Fate of major compounds in source-separated urine

K.M. Udert, T.A. Larsen and W. Gujer
Swiss Federal Institute for Environmental Science and Technology (EAWAG) and Swiss Federal Institute of Technology (ETH), 8600 Dübendorf, Switzerland (E-mail: udert@mit.edu; larsen@eawag.ch; gujer@eawag.ch)

Abstract Urine separation is a promising alternative to present-day waste water management. It can help to manage our nutrient flows in a sustainable way. Currently, techniques are being developed to recycle and treat source-separated urine. These techniques, however, must consider the spontaneous processes that change the separated urine. The initial cause of changes is the contamination with microorganisms, which can hardly be avoided in urine-collecting systems. The most important transformation processes are microbial urea hydrolysis, mineral precipitation and ammonia volatilisation. Additionally, a variety of microorganisms may grow in source-separated urine, because the content of biodegradable organic compounds is very high. These microorganisms may also include pathogens. In this paper we give an overview of the effects that the spontaneous transformation processes may have. We focus on nitrogen, phosphorus, magnesium, calcium, potassium, sulphur, organic substances, pathogens and the buffering capacity. The discussion is based on own experiences and literature reviews. This overview will help to develop appropriate technologies for urine recycling.

Keywords Ammonia volatilisation; NoMix; precipitation; urea hydrolysis; urine-collecting systems

Introduction
Present-day treatment of mixed waste water has several shortcomings: high amounts of resources – including drinking water – are consumed, valuable nutrients such as phosphorus, nitrogen or potassium are lost to the environment and micropollutants are eliminated insufficiently. Source separation of urine, which contributes most of the nutrients to waste water, is a promising alternative (Larsen et al., 2001; Udert, 2003). However, the nutrients in urine might not be available in a convenient form for fertilisers. Furthermore, urine contains micropollutants such as synthetic hormones, pharmaceuticals and their metabolites. These substances are mainly excreted via urine (Alder, 2002) and may be harmful to the ecosystems and human health (Daughton and Ternes, 1999). Today, many micropollutants reach the aquatic environment, because their degradation in waste water treatment plants is poor (Ternes, 1998).

Urine treatment might be necessary to produce an adequate fertiliser, but it might also be a suitable method to prevent the pollution of the environment with micropollutants. Developing a treatment method requires the knowledge about the concentration and behaviour of the major urine compounds. During separation, storage and transport, urine is subject to several spontaneous processes such as urea hydrolysis, precipitation, or volatilisation which change the urine composition significantly. In this paper we discuss the effect of spontaneous processes on major urine compounds. The understanding of these processes is crucial for developing appropriate technologies for urine recycling.
**Major processes**

Urine from healthy persons is quite stable and hardly contains any microorganisms. Significant changes in its composition are slow and affect mainly the organic fraction (Colombo, 1994). The changes that are described in this paper are due to the contamination with bacteria from faeces or from the urine-collecting system itself. The contact with bacteria cannot be prevented in normal NoMix toilets or waterless urinals. Urea-hydrolysing bacteria have the strongest effect on the urine composition. Since they are ubiquitous (Mobley and Hausinger, 1989), it takes little time until they occur in urine-collecting systems. Their enzyme urease catalyses the hydrolysis of urea to ammonia and bicarbonate. This process involves a strong pH increase (Table 1).

\[
\text{NH}_2(\text{CO})\text{NH}_2 + 2\text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{NH}_4^+ + \text{HCO}_3^-
\]

The pH increase triggers the precipitation of struvite (MgNH_4PO_4·6H_2O), hydroxyapatite (Ca_5(PO_4)_3(OH)) and occasionally calcite (CaCO_3) (Udert et al., 2003b, c).

The changes in the composition of undiluted urine due to urea hydrolysis and precipitation are shown in Table 1. They will be discussed in detail in the following sections. An additional consequence of the pH increase is the risk of ammonia volatilisation during storage, transport and application of urine. To clarify the different characteristics of urine we define source-separated urine as urine that has been collected in NoMix toilets or waterless urinals and that is contaminated with microorganisms. Additionally, we define stored urine as source-separated urine after complete urea hydrolysis and precipitation.

**Nitrogen**

In fresh urine, about 85% of nitrogen is fixed as urea and about 5% as total ammonia (Table 1). The rest of the nitrogen compounds are mainly creatinine, amino acids and uric acid (Ciba-Geigy, 1977). After urea hydrolysis, total ammonia accounts for 90% of the nitrogen in stored urine. Due to the increased pH, the concentration of ammonia NH_3 is significantly increased.

**Table 1** Reference values for fresh urine and stored urine. The concentrations in fresh urine are literature values compiled from various sources (Udert, 2003). The concentrations in stored urine are simulated values. (Udert et al., 2003c)

<table>
<thead>
<tr>
<th></th>
<th>Fresh urine</th>
<th>Stored urine(1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>CV% Data range</td>
</tr>
<tr>
<td>Total nitrogen</td>
<td>[gN·m⁻³]</td>
<td>9200 – 9200</td>
</tr>
<tr>
<td>Total ammonia</td>
<td>[gN·m⁻³]</td>
<td>480 – 8100</td>
</tr>
<tr>
<td>Ammonia NH₃(1)</td>
<td>[gN·m⁻³]</td>
<td>0.3 – 2700</td>
</tr>
<tr>
<td>Urea</td>
<td>[gN·m⁻³]</td>
<td>7700 – 0</td>
</tr>
<tr>
<td>Total phosphate(2)</td>
<td>[gP·m⁻³]</td>
<td>740 – 540</td>
</tr>
<tr>
<td>Calcium</td>
<td>[g·m⁻³]</td>
<td>190 – 0</td>
</tr>
<tr>
<td>Magnesium</td>
<td>[g·m⁻³]</td>
<td>100 – 0</td>
</tr>
<tr>
<td>Potassium</td>
<td>[g·m⁻³]</td>
<td>2200 – 2200</td>
</tr>
<tr>
<td>Total carbonate</td>
<td>[gC·m⁻³]</td>
<td>0 – 3200</td>
</tr>
<tr>
<td>Sulphate(3)</td>
<td>[gSO₄·m⁻³]</td>
<td>1500 – 1500</td>
</tr>
<tr>
<td>Chloride</td>
<td>[g·m⁻³]</td>
<td>3800 – 3800</td>
</tr>
<tr>
<td>Sodium</td>
<td>[g·m⁻³]</td>
<td>2600 – 2600</td>
</tr>
<tr>
<td>pH</td>
<td>[-]</td>
<td>6.2 – 9.1</td>
</tr>
<tr>
<td>Alkalinity(1)</td>
<td>[mM]</td>
<td>22 – 490</td>
</tr>
<tr>
<td>COD</td>
<td>[gO₂·m⁻³]</td>
<td>10000 – 10000</td>
</tr>
<tr>
<td>Volume</td>
<td>[lt]</td>
<td>1.25 – 1.25</td>
</tr>
</tbody>
</table>

(1) Simulated values
(2) 95–100% of total phosph (Ciba Geigy, 1977)
(3) about 90% of total sulphur (Ciba Geigy, 1977)
very high (Table 1). Ammonia is volatile and one may expect that substantial losses can occur during storage, transport or application of source-separated urine. These losses not only diminish the efficiency of nitrogen recovery, but volatilised ammonia can also have negative effects on the environment and human health (Galloway and Cowling, 2002).

Present research results show that the loss of ammonia is marginal in closed storage tanks (Fittschen and Hahn, 1998; Hellström and Johansson, 1999 and own unpublished results). The high solubility of NH₃ in water (the Henry coefficient is 0.00071 M(g)/M(aq) at 25 °C, Stumm and Morgan (1996)) prevents a large fraction of ammonia escaping to the tank atmosphere. Nevertheless, odour problems will occur if the tank is not properly closed. The NH₃ concentration in the headspace of the storage tank is low compared to the concentration in urine, but it certainly reaches values that are disturbing if not harmful. The theoretical equilibrium concentration with dissolved ammonia in a tank half full of undiluted urine is 2300 mgN/m³. This is far above the perceivable level of 7 to 14 mg/m³ and also above the toxic level of 210–280 mgN/m³ (KTBL, 1990). This maximum value will not be reached in storage tanks, because the ammonia exchange between urine solution and gas phase is very slow. Nevertheless, it must be considered that working in urine storage tanks can be harmful.

Ammonia volatilisation can be a major problem during the transport of source-separated urine. Especially the transport through the sewer (Larsen and Gujer, 1996) may be critical. To test this hypothesis, an ammonia solution was flushed through a straight sewer of 2000 m in length, 0.9 m in diameter and a slope of 0.09% in average (Buri and Schildknecht, 1998). The water flow was 20 l/s and the water temperature 15 °C. The results showed that the maximum loss of total ammonia under these conditions and at pH 9 would be 2% per hour. Although the decrease of total ammonia in urine might be low, the volatilised ammonia would cause considerable odour problems. Preliminary treatment of the source-separated urine may be necessary to prevent ammonia volatilisation during transport in common sewers.

While the ammonia loss is supposedly low during storage and transport, it might be high, if stored urine is spread as fertiliser. However, a study conducted by the Stockholm Water Company using stored urine showed that the ammonia losses were only 1 to 10%. Trailing hoses and sliding shoes were used to keep the volatilisation as low as possible (Johansson, 2001). Current experiences with liquid manure show much higher losses of ammonia during spreading on fields. Menzì et al. (1997) estimated that 50% of the total ammonia in liquid manure volatilises during spreading. Using alternative spreading techniques could reduce the ammonia loss by 30 to 60% (trailing hoses) or even by 90% (deep injection). However, the study also showed that the application of such techniques is restricted by the slope and area of the field and by the soil structure. More studies are needed to explain the differences between stored urine and liquid manure. Still, the very low ammonia losses found by the Stockholm Water Company were achieved by the use of sophisticated spreading techniques, which cannot be used on many fields as Menzì et al. (1997) pointed out.

Apart from the ammonia loss, the smell of stored urine may restrict its use on fields near residential areas. In the study of the Stockholm Water Company ammonia could be smelled for 24 hours after application (Johansson, 2001). Generally, a preliminary treatment of the source-separated urine can prevent the ammonia volatilisation. The main goals of this treatment should be lowering the pH or transforming the ammonia into a non-volatile nitrogen compound, e.g. nitrate (Udert et al., 2003d).

The concentration of dissolved nitrogen is also influenced by precipitation. Ammonium is one of the components of struvite. However, precipitation is not a major sink for nitrogen. The maximum amount of ammonium included in struvite is less than 1% of the total ammonia in source-separated urine (Udert et al., 2003a).
Phosphorus, calcium and magnesium

Today, phosphate rock (mainly francolite, a carbonate-fluorapatite) is the source for phosphorus production (Nathan, 1984), but the deposits of good quality are becoming scarce (Smil, 2000). Phosphorus recovery is therefore a major incentive for urine collection.

In fresh urine, between 95 to 100% of phosphorus is bound as dissolved phosphate (Ciba-Geigy, 1977). The phosphate concentration is strongly influenced by precipitation processes and so are the concentrations of the cations calcium and magnesium.

Struvite and hydroxyapatite make up most of the precipitates in urine-collecting systems. Both are phosphate minerals. Measurements and simulations showed that in undiluted urine about 30% of the soluble phosphate is incorporated in the solid phase of the precipitates (Udert et al., 2003a, b). This fraction varies with the composition of the urine. However, the fraction of precipitated phosphate increases with the hardness and the amount of flushing water (Figure 1). Calcium and magnesium are the limiting factors for the phosphate precipitation. In sparsely diluted urine they are completely included into the solid phase (Figure 1). The simulation results shown in Figure 1 give the maximum values for phosphate, calcium and magnesium precipitation. Measurements show that these values are nearly reached in slightly diluted urine (Udert et al., 2003c).

Some precipitation occurs in the trap and pipes causing blockages (Udert et al., 2003a). However, most of the phosphate minerals are incorporated in the urine sludge at the bottom of the collection tank (Udert et al., 2003c). This sludge is liquid and maybe pumped with the urine solution.

The partitioning of phosphorus in a soluble and solid fraction is important for the choice of possible recovery methods. Dissolved phosphate might be better available for plants. However, the advantage of phosphate precipitates is that the phosphorus is very concentrated and separated from most other urine compounds. Enhancing precipitation by adding calcium or magnesium sources may therefore be one method for phosphorus recovery from source-separated urine. Based on the sparse literature, data hydroxyapatite and struvite are assumed to be good slow-release fertilisers on acid soils (see Udert et al., 2003a). Hydroxyapatite is better suited as resource for the current phosphate industry, because it resembles phosphate rock (Driver et al., 1999). However, struvite precipitation is faster and easier to accomplish (Udert et al., 2003c).

![Figure 1](https://iwaponline.com/wst/article-pdf/54/11-12/413/431210/413.pdf)

**Figure 1** Fraction of solutes eliminated by precipitation in urine diluted with tap water (water hardness medium). Total dilution factor: total sample volume divided by urine volume. Usual dilution factors for urine-collecting systems are between 1 and 10. Total ammonia: ammonium and ammonia after all urea has been hydrolysed. All values are simulated (Udert et al., 2003b)
Potassium
In source-separated urine, precipitation is the only process that may significantly affect the potassium concentration. Potassium is known to be incorporated in struvite as well as in hydroxyapatite. In struvite, potassium can substitute ammonium (Schuiling and Andrade, 1999; Lind et al., 2000). However, in source-separated urine the molar total ammonia concentration is nearly fivefold higher than the potassium concentration. Therefore, one can assume that only little ammonium is replaced by potassium. In the completely hypothetical case that all ammonium in struvite would be substituted by potassium, the loss of soluble potassium would be less than 7% anyway.

In hydroxyapatite, potassium can substitute calcium, but the fraction of potassium in biologically formed hydroxyapatite is very low. In human bones and teeth potassium accounts for less than 0.1%wt (LeGeros and LeGeros, 1984). Potassium loss due to hydroxyapatite precipitation is presumably negligible.

Sulphur
Nearly 90% of sulphur in urine is found as sulphate. Other sulphur compounds are esters of sulphuric acid and neutral sulphur compounds (Ciba-Geigy, 1977). There are two processes that may significantly influence sulphate in source-separated urine: precipitation and biological reduction.

Sulphate may be incorporated in apatites. No data was found on sulphate incorporation in hydroxyapatite but sulphur contents in phosphate rock may serve as a first estimate. Nathan (1984) reported that the sulphur content of several phosphate rocks varied between 0.03 wt% and 1.6 wt% with a median of 0.8 wt%. This fraction is very small and one can assume that precipitation of sulphate is negligible in source-separated urine.

However, microbial processes are likely to reduce sulphate in source-separated urine. Sulphate is the most favourable electron acceptor in stored urine, since elemental oxygen, nitrate or nitrite are missing and the concentration of iron is very low. Additionally, urine contains appropriate electron donors such as fatty acids (Ciba-Geigy, 1977; Madigan et al., 2000). The product of sulphate respiration is hydrogen sulphide $\text{H}_2\text{S}$, a corrosive gas which causes odour problems and may be toxic to humans already at low concentrations. Sulphate-reducing bacteria are widely distributed in nature (Madigan et al., 2000), they may also invade stored urine.

Since microbial sulphate reduction is likely to occur in source-separated urine and may have detrimental impacts on the urine-collecting system and on human health, sulphate reduction should be a subject of further investigations.

Organic substances
The concentration of organic substances in urine is high, about 10,000 gCOD/m$^3$ (Table 1). On a COD basis organic acids, creatinine, amino acids and carbon hydrates are the main organic urine compounds (Ciba Geigy, 1977). On a molar basis urea, which has no COD, is the most important organic substance in fresh urine. 85% of COD in urine are easily biodegradable (Udert et al., 2003d). Biological degradation of the organic compounds will occur, if urine gets in contact with anaerobic microorganisms which can use the organic compounds as electron acceptors. One example stated above are the sulphate reducers. Fermenters may also grow in urine: Höglund et al. (1998, 2000) noticed that the bacteria of the fermenting genus Clostridium are persistent in stored urine. Methane production would be critical, but is unlikely because of the high ammonia concentration (Sprott and Patel, 1986). Not only anaerobic, but also aerobic degradation can occur, if substantial amounts of oxygen diffuse through the tank walls. We observed degradation of organic compounds
and even nitrification in collection tanks, which had been used for waste water storage before (unpublished data).

Organic substances are also included in precipitates. Höglund et al. (2000) found that the concentration of bacteria and organics in the urine sludge is substantially higher than in the urine solution. We measured a COD content of 0.18 gCOD/gTSS in the solids at the bottom of a urine collection tank (Udert et al., 2003d).

The organic substances in urine also include micropollutants. At the moment it is not known, whether these micropollutants are degraded or substantially precipitated during urine storage. Urine treatment may be necessary to eliminate harmful micropollutants.

Pathogens
Measurements of faecal sterols in stored urine indicated that transmissible pathogens in source-separated urine are mainly cross-contaminated from faeces (Schönning et al., 2002). Many microorganisms die off during urine storage. Höglund and Stenström (1999) assumed that a storage time of six months should be sufficient to lower the transmission risk below an acceptable limit. However, not all pathogens are eliminated after this time.

Höglund and co-workers (Höglund et al., 1998, 2000, 2002; Höglund and Stenström, 1999) determined the inactivation of several test pathogens in source-separated urine. Gram-negative bacteria (Aeromonas hydrophila, Escherichia coli, Pseudomonas aeruginosa, Salmonella senftenberg, Salmonella typhimurium) died off in a few days. Rhesus rotavirus and Salmonella typhimurium phage 28B were not detected anymore after several weeks. Similarly, most oocysts of the pathogenic protozoa Cryptosporidium parvum were killed after several weeks. The inactivation of faecal streptococci took weeks to months. However, bacteria of the genus Clostridium and ova of the intestinal roundworm Ascaris suum could still be found in high numbers after several months of storage. Höglund et al. (1998) found that high concentrations of streptococci are probably due to their growth in the tanks or pipes of the collection system. The endurance of Clostridia may be explained by the fact that these bacteria are obligate anaerobes and fermenters (Madigan et al., 2000). The conditions in stored urine possibly support their growth. However, for most other pathogens the alkaline pH values in stored urine and the high urine concentration are factors that facilitate their elimination. Additionally high temperatures (20°C instead of 4°C) are beneficial for die-off of pathogens (Höglund et al., 1998). Most likely, many pathogens, especially anaerobic ones, which only die off slowly in stored urine could be killed with aerobic treatment of stored urine.

In the collection tank, concentrations of bacteria were higher at the base than in the solution above (Höglund et al., 1998). Therefore, care must be taken while handling with urine sludge. It may contain an increased concentration of pathogens.

Buffer capacity and pH
The buffer capacity or alkalinity of urine strongly increases during storage due to urea hydrolysis. Simulations showed that urea hydrolysis raises the alkalinity from about 22 mM to nearly 490 mM (Table 1). The main buffering compounds are bicarbonate and ammonia. This increase affects the later treatment and application of urine. Due to the high buffer capacity, acid addition is not an economical method to prevent ammonia volatisation. The high buffer capacity also limits the fertiliser qualities of source-separated urine. If stored urine is directly applied to agricultural soils, the high pH combined with the high buffer capacity may affect bacterial nitrification and cause nitrite accumulation in soils (Burns et al., 1995). Nitrification to nitrate was achieved in laboratory reactors and it is a possible method to stabilise nitrogen in urine (Udert et al., 2003d). However, the high pH and buffer capacity requires exact process control.
Conclusions
The most important changes affecting the treatment of urine are:

- All urea is degraded and most of the nitrogen is available as total ammonia. Up to 33% of the total ammonia is volatile NH₃. Ammonia losses and odour problems will occur during transport and spreading of stored urine.

- The urine is alkaline with a pH around 9. The buffer capacity is so high that acid addition, e.g. to prevent ammonia volatilisation, is not economical.

- Practically all calcium and magnesium is precipitated. No more spontaneous precipitation will occur. This is beneficial for the biological treatment of stored urine (Udert et al., 2003d).

- The phosphorus is separated in two phases: at least 30% is fixed in precipitates and the rest is dissolved. Supplemental calcium or magnesium addition seems to be a favourable technique to concentrate phosphorus.

- Sulphate might be reduced to H₂S, if sulphate-reducing bacteria grow in the solution.

- The high fraction of biodegradable organic compounds may be a substrate for several aerobic and anaerobic microorganisms.

- Some pathogens may survive or even grow during urine storage, but most of them will be killed during the storage of urine.

References


