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BEHAVIOR OF FOUR SELECTED PHARMACEUTICALS DURING LONG-TIME STORAGE OF YELLOW WATER

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ABSTRACT

Urine from individuals without any medication as well as a freeze concentrate of this urine were spiked with carbamazepine, diclofenac, ibuprofen, and clofibrac acid in concentrations of 10 mg/l each and stored for 363 days in glass bottles under different conditions concerning temperature, pH, daylight/darkness, and mechanical agitation. At several times, samples were taken from each bottle and subsequent to solid phase extraction (SPE), concentrations of the four pharmaceuticals were measured by gas chromatography with flame ionisation detection (GC/FID). In the final sample at the end of the storage period analysis was performed by gas chromatography with mass selective detection (GC/MS). None of the four human pharmaceuticals was remarkably reduced irrespective of the storage conditions. Only for carbamazepine concentrations in the bottles exposed to daylight at room temperature both analytical methods indicated a slightly decreasing trend which was not substantial, however. The results suggest that there is need of a technology for pharmaceutical elimination from human urine to be utilised as fertiliser, because some pharmaceuticals are known to be very recalcitrant and they might contaminate the groundwater and even be transferred to crops.

KEYWORDS: pharmaceuticals, storage, yellow water

INTRODUCTION

Yellow water is a splendid lowly contaminated natural fertiliser which can contribute to food security in poor regions. However, it may be contaminated by fairly high concentrations of pharmaceuticals. A worst-case



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scenario would be agricultural application of urine of one medicated person on a small area. For carbamazepine, a daily defined dose of 1 g and a renal excretion rate of 2 to 3 % together with a daily excreted urine volume of 1.25 l will result in predicted concentrations in the person's yellow water of 16 to 24 mg/l. At present, there is no knowledge - but concern - about uptake of human pharmaceuticals by crops. Moreover, agricultural application of pharmaceutical-contaminated urine may lead to groundwater contamination. The antiepileptic carbamazepine, the antiphlogistics ibuprofen and diclofenac, as well as clofibric acid, the active metabolite of a couple of antilipidemic agents like e.g. clofibrate, have been detected in German groundwater samples and were therefore selected for this study.

Several yellow water treatment processes have been investigated for their suitability to remove human pharmaceuticals: Ozonation (Gulyas et al. 2007, Nguyen and Funamizu 2005), electro dialysis (Pronk et al. 2006a), nanofiltration (Pronk et al. 2006b), steam stripping (Tettenborn 2007), vacuum distillation (Tettenborn 2007), UV irradiation (Tettenborn 2007). However, these processes are sophisticated high-tech processes and energy-consuming (Gulyas et al. 2007, Tettenborn 2007). Therefore, the storage of urine as a simple process leading to hygienisation by pH augmentation due to ureolysis was investigated with respect to human pharmaceuticals removal by Butzen et al. (2005). In their study it was shown that diclofenac and tetracycline were efficiently removed during a six months storage period at pH 2, while sulfamethazine and sulfamethazol concentrations were decreased by 30 % (initial concentrations of pharmaceuticals: 0.1 mg/l). It has to be noted that for decreasing the pH of stored urine a high amount of acid is required because of the reasonable alkalinity of yellow water subsequent to complete ureolysis. In the neutral range, only tetracycline was reduced by about 20 %, while at pH 9 tetracycline was reduced by 30 to 40 %, sulfamethoxazol by 20 to 30 % and ibuprofen and carbamazepine by about 15 % within 6 months (Butzen et al. 2005).

In order to get some information about the behavior of pharmaceuticals present in urine under worst case conditions (high concentrations), yellow water spiked with the four selected substances in concentrations of 10 mg/l each was stored under different conditions for a year and the pharmaceuticals concentrations were analysed several times during the storage period.

MATERIALS AND METHODS

Urine was collected from volunteer unmedicated donors. The collected urine samples were combined. A part of this mixture was freeze-concentrated threefold according to Gulyas et al. (2004). Original urine and freeze concentrate were spiked with carbamazepine, diclofenac, ibuprofen, and clofibric acid in concentrations of 10 mg/l each. The spiked urine as well as the spiked concentrate were divided into 1 litre portions which were stored in glass bottles for 363 days in the dark at different temperatures (4°C, 20°C, room temperature varying between 12 and 38°C) and different pH (4, 7 and 10). The bottles were not agitated during storage (only prior to sampling the bottles were vigorously shaken) except one set stored at room temperature placed on magnetic stirrers. One non-agitated set of bottles was allowed to stand at room temperature in translucent glass bottles close to the laboratory window for investigating the influence of daylight. Samples were taken several times during the storage period. Pharmaceuticals were analysed by solid phase extraction (SPE) with abselutNEXUS cartridges (Varian) and gas chromatographic analysis of the SPE methanol eluates with flame ionisation detection (GC/FID) subsequent to derivatisation of clofibric acid, diclofenac and ibuprofen with trimethylsulfonium hydroxide (TMSH) directly in the injector; for details see Gulyas et al. (2007). For all gas chromatographic analyses dihydrocarbamazepine was used as a surrogate standard. Each sample taken at the end of the storage period was analysed by GC/MS. The following target ions were used for identification in GC/MS analyses: $m/z = 128$ (clofibric acid), $m/z = 161$ (ibuprofen), $m/z = 214$ (diclofenac), $m/z = 193$ (carbamazepine), $m/z = 195$ (dihydrocarbamazepine).

RESULTS AND DISCUSSION

In general, the results showed that none of the tested pharmaceuticals was substantially removed from the spiked yellow water during a several months storing period under all investigated storage conditions. The variation of GC/FID data were larger than or at least in the same range as the decrease of pharmaceutical concentrations after 363 days (see fig. 1 for the pharmaceutical carbamazepine). No or at the best marginal pharmaceutical removal was corroborated by the GC/MS analyses of the samples taken after 363 d storage

resulting in pharmaceutical concentrations as high as the initial concentrations regardless of the storage conditions. The GC/MS analyses were more reliable because the peak identification by selective target ions was more secure than by the nonspecific FID signals in the very complex organic matrix of urine. In non-spiked urine blanks no pharmaceuticals were detectable by GC/MS.

Interestingly, carbamazepine concentrations in yellow water stored in translucent glass bottles at the window ("daylight" in fig. 1) measured by GC/MS slightly decreased within the storage period at each investigated pH. This small decreasing trend of carbamazepine concentrations was also observed at all tested pH ranges with spiked threefold freeze concentrates of yellow water exposed to daylight in translucent bottles (data not shown). However, the decrease was very small (about 20 % within one year) and might also be attributed to analytical errors (e.g. with volume dosing when adding surrogate standard solutions etc.). Moreover, it was confusing that the photolabile substance diclofenac did not show this behavior (except for storage at daylight at pH 4; data not shown). On the other hand, Chiron et al. (2006) demonstrated that carbamazepine was degraded by UV irradiation when high chloride concentrations were present. They attributed the carbamazepine degradation to a radicalic mechanism caused by the interaction of UV photons, Fe^{3+} and chloride ions. However, the Duran glass bottles together with the window glass panes cannot be looked at as UV-translucent.

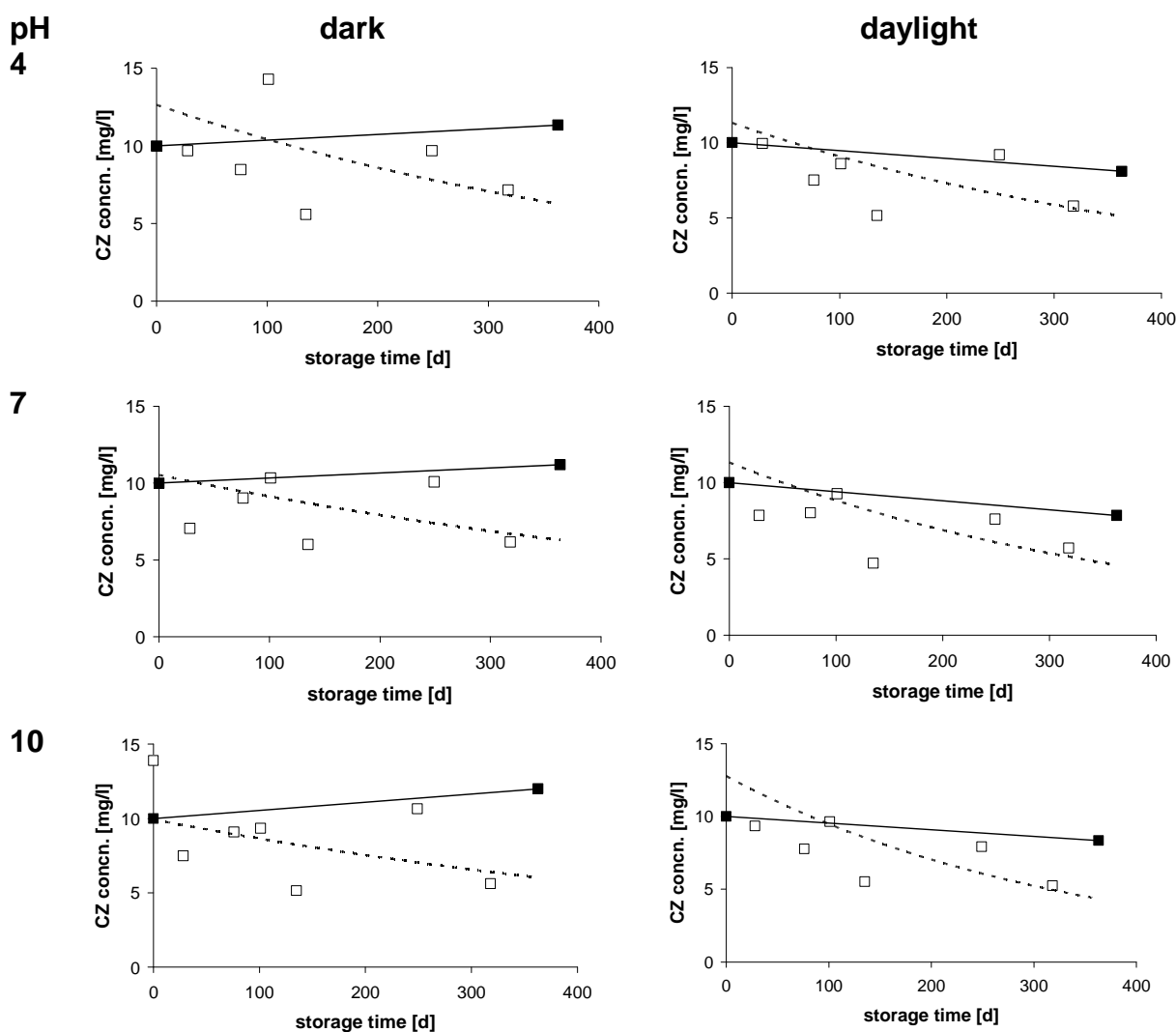


Figure 1 – Carbamazepine (CZ) concentrations in spiked non-concentrated urine during a 363 d storage period at different pH at room temperature in brown glass bottles (left) and translucent glass bottles (right); open squares: analysed by GC/FID; dark squares: initial concentration constituted by weighing and sample at the end of storage period analysed by GC/MS



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There is some contradiction between the data presented here and the results of Butzen et al. (2005). Butzen et al. (2005) found an efficient diclofenac removal by storing urine for six months at pH 2, but in this study no removal of the investigated pharmaceuticals – among them also diclofenac – was observed. This might be explained by the hypothesis that diclofenac is decaying at pH 2, while pH 4 may not be sufficiently acidic for diclofenac decomposition. That ibuprofen and carbamazepine concentrations were reduced by about 15 % in the investigation of Butzen et al. (2005), but not in the study presented here at an even higher pH may refer to the different initial pharmaceutical concentrations (0.1 mg/l vs. 10 mg/l). Moreover, analytical errors cannot be excluded for the study of Butzen et al. (2005), especially as the decrease of carbamazepine and ibuprofen concentrations was relatively small in their investigation.

CONCLUSION

At least high concentrations (10 mg/l) of the four investigated human pharmaceuticals are not reduced during storage of yellow water at pH 4, 7 or 10 irrespective of the storage temperature. Influence of daylight on carbamazepine was in the range of data variation and thus not reliably ascertained, although observed in all samples exposed to daylight. It has therefore to be considered that pharmaceuticals contained in urine derived from small collectives with several persons under medication can be transferred to groundwater or to crops when the yellow water is utilised as fertiliser. It is thus important to find an economic process for removing pharmaceuticals from yellow water which is also feasible for rural sites with decentralized ecological sanitation.

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