wood ash in the precipitation experiment was therefore considerably higher than in the dissolution experiment (32%).

3.1.4. Calcium

Calcium behaved similarly in both experiments. Starting at a concentration of 23.6 $mg \cdot L^{-1}$ in the dissolution experiment and 17.7 $mg \cdot L^{-1}$ in the precipitation experiment, a maximum peak was reached after about 0.5 h (41.5 $mg \cdot L^{-1}$ and 66.2 $mg \cdot L^{-1}$, respectively). The final concentration (17.9 $mg \cdot L^{-1}$ and 13.4 $mg \cdot L^{-1}$, respectively) was only slightly lower than the initial.

3.1.5. Potassium

Potassium behaved nearly identically in both experiments. Starting at a concentration of 1350 $mg \cdot L^{-1}$ in the dissolution experiment and 1330 $mg \cdot L^{-1}$ in the precipitation experiment, potassium reached the maximum concentration after 1 h (1860 $mg \cdot L^{-1}$ and 1850 $mg \cdot L^{-1}$, respectively). This increases corresponded to 60% and 61%, respectively, of the potassium, which was added in the form of wood ash.

3.2. XRD analysis

The wood ash and the precipitate from the precipitation experiment were analyzed with XRD analysis. The x-ray diffractograms showed that both the wood ash and the precipitate consisted of various crystalline phases, which

Table 6 *Settings for the PHREEQC simulations*

Compound	Setting
General urine composition	Table 1
Total inorganic carbon	100 mmol·L^{-1}
Acetate	Charge balance
Periclase (MgO)	Magnesium released in precipitation exp.: 8.5 mmol·L^{-1}
Fairchildite (K$_2$Ca(CO$_3$)$_2$)	Potassium released in both exp.: 6.7 mmol·L^{-1}
Sum of lime (CaO) and calcite (CaCO$_3$)	77.7 mmol L^{-1}

could not all be identified. The major phases identified are presented in Table 5***Table*** , in order of their abundance.

Calcite and quartz are the main compounds in wood ash and in the precipitate. The other minerals found initially in wood ash were not detected after precipitation. Periclase (magnesium oxide) was the only magnesium compound detected. Another mineral oxide, lime, was also prominent. Both compounds cause a pH increase when they dissolve in water or urine. Fairchildite was the only potassium compound found with XRD analysis. The abundance of bassanite was low. We did not consider it in our later discussion, because it probably constituted only small amounts of the total calcium in wood ash and its dissolution had little influence on the pH value. After precipitation, struvite and magnesian calcite were the two mineral phases identified besides calcite and quartz. No potassium compound was detected. Although they were likely present, the amounts of potassium compounds were probably low and could not be detected.

3.3. Computer simulations and further calculations

We used simulations to better understand how different precipitation and dissolution processes influence the concentrations in the dissolution and in the precipitation experiment.

The simulation input was based on the measurement results (Table 6). We assumed that all magnesium and all potassium was released by the dissolution of periclase and fairchildite. The XRD measurement did not allow us to quantify the fraction of calcite and lime. However, lime dissolution increases the pH value, so we fitted the lime fraction to the measured pH value. Since total inorganic carbon and organic anions have a strong influence on the buffer capacity, we added both compounds to the simulation according to literature values (Udert and Wächter, 2011). Acetate was used to represent organic anions and it was also used for the charge balance.

The fitted amount of initial lime was similar in both experiments (Table 7). On a molar basis, nearly half of the calcium was present as lime. The simulated magnesium and potassium concentrations fitted the measured values well. This was to be expected for potassium, because the potassium concentrations were only governed by the dissolution of fairchildite, but not by any precipitation process. However, the dissolved concentration of magnesium was determined by several processes: it was released by the dissolution of magnesium oxide and precipitated either as struvite or as nesquehonite (MgCO$_3$·3 H$_2$O). The latter only occurred in the dissolution experiment. The simulated phosphate and calcium concentrations were both substantially lower than the measurements.

Assuming that 99% of the phosphate was removed and no heavy metals were dissolved, we calculated the composition of the solid product based on the phosphorus content (Table 8). The resulting heavy metal concentrations were significantly higher than in common phosphorus fertilizers, which were analyzed in a study in Chile (Molina et al., 2009). Additionally, we calculated the total solid concentration, assuming that the amounts of lime, periclase and fairchildite given in Table 7 dissolved and struvite and calcite precipitated according to our simulations (Table 7). The resulting concentration of the total solids was 12.9 g·L^{-1}, which is higher than the amount of wood ash initially dosed (11.4 g·L^{-1}). Including the

Table 7 *PHREEQC simulation results and measurement results at t = 4 h*

		Phosphate depleted ureolyzed urine		Ureolyzed Urine	
		Simulated	Measured	Simulated	Measured
pH	[-]	9.17	9.17	9.22	9.21
Initial lime	[mmol·L^{-1}]	36	-	29	-
Initial calcite	[mmol·L^{-1}]	35	-	42	-
Initial fairchildite	[mmol·L^{-1}]	6.7	-	6.7	-
Final lime	[mmol·L^{-1}]	0.0	-	0.0	-
Final calcite	[mmol·L^{-1}]	78.3	-	78.1	-
Final fairchildite	[mmol·L^{-1}]	0	-	0	-
Final struvite	[mmol·L^{-1}]	0.15	-	6.0	-
Final nesquehonite	[mmol·L^{-1}]	3.25	-	0.0	-
Magnesium	[mg·L^{-1}]	173	174	61.9	63.1
Potassium	[mg·L^{-1}]	1870	1920	1852	1870
Calcium	[mg·L^{-1}]	0.47	17.9	0.40	13.4
Total phosphate	[mg·L^{-1}]	0.32	1.39	0.56	1.73

Table 8 *Estimated heavy metal content of the phosphorus fertilizer produced in our experiment compared to average heavy metal contents of common phosphorus fertilizers (Molina et al. 2009)*

| | Our product | | Molina et al. (2009) | | |
| | Average | Stdev. | Triple superphosphate | Monoammonium phosphate | Diammonium phosphate |
	[$g \cdot kgP^{-1}$]	[$g \cdot kgP^{-1}$]	[$g \cdot kgP^{-1}$]	[$g \cdot kgP^{-1}$]	[$g \cdot kgP^{-1}$]
Cadmium	0.850	0.090	0.140	0.019	0.020
Chromium	39.2	4.6	3.08	0.38	0.44
Copper	31.9	3.7	0.366	0.011	0.018
Nickel	1.49	0.17	0.052	0.022	0.028
Lead	18.1	1.2	0.080	0.026	0.046
Zinc	81.2	6.4	2.92	0.29	0.21

phosphorus in the wood ash, the total suspended solid concentration with respect to phosphorus was 34.4 $gTSS \cdot gP^{-1}$, which is 4.4 times higher than for pure struvite (7.9 $gTSS \cdot gP^{-1}$). The nutrient content of the simulated precipitate was 26 $gMg \cdot kgTSS^{-1}$, 25 $gK \cdot kgTSS^{-1}$, 7 $gN \cdot kgTSS^{-1}$, 29 $gP \cdot kgTSS^{-1}$ and 11 $gS \cdot kgTSS^{-1}$.

3.4. Financial value of struvite and wood ash as fertilizers in India

Using the model described in Section 2.8 (Financial Analysis), we found that the fitted values for the market price for nitrogen, phosphorus, potassium, magnesium and sulfur were good (coefficient of determination R^2 of 0.986). Based on theses values (Table 9), we calculated the hypothetical market price of struvite fertilizer for India to be 16.8 $INR \cdot kg^{-1}$. This value does not consider that the Government of India supports the fertilizer industry with Nutrient Based Subsidies (NBS) (Goyal, 2011), and therefore does not represent the overall financial value of struvite. Hypothetically, the struvite producer is also eligible for NBS. Accordingly, we estimated the maximum revenue that a producer of struvite fertilizer could obtain by including the NBS in the calculation of the financial value of struvite. In this way, the financial value of struvite increases by 34% to a value of 22.4 $INR \cdot kg^{-1}$. Table 9 shows the financial value of wood ash and the precipitate (see section 3.3 for the simulated composition of the precipitate). Wood ash already has a considerably high financial nutrient value (5.17 $INR \cdot kg^{-1}$) without precipitating phosphate. The nutrient value of the precipitate is even slightly lower (4.86 $INR \cdot kg^{-1}$) due to the loss of potassium and the increased amount of valueless solids. The actual market value of both the wood ash and the precipitate could be substantially higher, if the value of calcite, a common soil conditioner for acidic soils, was considered as well.

Finally, the financial value for ureolyzed urine is substantially lower than for struvite, wood ash or the precipitate, which is due to the high water content.

3.5. Costs of magnesium sources in India

The input costs calculated for struvite production with commercially available magnesium salts, bittern and wood ash are given in Table 10 and Table 11. The comparison of the

overall input costs shows that wood ash costs the least (up to a maximum of 2.8 INR·kg struvite^{-1}). Struvite production costs with commercially available salts (magnesium chloride 14.4 INR·kg struvite^{-1}, magnesium sulfate 18.6 INR·kg struvite^{-1} and magnesium oxide 11.9 INR·kg struvite^{-1}) are at least 4 times higher than with wood ash. The cost of bittern strongly depends on the transport distance. Close to the sea, bittern is competitive with wood ash (0.5 INR·kg struvite^{-1}), but further inland the costs can be even higher than commercial magnesium salts (21.4 INR·kg struvite^{-1}).

4. DISCUSSION

4.1. Available magnesium and calcium

The magnesium contained in the wood ash is not completely available for struvite precipitation. However, the magnesium availability was higher than what had been expected from the dissolution experiment. Our computer simulations showed that the likely reason is the precipitation of magnesium carbonate (e.g. nesquehonite, $MgCO_3 \cdot 3H_2O$) at high pH values. Formation of nesquehonite has also been observed by Hug and Udert (2011) during electrochemical magnesium disso-

Table 9 *Financial values of nutrients, struvite, wood ash, the precipitate and ureolyzed urine. The market values are based on retail prices in Tamil Nadu (Table 4) and the Nutrient Bases Subsidies NBS are given by Goyal (2011).*

| | Financial market value | Nutrient Based Subsidy | Overall financial value incl. NBS |
	[$INR \cdot kg^{-1}$]	[$INR \cdot kg^{-1}$]	[$INR \cdot kg^{-1}$]
Nitrogen	32.43	27.153	59.59
Phosphorus (P)	40.17	32.338	72.51
Potassium (K)	13.82	26.756	40.57
Magnesium Mg	99.54	-	99.54
Sulfur S	5.73	1.677	7.41
Struvite	16.79	-	22.42
Wood ash	5.17	-	7.73
Precipitate	4.28	-	6.07
Ureolyzed urine	0.12	-	0.23

Table 10 *Estimated struvite production costs using industrial grade magnesium salts in India.*

	Magnesium Chloride	Magnesium Sulfate	Magnesium Oxide
Chemical formula	$MgCl_2 \cdot 6H_2O$	$MgSO_4 \cdot 7H_2O$	MgO
Magnesium content [g·kg^{-1}]	117	96.6	508
Common dosage [mol Mg·mol P^{-1}]	1.1	1.1	1.5
Required input [kg·kg Struvite^{-1}]	0.93	1.13	0.29
Product price [INR·kg^{-1}]	15	16	40
Transport distance [km]	50	50	50
Transport cost [INR·kg^{-1}·km^{-1}]	0.01	0.01	0.01
Total input cost [INR·kg^{-1}]	15.5	16.5	40.5
Total input cost [INR·kg Struvite^{-1}]	14.4	18.6	11.8

lution. In the latter process, high pH values occur close to the electrode and trigger nesquehonite precipitation. In our study, the high pH values were caused by the dissolution of lime (CaO). We estimated the amount of lime with computer simulations by fitting the measured pH values. The two calculated amounts of lime (36 mmol·L^{-1} in the dissolution experiment, 29 mmol·L^{-1} in the precipitation experiment) are similar, but they differ by approximately 20%. The difference can be explained by measurement uncertainties of the urine composition, or by processes that have an effect on the pH value, but which have not been considered in the simulation. One example of a pH increasing process is the volatilization of ammonia. According to the simulations, the moles of lime (CaO) were almost the same as the moles of calcite ($CaCO_3$) present in the wood ash. Since calcite has a higher molecular mass, it was probably more abundant in the results of the XRD analysis.

In the precipitation experiment, wood ash released much more magnesium than what was expected from the dissolution experiment. We therefore conclude that the dosage ratio could be reduced significantly. If the dissolved magnesium in the precipitation experiment (63 mg·L^{-1}) is considered to be available for struvite precipitation, the wood ash dosage could be reduced from 11.4 g L^{-1} (dosage ratio 2.7 mol Mg mol P^{-1}) to 8.1 g L^{-1} (dosage ratio 1.9 mol Mg mol P^{-1}). The corrected dosage ratio is close to 1.5 mol Mg mol P^{-1}, a ratio commonly used for struvite production from urine with magnesium oxide (Etter et al. 2011).

4.2. Increasing the solubility of magnesium and calcium

The high calcite content ($CaCO_3$) indicates that the wood was burnt at low temperatures. This is to be expected from a residential fireplace. Other researchers showed that the furnace temperature strongly influences the composition of the wood ash. Olanders and Steenari (1995) used XRD to analyze wood ash samples that had been burnt at temperatures between 400 °C and 1150 °C. For temperatures of 650 °C and below, $CaCO_3$ and SiO_2 were the most abundant phases. $K_2Ca(CO_3)_2$ (fairchildite) occurred as well but no MgO was found. At temperatures of 700 °C and above, CaO was the predominant crystalline phase. MgO first occurred at 700 °C and became the second most abundant phase at temperatures above 700 °C, while $K_2Ca(CO_3)_2$ and SiO_2 could not be detected anymore. Similar results were reported by Misra et al. (1993).

The studies of Olanders and Steenari (1995) and Misra et al. (1993) suggest that at increasing temperatures MgO is formed from other magnesium minerals, possibly magnesium carbonates. Since MgO dissolves well in source-separated urine, we hypothesize that wood ash produced at high furnace temperatures (700°C or above) would be a better magnesium source than the wood ash that we used in our study. To produce such wood ash, more sophisticated furnaces, for example brick kilns (UN Habitat 1993), would be needed. The costs for such wood ash could be substantially higher than for wood ash from a conventional wood stove or fireplace.

4.3. Struvite is the phosphate precipitation product

The XRD measurements and the computer simulations confirmed that struvite was the main phosphate compound produced during the precipitation experiment. Calcium phosphate compounds such as hydroxylapatite ($Ca_5(PO_4)_3OH$) or octacalcium phosphate ($Ca_8H_2(PO_4)_6 \cdot 5H_2O$) were not found, but it is likely that they were formed at least in small amounts as transient compounds due to the release of calcium during lime (CaO) dissolution (Udert et al. 2003b). Another phosphate compound reported to occur in phosphate removal from source-separated urine is potassium struvite ($MgKPO_4 \cdot 6H_2O$) (Wilsenach et al., 2007). Although potassium was released during wood ash dissolution, the potassium concentrations were too low to trigger potassium struvite formation: the

Table 11 *Estimated struvite production costs using bittern and wood ash.*

		Bittern	Wood ash
Magnesium form		dissolved Mg^{2+} ions	solid MgO
Measured magnesium content [g·kg^{-1}]		102	34.2
Common dosage	[mol Mg·mol P^{-1}]	1.1	1.9
Required input	[kg·kg Struvite^{-1}]	1.07	5.50
Product price	[INR·kg^{-1}]	0	0
Transport distance	[km]	50 to 2000	0 to 50
Transport cost	[INR·kg^{-1}·km^{-1}]	0.01	0.01
Total input cost	[INR·kg^{-1}]	0.5 to 20.0	0 to 0.5
Total input cost	[INR·kg Struvite^{-1}]	0.53 to 21.4	0 to 2.75

compound was found neither in the X-ray diffractograms nor in the computer simulations.

4.4. Potassium is lost to the solution

Wood ash has been shown to be a good source of potassium in agricultural soils (Demeyer et al. 2001). Therefore, the substantial release of potassium to the urine solution has some important implications for the quality of the solid product. By using wood ash for phosphate recovery, the easily dissolvable potassium is lost to the bulk solution. It is not clear however, whether the lower availability of potassium impedes the use of the precipitate as a fertilizer: in experiments with wood ash, Etiegni et al. (1991b) showed that the high availability of potassium in wood ash reduced the growth of bush beans. Therefore, lower potassium availability might actually be an advantage of the precipitate over wood ash. However, this is merely an assumption based on literature. To determine the actual fertilizer value of the precipitate, detailed agricultural experiments with various soils and crops are needed.

4.5. Heavy metals

The wood ash used in our experiments contained higher amounts of heavy metals than other wood ash samples (Table 1) and especially phosphorus fertilizers (Table 8). The high content could be due to the uncontrolled wood ash production in a residential fireplace. The other wood ash samples shown in Table 1 were taken from large facilities or laboratory reactors. In the long term, the content of heavy metals determines the applicability of any fertilizer made with wood ash. Cadmium especially, has received considerable attention by researchers and legislators due to its high concentration in phosphorus fertilizers (Molina et al. 2009). Several countries have imposed maximum cadmium limits on phosphorus fertilizers. According to Molina et al. (2009), the standards range from 0.035 $gCd \cdot kgP^{-1}$ in The Netherlands to 0.34 $gCd \cdot kgP^{-1}$ in Japan. The estimated cadmium content of our product is 2.5 times higher than the highest standard. However, the high cadmium content might not be a problem for all wood ash. Our sample contained rather high amounts of heavy metals. Etiegni and Campbell (1991), for example, found less than 0.002 $g \cdot kg^{-1}$ cadmium in wood ash (Table 1). Furthermore, burning the wood ash at higher temperatures (700 °C or above) will reduce the heavy metal content in the final precipitate: due to the higher availability of magnesium, less wood ash has to be dosed and therefore fewer heavy metals are added. The quality of the wood ash is therefore crucial for the sustainability of this kind of struvite production.

4.6. Total amount of precipitate

In contrast to other precipitants, wood ash does not only produce struvite but a mixture of various minerals. The amount solids produced (i.e. total solid per gram phosphorus) is therefore high. Based on our simulations, the TSS to phosphorus ratio is 34.4 $gTSS \cdot gP^{-1}$. This corresponds to a phosphorus content of 3%, which is about 4 times lower than in struvite (13%) and about 15 times lower than in di-ammonium phosphate (DAP, 46%). The phosphorus content is also only about 2 times higher than in the initial wood ash (1.7%). If wood ash from high temperature furnaces is used

as a precipitant, the phosphorus content in the final precipitate could be increased. However, it will still be much lower than in common phosphorus fertilizers. What phosphate precipitation with wood ash produces is more like an enhanced soil conditioner with phosphorus than a phosphorus fertilizer: wood ash and the precipitate contain high levels of alkaline minerals (calcite or lime), which can be used to ameliorate acidic soils.

4.7. Financial value of struvite

The calculated financial value of struvite in India is very similar to the value calculated by Tilley et al. (2009) for Nepal: based on fertilizer prices in Kathmandu the financial value was calculated to be 41 NPR kg^{-1}(Nepalese Rupees), which corresponds to 25 INR·kg^{-1} (assuming an exchange rate of 0.62 INR·NPR^{-1} in April 2011). This is higher than the financial value we calculated for India (16.8 INR kg^{-1}). The reasons for the difference can be high import costs in Nepal and the subsidies for the fertilizer industry in India. The financial value of struvite in India would be 22.4 INR kg^{-1}, if struvite producers received the same subsidies as the Indian fertilizer industry. This value is very close to the financial struvite value calculated for Nepal.

4.8. Financial comparison of magnesium sources

Wood ash is a considerably cheaper magnesium source than industrially produced magnesium salts. Even bittern is more expensive than wood ash if the struvite production site is far from the sea where bittern is produced. For all magnesium sources except magnesium sulfate, the chemical input costs to produce struvite are lower than the estimated financial value of the struvite produced. However, this calculation does not include all of the costs for reactor construction and operation, urine collection and struvite transport and marketing. Transport costs especially, can make struvite production from source-separated urine financially unfeasible (Etter et al. 2011). Struvite production from urine is most interesting if it can be combined with public endeavors to promote sanitation. Wood ash could be a well-suited magnesium source for use in remote villages where industrially produced chemicals are either not available or too expensive, due to transport and intermediary costs. However, our study shows that wood ash cannot be compared directly with other magnesium sources. The main disadvantages of wood ash are the low magnesium availability and the possibly high heavy metal content. By producing wood ash in high-temperature furnaces, the magnesium availability could probably be increased to 100%, but the costs for such a wood ash product would be substantially higher. Our study also shows that wood ash itself has a financial market value (5.17 INR·kg^{-1}), which is even higher than the financial market value of the precipitate produced in our experiments (4.28 INR·kg^{-1}). The reduction of the market value is due to the loss of potassium from wood ash during the precipitation process. The nutrient needs of the soils dictate whether or not it is worth it to produce a fertilizer in which much of the potassium is substituted for phosphate.

5. CONCLUSIONS

- Wood ash can be used to precipitate phosphate from urine in the form of struvite. The efficiency of wood ash as a precipitant depends on the furnace temperature during wood burning. To support the formation of MgO, the temperatures should be 700°C or above. The precipitate produced using wood ash is a mixture of various minerals, with calcite as a main compound. In our experiments, the final phosphorus content in the precipitate was only about 3%.
- Wood ash is considerably cheaper than industrially produced magnesium sources and, at inland locations, cheaper than bittern. However, the precipitate is rather a soil conditioner enhanced with phosphorus than a phosphorus fertilizer. Therefore, a direct comparison with magnesium sources that produce pure struvite is not possible.
- Depending on the composition of the wood ash, the precipitate can contain heavy metals, which exceed the limits for phosphorus fertilizers in many countries. The heavy metal content in the product can be reduced by a controlled wood ash production process.
- Due to the high heavy metal content and the low nutrient content of the precipitate, wood ash is not a very suitable precipitant for struvite production. The use of wood ash for struvite production might be sensible, if (1) a strong need for a soil conditioner that also contains phosphate exists, (2) potassium is abundant in the soil and (3) no other cheap precipitant, such as bittern or magnesium oxide, is available.

6. ACKNOWLEDGEMENTS

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**Wood ash as a magnesium source for phosphorus recovery from source-separated urine**

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SUPPLEMENTARY INFORMATION

Estimation of the solubility constant for fairchildite

Navrotsky et al. (1997) determined the enthalpy ΔH and the entropy ΔS for the formation of fairchildite ($K_2Ca(CO_3)_2$) from K_2CO_3 and $CaCO_3$ at 298 °C

$$K_2CO_3(s) + CaCO_3(s) \leftrightarrow K_2Ca(CO_3)_2(s)$$
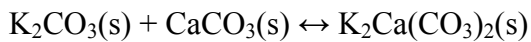
$$\Delta H = -38.7 \pm 3.2 \quad kJ \cdot mol^{-1}$$
$$\Delta S = 40.9 \pm 5.1 \quad J \cdot mol^{-1} \cdot K^{-1}$$

With these values the Gibbs free energy for the reaction can be calculated according to

$$\Delta G = \Delta H - T \cdot \Delta S$$
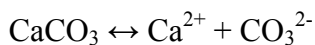
$$\Delta G = -17.3 \ kJ \cdot mol^{-1} \qquad \text{for } T = 298°C$$

The ratio of the solubilities (D) can be calculated as

$$D = e^{-\Delta G/R/T} \qquad \text{with } R = 8.314 \ J \cdot mol^{-1} \cdot K^{-1}$$

$$\log D = 3.0$$

For the calculation of the solubility constant for fairchildite we need the solubility constants for $CaCO_3$ (calcite) and K_2CO_3.
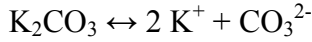
Solubility product of $CaCO_3$:

$$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$$

$$\log K_{sp,calcite} = -8.48 \qquad \text{Stumm and Morgan (1996)}$$

For K_2CO_3, a highly soluble salt, we have not found any solubility constant in the literature. As a first estimation, we calculate the solubility constant for K_2CO_3 with solubility data cited in Kamps et al. (2007)

$$8.1 \ mol \cdot kg_{water}^{-1} \qquad \text{at } 298°C$$

Due to the high solubility, the solution will have a very high ionic strength at equilibrium. At very high ionic strengths, the usual Davies approach cannot be used for calculating the ion activities. Instead we use the Pitzer approach in PHREEQC to calculate the ion activities of K^+ and CO_3^{2-} and obtain for dissolution of $8.1 \text{ mol·kg}_{water}^{-1}$

$$K_2CO_3 \leftrightarrow 2\,K^+ + CO_3^{2-}$$

$$\{K^+\} = \quad 20.6$$
$$\{CO_3^{2-}\} = \quad 8.31$$

Now, the solubility constant can be estimated with the ion activity product

$$K_{sp,K2CO3} = \{K^+\}^2 \cdot \{CO_3^{2-}\}$$

$$\log K_{sp,K2CO3} = 3.55$$

The solubility constant for fairchildite becomes

$$D = K_{sp,fairchildite} \cdot K_{sp,calcite} \cdot K_{sp,K2CO3} \cdot K_{sp,fairchildite}^{-1}$$

$$\log K_{sp,fairchildite} = \log K_{sp,calcite} + \log K_{sp,K2CO3} - \log D$$

$$\log K_{sp,fairchildite} = -8.0$$

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