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Behavior of Pharmaceuticals in Waste Water Treatment Plant in Japan

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Abstract The fate of pharmaceuticals in a wastewater treatment plant (WWTP) in Kumamoto, Japan with activated sludge treatment is reported. Selected pharmaceuticals were detected in influent. Results from the present study confirmed that Acetaminophen, Amoxicillin, Ampicillin and Famotidine were removed at a high rate (>90% efficiency). In contrast, removal efficiency of Ketoprofen, Losartan, Oseltamivir, Carbamazepine, and Diclofenac was relatively low (<50%). The selected pharmaceuticals were also detected in raw sludge. In digestive process, Indomethacin, Atenolol, Famotidine, Trimethoprim and Cyclofosamide were removed at a high (>70% efficiency). On the other hand, removal of Carbamazepine, Ketoprofen and Diclofenac was not efficient (<50%).

Keywords PPCP · WWTP · Activated sludge · Removal efficiency

Recently, the presence of chemicals that originate from the usage and disposal of pharmaceuticals and personal care products (PPCPs) in the environment is attracting social attention as new types of contaminants (Takada 2008). Unlike the chemicals previously categorized as contaminants, the evaluating impact to the aquatic organism is not determined (Azuma 2008). In addition, the appearance of resistant bacteria is one of the problems related to these PPCPs (Takada 2008). Many PPCPs are indispensable in our lives. However, limiting their use because of pollution prevention is not realistic (Takada 2008). Most PPCPs contained in sewage were removed, through biodegradation and adsorption to excess sludge by the activated sludge of the sewage treatment plant (Castiglioni 2006). Existence and behavior of PPCPs have been analyzed by LC/MS/MS (Narumiya et al. 2009), in order to assess the environmental impact of PPCPs. However, behavior of PPCPs in a peculiar environment over a certain period used in relatively large quantities has not been researched. In this rsearch, concentration of PPCPs in influent, processing line water, effluent, raw sludge, excess sludge, and dehydrated sludge were analyzed and removal efficiency was calculated. Seasonal change and residual tendencies of PPCPs in a Kumamoto municipal sewage treatment plant were clarified.

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Materials and Methods

Thickened sludge, digested sludge, return sludge, final sludge, sewage influent, processing line water, and effluent were collected from a municipal sewage treatment plant located in Kumamoto City, Japan at 10–11 am of February 5, June 18, August 27, and October 30 in 2009. The sampling conditions in the sewage plant are shown in Table 1. To composite samples collected for 24 h from influent and effluent of sewage, 0.1% NaN_3 was added to prevent biodegradation. Later, all samples were preserved at −40°C until pretreatment. Samples were centrifuged (3000 rpm, 3 min), and separated into a water phase and a solid phase. The solid phase of the samples was stored at −30°C until extraction, and the water phase of the samples was filtered with a 4-μm membrane filter and preserved at 5°C until extraction. The pretreatment method referred to Kolpin et al. (2002). Analysis of the PPCPs (Table 2) was carried

Table 1 Sampling conditions of the waste water

		31-Oct-08	5-Feb-09	18-Jun-09	27-Aug-09
Total influent quantity	(m^3)	52,444	52,605	53,966	52,536
Quantity of effluent	(m^3)	48,830	51,170	48,880	51,690
Water temperature of reactive tank	(°C)	26.1	21.3	27	28.8
SRT	(D)	8.1	8.8	13.8	15.8
Amount of excess sludge pulling out	(m^3)	744	696	339	654
Abundance of dehydration sludge	(t)	34.7	29.6	24.1	36.0

Table 2 Taget PPCPs

Compound name	LOD[a]	LOQ[b]	Fortified sample recoveries (%)			
			Water samples (n=3)	Sludge samples (n=3)		
				pH3	pH7	pH9
Famotidine	0.31	0.95	104	42	96	77
Atenolol	0.34	1.04	47	20	31	17
Acetaminophen	0.50	1.52	45	20	31	17
Trimethoprim	0.26	0.77	85	63	103	93
Ampicillin	0.84	2.54	300	146	135	323
Sulfamonomethoxine	0.13	0.39	37	26	32	11
Oseltamivir	0.30	0.92	72	68	74	85
Amoxicillin	1.39	4.23	60	17	46	30
Sulfamethoxazole	0.34	1.02	69	26	50	6
Cyclophosamide	0.27	0.81	75	58	73	56
Sulfadimefhoxine	0.13	0.39	67	26	45	21
Carbarn azepine	0.08	0.23	94	52	73	66
Ketoprofen	0.37	1.13	109	36	137	96
Crotamiton	0.15	0.45	125	0	1	1
Gliclazide	0.19	0.57	106	31	52	12
Indomefhacin	0.50	1.53	107	4	69	65
Diclofenac	0.16	0.49	141	1	77	97
Losartan	0.39	1.20	99	39	73	70

[a] *LOD* Limit of detection, [b] *LOQ* limit of quantity

out by an ESI-positive ion mode of LC/MS/MS (6,400 Series Triple Quadrupole LC/MS, Agilent, USA).

Results and Discussion

Concentrations of the selected PPCPs in the sewage influent are shown in Fig. 1. All selected PPCPs except Sulfadimethoxine and Sulfamonomethoxine were detected from the collected samples. The removal efficiency of the PPCPs by the sewage treatment process is shown in Fig. 2. Results show that 90% of Acetaminophen, Amoxicillin, and Ampicillin were removed. Gliclazide was also reduced at the high removal efficiency (>80%).On the other hand, the removal efficiency of Oseltamivir was merely 20%.

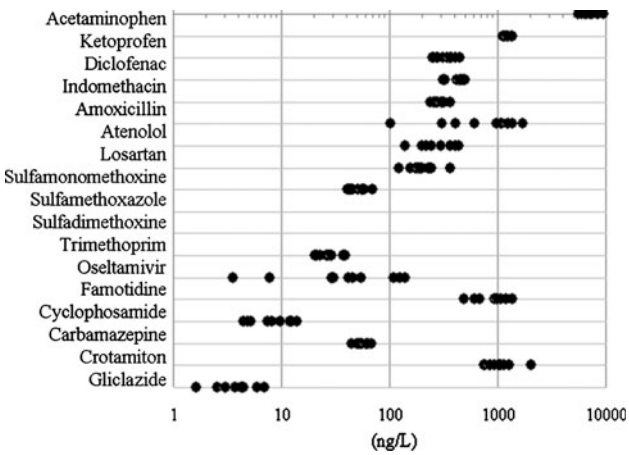

Fig. 1 Concentration of pharmaceuticals in influent water

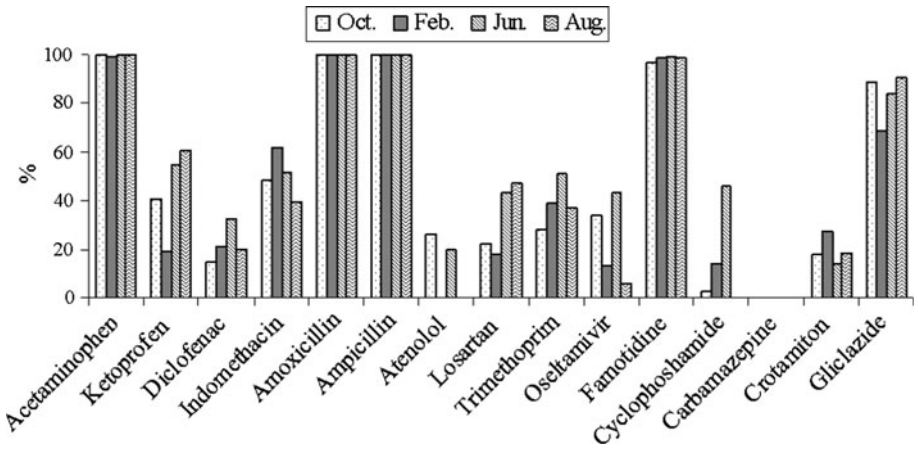

Fig. 2 Removal efficiency of PPCPs in the wastewater treatment plant

Most of Oseltamivir is known to be metabolited (>75%) to Oseltamivir Carboxylate (OC) in the human body (Fick et al. 2007). Previous reports have suggested that Oseltamivir Carboxylate (OC) was not removed by an activated sludge treatment processing (Ghosh et al. 2010). Previous studies and the present results indicate that a high stability of OC is in a conventional sludge treatment process. More than 98% of Famotidine was found to be removed in this research. However, in a previously conducted research, it is reported that 60% of Famotidine was removed in a similar sewage treatment plant (Radjenovic et al. 2009). The removal efficiency of Cyclophosamide and Carbamazepine was relatively low, 24% and −4% respectively. In the case of Carbamazepine, the concentration was found to increase during the activated sludge treatment process. Carbamazepine hydroxide, which was produced by metabolism in human bodies, might return to the original structure by reduction in the process (Radjenovic et al. 2009). Indometacin, Ketoprofen and Diclofenac were removed at the efficiency of 50%, 40% and 30% respectively. Yamamoto et al. (2007) reported that degradation rate of Ketoprofen was slow and the growth of the microorganism was accelerated in the batch examination. The removal efficiency of Diclofenac differs depending on the sewage treatment plant, and the relationship between sludge age and removal efficiency has been reported previously (Yamamoto et al. 2009). The removal efficiency of Atenolol was −24%, and Losartan was 33%. The results of Atenolol are inconsistent with the previous study that reported relatively high removal efficiency (>60%) (Radjenovic et al. 2009). The removal efficiency of PPCPs is influenced by sludge retention time (SRT) and the water temperature (Ternes et al. 2004). SRT and water temperature in sampling are shown in Table 1. The removal efficiency of PPCPs was reported to be relatively high when water temperature was high, and SRT was long (Ternes et al. 2004). In our result Losartan and Ketoprofen are applicable to these tendencies. Because the removal efficiency changes for other PPCPs at each season, possible influence of other factors beside SRT and the temperature were indicated. The seasonal variations in the concentration of PPCPs in the inflow sewage are shown in Fig. 3. All target chemicals were detected except Sulfadimethoxine and Sulfamonomethoxine. The concentration of Ampicillin and Amoxicillin tends to increase in winter. This indicates the increase in their primary usage as a cold medicine. The in crease in the concentration of Oseltamivir in winter can also be explained by its primary usage as an influenza medicine. The increasing trend in winter was also found as for Trimehtoprim. On the other hand, the concentration of Sulfamethoxazole used together as a ST mixture (Sulfamethoxazole-Trimethoprim Combination) did not show any increase in winter. Although Famotidine and Carbamazepine showed the highest concentration in spring, there was no seasonal tedency. As for Crotamiton, no increase was observed in winter, reflecting steady use as medical hand cream throughout the year. The concentrations of Acetaminophen, Ketoprofen, Indomethacin, and Diclofenac did not significantly increase. This could also be due to the steady usage as external anti-inflammation medicines for the people throughout the year. An increase in the concentration of Atenolol was noted in winter, while yet no significant change in the concentration increase of Losartan was able to be confirmed. Most of the fluctuations in the concentrations of PPCPs in the sewage influent among seasons can be explained by their primary usage. The medicines analyzed in this research were classifiable into antipyretic analgesic, influenza medicine, and antipruritic depending on the types of concentration fluctuation among seasons. Concentrations of PPCPs remaining in the raw sludge and the waste sludge samples are shown in Table 3. Amoxicillin, Ampicillin, Sulfamothoxazole, Sulfamethoxazole, Sulfadimethoxine and Sulfamonomethoxine were not detected in all sludge.

The output load of the medicine per day from the sewage treatment plant is shown in Table 4. Acetaminophen, Ampicillin, Amoxicillin, Famotidine, and Gliclazide were

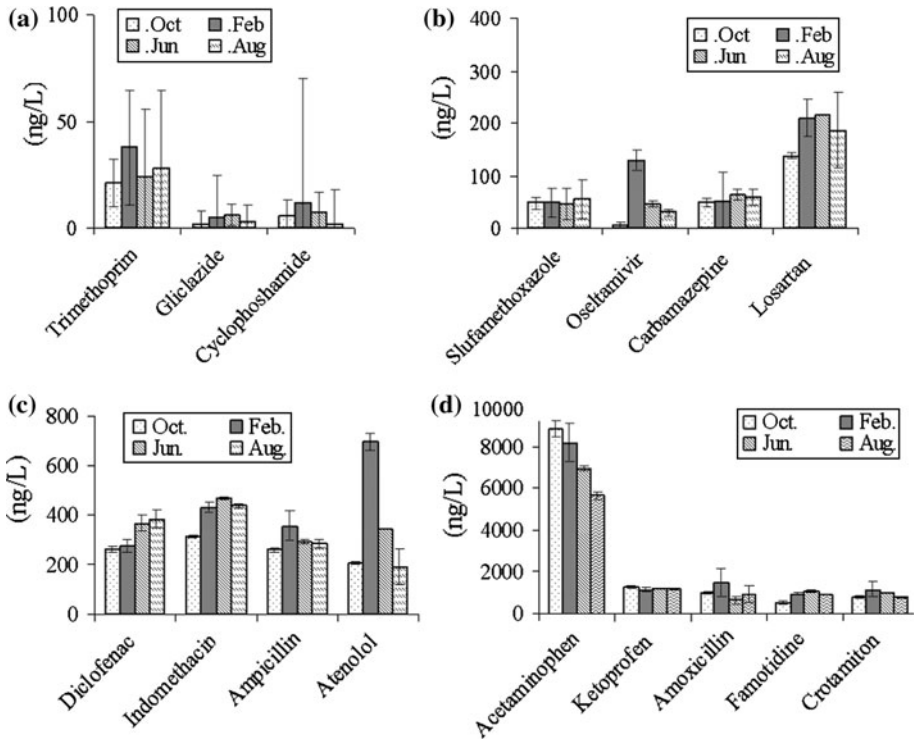

Fig. 3 Seasonal variations of PPCPs in influent

Table 3 Concentration of PPCPs in raw and sewage sludge

	Law sludge (ng/g)	Excess sludge (ng/g)
Acetaminophen	ND-258	ND
Ketoprofen	8.9–44	4.4–13
Diclofenac	8.1–29	6–29
Indomefhacin	24–57	23–77
Amoxicillin	ND	ND
Ampcillin	ND	ND
Atenolol	ND-86	ND-6.1
Losartan	25–86	8.0–26
Trimethoprim	ND-13	ND-15
Oseltamivir	ND-11	ND-5.3
Famotidine	70 ~ 285	ND-133
Cyclophoshamide	ND-15	ND-19
Carbanazepine	ND-12	1.9–12
Sulfamefhoxazole	ND	ND
Gliclazide	ND	ND

Table 4 Output loads of the PPCPs in effluent sewage and treated sludge

	Effluent sewage (g/day)	Treatment sluge (g/day)
Acetaminophen	ND-1.39	ND
Ampcillin	ND	ND
Amoxicilin	ND-0.02	ND
Oseltamivir	0.19–5.27	0.05
Trimethoprim	0.78–1.31	0.02–0.16
Sulfamefhoxazole	1.63–6.15	ND
Famotidine	0.62–0.92	ND-0.62
Cyclophoshamide	0.29–0.45	ND-0.12
Carbanazepine	2.73–6.88	0.04–0.13
Crotamiton	34.6–105.2	NA
Ketoprofen	23.8–61.3	0.09–0.33
Indometiiachin	8.20–14.1	ND-0.32
Diclofenac	10.8–27.4	0.11–0.42
Atenololo	14.3–32.3	ND-0.05
Losartan	5.17–18.0	0.11–0.13
Gliclazide	ND-0.14	ND-0.04

removed at the relatively high efficiency (80% or more) during the activated sludge treatment. Consequently, the chemical load of the effluent was low. On the other hand, some of the PPCPs were not removed, resulting in a relatively high load to the discharging site. Crotamiton, Ketoprofen, Atenolol, Diclofenac, and Losartan showed a relatively high load to the discharging site. Additionally Acetaminophen, Ampicillin, Amoxicillin, and Sulfamethozazole were not detected in the treatment sludge. During the treatment sludge process, they were removed at a low efficiency about 60% or less. Ketoprofen, Diclofenac, Losartan, and Carbamazepine comparatively occupied most of loads of the medicine in sludge. In this plant, the amount of average effluent water for a day is about 50,800 m^3. The average amount of treated sludge generated per day is about 32.6 t. Since sewage and sludge are the same level of concentrations, the PPCPs in

sludge have been 10^3 times more concentrated than those in sewage. In other words, it is thought that the daily load of PPCPs to water environments was influenced by effluent from a sewage treatment plant.

The fact that some PPCPs flow through the current sewage treatment plant virtually unprocessed, indicates that the current style of sewage treatment is insufficient to treat PPCPs. In the future, as for PPCPs with low efficiencies like Carbamazepine, the development of a new treatment processing is expected.

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