Fertilizer NPK from human urine and olive oil mill wastewaters

Manuel Jimenez Aguilar

ABSTRACT

The objective of this work was to determine how some wastewater acids could be used to prevent the decomposition of urea into ammonia during storage. The effect of storing human urine with olive oil mill wastewaters (OOMW) or water bubbled with CO₂ (BW), was studied. Moreover, the application of two levels of urine dissolved in water OOMW, has been studied in relation to the properties of two soils (loam and silty-clay loam). Our data provide evidence that human urine dissolved in OOMW significantly reduced the release of ammonium-N. Moreover, OOMW and CO₂ significantly lowered the pH. A dosage higher than 10% OOMW dissolved in fresh urine in volume could inhibit the hydrolysis of the urea for more than 6 months. Moreover, urine-N dissolved in OOMW significantly reduced the emission of nitrates from soils for 3 months, increasing K and P values. The application of urine with BW raised the soil pH and lowered the EC, but had no effect on nutrient contents. Thus, urine dissolved in OOMW and applied to soils could act as NPK-fertilizer. However, the impact of fertilization with human urine–OOMW–CO₂ requires further investigation with respect to crop production and pollution.

Key words | carbon dioxide, nitrogen conservation, olive oil wastes, organic wastes recycling, urine

INTRODUCTION

The plant nutrients consumed in human society today are lost through the established wastewater-treatment systems in industrialised countries as well as via insufficient or non-existent handling of sewage in the developing world. Human urine is a natural resource, which is available in all human societies, even the poorest ones. Urea is the main nitrogen component present in human urine. Urea fertilizer production has developed during the last few decades so that urea is one of the most important industrial nitrogen fertilizers. When urine becomes mixed with faeces, the mixture is much more difficult to handle hygienically outside of wastewater-treatment plants. To overcome this problem, urine-separating toilets have been introduced (Heinonen-Tanski et al. 2007). Separating urine from wastewater at the source reduces the costs of extensive wastewater treatment. Recovering the nutrients from urine and reusing them for agricultural purposes adds resource saving to the benefits. Source separation and reuse of human urine can decrease the environmental pollution of recipient waters and reduce the need for artificial mineral fertilizers (Behrendt et al. 2002).

The use of recycled urine, even if it is successfully separated from faeces, requires storage and transport. Storage offers a possible way of reducing the potential health risks from faecal pathogens (Hoglund et al. 2002).

In fresh urine the greater part of the nitrogen appears in organic form as urea CO(NH₂)₂. During hydrolysis, the pH rises and ammonium and bicarbonate ions are produced. Hydrolysed urine could be a resource of N and P because it could provide as much as 7,220 mg/L of N-NH₄ and 206 mg/L of P-PO₄. Complete hydrolysis requires 3–7 days (Liu et al. 2008). There is a strong relationship between pH and the fraction of urea decomposed in human urine. Thus, pH measurement could be used as a method to follow the decomposition rate of urea. A higher storage temperature and greater dilution increased the decomposition rate of
urea. The addition of acidic materials to urea may reduce urea hydrolysis and NH₃ volatilization. A one-time dosage of 60 meq sulphuric or acetic acid per litre of undiluted urine at the beginning of the storage period could inhibit the decomposition of urea for more than 100 days of storage in cans with multi-time dosages of urine (Hellström et al. 1999).

OOMW is produced in large amounts in Mediterranean countries. This material must be re-used to reduce its environmental impact and recover some nutrients. To solve the problems associated with OOMW, different elimination methods have been proposed based on evaporation ponds, thermal concentration and physico-chemical as well as biological treatments, including application on the soil (Roig et al. 2006). Many authors have observed phytotoxic effects in plants when this waste is used directly as an organic fertilizer. Such negative effects are associated with its high mineral-salt content, low pH and the presence of phytotoxic compounds, especially phenols. However OOMW contains a high organic load, as well as substantial amounts of plants nutrients and is a low-cost source of water, all of which favour its use as a soil fertilizer (Paredes et al. 1999). It has been demonstrated that OOMW can supply a large amount of potassium that may affect the Ca status of the soil and subsequently that of the plant (Gallardo-Lara et al. 1998). Moreover, OOMW can partially block the inorganic-N temporarily, reducing the issuance of nitrate for 2 months (Jimenez 2009). Thus, OOMW improves the efficiency of fertilizers to avoid any N-loss during the first irrigations.

Also, the atmospheric CO₂ must be reduced and reused. It could be absorbed from the air of chimneys or contamination focus into aqueous solutions (Tontiwachwuthikul et al. 1992). Dissolved CO₂ lowers tap-water pH due to the formation of carbonic acid which, like sulphuric and acetic acids used by Hellström et al. (1999), could inhibit the decomposition of urea.

Tap water or OOMW bubbled with CO₂ coming from a bottle of industrial gas can dissolve part of the bubbled CO₂. In this form, as dissolved inorganic carbon, the gas could enter the soil as CO₃ or HCO₃⁻ by means of fertilization or irrigation (Jimenez 2009).

Given that both OOMW and BW have acidic pH values, both might be useful to maintain the urine pH acidic and thus conserve nitrogen in urea form.

The aim of this work was to investigate the storage of urine in acidic wastewater mediums such as OOMW or BW and verify whether different urine concentrations stored in these mediums could inhibit the decomposition of urea over the long term. Also, it was to study the changes in soil properties with the input of urine dissolved in OOMW or BW after storage for some months. It was determined whether urine–OOMW–BW mixtures were useful as fertilizer NPK.

MATERIAL AND METHODS

The urine used in the experiments was my own urine. It has, on average, pH of 5.7; EC of 29.1 dS m⁻¹; NH₄-N of 7.5 g/L, Ca of 14 mg/L, K of 4.2 g/L, P-PO₄ of 191 mg/L. The OOMW, collected from St. Anthony oil mill of Viznar (Granada, Spain) in January 2009 had a pH of 4.2, EC of 13.5 dS m⁻¹, Ca of 370 mg/L, P-PO₄ of 195 mg/L, N-Kjeldahl of 63 mg/L, K of 7.3 g/L, and total polyphenols of 3.6 g/L, respectively. The CO₂ comes from an industrial gas cylinder supplied by the company Air Products Ltd. The urine and OOMW were diluted with tap water, pH of 7.8; EC of 0.22 dS m⁻¹, Ca of 38 mg/L, K of 0.6 mg/L or tap water bubbled for 2 min with CO₂ (pH of 6.0; EC of 0.30 dS m⁻¹).

Conservation tests

A previous laboratory experiment was carried out with different rates of urine–OOMW to evaluate the effect of OOMW on pH and ammonia-N. While for all treatments with water pH increased, reaching values close to 9, in the treatments with rates OOMW–urine higher 10% in volume, pH values remained close to 4.5.

Ammonium-N values found in each sample grew with urine concentration used. However, these values are approximately 10-fold smaller in OOMW dilutions than in water. This indicates that OOMW could be effective for the conservation of urine-N in urea form.

Test C1 – Two replications of 1 L of three dilutions of urine (1/10, 1/5, 1/1) per volume of tap water and OOMW were prepared in brown bottles. Also, replicates of the dilutions using BW–OOMW were prepared. All bottles were kept in the daylight laboratory for 6 months. Every month, pH values of
each bottle were measured using a pH/ion meter and at the same time the ammonia-N concentration in each sample was determined by distillation using the urea method of Keeney & Bremner (1967). For this, 10 mL of potassium phosphate buffer were added to 1 mL of each sample and, after distillation, released ammonia-N were valued with diluted sulphuric acid. No fungi appeared in any of the bottles.

**Fertilizer tests**

Two soils (loam and silt-clay-loam) from the farmlands of Granada (southern Spain) were studied. The characteristics of both soils are described in Jimenez (2009).

It has been shown that OOMW diluted with tap water more than 10-fold has no negative impact on the soil. So, OOMW must be diluted just when it is poured out on the soil.

Test F1 – Diluted urine with a concentration similar to urban wastewaters was used. To determine whether OOMW was useful for controlling the nitrate N soil emissions from diluted urine about like urban wastewaters. Experiments were conducted in the laboratory following a factorial design with two levels of urine and four levels of OOMW (A0, A1, A2, A3), with two replicates per sample for 3 months.

Treatments: A0 (1–2 mL of urine dissolved in 100 mL of water), A1 (1–2 mL of urine dissolved in 5 mL of OOMW and water to 100 mL), A2 (1–2 mL of urine dissolved in 10 mL of OOMW and water to 100 mL), A3 (1–2 mL of urine dissolved in 20 mL of OOMW and water to 100 mL). In each test, 20 g of each soil (loam and silt-clay-loam) were treated with 5 mL of each treatment and 5 mL of water.

Test F2 – With raw urine–OOMW. Experiments were conducted in the laboratory following a factorial design with two levels of urine and four levels of OOMW (A0, A1, A2, A3), for two types of water (tap water, BW water) with two replicates per sample for 15 weeks. One litre of different dilutions of urine–tap water and urine–raw OOMW by volume (D10, D5, D2) were stored for 2 months in brown bottles. A duplicate was made with urine–tap water and urine–raw OOMW mixtures subsequently bubbled with industrial CO2 for 2 min.

The treatments were: A0–2 mL of urine D5-water dissolved in 8 mL of water; A1–2 mL of urine D2-water dissolved in 9 mL of water; and A3–1 mL of urine D2-OOMW dissolved in 9 mL of water. All treatments were duplicated using BW. In each test, 20 g of soil were treated once with 10 mL of each treatment. Irrigation was applied once every 10 days with 10 mL of water. Dry soil samples were collected each 20 days to measure pH, EC, CaCO3, Ca, K, P-PO4, ammonium-N and nitrate-N. The ammonium-N was analysed according to Nelson (1983) and nitrate-N following Yang et al. (1998) in the extract of 1 g of soil with 20 mL of 1 N KCl. The EC and pH were measured in a 1:2.5 soil/water suspensions; the pH was monitored using a pH/ion meter, and EC using a conductivity meter (both Crison 2002 models). The CaCO3 analysis was made according to Drouineau (Loeppert & Suarez 1996). The K and exchangeable Ca were extracted with 1 M ammonium acetate at pH 7, a soil:solution ratio of 1:20, 2 h shaking (Steinberg & Hogel 1990), and then measured in a flame photometer and atomic-absorption spectrophotometer, respectively.

P-PO4 analysis was made by the method of Watanabe & Olsen (1965). The statistical analysis was performed using the PC computer program Statgraphics Plus 5.1.

To set the health standard of the fertilizer produced, *Escherichia coli* and other coliform bacteria were analysed by filtration in a soil and water extract (1:10), according to the method described in the Order SCO/778/2009, March 17, Department of Health and Consumption, on alternative methods for microbiological analysis of drinking water.

**RESULTS AND DISCUSSION**

**Conservation tests**

**Test C1**

Figures 1 and 2 show the evolution of the parameters in brown bottles. All treatments with water maintained a pH close to 9 whereas for OOMW treatments had a pH close to 4. However, BW registered an acidic pH (close to 6) for higher dilutions 5 and 10. For the highest concentration of urine, the pH rose to 8.4. Perhaps for this concentration of urine, a higher rate of CO2 should have been used.
The ammonium-N found in each bottle significantly decreased in samples with OOMW, but this also occurred with BW. This indicates that both OOMW and BW could be a useful method to inhibit the decomposition of urea.

In this work, two different wastewater acids were tested. It could be assumed that the fall in pH inhibited the decomposition of urea. Thus, it should be possible to use other wastewater acids with value as a fertilizer. For this, not just any acid is useful. Fertilization or irrigation with OOMW and BW have previously been shown to be a feasible method for reducing the environmental impact of OOMW, nitrates and CO₂ (Jimenez 2009). Thus, OOMW and CO₂ could be recycled by the fertilizer industry.

The pH value of fresh urine ranges from 5.6 to 6.8. According to Kissel et al. (1988) in the soil, part of the CO₃²⁻ precipitated as CaCO₃ when the soil pH rises to 8.8 and no CaCO₃ was detected down to pH of 7.1. Wilsenach et al. (2007) have indicated that between 75 and 95% of phosphate was recovered from source-separated urine through struvite precipitation when pH increased from 8.2 to 9.1. This implies that, as the treatments in the present study maintained the pH below those values, precipitation of calcite, struvite and hydroxyapatite could be reduced.

**Fertilizer tests**

The effects of urine–water–OOMW mixtures on soil parameters are shown in the Table 1 (diluted urine–OOMW) and Table 2 (raw urine–OOMW).
In samples treated with OOMW the pH rose over time, perhaps due to the production of NH$_3$ as a result of degradation and mineralization of nitrogenous organic compounds joined to low nitrate content.

The ammonium content was not influenced by the addition of OOMW. Ammonium fixation as opposed to the mineralisation of organic N from OOMW could account for this result. EC and nitrates significantly decreased in soils treated with urine–OOMW fertilizers, compared with the control. Nitrate reduction could explain lower EC decreasing and higher pH values, as these parameters were significantly correlated (Tables 3 and 4).

Mekki et al. (2006) reported that nitrifiers were strongly inhibited by untreated OOMW. According to Gamba et al. (2005) the polyphenols of OOMW inhibited the potential nitrification activity with a reduction in nitrite and nitrate contents. This could explain the fact that these parameters were significantly correlated with the polyphenol content in the OOMW (Tables 3 and 4).

The lack of nitrate N caused by OOMW application has been attributed to reversible N immobilization, such effects disappearing in 2 or 4 months (Jimenez 2009).

Soil-phosphorus levels remained high during the first 45 days and then fell drastically, indicating a possible precipitation and absorption by soil as calcium-ammonium phosphate, given that Ca levels also decreased after 2 months. According to Sierra et al. (2001), phosphorus values are considerably enhanced due to OOMW infiltration and phosphorus immobilization as calcium phosphate. Increased P extractability in reduced soils is attributed to the effect of pH and redox potential changes on Fe–P compounds and, to a lesser extent, attributed to organic acids and CO$_2$ released during the anaerobic decomposition of organic matter that can convert tricalcium phosphates to more soluble dicalcium phosphates and alter the solubility equilibria of Ca–P. Separately of phosphate fixation, in samples fertilized with raw OOMW, phosphate contents increased in accordance with different authors (Zenjari & Nejmeddine 2001; Mekki et al. 2006).

A considerable enrichment of available potassium in samples fertilized with OOMW also occurs, as has been reported previously by preceding authors. It must be due to the high content of this element in the OOMW. On the other hand, the degree of soil N, P, K fertilization can be modified according to mixture fresh or hydrolysed urine–OOMW rate used (the greater the urine, the greater the N rate).

The OOMW decreased soil exchangeable Ca (Gallardo-Lara et al. 1998). Sierra et al. (2001) also pointed out that untreated OOMW infiltration caused carbonates dissolution with changes in pH values. OOMW acidity was neutralized by carbonates presents in the high horizons, thus generating soluble calcium bicarbonate, which moves towards the lower horizons where it precipitates as calcium carbonate again. These carbonate mobilisation phenomena cannot be observed in our samples because horizons were mixed. Thus, in the present case, OOMW had only a slight influence on Ca and CaCO$_3$ contents, because the carbonates dissolution produced by OOMW could be neutralized by the carbonates precipitation due to pH increase by the mineralization of urea from urine and nitrogenous organic compounds from OOMW.
BW increases pH and reduces EC but has no influence on the nutrient content. BW, like other substances with acidic pH values, delays the decomposition of urea by maintaining the pH acidic. In basic soils, carbonic acid of BW should be neutralized by exchange bases (Ca, Mg, K) and precipitated in carbonate form. The amount of Ca and Mg precipitated increased with decreasing NH₃ losses. Precipitation of divalent cations boosted adsorption of NH₄ at soil exchange sites, thereby preventing the upward movement of NH₄ and subsequent NH₃ losses (Fenn & Miyamoto 1984). By means of urine, CO₂ could be fixed to soil in carbonate form.

Human urine is generally free of pathogens when excreted by a healthy person. However, the use of reclaimed wastewater for irrigation is an important route for the introduction of xenobiotic compounds into the environment. Pharmaceutical residues, which are reversibly adsorbed to soil, may be taken up by plants or have a negative impact on groundwater quality. The physico-chemical nature of organic matter (OM) affect sorption-desorption in soil layers. Generally, organic pollutants might be transferred from the soil irrigated with wastewater to different plant parts (Fatta-Kassinos et al. 2014).

In relation to the introduction and transmission of pathogens in the soil, Hoglund et al. (2002) have indicated that urine stored at 20 °C for at least 6 months may be considered safe to use as a fertilizer for any crop. On the other hand, low pH values appear to reduce the number of pathogens and can also have an impact on pharmaceuticals present in the urine. At pH 2, an inactivation level of between 50 and 95% has been found for some antibiotics (Hellström et al. 1999).

The treatment in the present study could be considered hygienically safe because firstly, the urine belonged to a healthy person, there was no contact with faeces at any time, and secondly it was stored for more than 6 months at room temperature and it has a low pH. However, in this study, the fertilized soil samples were microbiologically analysed and gave negative results. The Spanish Royal Decree of the Ministry of the Presidency 1620/2007 of 7 December (BOE 8.12.2007) established the legal regime of the reuse of treated water and the required quality for agricultural use. According to these quality criteria, the urine–OOMW mixture in the absence of pathogens (<1 UFC/100 mL) would be suitable for irrigation of all types of crops, including those with water-delivery systems that

| Table 2 | Main effect of raw urine–OOMW mixtures on soil parameters: pH, electrical conductivity (EC), nitrate N (NO₃), ammonium N (NH₄), calcium (Ca), potassium (K), phosphorus (P-PO₄) and lime (CaCO₃) |
|---|---|---|---|---|---|---|---|
| pH | EC (dS m⁻¹) | NO₃ (mg kg⁻¹) | NH₄ (mg kg⁻¹) | Ca (%) | K (mg kg⁻¹) | P-PO₄ (mg kg⁻¹) | CaCO₃ (%) |
| L | SCL | L | SCL | L | SCL | L | SCL | L | SCL | L | SCL | L | SCL |
| A0 | 8.15a | 8.12a | 0.51c | 0.91b | 64b | 132c | 13.6ab | 13.8ab | 0.86 | 1.11 | 259a | 332a | 72a | 87a |
| A1 | 8.48c | 8.44c | 0.42ab | 0.72a | 15a | 25a | 10a | 10.6a | 0.80 | 1.05 | 692c | 727c | 137c | 114b |
| A2 | 8.12a | 8.08a | 0.62d | 1.10c | 100c | 250c | 15a | 10.6a | 0.80 | 1.10 | 279a | 338a | 80a | 80a |
| A3 | 8.36b | 8.31b | 0.37a | 0.76a | 23a | 58b | 9.7a | 10.1a | 0.85 | 1.07 | 361b | 429b | 90b | 84a |
| Different letters within a column indicate different levels of significance (P < 0.05) according to Tukey’s test. |

Different letters within a column indicate different levels of significance (P < 0.05) according to Tukey’s test.
allow direct contact of reclaimed water with the edible plant parts for human consumption (100 CFU/100 mL maximum permissible value). This result was in accordance with Heinonen-Tanski et al. (2007), that in cucumber fertilized with urine, none of the cucumbers contained any enteric microorganisms (coliforms, enterococci, coliphages or clostridia).

However, urine treatment might be necessarily needed to produce an adequate fertilizer, but it might also provide a suitable method to prevent the pollution of the environment with micropollutants. Pronk et al. (2006), using nanofiltration for the separation of pharmaceuticals from nutrients in source-separated urine, managed to reduce 92% of all micropollutants in non-hydrolysed urine.

On the other hand, centralised aerobic wastewater-treatment plants should not be considered as the only possible solution for sustainable water and waste management in urban areas. A system with source control can avoid many problems of technology by respecting different qualities of wastewater and by treating them appropriately for reuse (Otterpohl et al. 1997).

An integrated system for wastewater treatment should consider the reuse of treated effluents (CO₂, OOMW) and urban wastewaters with the production of useful by-products (biogas, biofertilizer, production of microalgae from CO₂, etc.) (Rovirosa et al. 1995). So, the use of human urine, OOMW and CO₂ as an alternative source of multinutrient fertilizer could be achieved only by introducing new areas of scientific research.

CONCLUSIONS

There is a lineal relation between pH and the fraction of urea decomposed in human urine. The addition of acidic wastewater media such as OOMW or tap water bubbled with CO₂ into urine before storage could significantly decrease the decomposition rate of urea.

The urine–OOMW–BW mixtures could inhibit the hydrolysis of the urea for more than 6 months and could be useful for the conservation of ammonium-N.

Moreover, urine-N dissolved in OOMW significantly reduced the emission of nitrates from soils for 3 months, increasing K and П values. The application of urine with BW increased soil pH and reduced EC, but did not affect nutrient contents. Urine bubbled with CO₂ could reduce the atmospheric contamination.

Thus, human or animal urine dissolved in OOMW, applied on soils as fertilizer or irrigation, could act as NPK-fertilizer. However, the impact of fertilisation with human urine–OOMW–CO₂ requires further investigation with respect to crop production and pollution.
ACKNOWLEDGEMENTS

We thank Atarfe Agricultural Laboratory staff for their great support during the analytic work.

REFERENCES


