Methods for stabilising and concentrating human urine for use as a fertilizer

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Abstract Ever increasing demand for agricultural products causes an equally increasing demand for fertilizers. In the modern world though, these are produced from non-renewable sources, rather than from organic wastes, while at the same time lack of sanitation causes discharge of significant amounts of nutrients in the aquatic environment. Production of fertilizers from urine might be an option to, at least partially, solve both problems and close a cycle that needs to be closed again. However, to achieve this, a method must be devised to stabilize the urea present in urine, as under normal conditions this compound is rapidly hydrolysed, causing the loss of N to the atmosphere as NH_3. In this paper addition of common and low cost compounds to urine in order to stabilize nitrogen as urea are investigated, and it is concluded that the use of acetic acid (vinegar) may be an option for such a process.
Keywords: evaporation, urea stabilisation, fertilisation, resource oriented sanitation

INTRODUCTION

An ever increasing world population needs every day more food and other agricultural products. Thus, worldwide demand for fertilizers is increasing as well, but most fertilizers are now produced in unsustainable ways, like from fossil sources and phosphate mining. At the same time, increasing amounts of sewage are discharged in surface waters and, if treated at all, nutrient removal is often inadequate. In Brazil for instance, about 65 % of fertilizers are imported while 61 % of sewage is discharged without adequate treatment. Consequently, just as seen for carbon, the natural cycle of nutrients is broken, and rivers, lakes and oceans are suffering from eutrophication. As the nutrients available in human urine represent a significant part of the nutrients required for agriculture (Lind *et al.*, 2001), direct recycling of these nutrients to agriculture might be an option especially in densely populated regions with still low fertilizer use, like the semi urban areas in the Brazilian Northeast.

Urine separation is part of the Resource Oriented Sanitation concept, which is based on source-separation of different fractions of sewage, in order to permit reuse of resources. Several studies have demonstrated the value of urine as fertilizer (Heinonen-Tanski *et al.*, 2007; Tidaker *et al.*, 2007; Karak *et al.*, 2011; Kutu *et al.*, 2011). The nitrogen (N) present in urine is present in the form of urea, a molecule that tends to be rapidly hydrolysed in neutral environments (Figure 1) (Fidaleo *et al.*, 2003), leading to the loss of the N to the atmosphere in the form of ammonia. As a result, nitrogen present in urine can only be used for fertilizer production after developing a mechanism to protect it from hydrolysis, while transport of this material is only economically feasible when a major part of the water contained in it is removed (Gulyas *et al.*, 2014).

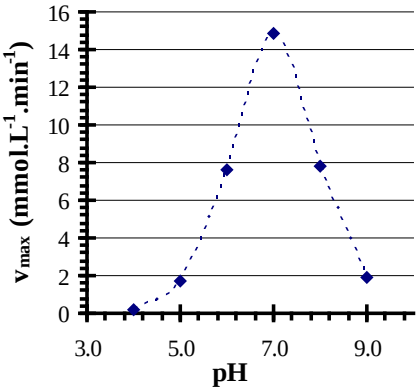

Figure 1: urea hydrolysis rate (Fidaleo *et al.*, 2003).

The loss of nitrogen can be prevented by means of acidification or alkalinisation, or by the use of urease inhibitors. Dewatering urine or separating the nutrients contained in it is the next step, but not so easy to achieve in a feasible way. A comprehensive review published by Maurer *et al.* in 2006 presented a wide range of technical options to treat collected urine, including: evaporation, freeze-thawing, reverse osmosis, acidification, nitrification, P-recovery by struvite formation, N-recovery by ion-exchange, ammonia stripping and *iso*-butylaldehyde-diurea (IBDU) precipitation, amongst others (Maurer *et al.*, 2006). However, the majority of the proposed methods are complex and not feasible to full scale application. More recently, others options were proposed, such as i) biological nitrification with distillation aiming at recovering all nutrients from source-separated urine in a dry solid fertilizer (Udert *et al.*, 2012), which requires a high energy input, ii) vertical gauze sheets as a simpler method to evaporate stored urine on-site, a method that showed to be promising at moderate evaporating conditions, where the rapid salt accumulation inhibits urea hydrolysis, but operating at low evaporating conditions caused the pH to raise causing ammonia loss (Pahore *et al.*, 2010). Following, iii), Gulyas *et al*. proposed the pre-treatment of stored urine by low-tech ammonia stripping to avoid nitrogen loss during solar evaporation (Gulyas *et al.*, 2014). Considering that a feasible, low energy, method with low operation and maintenance costs has not been established so far, the main objectives of this work were to study a way to stabilize nitrogen in urine by adjusting the pH to a value where urea hydrolysis does not occur (either $pH \leq 4{,}0$ or $pH \geq 10$), using readily available and easily handleable reagents, and to develop a simple evaporator that can be used in individual residences.

MATERIALS AND METHODS

Before starting the actual experiments with stabilisation of urine, the natural stability of the urine samples was determined in a preliminary test, in order to determine whether the urine could be stored in the laboratory before its use in the experiments, and under which conditions. In this preliminary experiment, the parameters $TN_{Kjeldahl}$ and NH_3-N were determined for the same samples as follows: i) freshly collected, ii) stored at ambient temperature, iii) stored in the fridge and iv) stored in a freezer. As ammonia was lost under all conditions, it was decided to use fresh urine (collected at most 4 hours before the experiment) for all experiments. Different methods for analysis of TN (Kjeldahl and Hach) and ammonia (Hach and an Orion ion-selective electrode) were also tested, partially because the mixtures with ashes and limestone would quickly become solid and measurements should not become a problem after the start of the experiments.

The mixed urine used for the experiments described here (Table 1) was obtained by collecting and mixing samples from a group of volunteers (50% Male, 50% Female, average age of the "donors" was 26.6 years). This mixed urine was analysed for temperature, turbidity, conductivity, pH, nitrite, nitrate, NH_3-N, $TN_{Kjeldahl}$, P, K, sulphate, sulphide, total solids (TS) and volatile suspended solids (VSS), according to "Standard Methods" (APHA *et al.*, 2005). Experiments were initiated immediately after sampling for initial analysis, to avoid any changes in composition, by adding amounts of potentially stabilizing compounds to an initial volume ($V_{initial}$) of 200 mL or 300 mL of fresh mixed urine. The samples, in triplicate, were stored in open 500 mL square glass vessels inside closed boxes in a temperature controlled room, with or without ventilation. Over time, evaporation was quantified by weighing, whilst periodically pH and nutrient concentrations ($TN_{Kjeldahl}$, NH_3, P, K) were determined as well. After almost total evaporation of the samples, a final analysis of the residual solid was performed and a recovery index for the nutrients was calculated.

Batch experiments with soluble stabilising compounds

Experiments were initiated according to the general procedure as stated above. Details of the mixtures are presented in Table 2. The first experiment was carried out in closed boxes, with forced ventilation, and the air passing through two absorption columns with sulfuric acid (before being admitted to the box and after), in order to permit quantification of the ammonia volatilization in each experiment (Figure 1). However, the admitted airflow was thus saturated with water vapour, and no evaporation of urine occurred. Thus the experiments 2 to 4 were carried out without the gas-washing bottle at the admission side, in a ventilated greenhouse, and ammonia volatilization was calculated from loss of $TN_{Kjeldahl}$. Ambient temperature, humidity, weight and pH were determined daily, whilst samples for analysis of N, P and K were collected after pre-defined intervals. After sampling, the weight of every vessel was determined again, in order to be able to correct for losses of water and solutes.

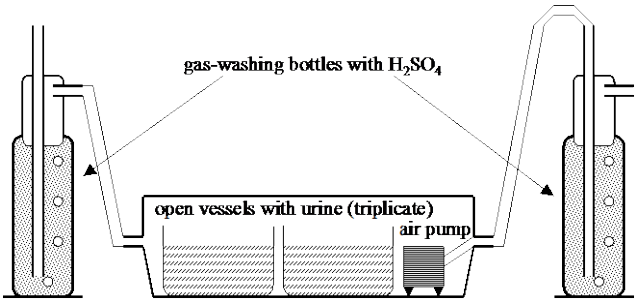

Figure 2: experimental setup with open vessels (triplicate) with urine and stabiliser contained in a sealed, ventilated box; each box containing only one set of triplicates. Air drawn in and expelled through gas washing bottles by means of small aquarium compressors. From experiment 2 on, gas-washing bottle at admission removed.

Table 1: Batch experiments conducted

Exp.	Stabilising agent tested	Ventilation	Conditions
1	bases (test of experimental setup)	forced	temperature controlled room (T_{amb} = 27.3 °)
2	acids (HCl, H_2SO_4, CH_3COOH)	natural	greenhouse (T_{amb} = 15.8 ± 5.8 °C)
3	bases (NaOH, ashes and limestone)	natural	greenhouse (T_{amb} = 28.0 ± 4,1 °C)
4	acids (H_2SO_4, CH_3COOH and BA)	natural	greenhouse (T_{amb} = 24,4 ± 6,6 °C)

After complete evaporation of the liquid from the vessels, a sample of the precipitate was withdrawn for final analysis, and in order to be able to close the balance of N, P and K. To avoid fungal growth, 60 mM of benzoic acid (BA; C_6H_5COOH; Vetec, Duque de Caxias-RJ, BR) was added as a fungicide during experiment 4.

Table 2: composition of the triplicates of experiments 1 and 2: urine stabilized with soluble stabilizers.

Exp.	Condition	Reagent	Conc. (M)	$pH_{initial}$	$V_{initial}$ (mL)	observations
2-U	urine	-	-	5.47	300	
2-SA	urine + acid	H_2SO_4	0.056	3.01	300	
2-HCl	urine + acid	HCl	0.064	2.96	300	
2-Hac	urine + acid	CH_3COOH	0.524	3.02	300	
2-NaOH	urine + base	NaOH	0.009	12.02	300	
4-SA1	urine + sulfuric acid	H_2SO_4	0.065	1.08	200	
4-SA2	urine + sulfuric acid	H_2SO_4	0.13	0.81	200	
4-SA3	urine + sulfuric acid	H_2SO_4	0.26	0.66	200	
4-SAF	urine + sulfuric acid	H_2SO_4	0.065	1.74	200	+ fungicide
4-HAc1	urine + acetic acid	CH_3COOH	0.13	3.5	200	
4-HAc2	urine + acetic acid	CH_3COOH	0.26	3.21	200	
4-HAc3	urine + acetic acid	CH_3COOH	0.52	3.01	200	
4-HAcF	urine + acetic acid	CH_3COOH	0.13	3.90	200	+ fungicide

Batch experiments with solid stabilizing compounds

The experiments were carried out according to the protocol described above, in triplicate, in open glass vessels of 500 mL. In these experiments, limestone (from Serra de Bodoquena-MS, BR) and ashes from sugarcane bagasse (from the boiler of a sugar factory/distillery in Sidrolandia-MS, BR) were used as conserving additives. These solids were added in volumetric proportion according to Table 3, based on density, to a graduated cylinder, after which the volume was completed to 200 mL or 300 mL with urine (the amount of urine actually used was determined by weighing). After thorough mixing, the content of the cylinder was transferred to the open vessel. Subsequently, samples for the initial analyses (solids, pH, $TN_{Kjeldahl}$ e NO_3-N, K) were withdrawn, and the vessels were placed in a temperature-controlled room (30.72 ± 1.97 °C) or in a greenhouse, according to Table 1 and Table 3. Daily, ambient temperature, humidity, weight and pH were determined, and at specific intervals samples were withdrawn for analysis of N, P and K. As in these experiments the samples were not homogeneous liquids, samples were taken and analysed as follows: a small amount (2.0 g) of sample was dissolved in 100 mL distilled water and homogenized. The suspension produced was then analysed using methods as described in "Standard Methods" (APHA *et al.*, 2005). The concentration was then calculated in terms of grams of compound per kg of experimental material, as both density and volume of the sample were unknown and varied during the course of the experiment. After sampling, the weight of every vessel was determined again in order to be able to correct all balances for loss of volume. After complete evaporation of all liquid, a sample of the remaining solid was taken for final analyses in the same way as for the previous series of experiments.

Table 3: composition of the samples used in the experiment with solid stabilizers

Exp.	alkaline conditions	proportion	$pH_{initial}$	ambient conditions
1-U	urine	-	6.4	forced evaporation (temperature controlled room)
1-Ci	urine + ashes	1+3	9.2	
1-Ca	urine + limestone	3+1	12.8	
1-CiCa	urine + ashes + limestone	2+1+1	12.8	
3-Ua	Urine	-	6.4	natural evaporation (greenhouse)
3-Ci	urine + ashes	1+3	9.2	
3-Ca	urine + limestone	6+1	12.6	
3-CiCa	urine + ashes + limestone	4+2+1	12.1	
3-Ub	urine	-	6.4	forced evaporation (greenhouse)

Experiments with a lab scale reactor

The faster the evaporation of water from urine occurs, the better, as a fast drying reduces nitrogen loss to the atmosphere. For rapid evaporation of the water contained in urine, a bench scale reactor was developed. The reactor consisted of i) a urine reservoir, ii) a heated, rotating drum for evaporating the water and iii) a system to collect the precipitate from the drum, as shown in the pictures (Figure 3). The reservoir of the reactor measured 19 x 9 x 5 cm (0.6 L), whilst the drum was 11 cm long and had a diameter of 8 cm. The drum was mounted on ball bearings and turned by a small motor, while a heating element inside the drum permitted heating the drum to 45 °C. Preliminary experiments were conducted in which the reactor was filled with 600 mL of urine, which was then evaporated. The reservoir was topped up continuously, whilst the concentrated solids were removed from the system. During the experiment, temperature, weight, pH and amount of precipitate were monitored.

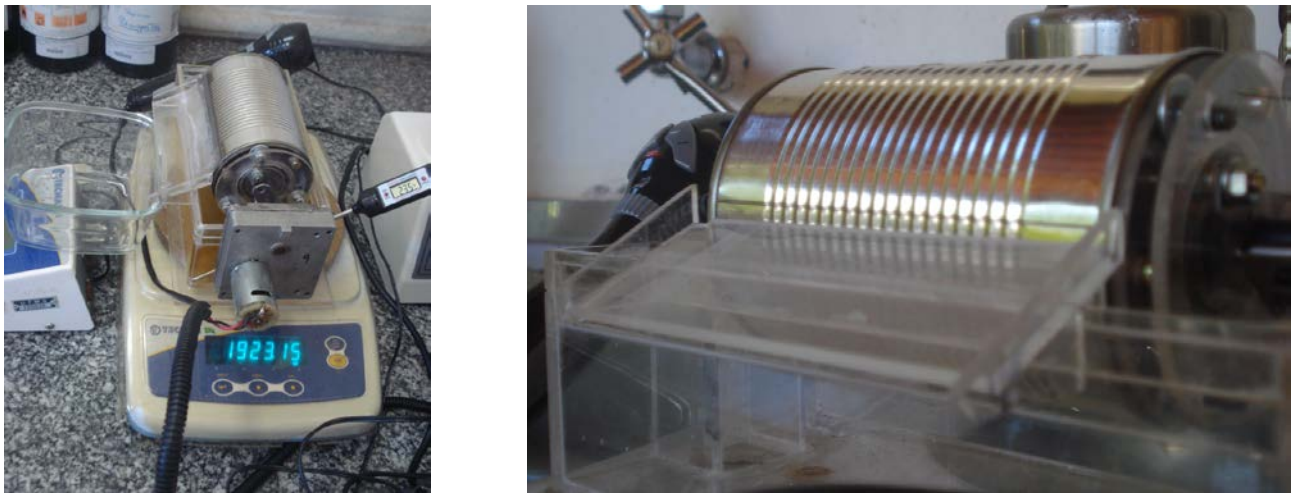

Figure 3: Experimental set up: the urine evaporating reactor and collection of the precipitate.

RESULTS AND DISCUSSION

The characterisation of the collected urine showed results comparable to those of Putnam and Udert (Putnam, 1971; Udert *et al.*, 2003). When urine is stored, part of the urea present may be hydrolysed, causing an increase of the pH and dissolved ammonia (NH_3), and loss of ammonia to the atmosphere, a process aggravated by the water loss occurring as a result of evaporation (Udert *et al.*, 2006). Addition of acids will reduce hydrolysis rates and also maintain the ammonia as NH_4^+, reducing evaporation losses (Equation 1).

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad \text{Equation 1}$$

Bases like NaOH or limestone may reduce hydrolysis rates as well, but will accelerate losses of ammonia, when formed. When acids are used to set the initial pH to a value of 3, the elevation of its pH will only occur after 10 days, when the urine volume has already been reduced by 50 % (Figure 4, left). Use of a weak acid like acetic acid requires a higher dose to obtain a low pH, but in compensation this higher dose will increase the buffering capacity of the system, such that in this case the pH reached a value of 4.35 only after 23 days (Figure 4). When higher concentrations of stronger acids are used (starting the experiment with a concentration of between 0.065 M e 0.27 M of acid, this still being only half of the amount of acetic acid used in the first experiments), rather than starting the experiment with a specific pH, the pH will actually drop even more during the experiment: urea conversion will not occur at all, avoiding liberation of the basic ammonia, NH_3, and with the loss of water, the concentration of acid increases and the pH decreases over time (Figure 4, right).

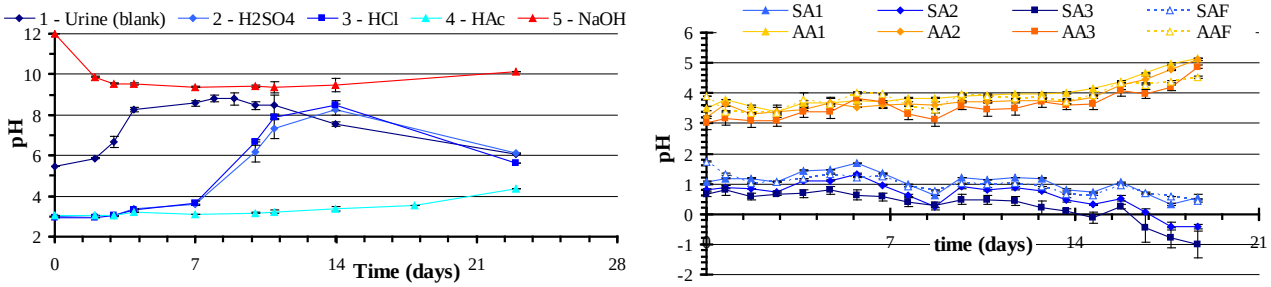

Figure 4: Evolution of pH during urine storage with evaporation. Left.: urine: plain and with H_2SO_4, HCl, acetic acid (HAc) and NaOH. Right.: acidified with equal amounts (0.12...0.52 N) of acetic (AA, $pH_{initial}$ = 3) and sulphuric acid (AS).

Nutrient (nitrogen, phosphorus, potassium) recovery in these experiments increases to the extent that the increase in pH during the experiment was impeded, with significant losses in the blank (urine without additives) and in the experiments where the pH before evaporation was around 3 but containing only a very low concentration of strong acids (Figure 5, left). In the experiments with higher concentrations of weaker acids (HAc_n series), nutrient recovery was complete (Figure 5, right).

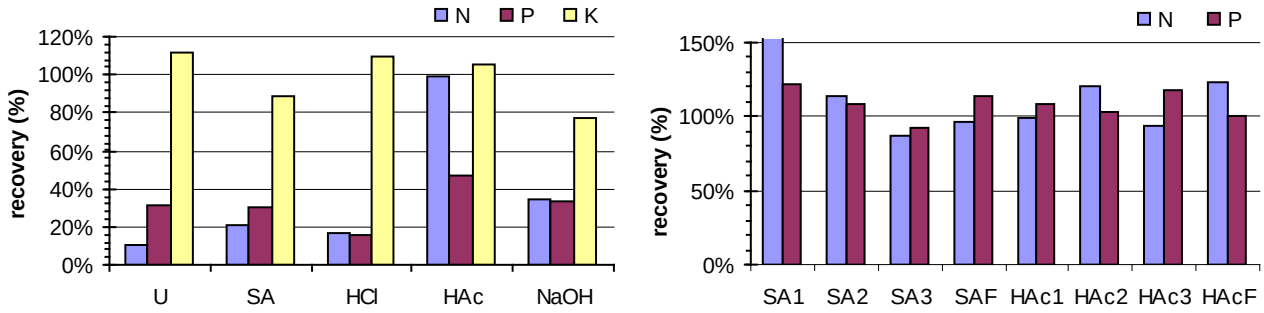

Figure 5 : recovery of nutrients N, P and K. Left: plain urine (U) and acidified with sulfuric acid (SA), hydrochloric acid (HCl) and acetic acid (HAc) until a $pH_{initial}$ = 3. Right: acidified with acetic acid (HAc_n) and sulfuric acid (SA_n) in concentrations between 0.065 M and 0.026 M.

Apart from acids, bases may also cause inhibition of urea hydrolysis (Figure 1). Thus, experiments were also conducted using sodium hydroxide (NaOH), ground limestone, and ashes obtained from incineration of sugarcane bagasse. However, the results were not as good in terms of recovery, as the results obtained using acids (Table 4).

Table 4: Results obtained with the tested basic compounds (sodium hydroxide, ground limestone, and ashes)

basic compound used	**$pH_{initial}$**	**N-recovery (%)**	**P-recovery (%)**
none (urine as collected)	6.40	11	31
sodium hydroxide	12	34	33
limestone (130 $g.L^{-1}$)	12.6	28	58
limestone (140 $g.L^{-1}$)	12.8	68	82
ashes	9.25	28	49
ashes + limestone	12.8	74	44

In the presence of sodium hydroxide (NaOH), the recovery of nitrogen was only 34%. With limestone, nitrogen recovery reached 68%, while using ashes (obtaining an initial pH of only 9.25) nitrogen recovery was only 28%. A problem with the use of basic compounds to reduce nitrogen losses however is that when urea hydrolysis is not totally avoided (as seemed to be the case in the experiments with the ashes and with NaOH), whatever amount of ammonia produced is immediately removed from the system, as in this case the equilibrium of equation 1 is situated completely on the right, the side representing the volatile form of ammonia. The amount of limestone needed to recover a significant portion of the nitrogen also will increase (a lot!) the weight of the fertilizer that will need to be transported after evaporation of the urine, as instead of only a few grams of nutrient containing paste, more than 140 grams of limestone impregnated with nutrients is produced.

To avoid excessive expenses with transport of urine, it is of vital importance that the volume of urine is reduced before its use as a fertilizer. However, evaporation of water is a process requiring lots of energy. It is thus essential to be able to realise this evaporation by natural means, like

sunlight and wind. The experiments as performed show that the rate of urine evaporation depends mainly of the temperature, but also on the amount of dissolved solids, as a higher temperature increases water partial pressure whilst the presence of solutes reduces this pressure, causing an increase and a decrease of the rate of evaporation during the experiments, respectively. On average, an amount of 300 mL of urine takes 20 days to evaporate, at a rate that becomes even smaller when the additive is a solid like limestone or ashes. The best option for a rapid reduction of the volume to be transported thus is the use of some external source of heat. In residences, recirculation of hot water, when a solar water boiler is available for instance, might be an option. And in industrial settings the use of residual heat, like for instance from cooling water of running engines, might present a viable solution.

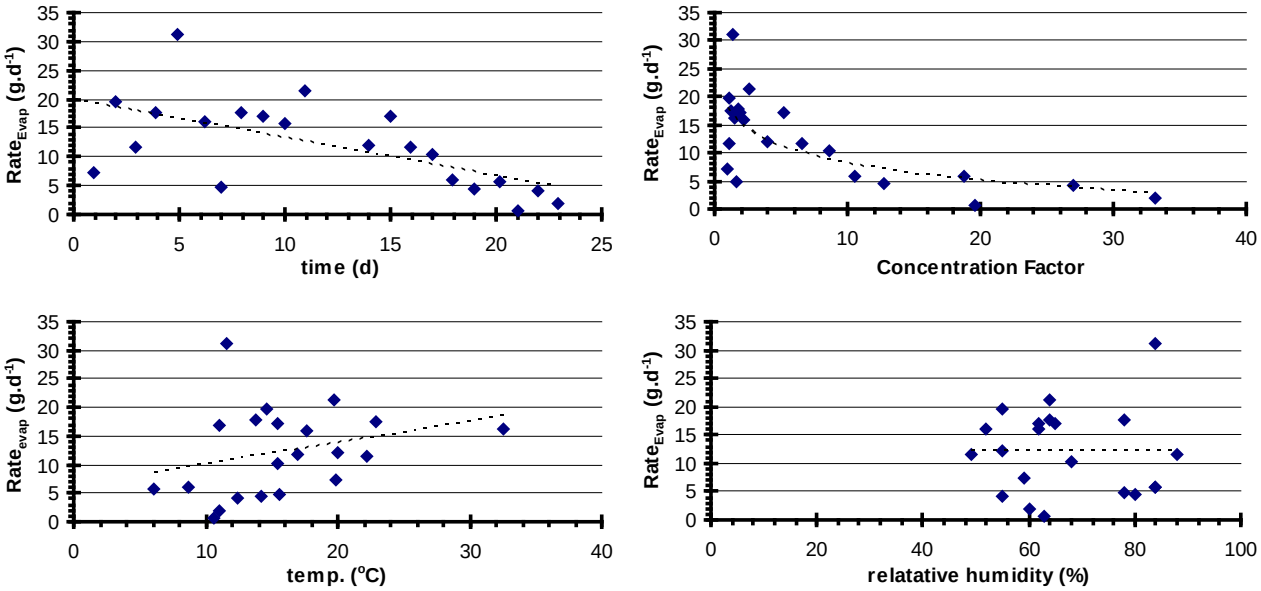

Figure 6: correlation between the rate of evaporation ($Rate_{Evap}$, in grams evaporated per day) with 4 parameters: the time of the experiment (upper left), the urine concentration factor (upper right), ambient temperature (lower left) and humidity of the air (lower right). The most important factor is the ambient temperature, but as can be expected from the reduction in vapour pressure, the concentration factor also plays an important role.

CONCLUSIONS

The best results for preserving nutrients contained in urine (almost 100% N-recovery) were obtained by means of acid conservation, using concentrations of ≥ 60 mM of strong, or ≥ 540 mM of weak acids (vinegar contains ≈ 1 M of acetic acid). Impeding urea hydrolysis using bases, for instance adding ≈ 140 g.L^{-1} of limestone, also works, but will result in a significant increase of the weight of the produced fertilizer. Good results with urine drying were obtained at elevated temperatures, and when no solids were added. From a practical point of view, the most appropriate option for nutrient conservation in urine is probably adding a 15% (v/v) amount of vinegar.

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