OCCURRENCE AND FATE OF PHARMACEUTICALS IN WASTEWATER SYSTEMS IN JAPAN

Yutaka SUZUKI, Koya KOMORI, Arata HARADA, Norihide NAKADA
and Makoto YASOJIMA
Water Quality Research Team, Water Environment Research Group
Public Works Research Institute
1-6 Minamihara, Tsukuba, Ibaraki 305-8516, Japan

ABSTRACT

Ten wastewater treatment plants were surveyed to clarify the occurrence and fate of pharmaceuticals and personal care products (PPCPs) in wastewater systems in Japan. It was found that the concentration of most PPCPs in influent wastewater ranged from hundreds to one thousand ng/L and that several patterns of PPCP removal in the treatment process existed according to the characteristics of PPCPs. From ecotoxicity tests and the concentration levels in wastewater, it was considered that some antiseptic agents and antibiotics may cause adverse effects on aquatic ecosystems if gray water is not collected and treated, or if the dilution rate of the receiving river is low.

KEYWORDS

Pharmaceuticals and personal care products, occurrence, fate, wastewater, ecotoxicity

INTRODUCTION

Recently, there has been growing public concern about the emergence of environmental pollution of water sources from pharmaceuticals and personal care products (PPCPs). Considering the routes by which PPCPs enter the water environment, wastewater treatment plants (WWTPs) may facilitate their initial entry. If PPCPs are not properly treated during the wastewater treatment process, they may contaminate the water environment, including drinking water sources.

Considering the current level of knowledge regarding this problem, it is necessary to clarify the fates of PPCPs in WWTPs to identify appropriate treatment methods. In our research, we analyzed the presence of PPCPs in several WWTPs to clarify the concentrations and fates of PPCPs at the various stages of wastewater treatment.

In addition, toxic effects of PPCPs on aquatic organisms were evaluated with ecotoxicity tests by comparing concentrations in wastewater and ecotoxicity results.

METHODS

Two sets of surveys were conducted for ten WWTPs that employ the conventional activated sludge process. The target PPCPs for the first set of surveys were six anti-inflammatories (aspirin, ketoprofen, ibuprofen, fenoprofen, naproxen, mefenamic acid), a phenolic antiseptic (triclosan), and three amide pharmaceuticals (crotamiton, diethyltoluamide, carbamazepine) (Figure 1). The target PPCPs for the second set of surveys were two antibiotics (levofloxacin (LVFX) and clarithromycin (CAM)) (Figure 2); these were selected because of their largest amount of consumption in Japan.

Twenty 4-hour water flow proportional composite samples were collected from several sampling locations in each WWTP. They were analyzed with GC/MS or LS/MS/MS after sample extraction and purification according to the methods of Nakada, N. et al. (2006) and Yasojima, M. et al. (2004).

In addition to the surveys in WWTPs, bench-scale wastewater treatment experiments were conducted using influent of a WWTP to investigate the mass balance of the antibiotics. The process was the conventional activated sludge process with the HRT of 8 hours and the SRT of 8 days.

Ecotoxicity of the PPCPs was evaluated with the Microtox test using *Vibrio Fisheri*, the algal growth inhibition test using *Pseudokirchneriella subcapitata*, and the *Daphnia* acute immobilization test (DAPHTOXKIT F MAGNA).

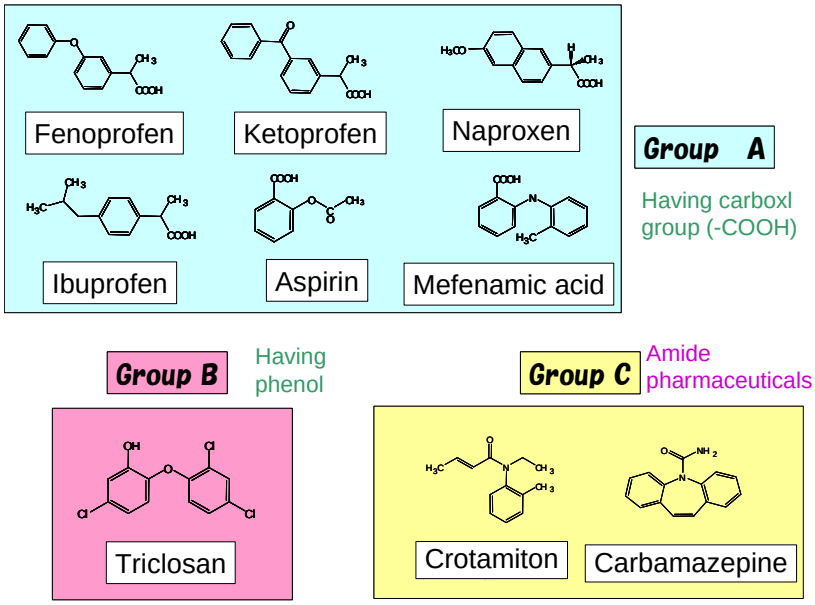


Figure 1 Anti-inflammatory drugs, etc. measured in the first set of surveys

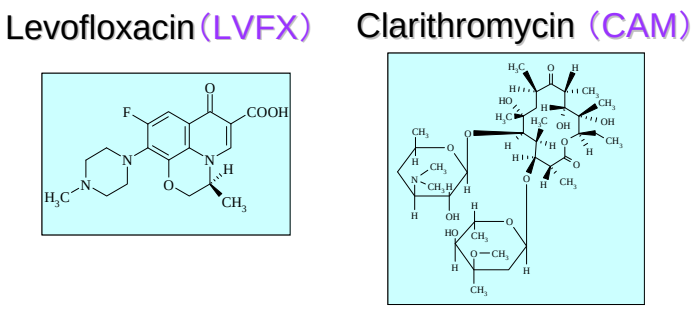


Figure 2 Antibiotics measured in the second set of surveys

OCCURRENCE AND FATE OF PHARMACEUTICALS

Anti-inflammatory drugs, etc.

The concentrations of dissolved PPCPs in the influent were of the order of hundreds of ng/L, except for carbamazepine which was of the order of tens of ng/L, and fenoprofen which was under the detection limit. Almost all of the PPCPs existed in the dissolved form except for triclosan.

Changes in dissolved concentrations along the stages of the treatment process are shown in Figure 3. No significant removal was observed in the primary sedimentation tank for all PPCPs, but the removal characteristics in the biological treatment differed according to the PPCPs; two anti-inflammatories (aspirin and ibuprofen) and triclosan were effectively removed, while the remaining anti-inflammatories (ketoprofen and naproxen) showed reductions of around 50%, and crotamiton and carbamazepine were hardly removed. From these characteristics, PPCPs were classified into three groups: the almost complete removal group, 50% removal group, and very low removal group (Table 1).

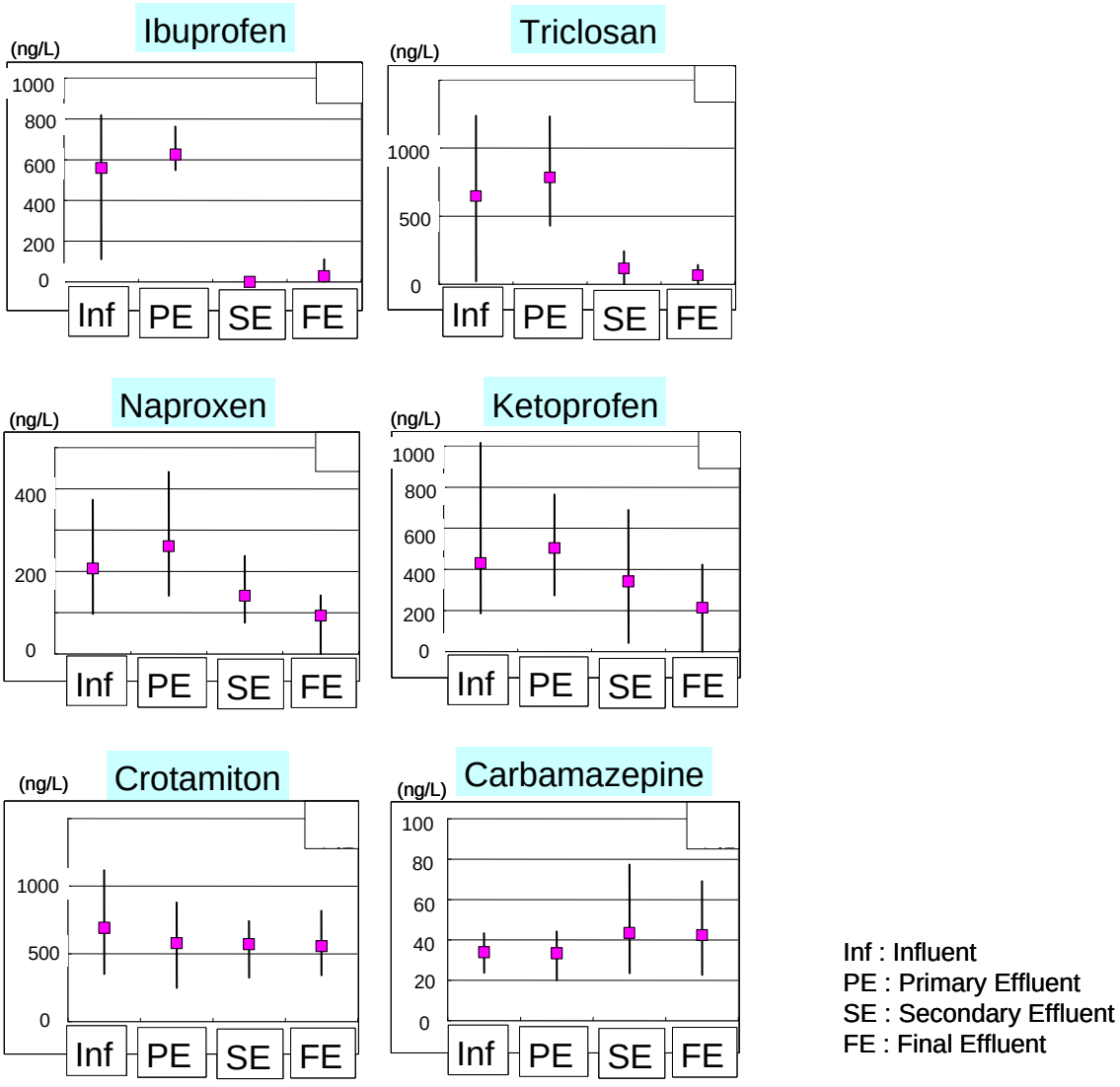
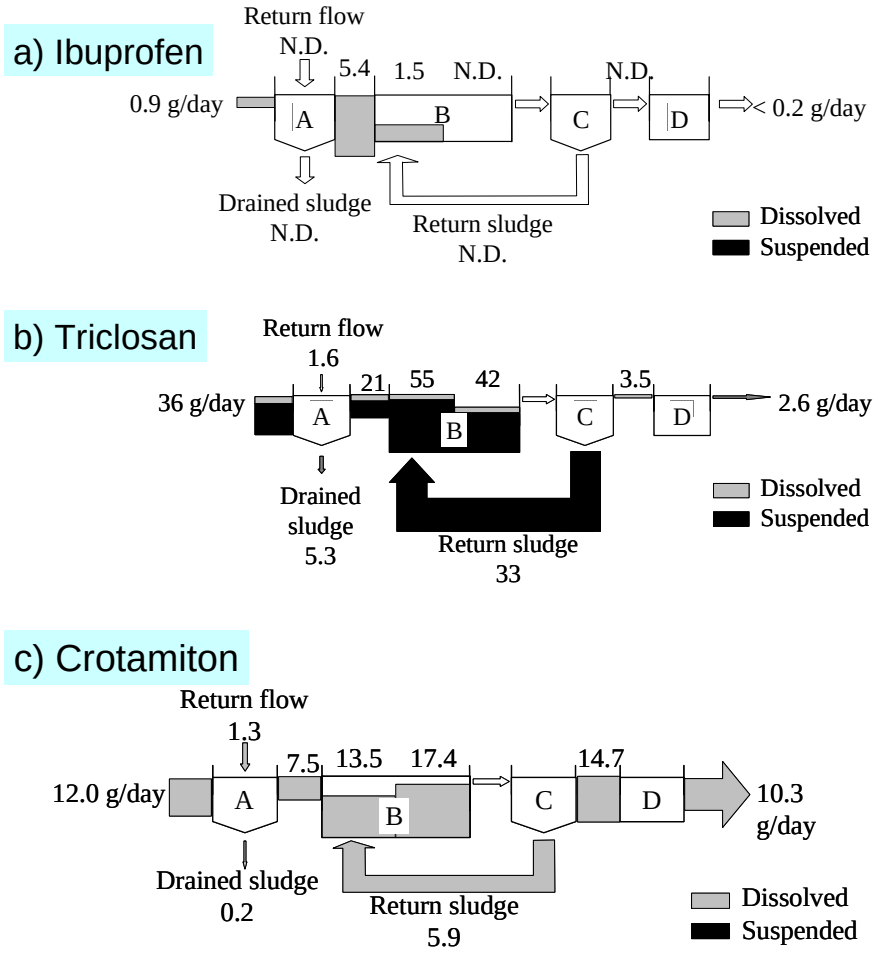


Figure 3 Changes in dissolved concentrations of anti-inflammatory drugs, etc. along the stages of the treatment process of WWTPs

Table 1　Average removal ratios of anti-inflammatory drugs, etc. in WWTPs

PPCPs		Removal ratio (%)
Aspirin	Anti-inflammatory	96
Ibuprofen	Anti-inflammatory	95
Triclosan	Antiseptic	90
Naproxen	Anti-inflammatory	55
Ketoprofen	Anti-inflammatory	50
Crotamiton	Itch-reliever	20
Carbamazepine	Antiepileptic	-25
Mefenamic acid	Anti-inflammatory	-240

The fates of PPCPs were evaluated by calculating the mass balance of PPCPs in the WWTPs (Figure 4). Ibuprofen was significantly removed and degraded by the activated sludge in the aeration tank, while triclosan was removed by adsorption to the activated sludge and accumulation in the sludge was observed. Crotamiton and carbamazepine hardly changed in the process.



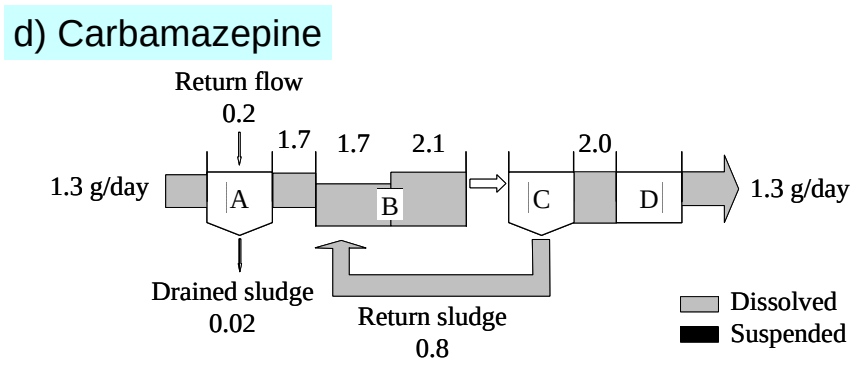


Figure 4 Mass balance of anti-inflammatory drugs, etc. in a WWTP

Antibiotics

Changes in dissolved concentrations of antibiotics along the stages of the treatment process of WWTPs are shown in Figure 5, and the mass balances of the antibiotics in the treatment process evaluated using a bench-scale plant are shown in Figure 6.

Dissolved concentration in the influent ranged from hundreds to one thousand ng/L, and the removal ratio in WWTPs was around 50%. For LVFX, an increase of dissolved concentration in the middle of the aeration tank was observed, which might have been caused by the desorption of LVFX from the activated sludge.

From the mass balance of the antibiotics, LVFX accumulated in the activated sludge in a high concentration, suggesting that the main mechanism of removal of LVFX was adsorption to the activated sludge. On the other hand, CAM accumulation in the sludge was small, which indicates that biodegradation by the activated sludge might happen.

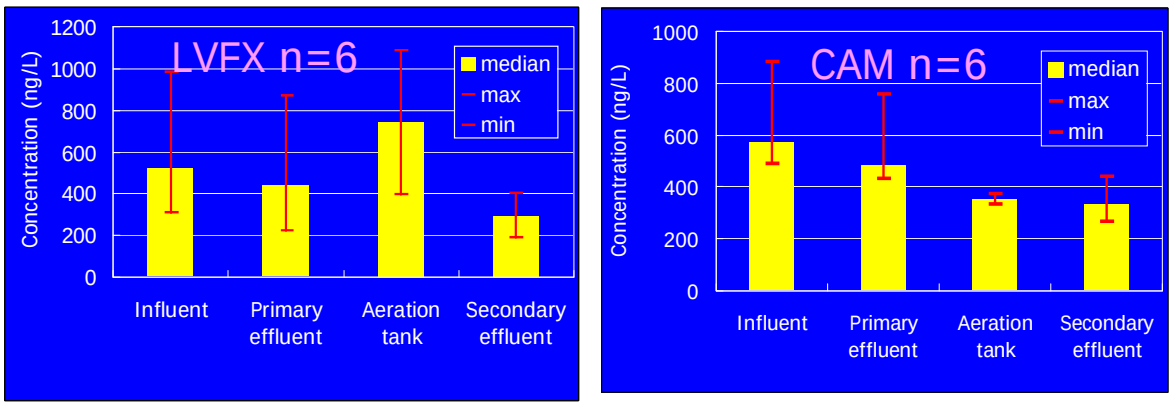


Figure 5 Changes in dissolved concentrations of antibiotics along the stages of the treatment process of WWTPs

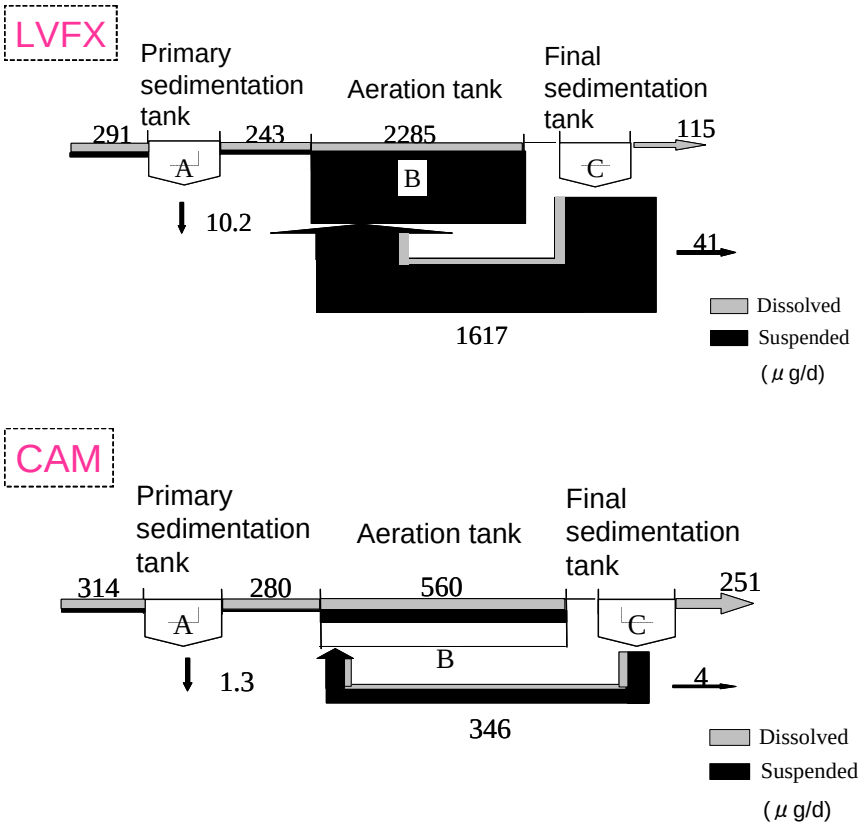


Figure 6 Mass balance of antibiotics in a wastewater treatment process

ECOTOXICITY

Ecotoxity of the PPCPs was evaluated with three kinds of bioassays. As shown in Table 2, triclosan (antiseptic agent) showed toxicity on bacteria and crustaceans at concentrations below 1 mg/L, and clarithromycin (CAM, antibiotic) inhibited algal growth at the concentration of 0.01 mg/L.

Table 2 Results of ecotoxicity tests

(mg/L)

PPCPs	Microtox test		Algal growth inhibition test	*Daphnia* acute immobilization test	
	EC50		EC50	EC50	
	5 min	15 min	96 hour	24 hour	48 hour
Aspirin	N.E.	N.E.	／	N.E.	N.E.
Triclosan	0.6	0.6	／	0.4	0.4
Crotamiton	57.6	N.E.	／	N.E.	N.E.
Levofloxacin	N.E.	N.E.	1.435	N.E.	N.E.
Clarithromycin	N.E.	N.E.	0.011	N.E.	N.E.

N.E. : No Effect

Comparing the EC50 with the PPCP concentration in the wastewater and treated wastewater, EC50 of triclosan for *Daphnia* immobilization was 1/400 of the wastewater concentration,

and EC50 of CAM for algal growth inhibition was 1/28 of the treated wastewater (Table 3).

Although the predicted no-effect concentrations (PNEC) of triclosan and CAM were not obtained precisely, triclosan could affect bacteria and crustaceans in an area without a sewerage system where triclosan in gray water may be directly discharged to the water environment. Furthermore, CAM in treated wastewater may affect algae in the water environment if the dilution rate of the receiving river is low.

Table 3 Comparison between EC50 and the concentration of wastewater

	EC50 (a)	Influent (b)	Final effluent (c)
Triclosan (μ g/L)	400	1	0.1
(b or c)/a		**1/400**	1/4000
Clarithromycin (μ g/L)	11	0.6	0.4
(b or c)/a		1/18	**1/28**

CONCLUSIONS

Surveys in wastewater treatment plants and ecotoxicity tests were carried out targeting pharmaceuticals and personal care products, and the following findings were obtained:

1) The concentration of most PPCPs in influent wastewater ranged from hundreds to one thousand ng/L.
2) Several patterns of PPCP removal in the treatment process were observed:
   a) effectively decomposed by activated sludge (some anti-inflammatory drugs)
   b) adsorbed to activated sludge (triclosan and levofloxacin)
   c) hardly changed (crotamiton and carbamazepine)
3) An antiseptic agent (triclosan) and an antibiotic (clarithromycin) showed ecotoxicity, and if gray water is not collected and treated or if the dilution rate of the receiving river is low, these PPCPs may cause adverse effects on aquatic ecosystems.

REFERENCES

Nakada, N. et al. (2006): “Pharmaceutical chemicals and endocrine disrupters in municipal wastewater in Tokyo and their removal during activated sludge treatment,” Water Research 40, 3297-3303

Yasojima, M. et al. (2004): “Development of analytical method for levofloxacin and clarithromycin in secondary effluent and their adverse effects on algal growth,” Journal of Japan Society on Water Environment, 27(11), 707-714 (in Japanese)