B−71 FATE OF URINARY COMPONENTS AND PHARMACEUTICALS IN STORAGE PROCESS OF URINE

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1. INTRODUCTION

Separation of urine at source has been a basic idea for more sustainable management of wastewater in household[1-7]. It is possible to prepare two main processes for source-separated urine: first one is onsite storage and second one is treatment of micro pollutants and recovery of nutrients *etc.* Various kinds of treatment and recovery methods have been investigated, however, compared to interests in phosphate, nitrogen and micro-pollutants, discussion about organic matter seemed to be not enough especially on the change in the character of urine during storage process. Therefore objectives of this study were 1) to prepare the list of urine components mainly focused on organic matter 2) to monitor the evolution of the urine components in storage process.

2. MATERIAL AND METHODS

(1) Collection and storage test of fresh urine

Fresh urine was collected from 189 volunteers (145 males and 44 females) in Hokkaido University within 4 hours around noon. After the collection, pharmaceuticals of carbamazepine, diclofenac and metoprolol were immediately added to fresh urine for pharmaceuticals' monitoring. For organic matter monitoring, 100 ml of the fresh urine was put into 100 ml of glass bottles (storage units). Every storage unit was stored in incubator (30 °C).

(2) Pretreatment and DOC determination

In 90 days storage test, sampling and analysis were conducted for several times. In every sampling process, urine pH was measured immediately after the storage units were opened. Then urine was filtrated by membrame filter with pore size of 0.45μm and UF membrane (MWCO 10 kDa, 1 kDa) and dialysis tube (MWCO 100 Da). By using these membrane, organic matter in urine was fractionated and their DOC were determined by TOC analyzer.

(3) Determination of amino acid, organic acid and pharmaceuticals in urine

Determination of organic acid was conducted by using the ion exclusion chromatography system. Amino acid analysis was conducted by using amino acid analyzer (HPLC: ModelL-8500, Hitachi). For the determination of pharmaceuticals, clean up and determination methods were followed by the OASIS technical notebook.

3. RESULTS AND DISCUSSIONS

(1) Compounds in very fresh human urine

Table 1 lists the comparison of major components measured in this study. As seen, most comparable values obtained in this study were similar to previous reports[8,9]. From the data obtained in this study, it was found that approximately 84% of organic matter in fresh urine was still unknown even though various compounds were determined; nitrogen species in urine were mostly described by four nitrogen species: urea, ammonia, uric acid and creatinin; major species of organic acid from fresh urine were the acetic acid, the lactic acid and the propionic acid; in amino acids the taurine and the histidine were slightly higher than other species.

(2) Fate of the fresh urine for 90 days storage

a) Transformation of organic matter

In this study, we monitored the organic matter in urine during the strorage process. Figure 1 shows the evolution of DOC including urea and DOC except urea. As seen, DOC except urea was on the stable level throughout the storage process whereas the DOC including urea constantly decreased. this indicated that main reduction of organic matter was degradation of urea. Regarding organic matter except urea, 10% reduction was found. Since stored urine usually provide pH more than 7 with ammonia on high level, then it might be difficult to assume methane production as anaerobic reaction of organic matter [10,11]. Udert *et al.* [12] reported more than 80% of dissolved COD of urine was biodegradable in aerobic condition whereas they discussed possibility for anaerobic biodegradation of organic matter in stored urine by citing previous reports[13,14].

Figure 2 shows the molecular weight distribution of the DOC except urea in storage process of urine. Simple result was found: 74% of organic matter were distributed in 100 Da - 1 kDa fraction in fresh urine whereas 84% of organic matter in stored urine presented in the fraction of less than 100 Da. It was found that the most of organic acid increased in the first 15 days during storage process (data not shown). That also supported the transformation of organic matter into smaller size.

c) Fate of pharmaceuticals

As shown in Fig.3, significant decrease of Tetracycline was found in stored urine at 30°C. Kakimoto and Funamizu[15] showed that the decomposition of Tetracycline profoundly related to levels of phosphate ion and Ammonia level in composting process of human feces. In urine, concentrations of phosphate and ammonium were much higher than in usual wastewater. It was therefore seemed to be reasonable that the tetracycline could decompose in storage process of urine. Slight decrease of the metoprolol was observed. Other pharmaceuticals used in this study did not decrease remarkably. It might be possible to assume that further three chemicals (Carbamazepine, Levfloxacin and Diclofenac) could be stable in simple storage process of urine. Carbamazepine was very stable even in the electro oxidation process[16]. Several results from previous studies showed that Levofloxacin was hard to decompose in wastewater treatment plant[17]. Diclofenac could decompose in wastewater treatment plant mainly because of bacteria[33]. Biodegradability of the diclofenac does increase in

Table 1 Comparison of components of fresh urine

		Urine [1][9]	Urine [2][8]	Our results
Dilution	(-)	1	1	1
pH	(-)	6.2	7.2	6.5
DOC	mg-C/l	-	*5546**	7300
COD	mg-C/l	-	3056	*4950**
Total N	mg-N/l	8830	-	6300
Urea	mg/l	-	12450	11800
Ammonia	mg-N/l	463	254	300
Phosphate	mg-P/l	800-2000***	367**	1100**
Na+	mg/l	3450	2670	2940
Cl]]\\\\\\\]-	mg/l	4970	3810	5180
Ca2+	mg/l	233	129	120
Mg^{2+}	mg/l	119	77	60
K+	mg/l	2737	2710	1760

*: Estimated by assumption of "DOC = C in Urea + C in COD".
**: Including alls system species of phosphate ion
***: Total phosphorous

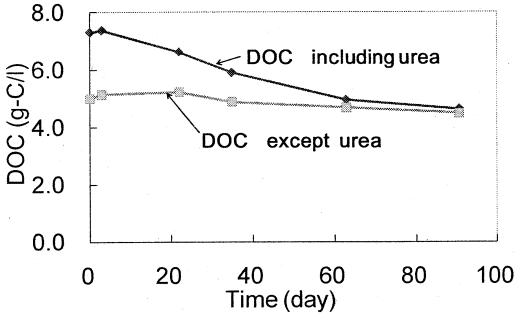

Figure 1 evolution of DOC in storage process

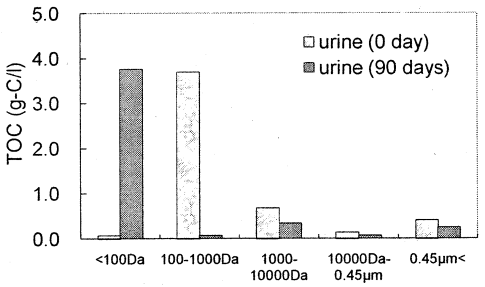

Figure 2 Molecular weight distribution of urine

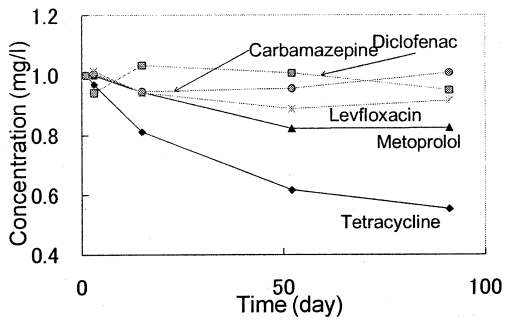

Figure 5 Pharmaceuticals in urine during strorage process

acidic condition that provides non-dissociation type. However, pH condition was relatively higher than pH 9 in stored urine. Thus it might be hard for diclofenac to decompose.

4. CONCLUSION

Study on source-separated urine was conducted. Conclusions obtained in this study were following:

(a) Lists of the components of very fresh urine were obtained: 40 species of amino acid, 7 species of organic acid, 4 species of nitrogen and 7 species of inorganic ion. However, more than 80% of organic carbon except Urea was still not determined in fresh urine.

(b) 90 days storage provided smaller molecules. The majority of organic matter in fresh urine was found in the fraction of 100Da-1000Da whereas it shifted into the fraction less than 100Da after long storage. However the main compounds less than 100Da was still unknown. In the storage unit, more than 90% of organic matter was not carbonated but they remained in dissolved type even after 90days storage at mild temperature. Some species of organic acid temporally increased but finally decreased.

(c) Declines of the Tetracycline and Metoprolol were found in simple storage unit with sealed at 30°C. However pharmaceuticals of Carbamazepine, Levfloxacin and Diclofenac were being on stable level throughout the storage process.

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