Field Survey on the Removal of Endocrine Disrupting Chemicals and Pharmaceutical Residues in Oxidation Ponds and Constructed Wetlands in Tropical Areas

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ABSTRACT
Field surveys were conducted to obtain fundamental information on the removal of endocrine disrupting chemicals (EDCs) and pharmaceutical residues (PRs) with conventional water quality parameters in wastewater treatment plants (WWTPs) in Thailand. Oxidation ponds and constructed wetlands were focused on because these systems are adapted in about 60% of municipalities. In the field surveys, water samples including the influent and effluent as well as water at the middle part of plants were taken from 6 WWTPs receiving municipal sewage or hospital wastewater. Totally 11 EDCs and PRs which have been detected frequently in public water body in Thailand were measured by LC-MS/MS. It was found that the EDCs and PRs were present in the range of 0.001 to 102 µg/L and 0.001 to 1 µg/L in the influents and effluents of WWTPs, respectively. Every pollutant was removed by WWTPs in different manner. More than 80% of naproxen and 70% of estrone were removed, while those of other pollutants such as p-acetaminophen, ibuprofen, DEET, and gemfibrozil were different among WWTPs. It was shown that oxidation ponds and constructed wetlands are effective to remove EDCs and PRs concurrently. However, a further study will be needed to evaluate precise removal performances and relations to design and operation parameters.

Keywords: constructed wetland, endocrine disrupting chemicals, field survey, oxidation pond, pharmaceutical residues

INTRODUCTION
Currently, as specific measures which lead to solve water shortage problems and to reduce water consumption, water reclamation has been practiced. Water purified in wastewater treatment plants (WWTPs) is reused (Ministry of Land, Infrastructure and Transport, Japan, 2005). Wastewater reclamation in WWTPs is desirable in terms of cost and feasibility because conventional treatment process and sewer system already exist (United Nations Environment Programme, 2005). As wastewater reclamation performances or treatment performances based on conventional water qualities such as BOD depend on design and operation conditions (Tchobanoglous and Burton, 1991), it is considered that removal efficiencies of trace pollutants also depend on these conditions (Miya and Onda, 2003; Hashimoto et al., 2007). In this study, endocrine disrupting chemicals (EDCs) and pharmaceutical residues (PRs) were focused on as trace toxic pollutants, because EDCs disrupt the endocrine function of human beings and wildlife and cause reproductive dysfunction and malignancies (Japan Environmental Agency, 2000). In addition, PRs such as antibiotics may affect the activity of bacteria at µg/L concentrations (Palaniappan et al., 2010); therefore, the impacts on the ecosystem have been of great concern.
Since EDCs and PRs are generally considered not easily biodegradable, they tend to accumulate in the aquatic environment, affect the ecosystem, and may promote the emergence of drug-resistance bacteria due to repeated recycling of water (Ministry of Land, Infrastructure, Transport, and Tourism, Japan, 2010). These problems should be considered in reclamation practice. Also, in recent reports on the treatment of EDCs and PRs, results were obtained mainly from the conventional activated sludge process or oxidation ditch process in urban areas (Niina et al., 2005; Lishman et al., 2006; Nakada et al., 2006; Jelena et al., 2009). There are few reports on other processes and suburban and rural areas.

In this study, field surveys were conducted to obtain fundamental information on the removals of EDCs and PRs with conventional water quality parameters such as biochemical oxygen demand (BOD), suspended solids (SS), and coliform in 6 different WWTPs in suburbs of tropical areas. EDCs and PRs measured were estriol, 17-β-estradiol, estrone, p-acetaminophen, ibuprofen, diethyl-m-toluamide (DEET), amoxicillin, sulfamethoxazole, tetracycline, gemfibrozil, and naproxen, which were selected due to relatively high concentration levels and frequent observations in public water body in Thailand. In addition, oxidation ponds and constructed wetlands were focused because these systems are adapted in about 60% of municipalities (Pollution Control Department, Thailand, 2010). Observed performances for the removals of EDCs and PRs were compared with those reported in conventional treatment processes.

METHODS
Field survey
In the six WWTPs in Thailand, sample collections were conducted. Six districts shown in the left part of Fig. 1 ((1) Sakon Nakhon, (2) Phon Thong, (3) Muang Suang, (4) U-Thong, (5) Suphanburi, (6) Petchaburi) were investigated. Dimensions of 6 WWTPs are listed in Table 1. In Sakon Nakhon and Petchaburi, treatment processes of stabilization pond and wetland were adopted. In Sakon Nakhon, stabilization pond is

![Fig. 1 - Map of Thailand (obtained through Google Earth) and photos of study sites.](image-url)
linked to wetland. On the other hand, in Petchaburi, stabilization pond and wetland exist separately. In Phon Thong and Muang Suang, a natural wetland and a constructed wetland were selected, respectively. In U-Thong and Suphanburi, stabilization pond was adopted.

Water sampling was conducted at three points in every plant, i.e. where wastewater flows into the treatment plants, halfway in the treatment plants, and where treated water was discharged. In Sakon Nakhon, U-Thong, Suphanburi, and Petchaburi, there are relatively large treatment plants managed by local governments, where influent wastewater to the plants is widely collected in the catchment areas. On the other hand, Phon Thong and Muang Suang have small facilities purifying wastewater discharged from hospitals. The treatment plants in the latter two sites were selected because it was expected that they were receiving relatively high concentration of EDCs and PRs.

**Water quality survey parameters**

The survey parameters were decided in terms of reusing wastewater in addition to the usual assessment, referring to the manual of water quality and others on reclamation of wastewater by the Ministry of Land, Infrastructure and Transport (2005), Japan. That is, in the manual, water quality parameters such as coliform, SS, pH, appearance, color, odor, and chlorine residues were described for washing, irrigation, landscape, and amenity reuse. Among them, the most important parameters such as coliform and SS were selected in terms of public health problem in addition to a conventional water quality parameter, BOD.

For a long-term reclamation of wastewater in the future, residual concentrations of PRs and EDCs are necessary to be considered. Eleven types of substances for EDCs and PRs, which have been detected frequently in public water body in Thailand, were selected and the concentration profiles were investigated. Substances covered in this study were estradiol, 17-β-estradiol, estrone, p-acetaminophen, ibuprofen, diethyl-m-toluamide (DEET), amoxicillin, sulfamethoxazole, tetracycline, gemfibrozil, and naproxen. Removal efficiency was calculated as a value of concentration difference between the influent and effluent divided by the influent concentration.
**BOD, Coliform, and SS analysis**
The conventional parameters analyzed were 5-day biochemical oxygen demand (BOD₅), coliform and total SS. All analyses were conducted referring to the standard methods (APHA, 1998). Chemical analysis was conducted in a laboratory of Environmental Research and Training Centre in Thailand.

**EDCs and PRs analysis**
These pollutants were analyzed using LC-MS/MS (Agilent Technologies HP 1100 series liquid chromatography coupled with SL 1100 series tandem mass spectrometry) after the extraction from filtered samples. The flow of pre-treatment is listed in Fig. 2. Analysis was conducted in a laboratory of Chulalongkorn University in Thailand. Average recoveries of the standard substances for 11 types of EDCs and PRs were in the range of 44 to 82%.

![Flow chart of pretreatment of EDCs and PRs in samples.](image-url)

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**Fig. 2 - Flow chart of pretreatment of EDCs and PRs in samples.**
RESULTS AND DISCUSSION
Conventional water quality parameters
Results of BOD, coliform, and SS analyses are shown in Figs. 3 to 5, respectively. While samples of three points were analyzed in each treatment plant, samples halfway in Petchaburi could not be collected due to difficulty in approaching the place with safety so only the inflow and outflow values are shown. Also, samples of Phon Thong could not be measured and no results are shown in Figs. 3 to 5. The BOD concentration

![Fig. 3 - Variation of BOD concentration.](image1)

![Fig. 4 - Variation of coliform concentration.](image2)

![Fig. 5 - Variation of SS concentration.](image3)
standard for discharged water from WWTPs is 20 mg/L or less in Thailand. However, if the last treatment unit is stabilization pond or oxidation pond, the standard for BOD is 50 mg/L or less so the two treatment plants in U-Thong and Suphanburi met the criteria. All treatment plants surveyed, except Petchaburi (wetland), met the criteria. Coliform was substantially removed in all treatment plants as shown in Fig. 4. The standard concentration for SS is 30 mg/L or less in Thailand, and there were 4 treatment plants that did not meet the criteria. This is because algae were discharged as a main component of SS in the effluent.

**Trace toxic substances**
Concentrations of PRs and EDCs in the influent and effluent are shown in Figs. 6 and 7, respectively. Circular plots in the figures indicate treatment plants having a stabilization pond, while square plots indicate treatment plants having a wetland. As for Sakon Nakhon, diamond plots are used because wastewater was treated by a combined pond and wetland system. Substances examined in this survey were present in the influent wastewater of almost all treatment plants and were removed by stabilization pond or wetland.

The range of concentration of trace toxic substances in the influent was 1 ng/L to $10^2$ µg/L as shown in Fig. 6. In Phon Thong, wastewater is from a hospital, so the effluent concentration range was 0.001 to 1 µg/L and was roughly one order of magnitude higher than others as shown in Fig. 7. This indicates that part of trace toxic substances which were not completely removed were discharged into the environment. Since some concentrations could not be detected by LC-MS/MS, they are not seen in Figs. 6 and 7. Removal efficiencies of each substance are shown in Fig. 8.

When removal efficiency is less than zero, the concentration of the effluent is greater than that of the influent. The gray part in the figure indicates the removal efficiencies reported for activated sludge process, which were referred to former studies (Miya and Onda, 2003; Carballa et al., 2004; Niina et al., 2005; Brown et al., 2006; Karthikeyan and Meyer, 2006; Lishman et al., 2006; Nakada et al., 2006; Hashimoto et al., 2007; Jelena et al., 2009; Lin et al., 2009). As shown in Fig. 8, more than 80% of naproxen and 70% of estrone were removed. However, the removal efficiencies of p-acetaminophen, ibuprofen, DEET, and gemfibrozil showed a variation with treatment plants. Similar variation of removal efficiencies with WWTPs was found in activated sludge processes. The removal efficiencies of ibuprofen, DEET, and tetracycline in Muang Suang, sulfamethoxazole in U-Thong, and gemfibrozil in Petchaburi were less than zero. According to a former study (Ministry of Land, Infrastructure and Transport, Japan, 2001), there is a relationship between trace toxic substances removals and hydraulic retention time (HRT). Therefore, the relationship was investigated by the results obtained from the field survey. Although the data were limited, the removal efficiencies of DEET, gemfibrozil, and naproxen tended to increase with increments of HRT or surface area. For example, in the treatment of hospital wastewater, removal efficiencies of most EDCs and PRs were larger in Phon Thong having larger surface area per wastewater flow rate (see Table 1) for wetland. In addition, the WWTP in Sakon Nakokhon, Petchaburi or U-thong having relatively longer HRT or larger surface area of stabilization ponds seem to have higher removal efficiencies of EDCs and PRs. Further research is necessary to clarify the relationship.
Fig. 6 - Concentrations of EDCs and PRs in influent wastewater.

Fig. 7 - Concentrations of EDCs and PRs in treated wastewater (effluent from treatment plants).

Fig. 8 - Comparisons of PRs’ removal efficiencies. Gray bars indicate ranges of removal efficiencies reported in activated sludge process.
CONCLUSIONS
In this study, field surveys of 6 WWTPs including 19 sampling sites were conducted. From the surveys, EDCs and PRs in the influent wastewater were detected in the range of 0.001 to 10² µg/L, while in the effluents were 0.001 to 1 µg/L, demonstrating that WWTPs using stabilization pond and wetland have the capability of removing these pollutants. More than 80% of naproxen and 70% of estrone were removed, while those of other pollutants such as p-acetaminophen, ibuprofen, DEET, and gemfibrozil were different among WWTPs. This indicates that EDCs and PRs were not removed completely and were released into the environment. Considering issues and costs in rural areas, wastewater treatment process using ponds and/or constructed wetland seems to be a feasible option in Thailand. However, a further study on precise performance evaluation of trace toxic substances besides conventional water quality parameters is necessary for promoting wastewater reclamation as well as the conservation of aquatic environment in suburban areas.

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