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Drying fresh human urine in magnesium-doped alkaline substrates: Capture of free ammonia, inhibition of enzymatic urea hydrolysis & minimisation of chemical urea hydrolysis

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ABSTRACT

Recycling urine can reduce the flux of reactive nitrogen in the environment. This paper presents a novel approach to recover all N (N_{tot}) from urine, including ammonia (TAN; about 5% of N_{tot}), which is usually volatilised when alkalised urine is dehydrated. As analytical methods for measuring N have a standard deviation of at least 5%, real fresh urine was fortified with ammonia ($urine_N$) or ammonia and phosphate ($urine_{NP}$) so that TAN comprised 10% of N_{tot}. The urine was then added to different magnesium-based alkaline substrates (MgO, $Mg(OH)_2$, $MgCl_2$ + $Mg(OH)_2$) and dried at 38 ℃. Chemical speciation modelling suggested that, irrespective of the substrate, >98% of N_{tot} in $urine_{NP}$ was recovered and 86% of TAN was precipitated as struvite. Experimental results showed that < 90% of N_{tot} was recovered when $urine_{NP}$ was dried in MgO and $Mg(OH)_2$, suggesting that no TAN was captured. However, all phosphorus and potassium and 93% (±5%) of N_{tot} and 30% of TAN were recovered when $urine_{NP}$ was dried in $MgCl_2$ + $Mg(OH)_2$, as the [Mg]:[NH_4]:[PO_4] molar ratio of 1.69:1.14:1.0 in urine favoured formation of struvite. Overall, this study demonstrated that all ammonia excreted in real fresh urine (unfortified, TAN < 5% N_{tot}) can be captured if urine is dried in substrates containing 3.7 g $MgCl_2{\cdot}6H_2O$ L^{-1} or 2.2 g $MgSO_4$ L^{-1}, but no calcium. Ammonia can also be captured if fresh urine is saturated with MgO or $Mg(OH)_2$ with high reactivity (<60 s citric acid test). If the drying substrate has pH > 10 throughout the treatment, urease enzyme-catalysed degradation of urea to ammonia is prevented, resulting in complete recovery of all nutrients. The end-product is a solid fertiliser containing 10–11% nitrogen, 1–2% phosphorus and 2–3% potassium.

1. Introduction

The supply of reactive nitrogen (N) is vital for life on earth [1]. In nature, the largely unreactive dinitrogen gas (N_2) present in the atmosphere is transformed into reactive forms (NH_3, NH_4, HNO_3, NO, NO_2, N_2O etc.) through biological N fixation [2]. However, for every unit of biologically fixed reactive N, more than three units of reactive N are currently fixed by anthropogenic activities [3]. The Haber-Bosch process, where ammonia (NH_3) is synthesised from atmospheric N_2, is the main pathway for artificial reactive N fixation. This process alone accounts for 1–2% of the world's energy consumption [4] and supplies most of the N fertilisers applied in agriculture. The food produced using Haber-Bosch N is estimated to support nearly half the world's population [5].

The Haber-Bosch process is highly optimised, but subsequent use of N in agricultural systems is inefficient. Only 4–14% of the Haber-Bosch N applied as fertiliser ends up in the human body as consumed protein [6]. This is because N is usually lost due to leaching, surface and subsurface runoff, and volatilisation [3127]. When lost, reactive N accumulates and cascades in the environment [2], where it can contribute to eutrophication [8], acidification of soils and waters [9] and associated loss of biodiversity [10]. The current flux of reactive N from terrestrial to aquatic ecosystems greatly exceeds its so-called planetary-level safe space [11].

The adult human body does not retain consumed N, which is excreted mostly via the urine fraction as urea (>85%), ammonia (<5%) and other N-containing organic compounds [12,13 14]. In conventional

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Nomenclature

$urine_N$	fresh human urine fortified with ammonia
$urine_{NP}$	fresh human urine fortified with ammonia and phosphate
N_{tot}	total nitrogen
TAN	Total Ammonia Nitrogen
EC	Electrical Conductivity
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
TS	Total Solids
VS	Volatile Solids
WB	Wet Basis
$mass.cf_{WB}$	mass concentration factor
$mass.red_{WB}$	mass reduction factor
$h_{1/2}$	half-life

wastewater systems, human urine is mixed with brownwater and greywater and collected as a single fraction in sewers that transport it to a treatment plant or in septic tanks or pit latrines. Globally, however, it is estimated that 80% of the wastewater produced in the world receives no treatment [15]. According to estimates made by Simha [16] using data from FAO [17] and the method for estimating the nutrient content of urine developed by Jönsson and Vinnerås [18], approximately 32 Tg N y^{-1} and 2.5 Tg phosphorus (P) y^{-1} are excreted via urine globally. Therefore, when untreated, wastewater can be a major source of reactive N in the environment [19 20].

Over the past century, wastewater treatment plants have evolved and have improved the efficiency of removal of different pollutants [21]. However, only treatment plants that apply tertiary treatment, i.e. steps for biological removal of N and biological/chemical removal of P, can produce effluents with substantially reduced flux of N. At present, such treatment plants can remove > 90% of P but only 50–75% of the N load [2223]. During biological N removal, about 4% of the N load to a treatment plant is also converted to N_2O, a potent greenhouse gas [24]. Today, tertiary wastewater treatment is carried out only in high-income countries [25] and, over the coming decades, a dramatic increase in global tertiary treatment capacity is highly unlikely [1520]. According to Eurostat [26], only 54% of the population in the European Union (EU) was connected to wastewater treatment plants with tertiary treatment in 2017.

Treating human urine at a central wastewater treatment plant only converts reactive N into unreactive N_2 gas [27]. However, if urine is collected at source [28], separately from the rest of the wastewater, it can be treated to produce a fertiliser [29]. This, if applied in agriculture, would help recycle N in the food system [30]. Such recycling would not only reduce the flux of reactive N from poorly treated wastewater, but could also replace nearly 25% of the Haber-Bosch N produced globally [16]. Human urine can be collected using urinals [31] or urine-diverting toilets [32] and treated by different methods, many of which have been reviewed recently [333435]. One of the most practical and effective ways of treating the collected urine is by subjecting it to alkaline dehydration [363738]. In this process, fresh human urine is alkalised immediately after collection by adding it to an alkaline substrate, which prevents urease-catalysed degradation of urea [3940]. The alkalised urine is then dehydrated to produce a solid fertiliser with high nutrient content (>10% N, 1–2% P, 4–8% potassium (K) on a dry matter basis) [4137]. If urine is dehydrated without alkalisation, then majority of the N can be lost as ammonia, which is produced due to the hydrolysis of urea during the collection of urine [424344].

Previous work by our research group showed that > 95% of the N present in urine can be recovered during alkaline dehydration [4537]. Ammonia, which makes up about 5% of all N excreted in fresh urine according to Friedler et al. [12], is usually lost during alkaline dehydration [4647]. However, reducing the indoor and outdoor emissions of ammonia from a urine dryer is important to achieve the requirements described in the ISO30500 standards for non-sewered sanitation systems. One approach to capture the ammonia is to precipitate it as struvite (magnesium ammonium phosphate, $NH_4MgPO_4{\cdot}6H_2O$) before the urine is dried [46]. For this, the urine would have to be supplemented with Mg^{2+}, since a molar ratio of 1:1:1 for [Mg]:[NH_4]:[PO_4] is needed to form struvite [48], and in fresh urine this ratio is usually 0.1:1:0.98 [13]. This study tested the hypothesis that all N excreted in urine can be captured by combining struvite precipitation with alkaline dehydration.

2. Methodology

2.1. Urine

Fresh human urine from approximately 20 donors (male and female, aged 25–66 years) was collected every day in 0.5 L polyethylene flasks, and used in experiments on the same day. The donations were pooled, mixed and divided into two batches. To the first batch ($urine_N$), 1.45 g NH_4Cl L^{-1} (27.1 mmol L^{-1}) was added and to the second batch ($urine_{NP}$), 1.45 g NH_4Cl L^{-1} (27.1 mmol L^{-1}) and 3.6 g $NaH_2PO_4{\cdot}H_2O$ L^{-1} (26.1 mmol L^{-1}) were added. These additions were made to fortify the collected urine with ammonia ($urine_N$) or ammonia and phosphate ($urine_{NP}$). The total N (N_{tot}) concentration and total ammonia nitrogen (TAN) concentration in the collected urine was assumed to be 5 g L^{-1} (0.36 mol L^{-1}) and 0.25 g L^{-1} (17.9 mmol L^{-1}), respectively. Adding NH_4Cl increased the TAN concentration to approximately 10% of N_{tot} in both $urine_N$ and $urine_{NP}$. This was necessary because the objective of the study was to quantify the recovery of TAN and the analytical methods for measuring N had a standard deviation of at least 5%. It was also assumed that the total P concentration of the collected urine was 0.3 g L^{-1} (3.16 mmol L^{-1}) and that all was in the form of phosphate ions.

2.2. Drying substrates

Three different alkaline Mg-based drying substrates were tested, magnesium oxide (MgO), magnesium hydroxide ($Mg(OH)_2$) and a mixture of $Mg(OH)_2$ and magnesium chloride hexahydrate ($MgCl_2{\cdot}6H_2O$). The substrates were of reagent grade and used without any pre-treatment.

2.3. Experiment

2.3.1. Set-up

The drying experiment was performed in square Petri dishes (Sarstedt, Germany; dimensions 100 mm × 100 mm × 20 mm) placed on two stainless steel racks inside the cavity (470 mm × 330 mm × 580 mm) of a modified benchtop incubator (Electrolux, Sweden). A fan (⌀ 12′′, 2300 rpm, Biltema, Sweden) installed at the bottom of the cavity introduced and distributed air inside the incubator. A wireless temperature sensor (TGU-4500, Tinytag) was used to monitor the temperature and relative humidity in the cavity.

2.3.2. Procedure

At the start of the experiment, 10 g of either MgO or $Mg(OH)_2$ was placed inside each Petri dish. For the substrate that contained magnesium chloride, 3.2 g $MgCl_2{\cdot}6H_2O$ was added to 10 g $Mg(OH)_2$ in order to increase the concentration of Mg^{2+} in urine so that the molar ratio of [Mg]:[NH_4] was approximately 1:1 (or by weight 1.35:1). For each drying substrate, there were 14 Petri dishes in total. The Petri dishes were divided into two equal batches, so that each batch received either $urine_N$ or $urine_{NP}$.

To start the treatment, 10 mL of either $urine_N$ or $urine_{NP}$ were added to Petri dishes containing 10 g of the drying substrate. The dishes were

then covered with lids and set aside for 30 min at room temperature (20 ± 0.5 °C), after which the lids were removed and the Petri dishes were transferred to the incubator to treat the urine by alkaline dehydration. After a fixed time duration, the Petri dishes were withdrawn from the incubator to mark the end of a drying cycle. To dry 10 mL more urine and to start a new drying cycle, the entire process was repeated. In total, 60 drying cycles were performed, so that at the end of the experiment the Petri dishes treated 600 mL of urine using 10 g of substrate. For the majority of the cycles (n = 46), the drying time in the incubator was <3 h, whereas for the rest drying was done overnight.

2.4. Sampling and analysis

Fresh urine used in the experiments was monitored for pH using a pH meter (Fisher Scientific accumet AE150, United States) attached to an electrode (Fisher Scientific accumet, 13–620-AE6, United States). Electrical conductivity (EC) was measured using a handheld EC meter (Cond 340i, WTW, Germany) connected to a probe (TetraCon 325, WTW, Germany). To characterise the urine, representative samples of $urine_N$ and $urine_{NP}$ were taken before every drying cycle, acidified to pH < 2 using 1 M HCl and refrigerated at 4 ℃. For these samples, N_{tot} and TAN were analysed colorimetrically using Spectroquant® test kits (Merck KGaA, Darmstadt, Germany) and a photometer (NOVA 60 A, Merck KgaA, Germany). For N_{tot} analysis, the urine was diluted 1000-fold, digested using the Spectroquant® Crack-Set 20 test kit (114963) and analysed for nitrate concentration in the range 1–25 mg L^{-1} using the Spectroquant® nitrate test kit (109713). For TAN analysis, the fresh urine was diluted 10-fold and analysed using the Spectroquant® ammonium test kit (100683) in the concentration range 2–150 mg L^{-1}. To measure the concentration of P, (K), calcium (Ca) and Mg in urine, inductively coupled plasma-optical emission spectroscopy (ICP-OES) was performed using an Optima Avio 200 (PerkinElmer, USA) optical emission spectrometer.

The Petri dishes were sampled destructively as singlets at the end of the 12th, 24th, 36th and 48th drying cycles, and as triplicates at the end of the 60th drying cycle (Supplementary Information, Fig. S1). The weight of the dishes at the end of the drying cycles was measured using a weighing balance (Kern KB 2000–2NM, Germany; 0.01 g precision). The substrate and dried urine collected in the dishes were then thoroughly mixed and analysed for total solids (TS), volatile solids (VS), $pH_{1:10}$, $EC_{1:10}$ and elemental composition. To determine TS content, the samples were dried at 105 ℃ for 12 h. They were then combusted (LH30/12, Nabertherm GmBH, Germany) at 550 ℃ for 6 h to determine VS. To account for loss of urea due to heat degradation during the measurements, the TS content of urine was adjusted as described in Simha et al. [37]. The pH and EC were measured in 1:10 (w/v) suspensions of the substrate in deionised water. To prepare the suspensions, 2 g of thoroughly mixed solids collected from the Petri dishes were diluted with 20 mL deionised water, mixed and allowed to rest in closed tubes for 48 h prior to measurements. Total N (N_{tot}) and total C (C_{tot}) content were measured by the Dumas combustion method, using an elemental analyser (LECO TruMac® CN, USA). The P and K content were measured by optical emission spectrometry (Optima Avio 200, PerkinElmer, United States).

2.5. Citric acid reactivity test

To determine the reactivity of the MgO and $Mg(OH)_2$ used in the experiments, a standard test used in the lime industry was performed [49]. In brief, 2 g of MgO or $Mg(OH)_2$ were added to 100 mL of 0.4 N citric acid and shaken with phenolphthalein until the colour of the solution changed from white to pink. The time required to neutralise the acid was recorded and the substrates were classified as having high reactivity (<60 s), medium reactivity (60–300 s) or low reactivity (>300 s).

2.6. Calculations

To analyse the effectiveness of the treatment in concentrating the volume of urine volume on a wet basis (WB), mass concentration factor ($mass.cf_{WB}$; Eq. 1) and percentage mass reduction ($mass.red_{WB}$; Eq. 2) were calculated [46]:

$$mass.cf_{WB} = \left(\frac{m_{substrate} + m_{urine}}{m_{end-product}}\right) (1)$$

$$mass.red_{WB} = \left(\frac{m_{substrate} + m_{urine} - m_{end-product}}{m_{substrate} + m_{urine}}\right) \times 100 (2)$$

where $m_{substrate}$, m_{urine} and $m_{end\text{-}product}$ is weight of the drying substrate at the start of the experiment, the total urine added in the experiment and the end-product, respectively.

To calculate the recovery of N from urine in the experiments, mass balances were calculated. To estimate the theoretical recovery of N as urea, the half-life ($h_{1/2}$) of urea was first estimated, as suggested in Simha et al. [41]. Based on the average temperature of the incubator (37.6 ℃), the half-life of urea in the pH range 2–12 was calculated to be 369 days. Using this, the recovery of urea in each drying cycle was estimated as [37]:

$$urea.rec_i = (urea.add_i + urea.rec_{i-1}) \times \left(1 - \frac{t}{2 \times h_{\frac{1}{2}}}\right) (3)$$

where $urea.rec_i$ is the amount of urea recovered in drying cycle i, $urea.add_i$ is the amount of urea added during that cycle, $urea.rec_{i\text{-}1}$ is the urea recovered in the previous cycle and t is the time difference between the cycles.

2.7. Statistical analysis

All statistical analyses were performed using RStudio version 1.2.5042 and R version 4.0.0 [50]. One-way analysis of variance (ANOVA) was performed to test whether the three drying substrates differed significantly in terms of N recovery, elemental composition and physicochemical properties. If differences were found, Tukey's honest significant difference (HSD) post-hoc test was applied. Prior to these analyses, the Shapiro-Wilk test for normality was run and homogeneity of variance was checked using the Brown-Forsythe-Levene test.

2.8. Thermodynamic modelling of chemical speciation

The chemical speciation in urine was modelled using an OLI Stream Analyzer [51] and the Mixed Solvent Electrolyte (MSE) model option in the software. The features of interest were the solubility of the different Mg compounds in $urine_N$ and $urine_{NP}$, the pH of the alkalised urine, the distribution of different elements between the liquid and the solid phase, and the concentration of the different solids formed at equilibrium. These results were used to describe the theoretical recovery of TAN as struvite. To explain the change in pH during alkaline dehydration, the influence of increasing absorption of CO_2 concentration in urine dosed with the Mg compounds was also modelled. The urine composition shown in Table 1 was used as the model input.

3. Results

3.1. Nutrient recovery

The mass balance calculations revealed that between 79% and 99% of the N in urine was recovered after the dehydration treatment (Table 2). According to the estimated half-life of urea (369 days), only 1% of N_{tot} would have degraded into ammonia because of chemical hydrolysis of urea. The N recovery varied over the course of the drying cycles, but there was no obvious trend (Table 2). In the uninterrupted

Table 1
Composition of fresh urine fortified with ammonia ($urine_N$) or ammonia and phosphate ($urine_{NP}$) and other inputs used for modelling the chemical speciation.

Analysis	Units	$Urine_N$	$Urine_{NP}$
Total N	mg L^{-1}	6540	6353
Urea	mg L^{-1}	12,736	12,417
NH_4^+	mg L^{-1}	772	723
PO_4^{3-}	mg L^{-1}	1211	3276
Ca^{2+}	mg L^{-1}	104	104.0
K^+	mg L^{-1}	1050	1061
Na^+	mg L^{-1}	1596	2134
Mg	mg L^{-1}	77	89
SO_4^{2-}	mg L^{-1}	1014	978
Cl^- simulated	mg L^{-1}	3864	3827
pH	[-]	6.52	6.11
EC (mS/cm)	mS cm^{-1}	15.87	17.14
Temperature	°C	25	25

Table 2
Recovery of nitrogen (N, %) in the different magnesium-based drying substrates at different treatment loads (L urine kg^{-1} substrate) of fresh urine fortified with ammonia ($urine_N$) or ammonia and phosphate ($urine_{NP}$).

Substrate	Urine	12 L kg^{-1}	24 L kg^{-1}	36 L kg^{-1}	48 L kg^{-1}	60 L kg^{-1}
MgO	$Urine_N$	79	84	82	82	86 ± 3
	$Urine_{NP}$	79	88	88	84	89 ± 2^{ab}
$Mg(OH)_2$	$Urine_N$	83	83	86	85	86 ± 6
	$Urine_{NP}$	85	85	84	86	85 ± 2^b
$MgCl_2$ + Mg $(OH)_2$	$Urine_N$	78	93	85	87	85 ± 4
	$Urine_{NP}$	85	99	88	82	93 ± $5^{a,*}$

urine treatment involving 60 drying cycles, the average N recovery was between 85% and 93%.

Values are mean ± standard deviation (n = 3) at 60 L kg^{-1}.

Different letters (a,b) indicate significant difference (α = 0.05) in N recovery.

Nitrogen recovery was found to depend on both the type of the alkaline substrate used and the type of fresh urine ($urine_N$ and $urine_{NP}$) added to the substrate. When $urine_N$ was dried, the N recovery was similar in all three substrates ($p = 0.93$). However, the N recovery was significantly different ($p < 0.1$) between the substrates when $urine_{NP}$ was dried. The recovery of N was highest when $urine_{NP}$ was dried using $MgCl_2$ + $Mg(OH)_2$ and was significantly different from $Mg(OH)_2$, but similar to MgO. For the substrate containing a mixture of $MgCl_2$ and Mg $(OH)_2$, the N recovery was higher ($p < 0.1$) when $urine_{NP}$ was dried (93 ± 5%) than when $urine_N$ was dried (85 ± 4%). According to the mass balance (Supplementary Information, Fig. S2), there was complete recovery of K in all three substrates. There was complete recovery of P when urine was dried in $Mg(OH)_2$ + $MgCl_2$, but the P recovery was only 67–78% in MgO and 71–76% in $Mg(OH)_2$. This was probably due to inefficient extraction of P from the dried products during the analytical measurements, as P cannot have been lost during the drying treatment since it does not volatilise.

3.2. Elemental composition of products

The elemental composition of the products obtained at the end of the treatment was calculated as a percentage of their TS content (Table 3). On a wet weight basis, the fresh urine used in the experiments contained 0.6% N, 0.05–0.1% P and 0.1% K, while the drying substrates initially contained none of these elements. The N content of the substrates progressively increased as more urine was dried in the same Petri dish (Fig. 1). At the end of the treatment (60 L urine treated kg^{-1} substrate), the N content of $urine_{NP}$ dried in $Mg(OH)_2$ was 11.6%, which was significantly higher than for the other two substrates ($p < 0.05$). For the N content of the products to exceed 10% of their TS content, the minimum volume of urine that needed to be dried was 65 L kg^{-1} MgO, 48 L kg^{-1} $Mg(OH)_2$ and 54 L kg^{-1} $MgCl_2$ + $Mg(OH)_2$. There was no significant difference in the P content of the products when the same type of urine was dried in different substrates. However, for the same substrate, drying $urine_{NP}$ resulted in products with higher P content than drying $urine_N$. The average K content of the products was 2.2% and was similar for all products.

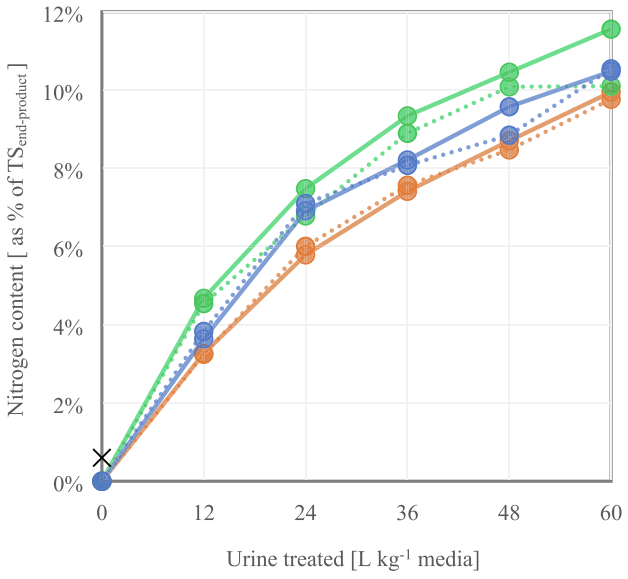

Fig. 1. Nitrogen (N) content (% of total solids, TS) of the products obtained by drying fresh human urine using three different alkaline substrates, MgO (●), Mg $(OH)_2$ (●) and $MgCl_2$ + $Mg(OH)_2$ (●). Solid lines represent fresh urine fortified with ammonia ($urine_N$), dashed lines represent fresh urine fortified with ammonia and phosphate ($urine_{NP}$). The N content of fresh untreated urine on a wet weight basis is also shown (×).

Table 3
Elemental composition (% of total solids, TS) of the products obtained after drying 60 L fresh urine fortified with ammonia ($urine_N$) and fresh urine fortified with ammonia and phosphate ($urine_{NP}$) per kg of the different magnesium-based drying substrates. The elemental composition of fresh untreated urine on a wet weight basis is also presented.

Element	Fresh Urine		MgO		$Mg(OH)_2$		$MgCl_2$ + $Mg(OH)_2$	
	$Urine_N$	$Urine_{NP}$	$Urine_N$	$Urine_{NP}$	$Urine_N$	$Urine_{NP}$	$Urine_N$	$Urine_{NP}$
N	0.64	0.64	9.9 (0.1)^{bc}	9.78 (0.4)^c	11.6 (0.6)^a	10.1 (0.2)^{ab}	10.5 (0.4)^{abc}	10.5 (0.5)^{abc}
P	0.05	0.11	0.5 (0.1)^c	1.9 (1.3)^{ab}	0.7 (0.1)^c	1.8 (0.2)^a	0.9 (0.3)^{bc}	1.9 (0.4)^a
K	0.1	0.1	1.9 (0.1)^a	2.6 (0.8)^a	2.1 (0.2)^a	2.1 (0.2)^a	2.5 (0.3)^a	2.1 (0.2)^a

Values are mean (standard deviation) for n = 3.
Within rows, values marked with different letters (a,b,c) are significantly different (α = 0.05).

3.3. Changes in physicochemical properties

The drying treatment was efficient in evaporating water and in reducing the volume of urine. Overall, the mass reduction was at least 90%, irrespective of the drying substrate used (Table 4). The calculated mass concentration factor varied between 16 and 25. The urine was most concentrated when it was dried using pure $Mg(OH)_2$, whereas it was least concentrated when it was dried using pure MgO. The mass concentration was always lower for $urine_{NP}$ than for $urine_N$. The total drying time for treating 600 mL of fresh urine at the average temperature achieved by the incubator (37.6 °C) was 11.5 d, which meant that an average drying rate of 5.3 kg urine m^{-2} d^{-1} was obtained. The drying rate did not differ significantly between the substrates ($p > 0.05$).

The pH and EC value was 6.5 ± 0.3 and 15 ± 2.0 mS cm^{-1}, respectively, in $urine_N$ and 6.1 ± 0.2 and 17.1 ± 2 mS cm^{-1}, respectively, in $urine_{NP}$. When $urine_N$ was added to MgO and $Mg(OH)_2$, a saturated solution with pH > 10 was formed at the start of the treatment (Fig. 2). However, when $urine_{NP}$ was added to these substrates, the initial pH was 9.8. When $urine_N$ or $urine_{NP}$ was added to $MgCl_2 + Mg(OH)_2$, the initial pH was only 9.6. During the course of the treatment, the pH of urine decreased in all three substrates. For MgO and $Mg(OH)_2$, the pH at the end of the treatment was significantly lower when treating $urine_{NP}$ ($p < 0.05$) than when treating $urine_N$. Even at this low pH, no enzymatic urea hydrolysis was observed, probably because no ureolytic bacteria entered the Petri dishes during the trials. In contrast to the pH, EC increased during the treatment, reflecting accumulation of urinary salts in the substrates. The substrate containing a mixture of $MgCl_2$ and $Mg(OH)_2$ was the most easily soluble in fresh urine and had the highest EC. The EC of the products after treating 60 L urine kg^{-1} substrate decreased in the order: $MgCl_2 + Mg(OH)_2 > Mg(OH)_2 > MgO$.

The citric acid reactivity test showed that the time required for MgO to neutralise the acid was 46 ± 5 s, indicating that it was highly reactive (<60 s), whereas the time required for $Mg(OH)_2$ was 448 ± 33 s, indicating that it had medium reactivity.

4. Discussion

4.1. Nutrient recovery

To recover all the nitrogen (N_{tot}) present in fresh urine, urea, TAN and nitrogen-containing organic compounds (other than urea) must be recovered. The boiling point of almost all the organic compounds (e.g. creatinine, uric acid, hippuric acid) excreted in urine is above 100 °C and they are more stable than urea [52]. Therefore, it can be assumed that they are not degraded during alkaline dehydration. In our previous studies on N recovery from urine [45413747], we focused primarily on recovering urea, since it accounts for > 80% of N_{tot} in fresh urine [1252]. We demonstrated that, to recover urea, it is necessary to inhibit enzymatic hydrolysis by alkalising fresh urine [4045] and to minimise chemical hydrolysis by optimising the urine dehydration rate [37]. A combination of these two processes results in > 90% recovery of N_{tot} [37], but TAN is usually lost when alkalised fresh human urine is dehydrated [46] because the vapour pressure of ammonia is higher than that of water. Therefore, the present study investigated the possibility of recovering all N excreted in alkalised urine (pH ≥ 10), including TAN.

Overall, 93% (±5%) of N_{tot} was recovered when fresh urine was dried in a mixture of magnesium chloride and hydroxide ($MgCl_2 + Mg(OH)_2$). In this substrate, after drying 24 L urine kg^{-1} substrate up to 99% of N_{tot} was recovered. All urine added in the drying experiments had around 10% of initial N_{tot} in the form of TAN, because it was fortified with ammonia. About 1% of the N_{tot} in urine was calculated to have transformed into TAN due to chemical hydrolysis of urea during the dehydration treatment (half-life of urea was 369 d, as drying temperature was 38 °C and total drying time was 11.5 d). Therefore, if there had been no TAN recovery during the treatment, <89% of N_{tot} would have been recovered. In other words, when the N_{tot} recovery was above > 89%, TAN was also captured (Table 2).

In struvite, the [Mg]:[NH_4]:[PO_4] molar ratio is 1:1:1 (or 1.35:1:5.26 by weight) [48]. In human urine, the formation of struvite is limited by Mg^{2+} since it is excreted in low concentrations [53]. The urine used in the present study contained<50 mg Mg L^{-1}. In $urine_N$, the average molar ratio of [Mg]:[NH_4]:[PO_4] was 0.08:1:0.3, whereas in $urine_{NP}$ the ratio was 0.08:1:0.8. This suggests that a maximum of 8% of TAN or < 1% of N_{tot} would eventually self-precipitate as struvite without external addition of Mg^{2+}. However, according to our chemical speciation modelling (Supplementary Information, Fig. S3), if the urine was saturated with $MgO/Mg(OH)_2$, about 26% of the TAN in $urine_N$ and 83% of the TAN in $urine_{NP}$ would precipitate as struvite. Mass balance calculations revealed that only 30% of TAN and 93% of N_{tot} was recovered from $urine_{NP}$, and only when treating it using a mixture of $MgCl_2$ and $Mg(OH)_2$. No TAN was recovered from $urine_N$, as the maximum N_{tot} recovery from this urine was 86%.

In $urine_N$, the initial phosphate concentration was relatively low and 30% of the P precipitated as hydroxylapatite ($Ca_5(PO_4)_3(OH)$). In $urine_{NP}$, which was fortified with phosphate, only 11% of the P was removed as hydroxylapatite (Supplementary Information, Fig. S3). According to thermodynamic modelling, the solubility of MgO in $urine_N$ and $urine_{NP}$ at 25 °C was 0.95 g L^{-1} and 1.5 g L^{-1}, respectively, whereas the corresponding $Mg(OH)_2$ solubility was 1.2 g L^{-1} and 1.9 g L^{-1}, respectively. Therefore, if $urine_N$ were saturated with these compounds, its molar ratio of [NH_4]:[Mg] would vary between 1.8 (MgO) and 2.1 ($Mg(OH)_2$), and struvite formation would be limited by Mg^{2+}. In $urine_{NP}$, the molar ratio would vary between 1.1 (MgO) and 1.2 ($Mg(OH)_2$). In a recent follow-up experiment, we observed that 10–60 min of continuous mixing may be required to saturate fresh urine with MgO or $Mg(OH)_2$ [54]. In the present study, fresh urine was added, but not mixed, with the two substrates and left undisturbed for 30 min before it was dried. In combination, these findings suggest that MgO and $Mg(OH)_2$ alone could not capture all the TAN present in $urine_N$ and $urine_{NP}$. In contrast, $MgCl_2{\cdot}6H_2O$ readily and completely dissolves when added to urine [55]. The molar ratio of [Mg]:[NH_4]:[PO_4] in $urine_N$ after being added to $Mg(OH)_2 + MgCl_2$ was 3.5:3.3:1.0, whereas the molar ratio in

Table 4
Mass reduction ($mass.red_{WB}$; %) and mass concentration factor ($mass.cf_{WB}$) obtained by drying fresh urine fortified with ammonia ($urine_N$) and fresh urine fortified with ammonia and phosphate ($urine_{NP}$) in the different magnesium-based substrates at different treatment loads (L urine kg^{-1} substrate).

Parameter	Urine treated [L kg^{-1} substrate]	MgO		$Mg(OH)_2$		$MgCl_2 + Mg(OH)_2$	
		$Urine_N$	$Urine_{NP}$	$Urine_N$	$Urine_{NP}$	$Urine_N$	$Urine_{NP}$
$mass.red_{WB}$	12	87.2	86.8	90.4	90.2	87.9	87.8
	24	92.1	91.8	93.8	93.6	92.6	92.4
	36	94.0	93.6	95.1	94.9	94.4	94.1
	48	94.8	94.2	95.7	94.8	94.8	94.7
	60	95.0	93.9	96.0	95.5	95.5	95.1
$mass.cf_{WB}$	12	7.8	7.6	10.5	10.2	8.3	8.2
	24	12.6	12.1	16.2	15.6	13.6	13.1
	36	16.6	15.7	20.6	19.7	18.0	17.0
	48	19.3	17.3	23.3	19.1	20.8	19.0
	60	19.8	16.3	25.1	22.2	22.2	20.3

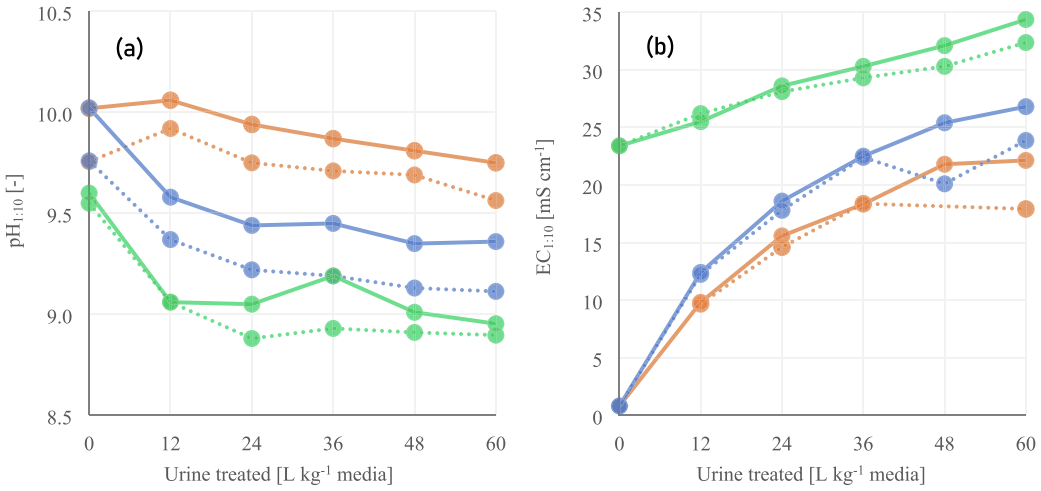

Fig. 2. (a) $pH_{1:10}$ and (b) $EC_{1:10}$ of the products obtained when fresh urine fortified with ammonia ($urine_N$, solid lines) and fresh urine fortified with ammonia and phosphate ($urine_{NP}$, dashed lines) was dried using MgO (●), $Mg(OH)_2$ (●) and $MgCl_2 + Mg(OH)_2$ (●).

$urine_{NP}$ was 1.69:1.14:1.0. Therefore, the only instance where capture of TAN and formation of struvite was largely unhindered was when $urine_{NP}$ was dried in the substrate containing $MgCl_2$ (Table 5).

Completely recovering the TAN present in fresh urine during alkaline dehydration is not straightforward, largely because of the speciation of ammonia in urine. In fresh urine (pH < 7), all the ammonia is in dissolved form, as TAN ($NH_4^+ + NH_{3(aq)}$) (Fig. 3). Alkalising the urine with KOH or $Ca(OH)_2$ shifts the ammonia equilibrium from NH_4^+ towards $NH_{3(g)}$. For instance, at 25 °C, if urine is alkalised with KOH (pH > 12) or saturated with $Ca(OH)_2$, 80% of the initial TAN is converted to $NH_{3(g)}$, which can be lost when the urine is dehydrated. In contrast, when urine is saturated with $MgO/Mg(OH)_2$ at 25 °C, the ammonia equilibrium irreversibly shifts away from $NH_{3(g)}$ as 83% of the initial TAN is precipitated in the form of struvite (Fig. 3). Increasing the temperature of urine saturated with $MgO/Mg(OH)_2$ has little effect on the speciation of ammonia or on the amount of struvite formed (or TAN captured). However, increasing the temperature reduces the solubility of $MgO/Mg(OH)_2$, which in turn reduces the pH of saturated urine from > 10 at 20 °C to 9.1 at 50 °C (Fig. 4).

4.2. Alkaline urine stabilisation

Another finding in this study was that none of the Mg-based drying compounds could maintain their initially high pH of 10, which is crucial for inhibiting enzyme-catalysed hydrolysis of urea. The pH drop was due to absorption of $CO_{2(g)}$ by urine during the drying treatment and carbonation of $Mg(OH)_2$, which resulted in formation of $MgCO_3$. The Ca present in fresh urine also precipitated as $CaCO_3$. However, there was poor agreement between the model-predicted drop in pH (Supplementary Information, Fig. S4) due to increasing CO_2 concentration in urine and the pH drop recorded in the experiments. When water removal was integrated into the model (to simulate the drying process) at a fixed $CO_{2(aq)}$ dosage of 400 mg L^{-1} urine, the pH drop was more in line with experimental observations (Supplementary Information, Fig. S5).

Table 5
Molar ratio of [Mg]:[NH_4]:[PO_4] in drying fresh urine fortified with ammonia ($urine_N$) and fresh urine fortified with ammonia and phosphate ($urine_{NP}$) when saturated with different magnesium compounds.

Substrate	$Urine_N$	$Urine_{NP}$
MgO	1.8 : 3.3 : 1.0	1.05 : 1.14 : 1.0
$Mg(OH)_2$	1.5 : 3.3 : 1.0	0.94 : 1.14 : 1.0
$MgCl_2 + Mg(OH)_2$	3.5 : 3.3 : 1.0	1.69 : 1.14 : 1.0

However, further research is needed to determine the dynamic change in pH during alkaline dehydration and how the drying conditions (e.g. airflow rate, temperature, humidity, substrate type) affect the absorption of CO_2. Preventing absorption of CO_2 by the urine/substrate is difficult, as this is a natural recarbonation reaction, and a drop in pH during alkaline dehydration must be anticipated.

It was observed that MgO and $Mg(OH)_2$ displayed differences in alkalinity, even though MgO hydrates to $Mg(OH)_2$ on dissolution in urine. Results of the citric acid reactivity test showed that MgO was highly reactive (<60 s), whereas $Mg(OH)_2$ showed medium reactivity. This suggests that the compounds were probably calcined at different temperatures. Calcination affects the reactivity and solubility of Mg compounds [49], and consequently also the pH of urine when it is saturated. Therefore when alkalising urine to prevent enzymatic urea hydrolysis, only high reactivity MgO or $Mg(OH)_2$ should be used. To measure reactivity, a simple test using citric acid can be performed, as described by van der Merwe and Strydom [56]. We did not perform the reactivity test for the substrate $MgCl_2 + Mg(OH)_2$, since $MgCl_2{\cdot}6H_2O$ is a neutral salt and the citric acid test measures the acid neutralising capacity of a substrate.

The substrate containing a mixture of $Mg(OH)_2$ and $MgCl_2$ performed best in terms of N recovery, but experienced the largest drop in pH. Thus, if $MgCl_2$ or $MgSO_4$ is used as part of the drying substrate for recovering TAN, it should be mixed with highly reactive MgO or some other Ca-free alkalising agent. Lastly, it must be noted that the pH of urine saturated with $MgO/Mg(OH)_2$ decreases with temperature (Fig. 4) and drops to < 10 above 30 °C. While this does not affect the recovery of TAN, it can increase the risk of microbial ureolysis, since the inactivation of urease by $Mg(OH)_2$ is reversible [57]. Therefore, a urine drying system that uses $Mg(OH)_2$ for alkalisation must operate between 20 and 30 °C to reduce the risk of ureolysis and capture all N_{tot}.

4.3. Implications for technology implementation

The results obtained in this study have many implications for the future implementation of alkaline urine dehydration technology. First, it was demonstrated that by doping an alkaline substrate with available Mg^{2+}, N could be completely recovered during the dehydration treatment. The fresh urine used in the experiments originally had < 3% N_{tot} as TAN and [Mg]:[NH_4]:[PO_4] ratio of 0.17:1:0.7. The TAN and phosphate concentration were artificially increased by preparing $urine_N$ and $urine_{NP}$, because the analytical procedures for measuring N have a standard deviation of at least 5% and quantifying TAN recovery would otherwise be difficult [58]. In real (non-fortified) fresh human urine,

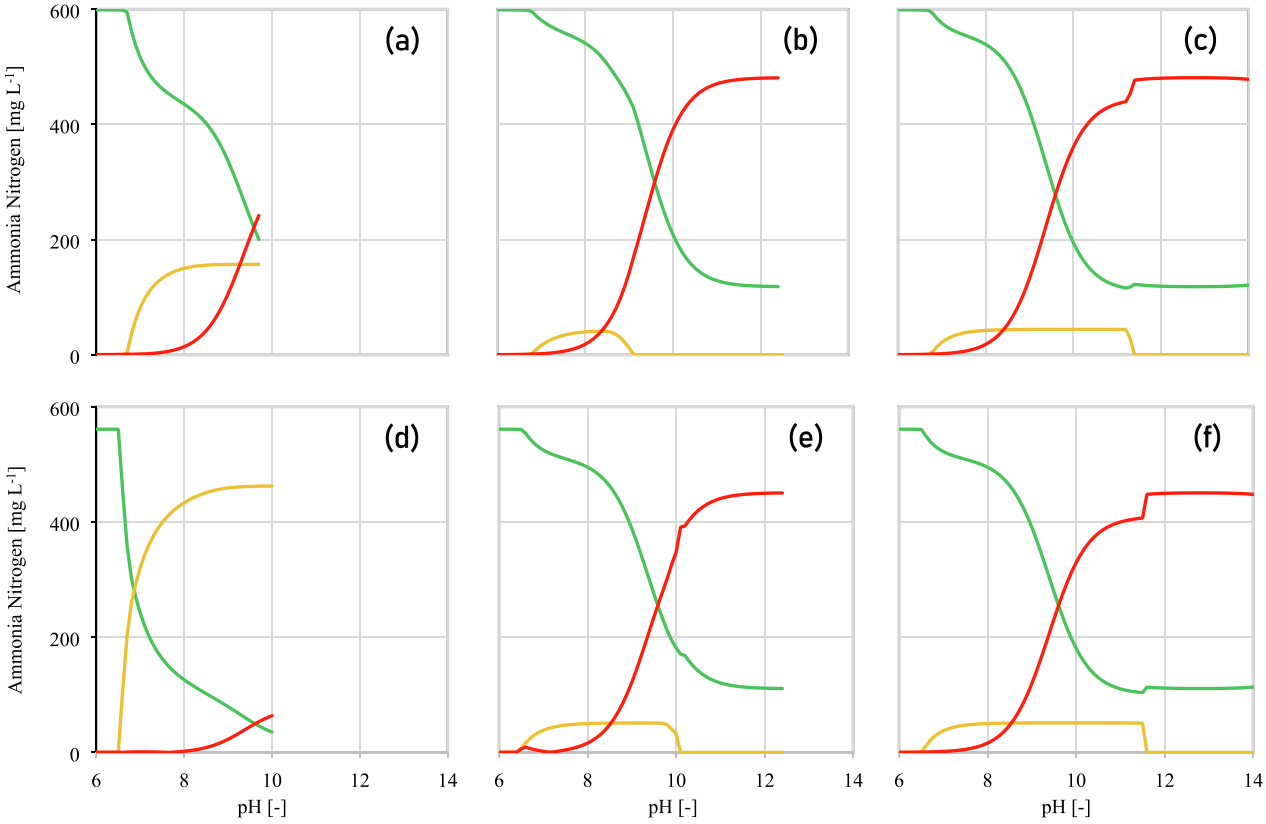

Fig. 3. Distribution of ammonia nitrogen between aqueous (green), solid (yellow) and gaseous (red) phases at 25 °C when fresh urine fortified with ammonia ($urine_N$) is saturated with (a) $MgO/Mg(OH)_2$, (b) $Ca(OH)_2$ and (c) KOH and when fresh urine fortified with ammonia and phosphate ($urine_{NP}$) is saturated with (d) $MgO/Mg(OH)_2$, (e) $Ca(OH)_2$ and (f) KOH. The pH of urine saturated with $Mg(OH)_2$, $Ca(OH)_2$ and KOH is approximately 10, 12.5 and 14, respectively, at 25 °C. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

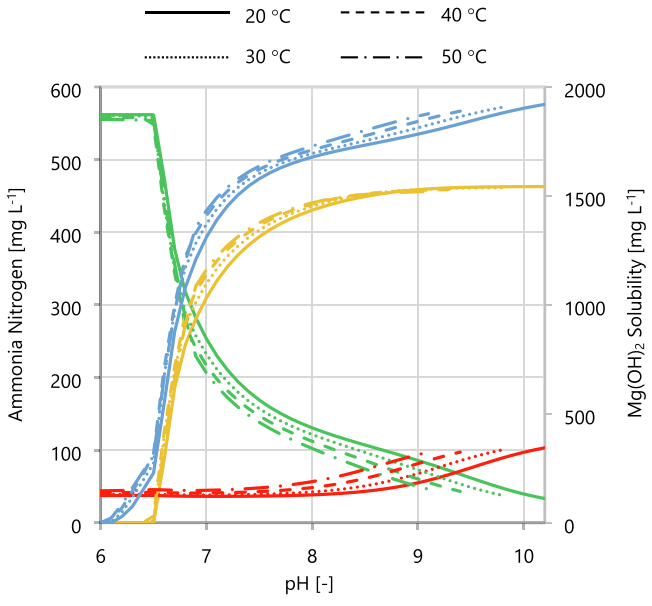

Fig. 4. Distribution of ammonia nitrogen (mg L^{-1}) between aqueous (green), solid (yellow) and gaseous (red) phases at different temperatures when fresh urine fortified with ammonia and phosphate ($urine_{NP}$) is saturated with $MgO/Mg(OH)_2$. The solubility of $Mg(OH)_2$ (blue) at the different temperatures and pH values is also shown. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

phosphate ions would not limit the capture of TAN as struvite, which was the case for $urine_N$. Assuming that real fresh urine contains 5% N_{tot} as TAN, then adding either 3.7 g $MgCl_2{\cdot}6H_2O$ L^{-1} or 2.2 g $MgSO_4$ L^{-1} urine would provide enough Mg^{2+} to precipitate all the phosphate and TAN in urine as struvite, leading to complete N_{tot} recovery when the urine is dried. In contrast, TAN capture by MgO and $Mg(OH)_2$ depends on their solubility in urine, which can vary considerably depending on the composition of urine [54]. Although both compounds can capture all the TAN in saturated urine, the technological design of the dryer (e.g. mixing required to achieve saturation) needed to promote struvite formation is unclear. Overall, the results suggest that to capture all the TAN excreted in urine (200 g cap^{-1} y^{-1} assuming TAN is 5% of N_{tot} and 4000 g N_{tot} cap^{-1} y^{-1} is excreted via urine [14]), about 0.38 kg MgO, 1.95 kg $MgCl_2{\cdot}6H_2O$ or 1.15 kg $MgSO_4$ cap^{-1} y^{-1} is required. The results also suggest that the recovery of TAN can be significantly affected by the treatment conditions, such as the alkaline substrate used (Fig. 3) and the drying conditions (e.g. temperature; Fig. 4). Formation of struvite in alkalised urine (pH $\leq$ 10) can be promoted by supplementing the urine with Mg^{2+} at temperatures $<$ 30 °C without any ventilation. In practice, the proposed approach can be integrated into the design of a urine dryer by using a sensor-based process controller that regulates the airflow, temperature, and drying rate, and by using a drying substrate that contains MgO, $MgCl_2{\cdot}6H_2O$ or $MgSO_4$. After every urination event, the controller can switch the dryer off for a fixed time duration to encourage the formation of struvite. However, not all TAN in urine can be captured in a urine dryer containing an alkaline Mg-based substrate if the urine is immediately subjected to drying.

5. Conclusion

Our study demonstrated that up to 99% of the N_{tot} present in urine is recovered when fresh urine is dehydrated in Mg-doped alkaline substrates. This was accomplished by combining three techniques (inhibition of enzymatic urea hydrolysis, minimisation of chemical urea hydrolysis and capture of free ammonia as struvite) as follows:

- First, the urease enzyme-catalysed degradation of urea (>80% of N_{tot} in urine) to ammonia was prevented by adding urine to MgO/$Mg(OH)_2$, which shifted the pH of fresh urine from < 7 to > 10. Since MgO/$Mg(OH)_2$ displays inverse solubility and because the inactivation of urease by alkalisation is reversible, it is recommended that urine is dried at temperatures < 30 °C.
- Second, the degradation of urea due to chemical hydrolysis during alkaline dehydration was kept below 1% by operating at pH 10 and drying temperature of < 40 °C, as the half-life of urea at these conditions was 369 d and the total drying time was 11.5 d.
- Third, free ammonia or TAN (usually < 5% of N_{tot} in fresh urine) was recovered, but only when urine was dehydrated in $MgCl_2$ + $Mg(OH)_2$. This substrate provided easily available Mg^{2+}, shifted the molar ratio of [Mg]:[NH_4]:[PO_4] in urine from 0.17:1:0.7 to 1.69:1.14:1.0, and encouraged the formation of struvite ($NH_4MgPO_4{\cdot}6H_2O$). All the TAN excreted in urine (200 g cap^{-1} y^{-1} assuming TAN is 5% of N_{tot} and 4000 g N_{tot} cap^{-1} y^{-1} is excreted via urine [14]) can be captured as struvite if alkalised urine is dehydrated in a substrate doped with 0.38 kg MgO, 1.95 kg $MgCl_2{\cdot}6H_2O$ or 1.15 kg $MgSO_4$ cap^{-1} y^{-1}. However, further research is required to identify how this study's results can be integrated into the design and operation of a urine dehydrator.

The current golden standard in sanitation is to collect all urban wastewater in mixed sewage systems and to treat it at centralised wastewater treatment plants. Even if these treatment plants were to be equipped with state-of-the-art processes like annamox, only 70–90% of the N, 95% of the P and < 6% of the K present in wastewater can be removed [59,60]. In contrast, if urine is collected and treated locally by alkaline dehydration, then 99% of the N and 100% of the P and K can be recovered. The product of the treatment is is a dry solid containing 10–11% N, 1–2% P and 2–3% K, which can be sold as fertiliser to recover the cost of the treatment. If all the urine produced in the world were to be treated using our approach, about 32 Tg N y^{-1} and 2.5 Tg P y^{-1} can be recycled as fertiliser. This would also lower the transgression of the planetary boundary for N and P by 35% and 25%, respectively.

CRediT authorship contribution statement

Anastasija Vasiljev: Conceptualization, Investigation, Data curation, Formal analysis, Writing – original draft. **Prithvi Simha:** Conceptualization, Methodology, Data curation, Formal analysis, Visualization, Writing – original draft, Supervision. **Natnael Demisse:** Conceptualization, Investigation, Writing – review & editing. **Caroline Karlsson:** Conceptualization, Investigation, Writing – review & editing. **Dyllon G. Randall:** Software, Validation, Formal analysis, Writing – review & editing. **Björn Vinnerås:** Conceptualization, Methodology, Writing – review & editing, Resources, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References

[1] D. Fowler, M. Coyle, U. Skiba, M.A. Sutton, J.N. Cape, S. Reis, L.J. Sheppard, A. Jenkins, B. Grizzetti, J.N. Galloway, P. Vitousek, A. Leach, A.F. Bouwman, K. Butterbach-Bahl, F. Dentener, D. Stevenson, M. Amann, M. Voss, The global nitrogen cycle in the twenty-first century, Philos. Trans. R. Soc. Lond. B Biol. Sci. 368 (1621) (2013) 20130164, https://doi.org/10.1098/rstb.2013.0164.

[2] J.N. Galloway, Aber, J. D., Erisman, J. W., Seitzinger, S. P., Howarth, R. W., Cowling, E. B., & Cosby, B. J., The nitrogen cascade, BioSc 53(4) (2003) 341-356. https://doi.org/10.1641/0006-3568(2003)053[0341:TNC]2.0.CO;2.

[3] B.L. Bodirsky, A. Popp, H. Lotze-Campen, J.P. Dietrich, S. Rolinski, I. Weindl, C. Schmitz, C. Muller, M. Bonsch, F. Humpenoder, A. Biewald, M. Stevanovic, Reactive nitrogen requirements to feed the world in 2050 and potential to mitigate nitrogen pollution, Nat. Commun. 5 (2014) 3858, https://doi.org/10.1038/ncomms4858.

[4] IFIA Ammonia Production: Moving Towards Maximum Efficiency and Lower Ghg Emissions, Fertilizer Facts, International Fertilizer Industry Association 2014.

[5] J.W. Erisman, M.A. Sutton, J. Galloway, Z. Klimont, W. Winiwarter, How a century of ammonia synthesis changed the world, Nat. Geosci. 1 (10) (2008) 636–639, https://doi.org/10.1038/ngeo325.

[6] J.N. Galloway, E.B. Cowling, Reactive nitrogen and the world: 200 years of change, Ambio 31 (2) (2002) 64–71, https://doi.org/10.1579/0044-7447-31.2.64.

[7] I. Pikaar, S. Matassa, K. Rabaey, B.L. Bodirsky, A. Popp, M. Herrero, W. Verstraete, Microbes and the Next Nitrogen Revolution, Environ. Sci. Technol. 51 (13) (2017) 7297–7303, https://doi.org/10.1021/acs.est.7b00916.

[8] R.J. Diaz, R. Rosenberg, Spreading dead zones and consequences for marine ecosystems, Sci 321 (5891) (2008) 926–929, https://doi.org/10.1126/science.1156401.

[9] J.H. Guo, X.J. Liu, Y. Zhang, J.L. Shen, W.X. Han, W.F. Zhang, P. Christie, K.W. T. Goulding, P.M. Vitousek, F.S. Zhang, Significant acidification in major Chinese croplands, Sci 327 (5968) (2010) 1008–1010, https://doi.org/10.1126/science.1182570.

[10] B.M. Campbell, D.J. Beare, E.M. Bennett, J.M. Hall-Spencer, J.S.I. Ingram, F. Jaramillo, R. Ortiz, N. Ramankutty, J.A. Sayer, D. Shindell, Agriculture production as a major driver of the Earth system exceeding planetary boundaries, Ecol. Soc. 22 (4) (2017), https://doi.org/10.5751/es-09595-220408.

[11] W. Steffen, K. Richardson, J. Rockstrom, S.E. Cornell, I. Fetzer, E.M. Bennett, R. Biggs, S.R. Carpenter, W. de Vries, C.A. de Wit, C. Folke, D. Gerten, J. Heinke, G. M. Mace, L.M. Persson, V. Ramanathan, B. Reyers, S. Sorlin, Sustainability. Planetary boundaries: guiding human development on a changing planet, Sci 347 (6223) (2015) 1259855, https://doi.org/10.1126/science.1259855.

[12] E. Friedler D. Butler Y. Alfiya Wastewater composition T.A. Larsen K.M. Udert J. Lienert Source Separation and Decentralization for Wastewater Management 2013 IWA Publishing 241 257.

[13] C. Rose, A. Parker, B. Jefferson, E. Cartmell, The Characterization of Feces and Urine: A Review of the Literature to Inform Advanced Treatment Technology, Crit. Rev. Env. Sci. Technol. 45 (17) (2015) 1827–1879, https://doi.org/10.1080/10643389.2014.1000761.

[14] B. Vinnerås, H. Palmquist, P. Balmér, H. Jönsson, The characteristics of household wastewater and biodegradable solid waste—A proposal for new Swedish design values, Urban Water J. 3 (1) (2006) 3–11, https://doi.org/10.1080/15730620600578629.

[15] UNESCO, The United Nations world water development report Wastewater: the untapped resource 2017 UNESCO 2017.

[16] P. Simha, Substituting nitrogen and phosphorous used in agriculture with human urine, 2021. https://osf.io/7ckax/.

[17] FAO, New Food Balances, Protein supply quantity, Food and Agriculture Organization of the United Nations (FAO), Rome, Italy, 2017.

[18] H. Jönsson B. Vinnerås Adapting the nutrient content of urine and faeces in different countries using FAO and Swedish data, Ecosan-Closing the loop 2004 Deutsche Gesellschaft fur Technische Zusammenarbeit Lubeck, Germany 623 626.

[19] Y. Tong, M. Wang, J. Penuelas, X. Liu, H.W. Paerl, J.J. Elser, J. Sardans, R. M. Couture, T. Larssen, H. Hu, X. Dong, W. He, W. Zhang, X. Wang, Y. Zhang, Y. Liu, S. Zeng, X. Kong, A.B.G. Janssen, Y. Lin, Improvement in municipal wastewater treatment alters lake nitrogen to phosphorus ratios in populated

regions, Proc Natl Acad Sci U S A 117 (21) (2020) 11566–11572, https://doi.org/10.1073/pnas.1920759117.
[20] P. van Puijenbroek, A.H.W. Beusen, A.F. Bouwman, Global nitrogen and phosphorus in urban waste water based on the Shared Socio-economic pathways, J. Environ. Manage. 231 (2018) 446–456, https://doi.org/10.1016/j.jenvman.2018.10.048.
[21] G.T. Daigger, Evolving urban water and residuals management paradigms: water reclamation and reuse, decentralization, and resource recovery, Water Environ. Res. 81 (8) (2009) 809–823, https://doi.org/10.2175/106143009x425898.
[22] T.A. Larsen, M. Maurer, K.M. Udert, J. Lienert, Nutrient cycles and resource management: implications for the choice of wastewater treatment technology, Water Sci. Technol. 56 (5) (2007) 229–237, https://doi.org/10.2166/wst.2007.576.
[23] M. Zamparas, V.C. Kapsalis, A.E. Kanteraki, E. Vardoulakis, G.L. Kyriakopoulos, M. Drosos, I.K. Kalavrouziotis, Novel composite materials as P-adsorption agents and their potential application as fertilizers, Global NEST Journal 21 (1) (2019) 48–57, https://doi.org/10.30955/gnj.002752.
[24] M.J. Kampschreur, H. Temmink, R. Kleerebezem, M.S. Jetten, M.C. van Loosdrecht, Nitrous oxide emission during wastewater treatment, Water Res. 43 (17) (2009) 4093–4103, https://doi.org/10.1016/j.watres.2009.03.001.
[25] T. Sato, M. Qadir, S. Yamamoto, T. Endo, A. Zahoor, Global, regional, and country level need for data on wastewater generation, treatment, and use, Agric. Water Manag. 130 (2013) 1–13, https://doi.org/10.1016/j.agwat.2013.08.007.
[26] Eurostat, Population connected to urban wastewater collecting and treatment systems, by treatment level, Eurostat - the Statistical Office of the European Union, 2020.
[27] Grigorios Kyriakopoulos, Vasilis Kapsalis, Konstantinos Aravossis, Miltiadis Zamparas, Alexandros Mitsikas, Evaluating Circular Economy under a Multi-Parametric Approach, A Technological Review. Sustainability 11 (21) (2019) 6139, https://doi.org/10.3390/su11216139.
[28] B. Vinnerås, H. Jönsson, The performance and potential of faecal separation and urine diversion to recycle plant nutrients in household wastewater, Bioresour. Technol. 84 (3) (2002) 275–282.
[29] M. Winker, B. Vinneras, A. Muskolus, U. Arnold, J. Clemens, Fertiliser products from new sanitation systems: their potential values and risks, Bioresour. Technol. 100 (18) (2009) 4090–4096, https://doi.org/10.1016/j.biortech.2009.03.024.
[30] P. Tidåker, B. Mattsson, H. Jönsson, Environmental impact of wheat production using human urine and mineral fertilisers – a scenario study, J. Cleaner Prod. 15 (1) (2007) 52–62, https://doi.org/10.1016/j.jclepro.2005.04.019.
[31] C.P. Flanagan, D.G. Randall, Development of a novel nutrient recovery urinal for on-site fertilizer production, J. Environ. Chem. Eng. 6 (5) (2018) 6344–6350, https://doi.org/10.1016/j.jece.2018.09.060.
[32] Joel Gundlach, Michael Bryla, Tove A. Larsen, Lotte Kristoferitsch, Harald Gründl, Markus Holzner, Novel NoMix toilet concept for efficient separation of urine and feces and its design optimization using computational fluid mechanics, Journal of Building Engineering 33 (2021) 101500, https://doi.org/10.1016/j.jobe.2020.101500.
[33] T.L. Chipako, D.G. Randall, Urine treatment technologies and the importance of pH, J. Environ. Chem. Eng. 8 (1) (2020) 103622, https://doi.org/10.1016/j.jece:2019.103622.
[34] Robin Harder, Rosanne Wielemaker, Tove A. Larsen, Grietje Zeeman, Gunilla Öberg, Recycling nutrients contained in human excreta to agriculture: Pathways, processes, and products, Crit. Rev. Env. Sci. Technol. 49 (8) (2019) 695–743, https://doi.org/10.1080/10643389.2018.1558889.
[35] T.M.P. Martin, F. Esculier, F. Levavasseur, S. Houot, Human urine-based fertilizers: A review, Crit. Rev. Env. Sci. Technol. (2020) 1–47, https://doi.org/10.1080/10643389.2020.1838214.
[36] J. Senecal, A. Nordin, P. Simha, B. Vinneras, Hygiene aspect of treating human urine by alkaline dehydration, Water Res. 144 (2018) 474–481, https://doi.org/10.1016/j.watres.2018.07.030.
[37] Prithvi Simha, Cecilia Lalander, Annika Nordin, Björn Vinnerås, Alkaline dehydration of source-separated fresh human urine: Preliminary insights into using different dehydration temperature and media, ScTEn 733 (2020) 139313, https://doi.org/10.1016/j.scitotenv.2020.139313.
[38] P. Simha J. Senecal D.J.I. Gustavsson B. Vinnerås Resource recovery from wastewater: a new approach with alkaline dehydration of urine at source A. Pandey R. Kataki D. Pant S. Khanal Current Developments in Biotechnology and Bioengineering: Sustainable Bioresources for Emerging Bioeconomy 2020 Elsevier Publications The Netherlands.
[39] B. Krajewska, Ureases I. Functional, catalytic and kinetic properties: A review, J. Mol. Catal. B Enzym. 59 (1-3) (2009) 9–21, https://doi.org/10.1016/j.molcatb.2009.01.003.
[40] D.G. Randall, M. Krahenbuhl, I. Kopping, T.A. Larsen, K.M. Udert, A novel approach for stabilizing fresh urine by calcium hydroxide addition, Water Res. 95 (2016) 361–369, https://doi.org/10.1016/j.watres.2016.03.007.
[41] P. Simha, C. Karlsson, E.-L. Viskari, R. Malila, B. Vinnerås, Field Testing a Pilot-Scale System for Alkaline Dehydration of Source-Separated Human Urine: A Case Study in Finland, Front. Environ. Sci. 8 (2020), https://doi.org/10.3389/fenvs.2020.570637.
[42] S. Antonini, P.T. Nguyen, U. Arnold, T. Eichert, J. Clemens, Solar thermal evaporation of human urine for nitrogen and phosphorus recovery in Vietnam, Sci. Total Environ. 414 (2012) 592–599, https://doi.org/10.1016/j.scitotenv.2011.11.055.
[43] D.N. Bethune, Angus Chu, M.C. Ryan, Passive evaporation of source-separated urine from dry toilets: a lab study, J.WaterSanit.Hyg.Dev 4 (4) (2014) 654–662, https://doi.org/10.2166/washdev.2014.058.
[44] M.M. Pahore, K. Ushijima, R. Ito, N. Funamizu, Fate of nitrogen during volume reduction of human urine using an on-site volume reduction system, Environ. Technol. 33 (1–3) (2012) 229–235, https://doi.org/10.1080/09593330.2011.560192.
[45] J. Senecal, B. Vinneras, Urea stabilisation and concentration for urine-diverting dry toilets: Urine dehydration in ash, Sci. Total Environ. 586 (2017) 650–657, https://doi.org/10.1016/j.scitotenv.2017.02.038.
[46] P. Simha, J. Senecal, A. Nordin, C. Lalander, B. Vinnerås, Alkaline dehydration of anion–exchanged human urine: Volume reduction, nutrient recovery and process optimisation, Water Res. 142 (2018) 325–336, https://doi.org/10.1016/j.watres.2018.06.001.
[47] P. Simha, C. Friedrich, D.G. Randall, B. Vinnerås, Alkaline Dehydration of Human Urine Collected in Source-Separated Sanitation Systems Using Magnesium Oxide, Front. Environ. Sci. 8 (2021), https://doi.org/10.3389/fenvs.2020.619901.
[48] M. Ronteltap, M. Maurer, W. Gujer, Struvite precipitation thermodynamics in source-separated urine, Water Res. 41 (5) (2007) 977–984, https://doi.org/10.1016/j.watres.2006.11.046.
[49] C.A. Strydom, E.M. van der Merwe, M.E. Aphane, The effect of calcining conditions on the rehydration of dead burnt magnesium oxide using magnesium acetate as a hydrating agent, JTAC 80 (3) (2005) 659–662.
[50] I. RStudio RStudio Team RStudio: Integrated Development for R 2016.
[51] OLI Systems Inc. OLI Stream Analyser 2020.
[52] D.F. Putnam Composition and concentrative properties of human urine 1971 National Aeronautics and Space Administration.
[53] H. Jönsson, T.A. Stenström, J. Svensson, A. Sundin, Source separated urine-nutrient and heavy metal content, water saving and faecal contamination, Water Sci. Technol. 35 (9) (1997) 145–152.
[54] C.K. Deb, P. Simha, D.G. Randall, B. Vinnerås, Solubility curves for MgO and Mg (OH)2 in fresh urine, in preparation.
[55] S.G. Barbosa, L. Peixoto, B. Meulman, M.M. Alves, M.A. Pereira, A design of experiments to assess phosphorous removal and crystal properties in struvite precipitation of source separated urine using different Mg sources, Chem. Eng. J. 298 (2016) 146–153, https://doi.org/10.1016/j.cej.2016.03.148.
[56] E.M. van der Merwe, C.A. Strydom, Hydration of medium reactive magnesium oxide using hydration agents, JTAC 84 (2) (2006) 467–471.
[57] M. Geinzer, Inactivation of the urease enzyme by heat and alkaline pH treatment, Department of Energy and Technology Swedish University of Agricultural Sciences Uppsala (2017).
[58] A. Vasiljev, Safe nutrient recovery of human urine as a crop fertilizer: capture of the free ammonium nitrogen during alkaline urine dehydration, eneng,, South-Eastern Finland University of Applied Sciences Mikkeli (2020), 71.
[59] M. Laureni, P. Falas, O. Robin, A. Wick, D.G. Weissbrodt, J.L. Nielsen, T.A. Ternes, E. Morgenroth, A. Joss, Mainstream partial nitritation and anammox: long-term process stability and effluent quality at low temperatures, Water Res. 101 (2016) 628–639, https://doi.org/10.1016/j.watres.2016.05.005.
[60] P. Simha, Alkaline Urine Dehydration: How to dry source-separated human urine and recover nutrients?. PhD Thesis, Swedish University of Agricultural Sciences, Uppsala, Sweden. Acta Universitatis Agriculturae Sueciae 2021:28 [eISBN 978-91-7760-735-9]. URL: https://pub.epsilon.slu.se/23473/.