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Determination of urine-derived odorous compounds in a source separation sanitation system

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ABSTRACT

Source separation sanitation systems have attracted more and more attention recently. However, separate urine collection and treatment could induce odor issues, especially in large scale application. In order to avoid such issues, it is necessary to monitor the odor related compounds that might be generated during urine storage. This study investigated the odorous compounds that emitted from source-separated human urine under different hydrolysis conditions. Batch experiments were conducted to investigate the effect of temperature, stale/fresh urine ratio and urine dilution on odor emissions. It was found that ammonia, dimethyl disulfide, allyl methyl sulfide and 4-heptanone were the main odorous compounds generated from human urine, with headspace concentrations hundreds of times higher than their respective odor thresholds. Furthermore, the high temperature accelerated urine hydrolysis and liquid–gas mass transfer, resulting a remarkable increase of odor emissions from the urine solution. The addition of stale urine enhanced urine hydrolysis and expedited odor emissions. On the contrary, diluted urine emitted less odorous compounds ascribed to reduced concentrations of odorant precursors. In addition, this study quantified the odor emissions and revealed the constraints of urine source separation in real-world applications. To address the odor issue, several control strategies are recommended for odor mitigation or elimination from an engineering perspective.

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Introduction

In recent years, the concept of source separation system has attracted increasing attention due to the improvement in the wastewater management practice (*e.g.*, water conservation, biogas production, and nutrient recovery) (Bracken et al., 2007). The key to a source separation system is the use of urine diverting toilet, which can effectively separate the human excreta into yellow water (urine) and brown water (feces). The source-separated urine can be utilized in agriculture after sufficient storage, or nutrient (NPK) recovery by engaging different urine treatment processes (Maurer et al., 2006; Larsen et al., 2009; Zhang et al., 2014).

Unlike the conventional wastewater treatment plants (WWTP), source separation-based facilities are designed to deal with wastewater streams with distinct physicochemical characteristics and potentially confront with more severe odor issues. Odor emissions have been investigated in WWTP, animal farms, food-processing plants, *etc.* (Easter et al., 2005; Kleeberg et al., 2005; Van Groenestijn and Kraakman, 2005).

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However, there is limited information on odor emissions derived from urine source separation systems. The odorous compounds present in urine could be influenced by gender, age, diet, physiological and hormonal status, and use of drugs (Edman and Brooks, 1983; Guernion et al., 2001). Some studies were conducted to identify the odorous substances that could serve as potential indicators for diseases or specific metabolic syndromes (Bolodeoku and Donaldson, 1996). Hiroshi et al. (2001) determined the malodorous substances derived from human excreta (feces and urine) using thermal-desorption cold-trap and gas chromatography–mass spectrometry. Their results showed that fatty acids were the main malodor-causing substances, and other odorous compounds included sulfur-containing compounds (hydrogen sulfide and methyl mercaptan) and nitrogen-containing compounds (ammonia, pyridine, pyrrole, indole, skatole and trimethylamine). It is important to recognize that odor could be an important issue of source separation systems because odor-related complaints could change the public acceptance of those systems.

Based on the source separation concept, systematic investigations on urine management were conducted in our previous studies. Urine hydrolysis was studied in open systems showing that hydrolysis process could be accomplished in 2 days at high temperature (35°C) by adding 20% stale urine (Zhang et al., 2013). In that study, it was also proven that electrical conductivity could serve as an ideal indicator for urine hydrolysis monitoring. Further studies indicated that phosphorus recovery from the hydrolyzed urine could be achieved through induced struvite precipitation using seawater as magnesium source, while nitrogen harvesting was accomplished by air stripping and subsequent acid adsorption (Liu et al., 2013, 2014). Afterwards, hydroponic system was applied to further polish the urine effluent in order to meet the discharge standards (Yang et al., 2015). Despite of the very promising results, the urine treatment systems were subjected to odor emissions which could obstruct real-world applications. The emitted compounds were generally non hazardous to human health, but unpleasant conditions were formed in the open treatment lines, especially when high temperatures were applied. It is therefore necessary to determine the odor emissions from source-separated urine in order to develop effective odor control strategies.

The main purpose of this study was to determine, both qualitatively and quantitatively, the odorous substances in the headspace of urine storage tank during the hydrolysis process. The effects of temperature, dilution, stale/fresh urine ratio on the odorous emissions were investigated as well. The findings from this study could provide a useful reference for the odor control, while several methods are proposed to mitigate or eliminate odorous emissions.

1. Materials and methods

1.1. Chemicals

All reagents used in this study were of analytical grade. Six odorant standards including dimethyl disulfide (DMDS), allyl methyl sulfide (AMS), 4-heptanone, allyl methyl disulfide (AMDS), methyl propyl disulfide (MPDS), and menthol were provided by Sigma-Aldrich (Singapore) with high purity (98%).

1.2. Batch experiments

Fresh urine was collected from 25 healthy adults and stored in a sterile plastic tank. Batch experiments were carried out in glass carboys (5 L) to monitor the urine hydrolysis process and determine the odorous emissions under different conditions, including two temperatures (23, 35°C), three dilution factors (no dilution, 1:2, 1:5) and fresh/stale urine ratio (4:1). Each carboy was loaded with 1 L of urine solution. The urine-loaded carboys were then capped with a liquid sampling port and two gas sampling outlets as well as one gas inlet.

1.3. Chemical analysis of urine samples

The ammonium concentration in urine samples was measured using a DR 2800 spectrophotometer based on the salicylate method (Hach, USA). The pH-value was measured with a D-54 pH meter (Horiba, Japan). The volatile fatty acids (VFA) in urine samples were determined by gas chromatography (Agilent Technologies 7890A, USA) equipped with a flame ionization detector and a DB-FFAP capillary column (30 m × 0.32 mm i.d. × 0.50 μm film thickness, J&W Scientific, Agilent). The collected urine samples were first filtered through 0.45 μm cellulose acetate membrane filters and the injection volume was 1 μL. At least two parallel replicates were engaged throughout the study for quality assurance.

1.4. Odor quantification analysis

Odorous gas sample was actively collected from the carboy headspace using two digital air sampling pumps (GilAir Plus, USA) operated at a flow rate of 100 mL/min. A total volume of 1 L gas sample was aspirated and passed through a stainless steel sampling tube packed with 130 mg Tenax TA adsorbent (Perkin Elmer, USA).

Gas analysis was then carried out with a thermal desorber (TD-100, Markes International, Llantrisant, UK) followed by gas chromatography–mass spectrometry (TD-GC/MS) (7890A/5975C, Agilent). A two-stage desorption process was applied to desorb the target compounds from the Tenax TA sorbents. The desorption temperature was set at 280°C for 10 min, and then at 320°C for 5 min. The flow rate of carrier gas (N_2) was held at 100 mL/min and the cold trap temperature was kept at 0°C. The split ratios for sample injection were adjusted between 1:10 and 1:200 according to the concentrations of target compounds collected in the sampling tubes. The oven temperature program was 40°C hold for 10 min, ramping to 250°C at 10°C/min and held for 5 min. A DB-5 ms capillary column (30 m × 0.25 μm i.d., thickness 0.25 mm) was used to effectively separate the target compounds with a helium flow rate of 1.2 mL/min. The MS was operated in electronic ionization (EI mode) and scan mode. The target compounds were quantified with external calibration curve established over a range of standard concentrations: 22, 44, 110, 220 and 440 mg/L. 2 μL of standard solution was injected into the Tenax TA sorbent with 100 mL/min carrier gas (N_2) for 5 min.

2. Results and discussion

2.1. Ammonia emissions during urine hydrolysis

Fig. 1a shows the ammonium concentrations in the liquid during the hydrolysis process under different experimental conditions. The ammonium concentrations were increased with elapsed storage time because of the continuous conversion of urea into conductive ammonium ions. Once the ammonium was formed, ammonia gas was emitted with a strong pungent odor. Assuming that ammonia emission in a closed system reaches to gas–liquid equilibrium at the given condition, ammonia concentration in gas phase is dependent on the equilibria of ammonia absorption, ammonia hydrolysis and water dissociation, and can be described by Eq. (1) (Seinfeld and Pandis, 1998).

$$C_{NH_3,g} = \frac{1.90 \times 10^3 \times \exp\left(-\frac{4111}{T}\right)}{\left(1 + 10^{-pH} \times 6.07 \times 10^{-5} \times \exp\left(\frac{2365}{T}\right)\right) \times T} \times C_{NH_4^+,l} \quad (1)$$

where $C_{NH_4^+,l}$ (mg/L) is total ammonium concentration in liquid; $C_{NH_3,g}$ (mg/L) is the free ammonia concentration in the gas phase under equilibrium; T (K) is the temperature of liquid.

Ammonia emission was then calculated using Eq. (1) based on the measured ammonium concentration, temperature and pH (Fig. 1b). The effect of temperature on the ammonia emission was investigated using fresh urine without dilution stored at 23 and 35°C. The emissions were low after 2 day storage under both temperatures. At 23°C, the ammonia emission increased significantly during the storage time of 3–10 days, and reached 433 mg/m^3 at day 10. However, at 35°C, the ammonia emission increased drastically from 4 to 954 mg/m^3 during the storage time of 3–6 days, and then remained stable around 1100 mg/m^3. The temperature had great influence on ammonia emission mainly because of the formation of ammonium in the liquid. At 23°C, the ammonium concentrations in the fresh urine increased from 239 to 2696 mg/L with a conversion rate of around 96 mg/L NH_4^+/day. At 35°C, the ammonium concentration increased with a conversion rate 458 mg/L NH_4^+/day for five days, and then stabilized at 33 mg/L NH_4^+/day. The higher temperature significantly enhanced the enzymatic conversion of urea into ammonium due to successful growth of urease-positive bacteria. With the formation of ammonium, pH was also increased from 6 to 9. Both high ammonium concentration and high pH were favorable for the conversion of ammonium ion into free ammonia in the liquid. The higher temperature enhanced the mass transfer of free ammonia from liquid to gas phase as well.

The effect of stale/fresh urine ratio on the ammonia emission was investigated using fresh urine mixed with 20% (V/V) stale urine without dilution at 35°C. The ammonia emission of mixed urine was higher than fresh urine during the storage time of 1–5 days, but they followed similar trend after a longer storage time. The addition of stale urine into the fresh urine accelerated the ammonia emission, because it introduced more urease-positive bacteria into the urine solution, which enhanced the conversion of urea to ammonium with an increasing pH. According to Eq. (1), about 30% of ammonium was converted into free ammonia molecules in alkaline urine. When the urea was fully hydrolyzed after 10 day storage time, ammonium concentration remained stable.

The effect of dilution ratio on the ammonia emission was investigated using mixed urine with a dilution factor of 2 at 35°C. The diluted urine reached to a similar alkaline pH as undiluted urine due to the strong buffering capacity formed after complete hydrolysis. As expected, the ammonia emissions from the diluted urine were about half of those from the undiluted urine. This was mainly due to the reduction of ammonium ions and therefore the free ammonia in the diluted urine. The retarded liquid–gas mass transfer of free ammonia molecules resulted in a significant reduction in total ammonia emission according to Eq. (1).

Compared to odor threshold, the maximum ammonia concentrations in the headspace were almost 3500 times higher. Therefore, ammonia gas is considered an important odor burden during urine hydrolysis. In an open system, the transmitted urease-positive bacteria from air might shorten the time needed for complete urine hydrolysis (Zhang et al.,

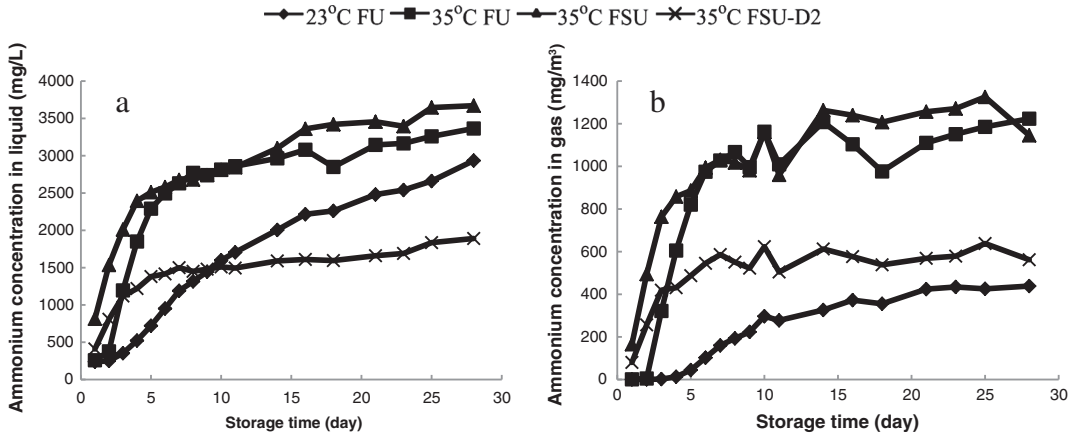

Fig. 1 – Variations of the ammonium concentrations in liquid (a) and in headspace gas (b) during the hydrolysis process under different conditions (23°C FU: fresh urine stored at 23°C; 35°C FU: fresh urine stored at 35°C; 35°C FSU: fresh urine mixed with 20% (V/V) stale urine (mixed urine) stored at 35°C; 35°C FSU-D2: mixed urine with a dilution factor of 2 stored at 35°C).

2013). In this case, ammonia molecules could continuously emit from the liquid due to prompt diffusion into the surrounding air. Theoretically, the majority of ammonium ($C_{NH_4^+,l}$ in Eq. (1)) in urine would ultimately transmit in to ambient air in an open system. From an engineering perspective, a closed system for urine collection and subsequent treatment is needed to prevent the emission of ammonia and other odorous gases.

2.2. Identification of odorous organic compounds

This study also identified the organic malodorous compounds emitted during urine hydrolysis, especially those with high concentration but low threshold limit of olfactory sensitivity. Fig. 2 shows the chromatogram of volatile organic compounds (VOCs) collected in the headspace of fresh urine at Days 1, 5 and 10 at 35°C. A total of 60 compounds were identified in the headspace of urine by comparing their mass spectra with the National Institute of Standard Technology library data. Table 1 lists the VOCs identified in this study in comparison with several other studies targeting at the odor emissions from human excreta and WWTPs. Totally 131 volatile organic compounds are included in Table 1, and they are classified in eight groups, namely, S-containing compounds, N-containing compounds, volatile fatty acids, ketones, aldehydes, alcohols, aromatic hydrocarbons and others. The compounds identified in this study were mainly S-containing compounds (13), ketones (17) and aromatic hydrocarbons (11). Among them, six volatile organic compounds were considered as the main odorous compounds (AMS, DMDS, AMDS, MPDS, 4-Heptanone and Menthol) and their characteristics are further listed in Table 2. It is noteworthy that the concentration ranges detected were much higher than their threshold limits.

It has been reported in the literature that VFAs were the predominant odorants in human waste (Hiroshi et al., 2001). In this study, only acetic acid was detected in the headspace gas of fresh urine around 0.005 mg/m^3 in the first few days, whereas other VFAs were detected only in the urine solution.

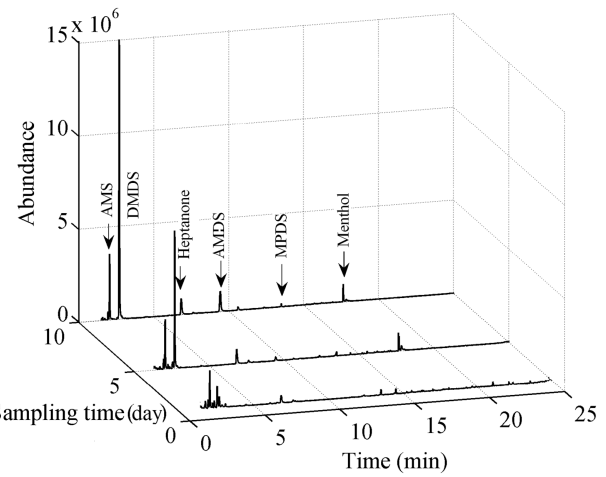

Fig. 2 – Chromatogram of volatile organic compounds detected in the headspace of fresh human urine at Days 1, 5 and 10 of storage at 35°C.

Acetic and propionic acid were the two most abundant compounds with liquid concentrations 240–420 and 74–148 mg/L, respectively. The concentrations of butyrate and isovalerate acid were 17.6–35.2 and 30.6–40.8 mg/L, respectively. In the alkaline urine solution, VFAs existed mainly in ionic forms due to their low dissociation constants (pK_a). The pK_a for acetate, propionate, butyrate, isovalerate and isocaproate are 4.75, 4.87, 4.82, 4.86 and 5.12, respectively. Hence, the emission of VFA species into the headspace was marginal under all conditions.

2.3. Factors affecting odor emissions

2.3.1. Effect of temperature

Fig. 3a–b shows the total organic odor emissions from fresh human urine in 10-day storage time under 23 and 35°C, respectively. The total amount of odor emission from human urine at 23°C was around 0.5 mg/m^3 in the first 3 days, and then increased drastically to 4 mg/m^3 at Day 4 and gradually to 7 mg/m^3. At higher temperature 35°C, the total amount of odor emission increased rapidly from 1.5 to 5.7 mg/m^3 in the first 3 days, and then increased gradually to 18.3 mg/m^3. It was observed that urine became more odorous with an elapsed storage time due to continuous urine hydrolysis. The higher temperature induced higher odor emission nearly three times compared to room temperature.

Among the organic odorous compounds, DMDS was the main contributor. At 23°C, the concentration of DMDS increased from 0.15 to 5.6 mg/m^3 in the course of 10 days with an increasing proportion from 56 to 80% of the total odor emission. At 35°C, the concentration of DMDS increased from 0.1 to 11.0 mg/m^3, making the proportion of DMDS emission increase from 43 to 60%. DMDS is mainly originated from dietary sources such as vegetables, cheese, fish, meat, baked goods and beverages (Mochalski et al., 2012). The generation of DMDS from urine was minor in the first day at both temperatures. Within the first 3 days of storage at 35°C, the concentration of DMDS dramatically increased to a 10-fold level compared to that at 23°C. The increase of DMDS might be attributed to the oxidation of methanethiol, which was enzymatically converted from methionine by bacteria (Tangerman, 2009). A higher temperature could enhance the microbial activity of bacteria and therefore the oxidation rate of methanethiol, leading to a stronger emission of DMDS. With the growth of bacteria, the DMDS emission at 23°C also increased rapidly. It should be noted that DMDS has an extremely low odor threshold (1.1–29 μg/m^3) that even the initial emitted concentration was one hundred times higher than the odor threshold concentration. Therefore, DMDS was considered as one of most odorous compounds emitted from human urine.

AMS was another main odorous compound emitted from human urine. The concentration increased gradually from 0.09 to 1.0 mg/m^3, occupying a proportion of 35%–14% of the total odor emission at 23°C. At 35°C, the concentration increased from 0.08 to 2.6 mg/m^3 over the same storage time and the proportion in the total odor emission decreased from 35% to 11%. AMS has been identified as one of the main volatile organic compounds that causes malodorous breath after garlic consumption, which is formed from allyl mercaptan (Munch and Barringer, 2014).

Table 1 – Comparison of odorant compounds emitted from human urine and WWTPs.

Classification	Odor source	WWTPs [a]	Feces and urine [b]	Urine [c]	Urine in current study
	Analytical method	GC/MS	TD-GC/MS	SPME-GC/MS	TD-GC/MS
S-containing compounds	Allylisothiocyanate			√	
	Allyl methyl sulfide				√
	Dimethyl disulfide	√		√	√
	Diallyl disulfide				√
	Di-2-propenyl trisulfide				√
	Dimethyl sulfide	√		√	√
	Dimethyl sulfone			√	
	Dimethyl tetrasulfide				√
	Dimethyl trisulfide	√		√	√
	Hydrogen sulfide	√	√		
	Isothiocyanocyclohexane			√	
	Methanethiol		√	√	
	Methyl 2-propenyl disulfide				√
	Methyl 2-propenyl trisulfide				√
	Methyl pentyl disulfide				√
	Methyl propyl disulfide				√
	3,3′-Thiobis 1-propene				√
N-containing compounds	Ammonia	√	√		√
	Chloramine	√			
	Dichloramine	√			
	Indole	√	√		√
	3-Methyl 1H-indole		√		
	Methyl pyrazine				√
	1-Methyl pyrrole			√	
	Phenyl formamide		√		
	Pyridine	√			
	Pyrrole		√	√	√
	Skatole	√	√		
	Trimethylamine	√	√		
	Trimethylpyrazine				√
	2,4,6-Trimethyl pyridine				
Volatile fatty acids	Acetic acid		√		√
	Butanoic acid		√		
	Dimethyl propanedioic acid		√		
	3-Methyl butanoic acid				
	Pentanoic acid		√		
	Propanoic acid		√		
	i-Valeric acid		√		
	n-Valeric acid		√		
Ketones	Acetone			√	
	2-Butanone			√	
	Camphor		√		
	2-Heptanone			√	√
	4-Heptanone			√	√
	2-Hexanone				√
	3-Hexanone			√	√
	3-Methyl 2-butanone			√	
	3-Methyl 2-hexanone				√
	4-Methyl 3-hexanone				√
	5-Methyl 3-hexanone				√
	6-Methyl 3-heptanone				√
	3-Methyl 6-(1-methylethyl) cyclohexen 1-one				√
	2-Methyl 4-pentanone	√		√	
	3-Methyl 2-pentanone			√	
	5-Methyl 2-propenyl cyclohexanone				√
	2-Nonanone				√
	2-Octanone				√
	3-Octanone				√
	2-Pentanone			√	√
	3-Penten 2-one			√	
	2-Propanone		√		

Table 1 (*continued*)

Classification	Odor source	WWTPs [a]	Feces and urine [b]	Urine [c]	Urine in current study
	Analytical method	GC/MS	TD-GC/MS	SPME-GC/MS	TD-GC/MS
Ketones	2-Undecanone				√
	2-Tridecanone				√
	1,7,7-Trimethyl bicycle[2.2.1]heptan 2-one				√
Aldehydes	2,4-Decadienal	√			
	1-Dodecanal	√			
	Heptanal	√			
	Hexanal			√	
	2-Methyl butanal			√	
	2-Methyl 2-butenal			√	
	1,2 Methyl propanal		√		
	2-Methyl propanal			√	
	Octanal			√	
	Pentanal			√	
	Propanal			√	
Alcohols	1-Butanol	√			√
	2-Butanol		√		
	Borneol				√
	Cis 3-Hexen 1-ol	√			
	3,7-Dimethyl 1,6-octadien-3-ol				√
	2-Ethyl 1-hexanol				√
	2-Heptadecanol		√		
	Menthol				√
	2-Methylisoborneol	√			
	1-Methyl 4-(1-methylethyl) cyclohexanol				√
	2-Methyl propanol		√		
	2-Pentanol				√
	2-propanol		√		
	2-Propyl 1-heptanol				√
Aromatic hydrocarbons	Butylatedhydroxytoluene				√
	Chloro benzene		√		
	1,2-Dichloro benzene		√		√
	1,4-Dichloro benzene	√			√
	2,3-Dihydro 5-methyl 1H-indene		√		
	1,3-Dimethyl benzene	√	√		
	Ethyl benzene		√		√
	1-Ethyl, 2-methyl benzene	√	√		
	4-Ethyl, 2-methoxy phenol				√
	3-Ethyl phenol		√		
	4-Ethyl phenol				√
	Eugenol				√
	Methyl benzene				√
	3-Methyl phenol		√		
	4-Methyl phenol				√
	Naphthalene		√		
	Phenol		√		√
	Styrene	√			
	Toluene	√		√	√
	2,4,6-Trichloroanisole	√			
	1,2,3-Trimethyl benzene		√		
	1,4,6-Trimethyl naphthalene		√		
Others	Carvone			√	
	Cineole		√		
	Cyclododecane		√		
	Decane		√		
	2,6-Dimethyl 1,3,6-heptatriene				√
	1,3-Dithiane				√
	D-Limonene	√			√
	Dodecane		√		
	Ethyl acetate			√	
	Furan			√	√
	Geosmin	√			
	Heptadecane		√		

(*continued on next page*)

Table 1 (*continued*)

Classification	Odor source	WWTPs [a]	Feces and urine [b]	Urine [c]	Urine in current study
	Analytical method	GC/MS	TD-GC/MS	SPME-GC/MS	TD-GC/MS
Others	Hexadecane		√		
	Methyl acetate			√	
	3-Methyl furan			√	
	8-Methyl heptadecane		√		
	2-Methyl 1-propene		√		
	1-Phenyl ethanone		√		
	1,1,1-Triethoxy ethane				√

Notes:
[a] Lebrero et al. (2011);
[b] Hiroshi et al. (2001);
[c] Mochalski et al. (2012).

It was observed that the concentration of 4-heptanone in the headspace increased from 0.04 to 2.2 mg/m^3 at 35°C with a proportion of 15% in the total odor emission, whereas its concentration was very low at 23°C with a proportion only 2%. The temperature seems to have significant influence on the formation and emission of 4-heptanone. 4-heptanone is considered as an important product of β-oxidation of 2-ethylhexanoic acid, which is a metabolic product of the plasticizer di-(2-ethylhexyl)-phthalate (Wahl et al., 2004; Walker and Mills, 2001). It has been used as one of the essential biomarkers of human urine and is listed as a major fraction of the volatile constituents (Mochalski et al., 2012). Although both AMS and 4-heptanone had lower concentrations than DMDS, they were still considered as two main odor contributors due to their very low threshold concentration.

In addition, AMDS, MPDS and menthol were also detected in the urine headspace. Their concentrations were relatively low in both temperatures and contributed 2%, 1% and 0.5% (at 23°C) and 6%, 1% and 5% (at 35°C) to the total odor emission, respectively. Particularly, the concentration of menthol increased from 0.002 to 0.7 mg/m^3 at 35°C. The major form of menthol in human urine is menthol glucuronide, which could be converted to menthol in the presence of glucuronidase enzyme. A higher temperature enhanced the conversion and subsequent emission of menthol.

2.3.2. Effect of stale/fresh urine ratio

Fig. 3c presents the total odor emissions of human urine by adding 20% stale urine in 10-day storage at 35°C. The total amount of odor emissions under such condition was enhanced compared to fresh urine as shown in Fig. 3b. By the addition of stale urine, more bacteria were introduced to biologically convert macromolecules into various products including volatile odorous compounds. Particularly, the concentration of DMDS emitted from the enhanced hydrolysis process was 3 times higher in the first 2 days. The increase of DMDS emission was probably originated from the stale urine as well as the enhanced hydrolysis of fresh urine. However, after the initial two days, there was no significant distinction in the odor emission among these two conditions (Fig. 3b vs. c).

It should be noted that the concentration of menthol emitted from fresh urine was higher than that from the urine mixture. The addition of stale urine introduced extra glucuronidase enzyme that further enhanced the conversion of menthol. Menthol has a short half-life of about 75 min in human body (Benowitz et al., 2010). Therefore, the menthol emitted from the urine mixture had a lower concentration. The stale/fresh urine ratio had little influence on the emissions of the other compounds.

In a source separation sanitation system, the efficiency of urine treatment is largely determined by the time needed for complete urea hydrolysis. It is therefore important to accelerate

Table 2 – Detection of main odorant compounds in the head space of human urine in this study.

Type of compound	Compounds	Concentration range detected (μg/m^3)	Threshold [a] (μg/m^3)	Odor description
S-containing compounds	Allyl methyl disulfide	90–2582	22–124	Alliaceous, garlic
	Allyl methyl sulfide	7–1550	0.06–60	Alliaceous, garlic, onion
	Dimethyl disulfide	100–10,997	1.1–29	Rotten cabbage
	Methyl propyl disulfide	3–251	0.9	Sulfurous, onion, radish
N-containing compounds	Ammonia	0–1250,000	210–350	Pungent, irritating
Alcohols	Menthol	1.3–733	0.5–33	Mint
Ketones	4-Heptanone	10–2207	0.08–0.7	Fruity, cheese, sweet

Notes:
[a] Refer to odor thresholds for chemicals with established occupational health standards, American Industrial Hygiene Association. USA (2009) and the Reference guide to odor thresholds for hazardous air pollutants listed in the clean air act amendments of 1990, EPA/600/R-92/047 (USA) (2009).

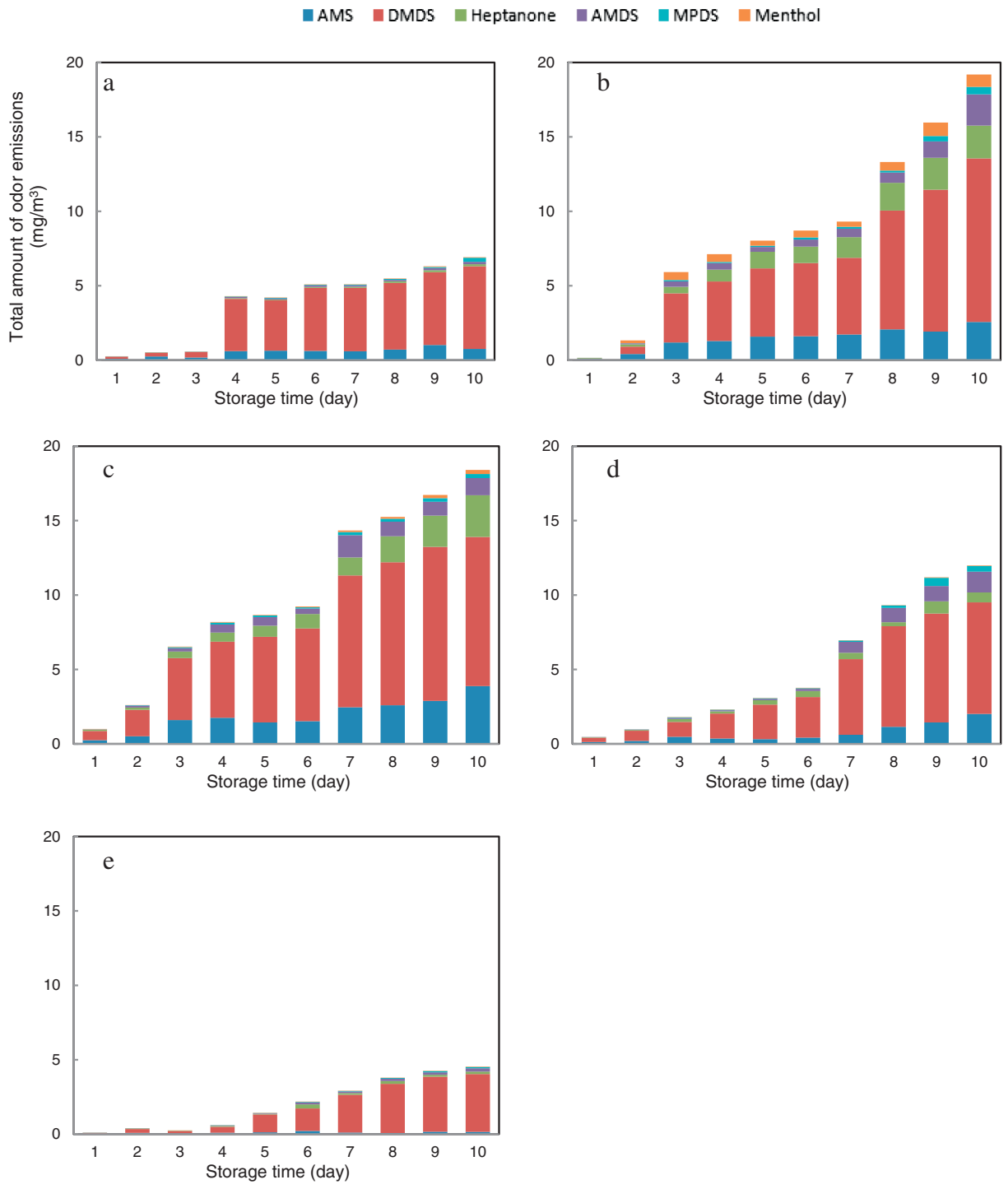

Fig. 3 – Total amount of odor emissions from human urine in the course of 10-day storage: (a) fresh urine stored at 23°C; (b) fresh urine stored at 35°C; (c) mixed urine stored at 35°C; (d) mixed urine with a dilution factor of 2; (e) mixed urine with a dilution factor of 5.

the urine hydrolysis in order to accomplish quick nutrient recovery. It has been proven that both nitrogen and phosphorus could be well recovered in less than 2 hr after hydrolysis (Liu et al., 2013, 2014). On the other hand, accelerating the hydrolysis process could significantly shorten the time of odor emissions. In case urine hydrolysis is shortened to 6 days, the total odor emissions would be reduced by 50% compared to 10 days. The recovery of nutrients could take place in a less odorous environment.

2.3.3. Effect of urine dilution ratio

The effect of urine dilution ratio on odor emission from urine mixture (20% stale urine) was further investigated at 35°C. Fig. 3d–e shows the total odor emissions of human urine at two different dilution ratios (2 and 5). Dilution significantly reduced the concentrations of precursor odorous compounds in solution and consequently mitigated the odor emission. With dilution factors of 2 and 5, the total odor emissions were reduced to

average 46% and 10%, respectively. These trends could be explained by the reduction in the formation of these odorous compounds during urine hydrolysis. According to Henry's law, the solubility of a given gas in a liquid is directly proportional to the partial pressure of the gas above the liquid. It also means the concentration of the evaporated gas is directly proportional to the concentration of the dissolved gas in liquid at an equilibrium status in a closed system. The concentrations of these compounds in the solution halved when the urine was diluted with the same volume of deionized water, causing accordingly reduced concentrations of the odorous compounds emitted.

2.4. Odor control strategies

There are limited investigations on odor control strategies that have been applied in source separation systems, although such systems are increasingly applied globally. Table 1 summarizes that sulfur compounds, ammonia and volatile organic compounds are also priority odorants generated in WWTPs (Lebrero et al., 2011). Odor control in WWTPs has been investigated by using different physicochemical or biological technologies such as chemical scrubber, activated carbon adsorption, and biofilter (Burgess et al., 2001). These technologies can be potentially used to control the odorous compounds emitted from source-separated urine.

Chemical scrubbers are one of the most widely used approaches used for odor abatement because of extensive experience in design and operation, short gas retention time and high robustness when properly operated (Gabriel and Deshusses, 2004). The removal efficiencies are in the range from 85% to 99% for H_2S, DMDS and dimethyl sulfide and higher than 99% for ammonia (Muirhead et al., 1993; Thompson et al., 1995). However, high requirement and the hazardous nature of oxidants and by-products generated present serious challenges in a long-term operation from the sustainable development perspective (Jeavons et al., 2000). Activated carbon adsorption is another option to remove the odorous compounds. The removal efficiencies are normally as high as 90%–99% for hydrogen sulfide and DMDS (Jeavons et al., 2000) and 90% for ammonia (Anfruns et al., 2008). But the high cost for adsorbent and its regeneration would probably constrain its wide implementation (Lebrero et al., 2011).

Compared to physicochemical technologies, biological technologies such as biofilters, biotrickling filters and bioscrubbers can be more cost-effective and environmentally friendly. The odorous compounds are essentially converted into innocuous compounds such as CO_2, H_2O and biomass at ambient pressure and temperature. The removal efficiencies are 80%–100% for sulfur compounds and 99%–100% for ammonia (Burgess et al., 2001; Easter et al., 2005). However, it has been reported that the adsorption of ammonia at relatively high concentration could increase the pH of the carrier material in biofilter and further inhibit the degradation of sulfur-containing compounds (Smet and Van Langenhove, 1998). Since ammonia emission from source-separated urine is substantial, it is recommended to remove ammonia from the odorous gas before entering biofilters. The main limitations of using biofilters include the requirement of large areas and operation/maintenance issues (Revah and Morgan-Sagastume, 2005). Bioscrubbers and biotrickling filters are only capable of removing compounds with an air-water partition coefficient (Henry's Law constant) lower than 0.01 (Dolfing et al., 1993), and, thus, they are unsuitable for the removal of DMDS with an air-water partition coefficient of 0.04.

Besides, advanced oxidation processes can be used to effectively remove various volatile organic compounds. For example, photocatalytic oxidation (PCO) is a promising technology for removing toxic organic compounds from air. PCO is cost-effective and can be carried out at room temperature and atmospheric pressure, with good catalyst stability (Jeong et al., 2004). The photocatalytic degradation of DMDS was investigated using the supported TiO_2-based catalysts (Chuang and Luo, 2013) and a relatively high removal efficiency of 80%–90% was achieved. However, the photochemical oxidation was incomplete in this process. Rather than oxidizing organic pollutant to CO_2 and H_2O, the oxidation process sometimes intercepted, producing some unintended by-products which can be toxic or irritating and may be less acceptable than their precursors (Sun et al., 2008).

3. Conclusions

This study determined the odorous compounds emitted from source-separated human urine during the hydrolysis process. Ammonia, DMDS, AMS and 4-Heptanone were the most dominant odorants emitted. Their concentrations in urine headspace gradually increased during urine hydrolysis process, and were hundreds of times higher than their odor threshold when urine was fully hydrolyzed. Besides, high temperatures significantly enhanced the odor emission from urine due to an accelerated formation of the odorous compounds and mass transfer to the headspace. Fresh urine mixed with 20% stale urine could emit more odorous compounds due to the introduction of urea-positive bacteria triggering urine hydrolysis. Diluting the urine with water reduced the concentrations of odorants in the liquid and therefore decreased their emission into the gas. This study also assessed different technologies that can be potentially used for odor treatment and mitigation, and future work is recommended to effectively remove the unpleasant odorous compounds from source-separated urine.

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