Science of the Total Environment xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Urea stabilisation and concentration for urine-diverting dry toilets: Urine dehydration in ash

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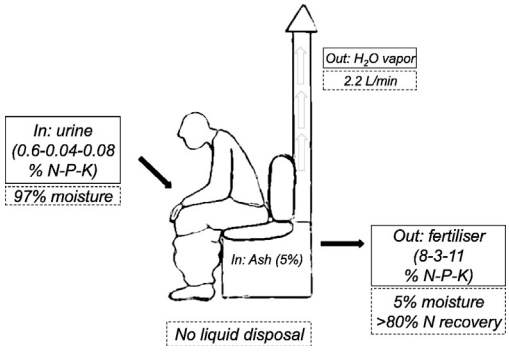
HIGHLIGHTS

- Human urine contains plant nutrients that can be concentrated to produce fertiliser.
- Increasing pH of urine inhibits urease enzymes from hydrolysing urea.
- Urine is reduced by 95%, while preserving up to 90% of the urea.
- No liquid disposal required from the toilet
- End product is a dry fertiliser with 7.8% N, 2.5% P and 10.9% K.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 November 2016
Received in revised form 3 February 2017
Accepted 5 February 2017
Available online xxxx

Editor: Simon Pollard

Keywords:
Alkalisation
Ash
Dehydration
Fertiliser
Human urine
Plant nutrients

ABSTRACT

Human excreta contain the same nitrogen, phosphorus and potassium (N-P-K) as the fertilisers used to produce the food consumed. However, human excreta are considered unwanted waste throughout the world, creating humanitarian and environmental problems. In order to replace the nutrients removed from fields during crop harvesting, more fertilisers are manufactured, in processes contributing to environmental changes at global level. The limitation of human urine as a fertiliser is its low nutrient concentration compared with commercial fertilisers. This study developed a technique to increase the N concentration (from 0.6% to >6%) through urine dehydration to produce a dry fertiliser of monetary value and avoid the need for liquid disposal from the toilet. The technique is intended for a container-based sanitation system that collects, contains, treats and reduces the volume of urine within the container. In tests, fresh human urine was added at various intervals to wood ash at 35 °C and 65 °C, to alkalise and thus inhibit the enzyme urease from catalysing hydrolysis of urea to ammonia. Mass balance calculations demonstrated a 95% reduction during dehydration, while preserving up to 90% of the N. Such a system would greatly simplify the logistics and costs of storage, transportation and application of urine as a fertiliser. The truly innovative feature is the final product: a dry powder with 7.8% N, 2.5% P and 10.9% K by weight, i.e. equivalent to commercial fertiliser.

1. Introduction

The saying 'we are what we eat' is only part of the story. What we eat is what we excrete, and this means plant nutrients. Human excreta contain the same nitrogen, phosphorus and potassium (N-P-K) as the

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http://dx.doi.org/10.1016/j.scitotenv.2017.02.038

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fertilisers used to produce the food consumed (Winker et al., 2009). However, human excreta are considered unwanted waste throughout the world, creating humanitarian and environmental problems (Baum et al., 2013). In order to replace the nutrients removed from the fields during harvesting more fertilisers are manufactured in industrial processes that are contributing to environmental changes at global level (Rockström et al., 2009). Recycling human excreta back to agricultural fields would reduce the current dependence on fossil fuel-derived fertilisers (Ramírez & Worrell, 2006). It would also improve crop yields in e.g. sub-Saharan Africa, where fertiliser application is low (FAO, 2015), and protect marine ecosystems in the Baltic Sea by limiting the flow of excess nutrients to surface waters (Rockström et al., 2009).

Urine, rather than faeces, contains the majority of the nutrients excreted annually: 80–90% of the total 4 kg of N excreted, 50–80% of the 0.4 kg of P and 80–90% of the 1 kg of K (Vinnerås et al., 2006). The main limitation with using urine as a fertiliser is that it is mostly water (97%), meaning that the concentration of nutrients is low. For example, the N concentration in urine is 0.6% (Vinnerås et al., 2006), whereas that of the manufactured fertiliser urea is 46%. Lower nutrient concentrations require larger quantities of urine to be applied per hectare as fertiliser, which creates logistics problems in terms of storage (as approx. 550 L of urine are produced per person and year) and increases the costs of transportation and application. Hence urine, as excreted, is not a competitive fertiliser. To better utilise the nutrients, the excess water in urine needs to be removed.

Concentrating the nutrients in urine while retaining N is challenging. Approximately 85% of the N in urine is initially present in non-volatile form, as urea ($CO(NH_2)_2$). Once excreted, the urea is quickly hydrolysed to volatile form, ammonia (NH_3), in a reaction that is catalysed by urease enzymes (urea amidohydrolase, EC 3.5.1.5) (Eq. (1)). The carbamate (H_2N-COOH) produced in this reaction then spontaneously hydrolyses into carbonic acid (H_2CO_3) and releases a second NH_3 molecule (Krajewska, 2009). The volatility of NH_3 means that urine cannot simply be dehydrated, but stopping the urease enzyme is also a challenge.

$$H_2N\text{–}CO\text{–}NH_2 + H_2O \overset{\text{Urease}}{\rightarrow} H_2N\text{–}COOH + NH_3 \overset{H_2O}{\rightarrow} H_2CO_3 + 2NH_3 \quad (1)$$

$$H_2N\text{–}CO\text{–}NH_2 \overset{\text{Uncatalysed}}{\rightarrow} HN{=}C{=}O + NH_3 \overset{2H_2O}{\rightarrow} H_2CO_3 + 2NH_3 \quad (2)$$

Urease is a group of highly proficient natural enzymes used in plants, algae, fungi and several microorganisms to catalyse the hydrolysis of urea (Ciurli et al., 1999). The structure varies between different urease-forming bacteria (enzyme molar mass range 190–300 kDa; Krajewska, 2009), but all have a common feature of two nickel ions at the active site. Urease is an extracellular enzyme that can be immobilised on particles and there continue its degradation of urea (Ciurli et al., 1996). Urease enzymes are most commonly known for their role in soil fertilised with urea but, unknown to most toilet users, human faeces contain large amounts of urease-forming bacteria (Wozny et al., 1977). Even in urine-diverting dry toilets, these urease enzymes accumulate in urine piping systems due to cross-contamination from faeces and biofilm formation on the pipe surface and cause rapid hydrolysis of urea to NH_3 (Vinnerås, 2002).

The potential source of nutrients in human urine has led to various trials to concentrate urine that has already been hydrolysed. Examples include NH_3 stripping (Antonini et al., 2012), nitrification (Udert et al., 2015), electrolysis (Udert et al., 2015), struvite formation by the addition of magnesium (Etter et al., 2011), and reverse osmosis, many of which are reviewed in Maurer et al. (2006). However, the implementation of such treatments is limited due to the sensitivity, high requirements for chemical inputs or the complexity of the system. In addition, most of the concentrating techniques collect only some of the elements in the concentrated fraction, e.g. N in NH_3 stripping and P in struvite.

Another approach is to first pre-treat the urine to limit the urease activity to enable dehydration of the excess water in urine. To limit the urease enzymes in agricultural soils, inhibitors such as N-(n-butyl) thiophosphoric triamide are being developed (Parker et al., 2012). However, due to the potential risks to human and environmental health (Ciurli et al., 1999), they cannot be considered a viable option for use in household toilets. The urease enzymes can also be limited by pH and temperature (Hotta & Funamizu, 2008; Huang & Chen, 1991; Sizer, 1940). Examples of stabilisation techniques include acidification (Hellstrom et al., 1999), alkalisation (Randall et al., 2016), freeze-thaw (Lind et al., 2001) and salinisation (Pahore et al., 2011), so that the N is preserved as urea and the excess water in the urine can be removed by dehydration. When the urease enzyme is limited by elevated pH and/or elevated temperature, then uncatalysed urea hydrolysis occurs (Eq. (2)) (Jespersen, 1975). However, this uncatalysed hydrolysis is 10^{10} times slower than enzyme-catalysed hydrolysis (Table 1).

Stabilising urine by alkalisation is an attractive option, as there are several sources of strong bases available and as alkalisation of soils in the humid northern temperate and humid tropic zones is a common existing practice for treating acidic soils (FAO, 1986). Calcium hydroxide ($Ca(OH)_2$) has been demonstrated to effectively increase the pH above 12 and inhibit the urease activity in a chemical reactor prior to drying in a separate system (Randall et al., 2016). The objective of the present study was to test the alkalinisation approach using another alkaline medium, wood ash, and performing the drying continuously in the same alkalising bed. Wood ash was selected not just for its high initial pH (>12.5), but also for its high surface area, to enable faster dehydration of the urine. The aim was to retain the majority of N (>90%) in a continuous drying process with daily addition of fresh source-separated urine. The urine was dehydrated under constant ventilation at two elevated temperatures, 35 and 65 °C. The approach is intended for container-based sanitation systems where the urine is diverted during excretion and collected, contained, treated and reduced within the same container. The installation of such a technique, along with full servicing from a central provider, would offer the experience of a flush toilet ('flush and forget') at an affordable cost. A container-based-sanitation system requires no pit, plumbing or sewer connection, greatly reducing the cost and complexity of the system. The potential for container-based sanitation technologies is immense, with 4.1 billion people currently lacking access to improved sanitation systems (Baum et al., 2013).

2. Methodology

2.1. Human urine

Human urine from one woman and one man in their mid-20s was collected in new containers 4 days a week, in the morning. The initial density and pH of the urine were measured and a cumulative samples was stored frozen until the end of the experiment. The N concentration was analysed at the end of the experiment by Koroleff's method, using an N (total)-Spectroquant Cell test kit (1.14763.0001, Merck-Chemicals).

Table 1
Examples of the half-life of urea varying on temperature, pH and catalyst.

	t½
Unanalysed (neutral pH, 25 °C)[a]	40 yrs
20 °C (pH > 10)[b]	Neg. at 32 days
38 °C (pH < 12)[c]	3.6 yrs
65 °C (pH < 12)[d]	15.3 days
65 °C (pH > 12.5)[d]	14.1 days
Enzymatic (Jack-bean, neutral pH, 25 °C)a	0.02 s

[a] (Callahan et al., 2005).
[b] (Kabdaşlı et al., 2006).
[c] (Zerner, 1991).
[d] Derived from Warner (1942).

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2.2. Wood ash

Two ash sources were used: *Agrol* from Agrol Värmepellets (wood pellets) produced by Agroenergi Neova Pellets AB, Sweden; and *Birch* from birch trees grown in central Sweden. Both were combusted in a residential fireplace in Sweden. The ash was sieved (<Ø1 mm), dried (65 °C, 24 h) and stored in 3-L sealed containers. Initial N concentration was measured as total N by dry combustion (Tru Mac). Initial phosphate-P (PO_4-P) and K concentrations were measured using ICP (ICP Optima 7300 DV Swedish Standard: SS 02 83 11).

2.3. Experimental set-up

Two treatments, *Static* and *Dose* ash beds, were tested in triplicate at the two chosen temperatures of 35 and 65 °C. In the Static ash bed treatments, 50 g of ash were added initially to each of the 250 mL plastic containers and after each urine application the contents were stirred for 5 s. In the Dose ash bed, ash was added with each urine application at 5% (ash/urine, w/w) and the contents were not stirred. The evaporation temperature of 65 °C was initially selected because a similar temperature has been achieved inside a solar urine dehydrating unit in Vietnam (Antonini et al., 2012). However, due to the shortened half-life of urea at 65 °C, a second trial was conducted at 35 °C to compare the N retention. Both temperature trials were performed in incubators with two DC 12 V computer fans for ventilation (fan 1: 0.25A (40 mm by 20 mm, Model AD0812HS-A70GL); and fan 2: 0.33A (70 mm by 15 mm, Model AFB0712HB) consuming 6.96 W combined; Delta Electronics, Taiwan). In the 35 °C trial, fresh urine was added four times a week at a rate of 3.8 L/m^2 ash bed and the treatment was run for 46 days, followed by 51 days with no urine addition, to monitor any change in pH due to ventilation. In the 65 °C trial, fresh urine was initially added at 8.9 L/m^2 (Days 0–15) but the evaporation rate was too low to completely dehydrate the urine within 24 h. From Day 16 onwards, 5.1 L/m^2 were added four days a week and the treatment ran for 41 days.

2.4. Sampling and analysis

The pH was measured weekly and the wet ash was returned to the container. No urine was added on the day that pH was measured. In the 65 °C trial, the N concentration was measured ($n = 3$) on three occasions during the experiment (Days 20, 33 and 41), as NH_3-N by an ammonia electrode probe (Metrohm AG, Switzerland). Before these measurements, the urea was hydrolysed to NH_4^+/NH_3 by adding 100 mg ash to a solution of 30 mL deionised water, 5 mL M/15 phosphate buffer (pH 7.2) and Jack-bean urease (lyophilised urease 5 U/mg, EC 3.5.1.5; Merck, Germany and 5000 U urease enzymes per g assumed concentration of urea) in a centrifuge tube with an O-ring. The tubes were incubated at 37 °C for 24 h on a shaker table for optimal temperature and contact with the enzymes. After the hydrolysis, to shift the equilibrium between NH_4^+ and NH_3 towards NH_3, the solution was alkalised to pH >12 by addition of 0.5 mL 10 M sodium hydroxide (NaOH). In the 35 °C trial, the N concentration was measured as total N dry combustion (Tru Mac) at the end of the experiment. This method was used as there was an issue with the NH_3-N electrode probe. The P and K concentrations were analysed at the end of the experiment, as described above for wood ash (Section 2.2).

2.5. Statistical analysis

The experiment had a complete randomised design and the data were analysed by analysis of variance (ANOVA) using SAS 9.2 software (SAS Institute Inc., Cary, NC). The power of the test was computed by calculating the standard deviation (SD) from the coefficient of variance (CV) and the mean (SAS 9.2, 2009); a power ≥ 0.8 was accepted. The effects of the treatments were computed by pair-wise comparisons with Duncan multiple range tests at $\alpha = 0.05$.

3. Results

3.1. Nitrogen concentration

Dehydrating urine in the alkaline medium of wood ash succeeded in eliminating the need for liquid disposal, while retaining the majority of N. The 35 °C trial retained significantly more N than the 65 °C trial ($P < 0.001$). At 35 °C, the Static bed retained 90% of the N added with urine and the Dose bed retained 82% (Fig. 1a) ($P < 0.001$). At 65 °C, the N retention peaked at 66% for the Static bed and 64% for the Dose bed, in both cases on Day 33 (Fig. 2a). The Dose bed in the 35 °C trial had the highest N concentration, followed by the Dose bed in the 65 °C trial (the 65 °C trial received 26% more urine than the 35 °C trial because of the higher evaporation and thereby application rate). The Static bed had a lower N concentration but retained more of the N applied (Fig. 1 and Fig. 2), because in both temperature trials the Static bed had a higher mass of ash (50 g) than the Dose bed (18.75–24 g ash) per unit volume of urine applied. The initial pH of the Agrol ash ranged from 13.1 to 13.7, while the initial pH of the Birch ash was 12.4, but there was no significant difference between the two ashes. The initial concentration of N in the two ashes was below the detection limit (10 mg/L). The power of the test was >0.999 for the parameters measured.

3.2. Mass reduction

The treatment concentrated the nutrients to produce a dry N-P-K fertiliser (approx. 5% moisture) with concentrations as high as 7.8–2.5–10.9 (Table 2). In order to maintain pH above 10.5, a urine to ash ratio of 20:1 was required. Fig. 3a and b show the mass balance for the nutrients and moisture in the final dried ash/urine product from the Dose ash treatment described in Table 2. Phosphate, K and other macro- and micronutrients were accumulated in the ash and complemented the N-rich urine, resulting in the balanced nutrient content required in a fertiliser.

3.3. Change in pH

In both temperature trials, the pH decreased and stabilised at approx. 10.5 within the first two weeks (Fig. 1b and Fig. 2b) except in the Static bed at 35 °C, which stabilised after three weeks. In the 35 °C trial, urine application was stopped on Day 47 and the pH was measured again on Day 97. During that time, the pH decreased from 10.7 to 10.3, with no difference between the treatments ($P < 0.05$). The pH in the controls (where water was added instead of urine) decreased at the same rate as in the treatments and had the same pH level as in the treatments up until the last measurement on Day 97, when it was lower (10.1) than in the treatments (10.3) ($P < 0.05$).

On Day 33 in the 65 °C trial, when the N concentration peaked, the pH was higher in the Static bed (10.6) than in the Dose bed (10.4) and within the treatments there was no different between the ash types ($P > 0.05$). After the peak, urine application was paused twice (data not shown) between Days 44 and 61 and again between Days 78 and 95, in which periods the pH of the ash decreased (≤10.5) and the NH_3-N concentration decreased to <38% of the total amount of NH_3-N added. This indicates that the N loss was due to temperature and not pH, as the N loss was minimal at 35 °C during the same period.

3.4. Calculating loss of urea

From the half-life values of urea (Table 1), an arithmetic series (Eq. (3)) was derived to calculate the amount of urea that would otherwise have been hydrolysed. Based on the results, the non-enzymatic N loss

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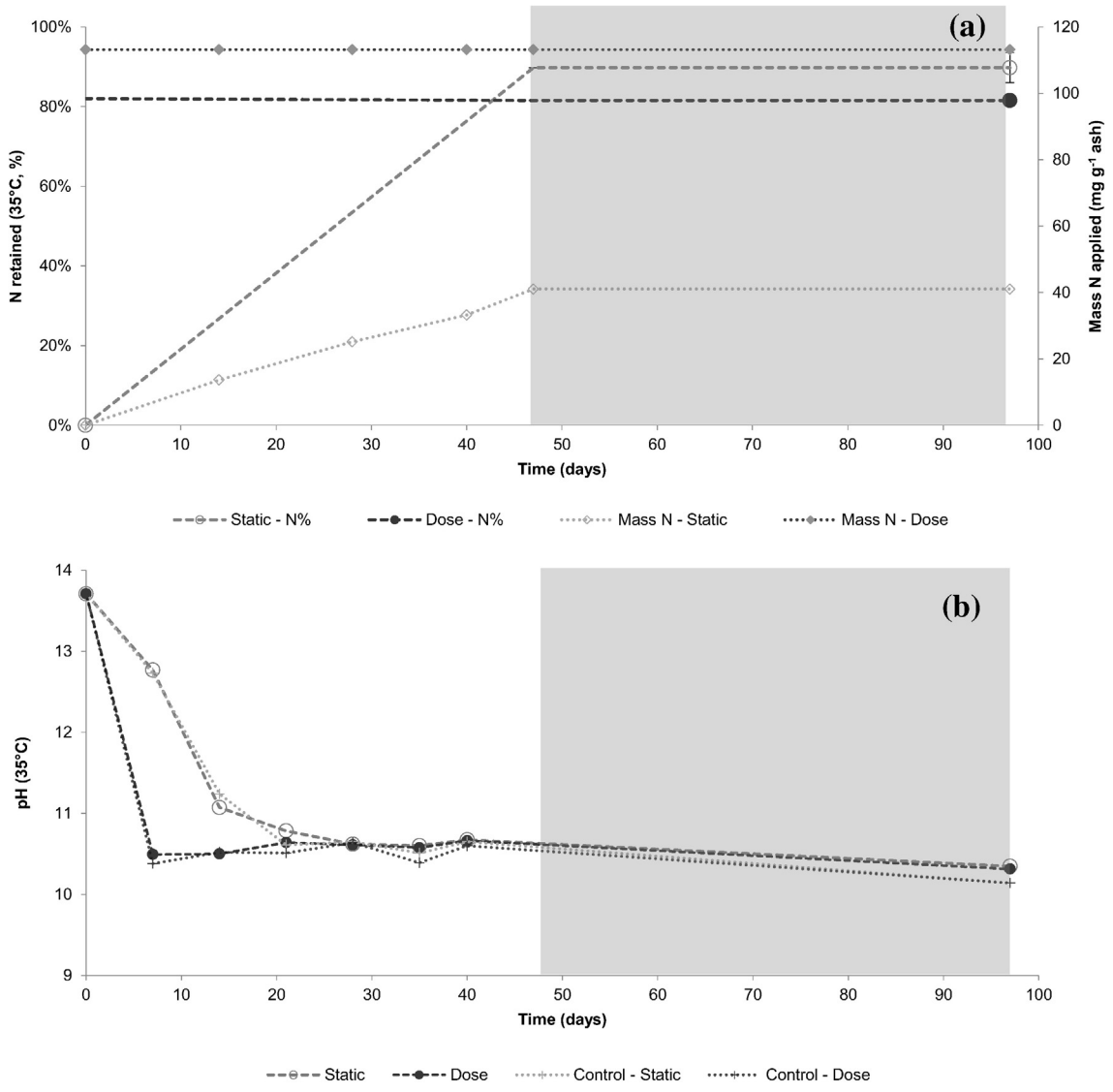

Fig. 1. a) Retained N-total (left axis) and mass of N added per g ash (right axis) over time and b) pH at 35 °C. The grey areas indicate a pause in urine application. For the pH, the standard deviation was too small (<0.15) to be displayed clearly.

was calculated for the initial pH of the ash and the temperature of the treatments (Table 3).

$$x = \sum_{n=1}^{d} n * \frac{x_o}{2 * t½} \quad (3)$$

where x is mass of urea hydrolysed, x_o is initial mass of urea, d is number of days in the given pH range and t½ is half-life for the given pH range and temperature.

Based on the measured and modelled N losses in the treatments, Fig. 4 illustrates the estimated N losses over 20 days.

4. Discussion

4.1. Mass reduction

Dehydrating human urine in an alkaline environment (pH >10.5) under high ventilation conditions reduced the ingoing mass (urine and ash included) by 93% in both temperature trials. Such a dehydration treatment process in a urine-diverting dry toilet would require no liquid disposal of the urine. This would greatly simplify the logistics and costs of storage, transportation and application as fertiliser, while also making a competitive fertiliser. The annual volume of urine produced per person (approx. 550 L/yr) would be reduced to 40 kg/yr (including the mass of ash required). The urine could be collected, contained, treated and reduced, all in the same collection container. An additional advantage of using high pH for inhibiting urease activity is the long-term effect compared with other methods. The remaining elevated pH would continue to inhibit contamination or regrowth of urease-producing bacteria within the end product (Nyberg et al., 2011). In other treatments, such as oxidation, that have good initial inhibition, regrowth of urease-producing bacteria post-oxidation leads to hydrolysis of urea (Zhang et al., 2013).

The dehydration process produces a urine-based fertiliser that is more concentrated than manures (Penhallegon, 2003) with similar nutrient ratio to some mineral fertilisers, such as combined potassium nitrate and ground rock phosphate (FAO, 1991). This urine/ash fertiliser has a potential monetary value of approximately US$80 ton^{-1} on the global commodity market, compared with the December 2016 cost of urea (US$216 ton^{-1} with 46% N), potash (US$215 ton^{-1} with 52% K) and phosphate rock (US$103 ton^{-1} with 14% P) (World Bank, 2017). Furthermore, all other macro- and micronutrients found in the urine (Vinnerås et al., 2006) would remain in the final dried product. In this final product, the P can be assumed to occur mainly in the form of

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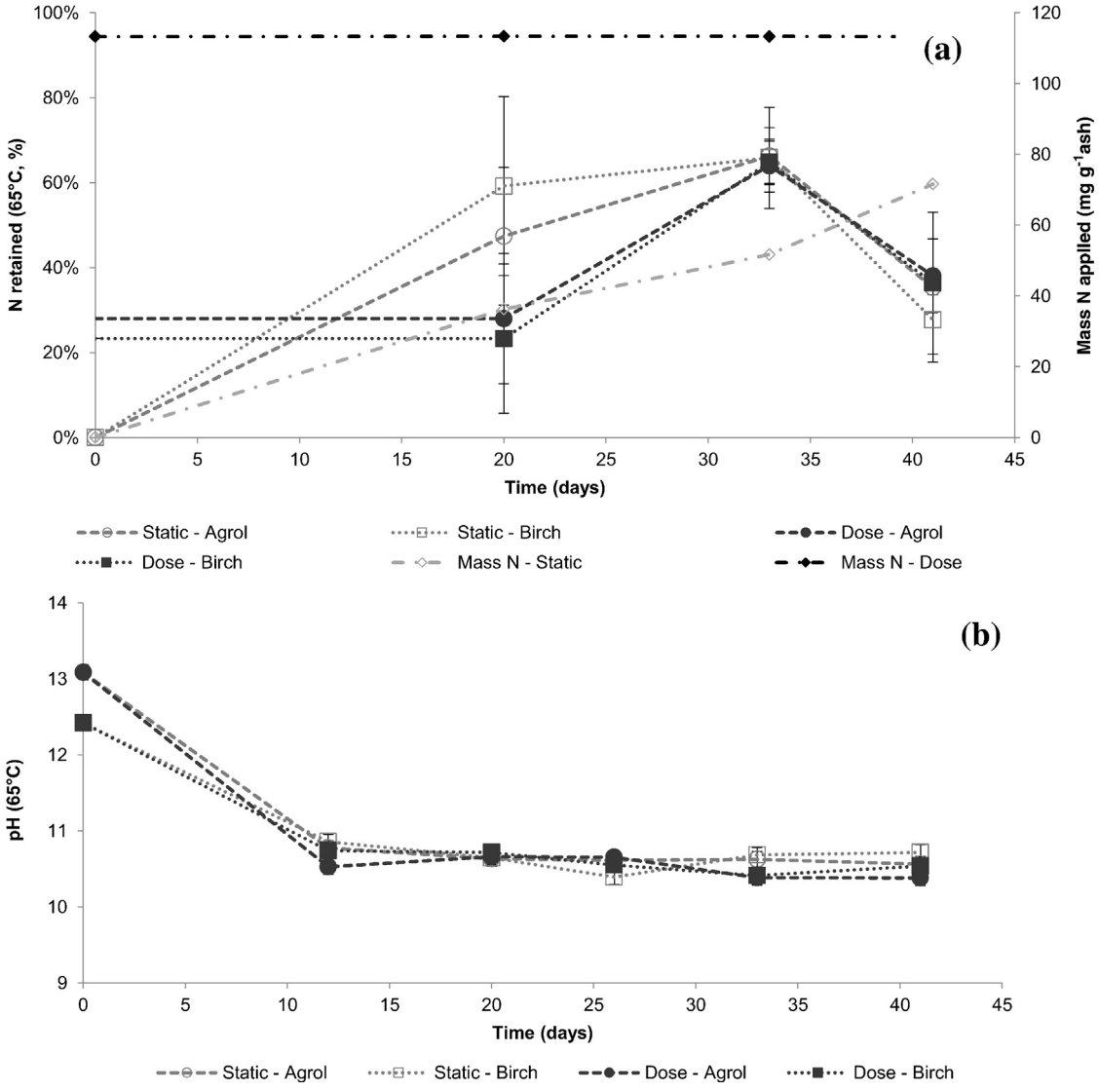

Fig. 2. a) Retained N as NH_3-N (left axis) and the mass of N applied per g ash (right axis) over time and b) pH at 65 °C. For the pH, the standard deviation was too small (<0.15) to be displayed clearly.

precipitated metal phosphates such as struvite ($MgNH_4PO_4 \cdot 6H_2O$) and hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$), due to the high pH and the added Mg and Ca from the ash (Udert et al., 2003). The K can be assumed mainly to remain its original salt forms, such as KCl, K_2SO_4, $KHCO_3$ and K_3PO_4 (Putnam, 1971). Urine has lower heavy metal concentrations than manufactured fertilisers (Jönsson et al., 1997), but the concentrations in different wood ash sources would need to be considered. The salt content of the urine/ash fertiliser (approx. 4.3%; Putnam, 1971) may also need to be taken into consideration if applied in arid areas.

Table 2
Fertiliser characteristics of dried urine and ash. Values based on initial concentrations and applied urine for the two temperature trials (35 °C and 65 °C) with the two systems for adding ash: Static and Dose ($n = 3$; standard deviation in brackets).

Initial	Nutrient concentration (%)			Moisture content, %
	N	P	K	
Urine (liquid)	0.57 (0.13)	0.06 (0.01)	0.29 (0.18)	97.1
Agrol ash	0.0 (0.0)	1.2 (0.0)	7.8 (0.0)	1.8 (0.01)
Birch ash	0.0 (0.0)	1.6 (0.0)	9.6 (0.0)	1.6 (0.00)
35 °C Trial				
Static - Agrol	3.4 (0.09)	1.8 (0.05)	9.1 (0.22)	4.6 (0.21)
Dose - Agrol	7.8 (0.09)	2.5 (0.05)	10.9 (0.26)	5.1 (1.01)
65 °C Trial				
Static - Agrol	3.3 (0.16)	2.1 (0.05)	12.2 (0.22)	3.9 (0.13)
Static - Birch	3.3 (0.36)	2.5 (0.03)	13.9 (0.20)	4.2 (0.21)
Dose - Agrol	6.9 (0.29)	2.4 (0.05)	13.3 (0.26)	4.9 (0.00)
Dose - Birch	6.9 (0.23)	2.8 (0.04)	15.1 (0.22)	5.3 (0.00)

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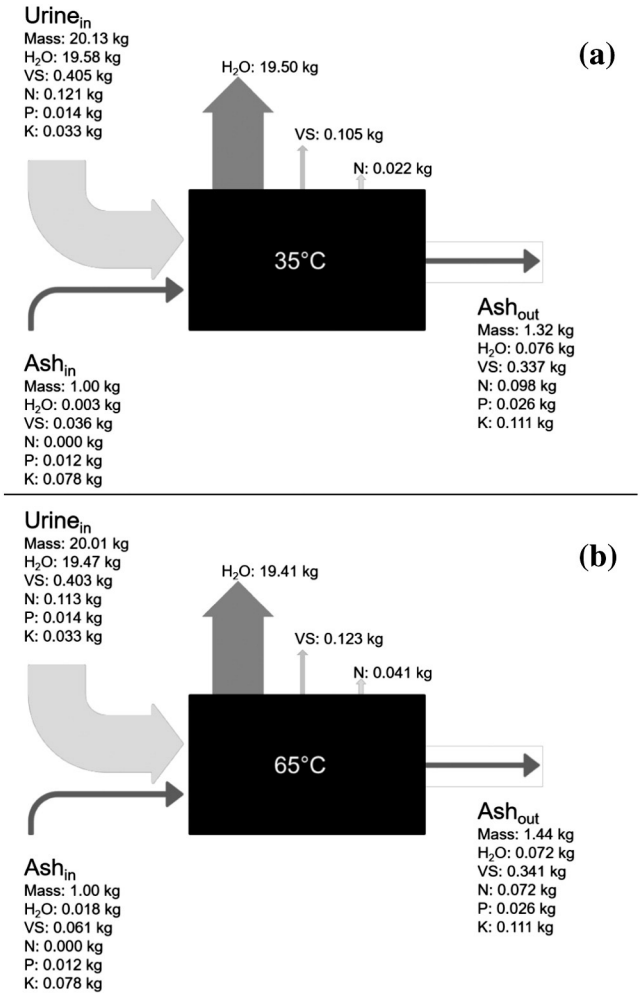

Fig. 3. Measured mass balance for dehydrating 20 L urine with 1 kg ash at a) 35 °C and b) 65 °C for the Dose ash bed, where ash (5% weight of urine) and urine were added at the same time. The excess water (H_2O) in the urine was evaporated, reducing the mass by 93%, in both temperature trials, producing a dry fertiliser. The nitrogen (N) loss is included in the volatile solids (VS).

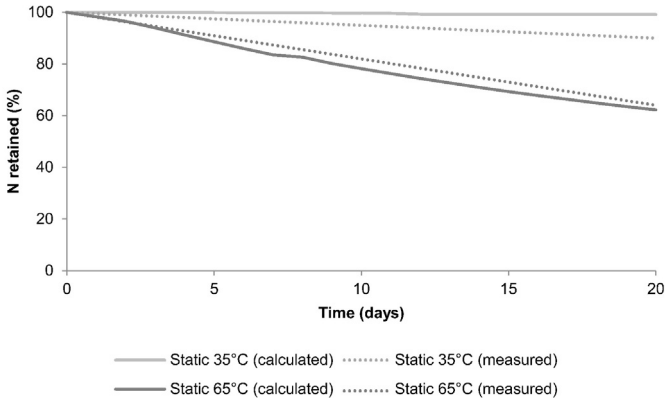

Fig. 4. Calculated percentage of N lost over time from the Static and Dose ash beds at two temperatures (35 and 65 °C) based on Eq. (3). The Static 65 °C calculated line is non-linear due to the shift at Day 7 when the pH dropped below 12.

4.2. Nitrogen losses

The elevated pH was used to inhibit enzymatic degradation of the urea, but N losses were still experienced during the dehydration process (Fig. 3). These N losses were mainly due to two factors. First, approximately 5% of the N initially excreted is already in the form of NH_3 (Udert et al., 2006), and this would volatilise immediately during the high pH dehydration process. Moreover, other N-containing organic substances could be degraded to NH_3 and lost by evaporation (Putnam, 1971). Second, urease enzymes are not the only parameters causing urea hydrolysis, as pH and temperature also hydrolyse urea. Urea is considered to be a stable molecule between pH 2 and 12, but outside this range non-enzymatic decomposition of urea occurs (Zerner, 1991). Therefore, while the highly alkaline conditions of the treatment were limiting for urease enzymatic activity, non-enzymatic hydrolysis by the elimination reaction (promoted in strong alkaline solutions; pKa = 14) was still occurring. In addition, the rate of hydrolysis increases with increasing temperature (thermo-degradation of urea) and increasing pH (Randall et al., 2016), although it is still considerably slower than the enzymatic rate (Table 1).

At 35 °C, up to 5% of urea would have been hydrolysed and lost due to pH and temperature (initial pH 13) (Table 3). In the Static treatment, the N loss at high pH may have been underestimated, as the half-life was based on the pH being below 12. However, Kabdaşlı et al. (2006) observed no N loss at pH >12 after 32 days. In the Dose treatment, the non-enzymatic loss was calculated and accounted for only 5%-units of the 18% N loss, according to Eq. (3). Hence other factors could also be at play, such as (a) some enzymatic activity occurring at the end of the study when the pH was reaching 10; and (b) localised pockets of ash with lower pH (<10).

At 65 °C, the potential loss was up to 54%, whereas the actual loss was 35%. There are three main factors explaining the differences in non-enzymatic loss in Table 3. First, the actual temperature in the dehydrating bed fluctuated over time with addition of the urine (37 °C) and the energy consumption during evaporation, and hence there was less thermo-degradation of the urea than calculated. Second, there was potential formation of struvite (NH_4MgPO_4), capable of capturing 16–25% of the total N in the added urine (overestimation with the assumption that all P from Table 2 formed struvite). The struvite

Table 3
Non-enzymatic loss of N during temperature trials in Static and Dose ash at 35 °C (97 days) and 65 °C (33 days) with Agrol ash. The loss (%) was calculated with half-time decay rates based on the daily average amount of urine added and then number of days that the pH was above and below pH 12 at the given temperature. For the trial at 35 °C, 2% accounts for the N loss during the pause of 52 days. The N retained were measured values (n = 3).

	pH >12		pH <12		Non-enzymatic N loss (%)	N retained %)	Difference (%)
	No. of days	t½	No. of days	t½			
35 °C							
Static	12	3.6 yrs[a]	33	3.6 yrs[b]	4.9	90	7.1
Dose	5	3.6 yrs[a]	40	3.6 yrs[b]	4.9	82	15.1
65 °C							
Static	7	14.1 days[c]	26	15.3 d[c]	53.6	64	−17.6
Dose	5	14.1 days[c]	28	15.3 d[c]	50.7	66	−16.7

[a] Limited data found for pH >12 at 35 °C and therefore the same value as for pH < 12 was used, as studies by Kabdaşlı et al. (2006) found no N loss at pH >12 after 32 days.
[b] (Zerner, 1991).
[c] Derived from data in Warner (1942).

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potential in the urine alone (without the P from the ash) would be at least 7% of the total N added. Third, as with the 35 °C trial, there may have been some enzymatic activity in pockets with lower pH (<10) during the temperature fluctuations. Enzymatic activity may be reduced above 60 °C (Sizer, 1940) and therefore the loss of N in the 65 °C trial was predominantly due to non-enzymatic hydrolysis (Eq. (2)) by elevated temperature and pH.

The N retention in the treatments was similar or higher (64–89.9%) than in other mass-reducing urine treatments such as solar drying (68%; Antonini et al., 2012); ash/lime beds (54–75%; Dutta & Vinnerås, 2016), struvite and nitrification (actual N recovery rate not specified due to N losses during storage) (Udert et al., 2015); NH_3 adsorption on zeolite and wollastonite (65–80%; Lind et al., 2000); and evaporation on gauze sheeting with high salt concentrations (85%; Pahore et al., 2011). Thus ash treatment is not only as efficient or more efficient at retaining N, but the end product is a dry powder that is lighter to transport and easier to apply with conventional fertiliser spreaders than the end product from most other systems, which is generally a slurry that is less concentrated and thereby heavier to transport and more difficult to apply in the field.

4.3. Dehydration

The dehydration is based on passive aeration, relying on steam pressure to transfer water from liquid to gas phase, after which the gas is removed. The outgoing gas would not be saturated due to the high ventilation rate. The large surface area provided by the ash increases the evaporation rate and prevents formation of an oily surface that might limit evaporation, as observed in other urine-dehydrating systems (Hellstrom et al., 1999). High initial relative humidity (RH) and inlet temperature would greatly diminish the evaporation rate. However, with increased temperature, the water-holding capacity of the air increases exponentially, to 40 g/kg dry air at 35 °C and 200 g/kg dry air at 65 °C. Warming the inlet air, either by solar or electricity, would help immensely. For example, to dehydrate 1 L of urine, the air flow requirement would decrease from 616.8 L min^{-1} at 20 °C to 2.23 L min^{-1} by heating the air to 35 °C or even lower, to 0.34 L min^{-1}, by heating the air to 65 °C (based on 70% RH in incoming air and on a 12 h per day drying period). A small solar panel (30 × 20 cm, US$25.00 (Amazon, 2017)) would be ample power for a small computer size fan (60 mm by 25 mm, DC 12 V, 3.1 W, US$9.15, (OrionFans, 2017)) with a sufficient air flow rate of 750 L m^{-1}.

4.4. Implementation potential

In the ash treatments, the urine was collected, contained, treated and reduced within the same container and no offensive odours were detected. Both dehydration temperatures functioned to produce a dry end product with high N-P-K concentration (Table 2). However, dehydration at 65 °C (5.1 L urine per kg/m^2 ash a day) enabled faster treatment than dehydration at 35 °C (3.8 L urine per kg/m^2 ash a day), requiring a longer dehydrating period for the same volume of urine. The saturation of the ash bed is not limited by the mass of urine added, but by the mass of carbon dioxide absorbed from the ventilation. As seen from the controls (Fig. 1), where only water was added, the pH decreased at the same rate as in the urine treatments. To further optimise the system, the incoming air could be stripped of carbon dioxide by an acid treatment. The evaporation rate could be further improved by optimisation of beds. Depending on the design of the system and the frequency with which the ash bed would need to be changed, operating at 65 °C enables flexibility where either the surface area can be decreased or the capacity increased with <20% N loss over 10 days. One limitation of this system would be drying at ambient temperatures at high initial RH%, which could be greatly reduced by increasing the air temperature to 65 °C by solar heating. The system presented here is a low-cost addition to the urine-diverting sanitation system that would greatly improve urine-based fertiliser management with a dry fertiliser product comparable to commercial fertiliser.

5. Conclusions

This study provides proof of concept that an alkaline ash-based dehydrating bed can efficiently retain N (64–89.9%) as urea so that the excess water in urine can be dehydrated (95%) with minimal N loss at a loading rate of 20 L urine per kg ash. A Static ash bed retains more N and would be simpler to operate than adding ash with every use as in a Dose bed system. Dehydrating the urine at higher temperature provides flexibility to either increase capacity or decrease the required surface area of ash. Installing such a dehydration system in existing urine-diverting dry toilets would greatly simplify the logistics and costs of storage, transportation and fertiliser application, as there would be no liquid disposal. The urine can be collected, contained, treated and reduced within the same collection container to produce a dry end product with high N-P-K concentration (up to 7.8–2.5–10.9), i.e. a fertiliser with monetary value.

Acknowledgement

This study was supported by The Swedish Research Council VR for the project Productive on-site sanitation system: New value chain for urine based fertiliser [grant number 2015-03072].

References

Amazon, 2017. Eco-worthy 10 W solar panel. Generators & Portable Power > Solar & Wind Power > Solar Panels, Amazon.com Inc.
Antonini, S., Nguyen, P.T., Arnold, U., Eichert, T., Clemens, J., 2012. Solar thermal evaporation of human urine for nitrogen and phosphorus recovery in Vietnam. Sci. Total Environ. 414, 592–599.
Baum, R., Luh, J., Bartram, J., 2013. Sanitation: a global estimate of sewerage connections without treatment and the resulting impact on MDG progress. Environ. Sci. Technol. 47, 1994–2000.
Callahan, B.P., Yuan, Y., Wolfenden, R., 2005. The burden borne by urease. J. Am. Chem. Soc. 127 (31), 10828–10829.
Ciurli, S., Benini, S., Rypniewski, W.R., Wilson, K.S., Miletti, S., Mangani, S., 1999. Structural properties of the nickel ions in urease: novel insights into the catalytic and inhibition mechanisms. Coord. Chem. Rev. 190–192 (0), 331–355.
Ciurli, S., Marzadori, C., Benini, S., Deiana, S., Gessa, C., 1996. Urease from the soil bacterium bacillus pasteurii: immobilization on Ca-polygalacturonate. Soil Biol. Biochem. 28 (6), 811–817.
Dutta, S., Vinnerås, B., 2016. Fertilizer from dried human urine added to ash and lime – a potential product from eco-sanitation system. Water Sci. Technol. 74 (6), 1436–1445.
Etter, B., Tilley, E., Khadka, R., Udert, K.M., 2011. Low-cost struvite production using source-separated urine in Nepal. Water Res. 45 (2), 852–862.
FAO, 1986. Efficient fertilizer use in acid upland soils of the humid tropics. Food and Agricultural Organization.
FAO, 1991. Manual on fertilizer statistics. Food and Agriculture Organization of the United Nations.
FAO, 2015. World fertilizer trends and outlook to 2018. Food and Agriculture Organization of the United Nations.
Hellstrom, D., Johansson, E., Grennberg, K., 1999. Storage of human urine: acidification as a method to inhibit decomposition of urea. Ecol. Eng. 12, 253–269.
Hotta, S., Funamizu, N., 2008. Inhibition factor of ammonification in stored urine with fecal contamination. Water Sci. Technol. 58 (6), 1187–1192.
Huang, T.-C., Chen, D.-H., 1991. Kinetic study of urease-catalysed urea hydrolysis. J. Chem. Technol. Biotechnol. 52 (4), 433–444.
Jespersen, N.D., 1975. Thermochemical study of the hydrolysis of urea by urease. J. Am. Chem. Soc. 97 (7), 1662–1667.
Jönsson, H., Stenström, T.-A., Svensson, J., Sundin, A., 1997. Source separated urine-nutrient and heavy metal content, water saving and faecal contamination. Water Sci. Technol. 35 (9), 145–152.
Kabdaşlı, I., Tünay, O., İşlek, Ç., Erdinç, E., Hüskalar, S., Tatlı, M.B., 2006. Nitrogen recovery by urea hydrolysis and struvite precipitation from anthropogenic urine. Water Sci. Technol. 53 (12), 305–312.
Krajewska, B., 2009. Ureases I. Functional, catalytic and kinetic properties: a review. J. Mol. Catal. B Enzym. 59 (1–3), 9–21.
Lind, B.-B., Ban, Z., Bydén, S., 2001. Volume reduction and concentration of nutrients in human urine. Ecol. Eng. 16 (4), 561–566.
Lind, B.B., Ban, Z., Byden, S., 2000. Nutrient recovery from human urine by struvite crystallization with ammonia adsorption on zeolite and wollastonite. Bioresour. Technol. 73 (2), 169–174.
Maurer, M., Pronk, W., Larsen, T.A., 2006. Treatment processes for source-separated urine. Water Res. 40 (17), 3151–3166.

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Nyberg, K.A., Vinnerås, B., Lewerin, S.S., Kjellberg, E., Albihn, A., 2011. Treatment with Ca(OH)2 for inactivation of *Salmonella typhimurium* and *Enterococcus faecalis* in soil contaminated with infected horse manure. J. Appl. Microbiol. 110 (6), 1515–1523.
OrionFans, 2017. OD6025-12HH Series. DC Fans. Orion Fans, Dallas, Texas.
Pahore, M.M., Ushijima, K., Ito, R., Funamizu, N., 2011. Fate of nitrogen during volume reduction of human urine using an on-site volume reduction system. Environ. Technol. 33 (2), 229–235.
Parker, D.B., Rhoades, M.B., Cole, N.A., Sambana, V.P., 2012. Effect of urease inhibitor application rate and rainfall on ammonia emissions from beef manure. Trans. ASABE 55 (1), 211–218.
Penhallegon, R., 2003. Nitrogen-Phophorus-Potassium Values of Organic Fertilizers. Oregon State University Extension Service.
Putnam, D.F., 1971. Composition and Concentrative Properties of Human Urine. McDonnell Douglas Astronautics Company - Western Division.
Ramírez, C.A., Worrell, E., 2006. Feeding fossil fuels to the soil: an analysis of energy embedded and technological learning in the fertilizer industry. Resour. Conserv. Recycl. 46 (1), 75–93.
Randall, D.G., Krähenbühl, M., Köpping, I., Larsen, T.A., Udert, K.M., 2016. A novel approach for stabilizing fresh urine by calcium hydroxide addition. Water Res. 95, 361–369.
Rockström, J., Steffen, W., Noone, K., Persson, A., Chapin, F.S., Lambin, E.F., Lenton, T.M., Scheffer, M., Folke, C., Schellnhuber, H.J., Nykvist, B., de Wit, C.A., Hughes, T., van der Leeuw, S., Rodhe, H., Sorlin, S., Snyder, P.K., Costanza, R., Svedin, U., Falkenmark, M., Karlberg, L., Corell, R.W., Fabry, V.J., Hansen, J., Walker, B., Liverman, D., Richardson, K., Crutzen, P., Foley, J.A., 2009. A safe operating space for humanity. Nature 461 (7263), 472–475.
Sizer, I.W., 1940. The activation energy of urea hydrolysis catalyzed by soy bean urease. J. Biol. Chem. 132, 209–218.
Udert, K.M., Buckley, C.A., Wächter, M., McArdell, C.S., Kohn, T., Strande, L., Zöllig, H., Fumasoli, A., Oberson, A., Etter, B., 2015. Technologies for the treatment of source-separated urine in the eThekwini municipality. Water SA 41 (2), 212–221.
Udert, K.M., Larsen, T.A., Biebow, M., Gujer, W., 2003. Urea hydrolysis and precipitation dynamics in a urine-collecting system. Water Res. 37 (11), 2571–2582.
Udert, K.M., Larsen, T.A., Gujer, W., 2006. Fate of major compounds in source-separated urine. Water Sci. Technol. 54 (11–12), 413–420.
Vinnerås, B., 2002. Possibilities for sustainable nutrient recycling by faecal separation combined with urine diversion. Department of Agricultural Engineering, Vol. Doctoral. Swedish University of Agricultural Sciences, Uppsala, p. 88.
Vinnerås, B., Palmquist, H., Balmer, P., Jönsson, H., 2006. The characteristics of household wastewater and biodegradable solid waste — a proposal for new Swedish design values. Urban Water 3, 3–11.
Winker, M., Vinnerås, B., Muskolus, A., Arnold, U., Clemens, J., 2009. Fertiliser products from new sanitation systems: their potential values and risks. Bioresour. Technol. 100, 4090–4096.
Warner, R.C., 1942. The Kinetics of the Hydrolysis of Urea and Arginine. J. Biol. Chem. 142 (2), 705–723.
WorldBank, 2017. Commodity Markets Outlook - Investment Weakness in Commodity Expoerters. A World Bank Quarterly Report. Washington, The World Bank. Q1, pp. 22–30.
Wozny, M.A., Bryant, M.P., Holdeman, L.V., Moore, W.E., 1977. Urease assay and urease-producing species of anaerobes in the bovine rumen and human feces. Appl. Environ. Microbiol. 33 (5), 1097–1104.
Zerner, B., 1991. Recent advances in the chemistry of an old enzyme, urease. Bioorg. Chem. 19 (1), 116–131.
Zhang, Y., Li, Z., Zhao, Y., Chen, S., Mahmood, I.B., 2013. Stabilization of source-separated human urine by chemical oxidation. Water Sci. Technol. 67 (9), 1901–1907.

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