Occurrence of Pharmaceuticals and Personal Care Products in Wastewater Systems

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1. Introduction

Recently, there has been a growing public concern about the emergence of environmental pollution of water sources from pharmaceuticals and personal care products (PPCPs). Considering the route PPCPs take to reach water environment, wastewater treatment plants (WWTPs) may facilitate their initial entry. If PPCPs are not properly treated during the wastewater treatment process, they can contaminate 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 along the units of wastewater treatment.

In addition, toxic effects of antibiotics on aquatic organisms were evaluated with ecotoxicity tests, and ecological risk of the antibiotics was evaluated by comparison between concentrations in water environment and ecotoxicity results.

2. Survey Sites and Methods

Surveys were conducted in four or six WWTPs employing conventional activated sludge process, depending on the type of the PPCPs. Twenty four-hour water flow proportional composite samples were collected from several sampling locations in each WWTP.

The target PPCPs were four anti-inflammatories (aspirin, ketoprofen, ibuprofen, naproxen), a phenolic antiseptic (triclosan), three amide pharmaceuticals (crotamiton, diethyltoluamide, carbamazepine) and two antibiotics (levofloxacin, clarithromycin). They were analyzed with GC/MS or LS/MS/MS after sample extraction and purification according to the methods by Nakada,N. et al.(2006) and Yasojima, M. et al.(2006). Ecotoxicity was evaluated with the tests using bacterium, alga and crustacean.

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3. Occurrence and Fate of PPCPs

The PPCP concentrations in the influent were of the order of hundreds ng/L, except for carbamazepine of the order of tens ng/L. Almost all of the PPCPs existed in the dissolved form except for triclosan and antibiotics, which might be the reason for no remarkable decrease after the primary sedimentation tank.

During the biological treatment, two anti-inflammatories (aspirin and ibuprofen) and triclosan were effectively removed, while the remaining anti-inflammatories (ketoprofen and naproxen), diethyltoluamide and antibiotics showed around 50% reduction, and crotamiton and carbamazepine was hardly removed.

The fates of PPCPs were evaluated by calculating the mass balance of PPCPs in the WWTPs. Ibuprofen was significantly removed and degraded by the activated sludge in the aeration tank (Figure 1), while triclosan was removed by the adsorption to the activated sludge and the accumulation in the sludge was observed (Figure 2). Antibiotics was removed mainly by the adsorption to the activated sludge, and accumulation in the sludge was observed.

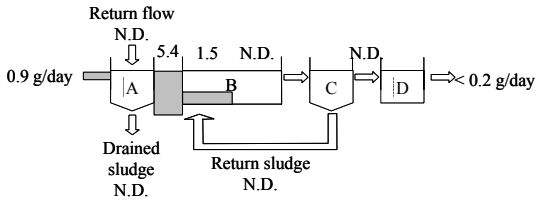

Figure 1 Mass balance of ibuprofen in WWTP

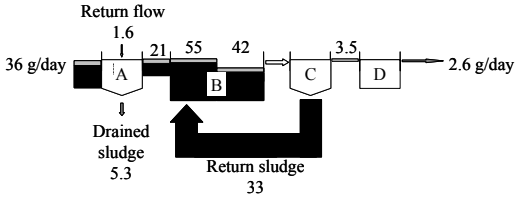

Figure 2 Mass balance of triclosan in WWTP

4. Ecotoxicity of Antibiotics

Microtox test using marine fluorescent bacterium and Daphnia immobilization test showed that levofloxacin (LVFX) and clarithromycin (CAM) have no acute toxicity on bacterium. Meanwhile, algal growth inhibition test revealed that LVFX and CAM have a toxicity to microalga, but the phytotoxicity of CAM was about 100 fold higher than that of LVFX.

Comparison of the concentration in aquatic environment and PNEC indicates that CAM discharged into aquatic environment may affect algae if dilution rate is low.

Reference

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.(2006) Occurrence of levofloxacin, clarithromysin and azithromycin in wastewater treatment plant in Japan, Wat. Sci. & Tech., 53(11), 227-233

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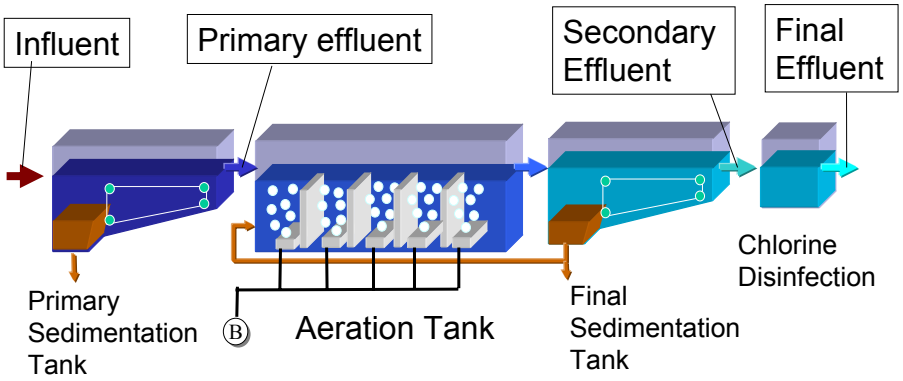
1. Introduction

- Growing public concern about the environment pollution of pharmaceuticals and personal care products (PPCPs)
- From existing research, wastewater treatment plants (WWTPs) may facilitate the initial entry of PPCPs to water environment
- It is important to clarify the occurrence and fates of PPCPs in WWTPs to evaluate both the effect of treated wastewater on water environment and the performance of WWTPs to remove PPCPs

- In our research, we conducted surveys in several WWTPs to clarify the concentrations and fates of PPCPs along the units of wastewater treatment.
- In addition, toxic effects of PPCPs on aquatic organisms were evaluated with ecotoxicity tests.

2. Occurrence and Fate of PPCPs (Anti-inflammatory Drugs, etc.) in WWTPs



Treatment method : Conventional activated sludge process
Treatment capacity : 22,500～700,000 m^3/d
Number of plants surveyed : 4
Sampling : Composite sample taken every 2 hours

PPCPs grouping by structural characteristics

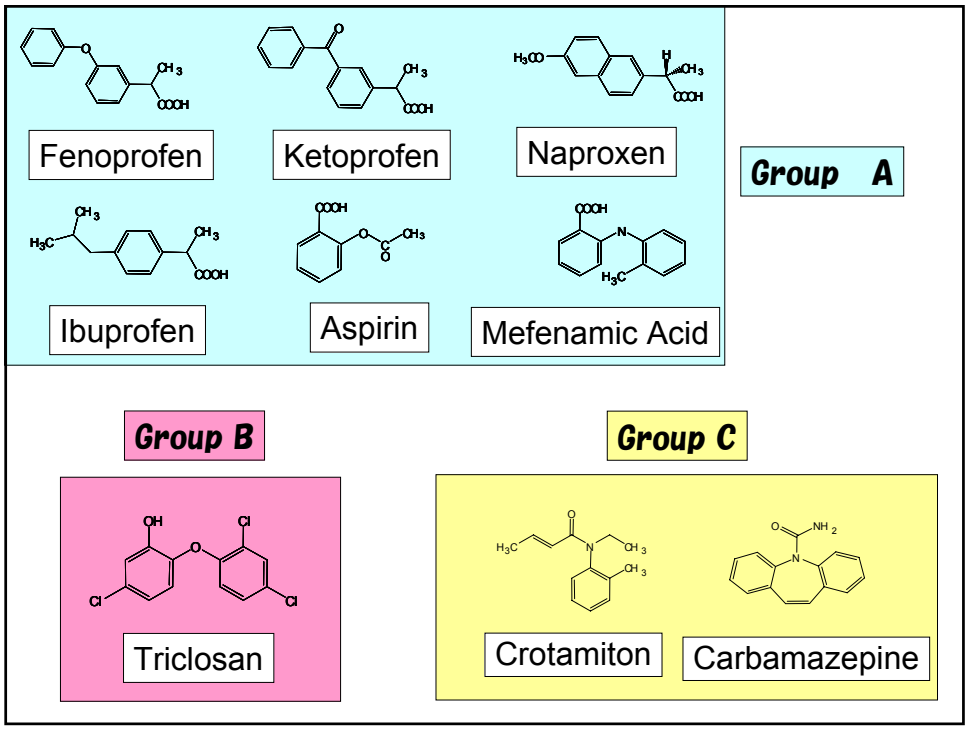
- Anti-inflammatory drugs: Aspirin, Ibuprofen, Fenoprofen, Naproxen, Mefenamic Acid, Ketoprofen

  Having carboxl group (-COOH) — **Group A**

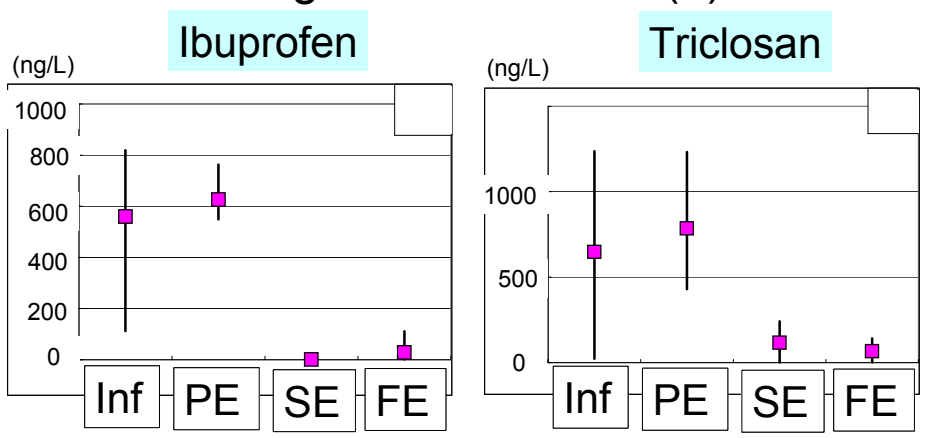
- Phenolic antiseptic: Triclosan

  Having Phenol — **Group B**

- Amide pharmaceuticals:
  Crotamiton (relieve itching)
  Carbamazepine (Antiepileptic) — **Group C**

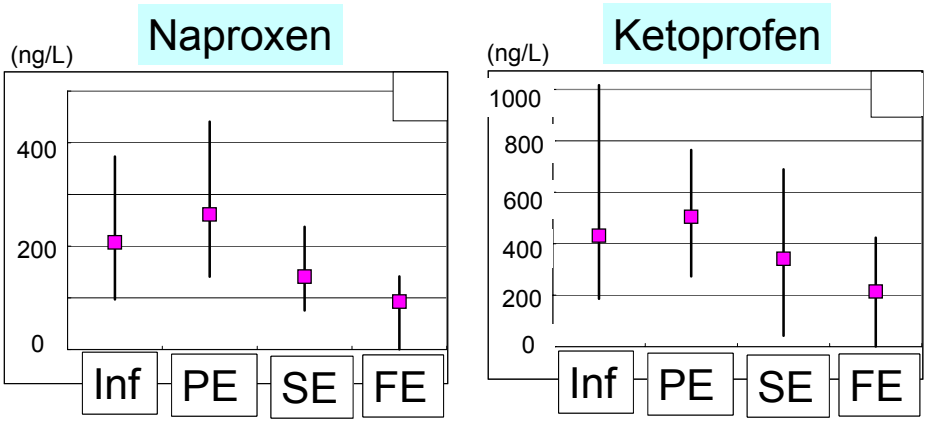


Dissolved phase concentration change along treatment units (1)



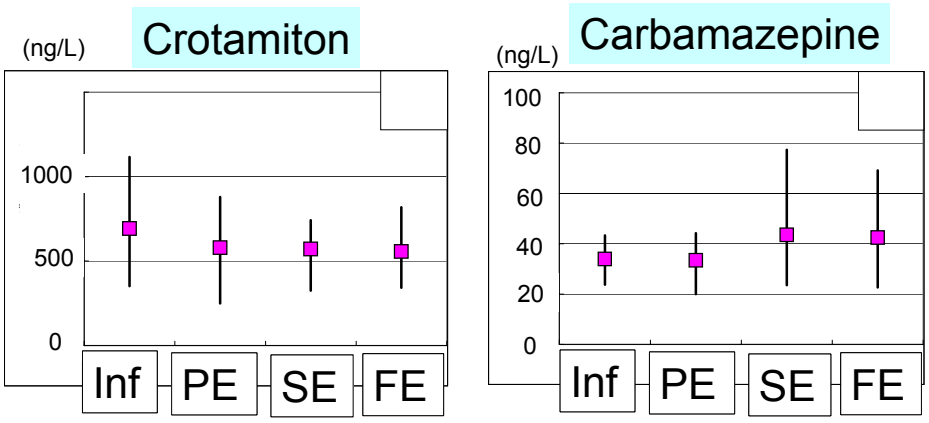
Inf : Influent
PE : Primary Effluent
SE : Secondary Effluent
FE : Final Effluent

Dissolved phase concentration change along treatment units (2)



Inf : Influent
PE : Primary Effluent
SE : Secondary Effluent
FE : Final Effluent

Dissolved phase concentration change along treatment units (3)



Inf : Influent
PE : Primary Effluent
SE : Secondary Effluent
FE : Final Effluent

Average PPCP removal ratio 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	relieve itching	20
Carbamazepine	Antiepileptic	-25
Mefenamic acid	Anti-inflammatory	-240

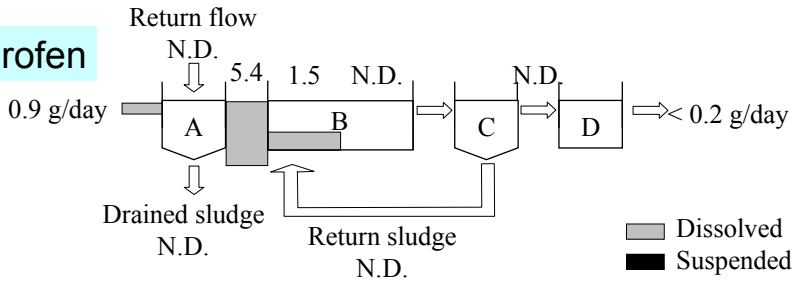
From the survey of 4 WWTPs,

- PPCPs (anti-inflammatory drugs, etc) concentraion in dissolved phase in influent ranged from hundreds to one thousand ng/L except for Carbamazepine

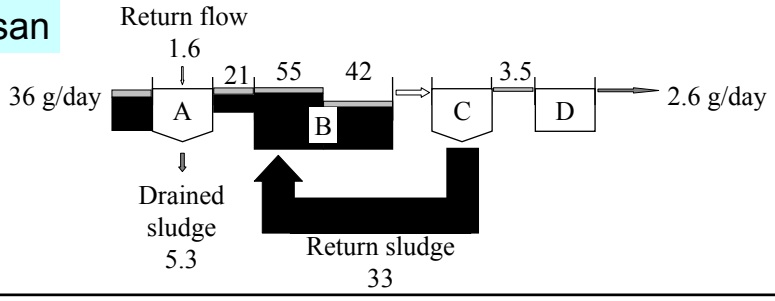
- PPCPs could be classified into three groups by the removal ratio in WWTPs

Mass balance of PPCPs including solid phase concentration

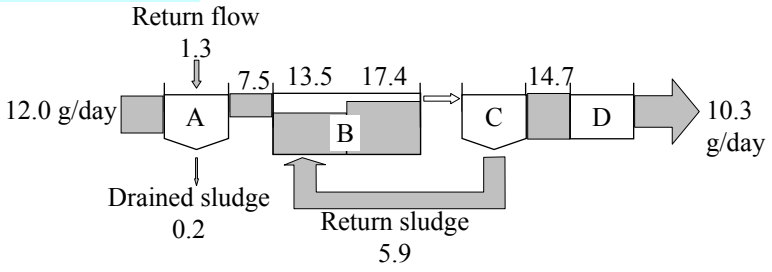
a) Ibuprofen



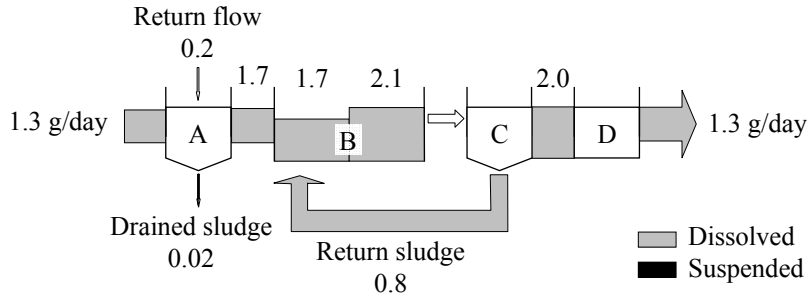
b) Triclosan



c) Crotamiton



d) Carbamazepine



From the mass balance survey in a WWTP,

-Almost of all of the PPCPs existed in the dissolved phase, except for Triclosan which mostly existed in solid phase.

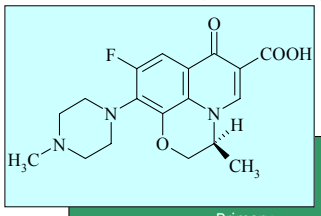
-Ibuprofen was decomposed in the biological treatment process effectively

-Triclosan was removed by the adsorption to the activetaed sludge, and was accumulated in the activated sludge in a high concentration.

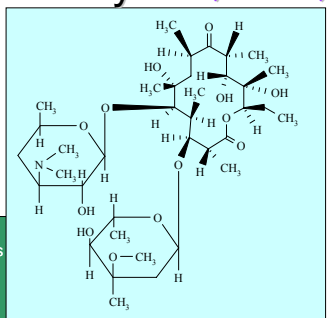
- Crotamiton and Carbamazepine was hardly changed in the process

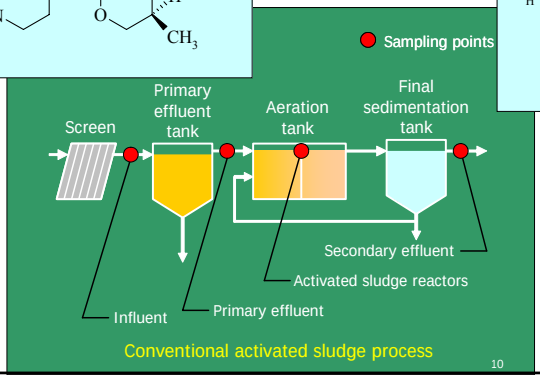
3. Occurrence and Fate of Antibiotics in WWTP

Levofloxacin (LVFX)

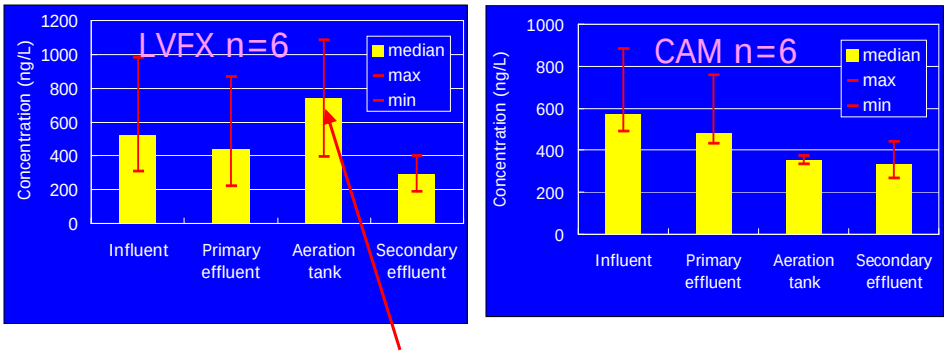


Clarithromycin (CAM)





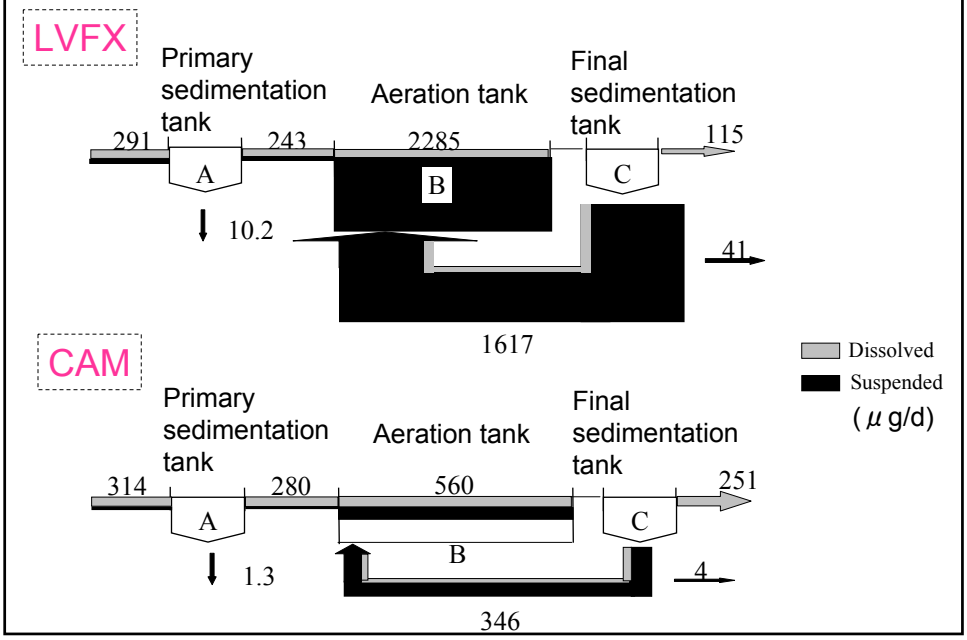
Concentration change of antibiotics along treatment units



Effect of return sludge?
or deconjugation?
or other factors?

11

Mass balance of antibiotics



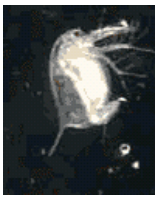
From the survey of antibiotics,

- Antibiotics concentration in the influent ranged from hundreds to one thousand ng/L, and the removal ratio in WWTPs was around 50%
- LVFX was removed by the adsorption to the activated sludge, and was accumulated in the activated sludge in a high concentration
- CAM accumulation in the sludge was small, which might indicate biodegradation by the activated sludge

4. Effect of PPCPs on Aquatic Organisms

Ecotoxicity tests (acute toxicity) applied

- Bacterium: Microtox test
- Alga: Algal growth inhibition test
- Crustacean: *Daphnia* acute immobilization test



Results of Ecotoxicity tests

(mg/L)

PPCPs	Microtox test		Algal growth inhibition test	*Daphnia* acute immobilization test	
	EC50		EC50	EC50	
	5min	15min	96hour	24hour	48hour
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

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**

From the ecotoxicity tests,

- Antiseptic agent (Triclosan) showed toxicity on Bacterium and Crustacean
- Antibiotics showed inhibition to Algal growth
- The toxic effect concentration was in the order of mg/L except for Clarithromycin
- Clarithromycin in treated wastewater might be evaluated to have toxic effect on Alga if NOEC is obtained

Conclusion

- The concentration of most PPCPs in influent ranged from hundreds to one thousand ng/L
- Several patterns of PPCP removal in the treatment process were observed;
  a) effectively decomposed by activated sludge
  b) adsorbed to activated sludge
  c) hardly changed
- Some PPCPs showed ecotoxicity, but the concentration of the order of mg/L
- Antibiotic in treated wastewater might be evaluated to have toxic effect on Alga