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Occurrence and removal of hazardous chemicals and toxic metals in 27 industrial wastewater treatment plants in Korea

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ABSTRACT

For better understanding of the occurrence and the fate of hazardous chemicals and toxic metals through industrial wastewater treatment plants (WWTPs), 27 WWTPs in Korea with each capacity over 2,000 m^3/d were surveyed. The sampling campaign was conducted in July through September, 2012 three times at each WWTP for 22 hazardous chemicals and toxic metals in influents and effluents. Concentrations of benzene, mercury, 1,1-dichloroethylene, and arsenic in influents to the WWTPs were relatively high (i.e. above the effluent limits for indirect dischargers in industrial complex). Counting phase transfers for the treatment, average removal rates of volatile organic compounds and metals were over 70 and 60%, respectively. However, neither treatment processes nor conventional pollutants exhibited significant correlation with the non-conventional pollutants, possibly due to complexity of operations in full scale plants. Removal rates of selenium (30%) and 1,4-dioxane (18%) were lower than other chemicals and metals. Since selenium and 1,4-dioxane were detected at a few WWTPs, it may be more efficient to manage concerning non-conventional pollutants at each WWTPs rather than establishing a universal limits for all WWTPs.

Keywords: Industrial wastewater; Hazardous chemicals; Toxic materials; Heavy metal; Effluent limits

1. Introduction

During the past decades rapid industrialization in Korea have been putting an increasing strain on the water resource requirements, and the demands for quality water resources in the industries are increasing [1]. In the meantime, pollutant loads to the watersheds have been increasing thus threatening sustainability of water bodies and ecosystems [1,2]. Especially, hazardous chemicals and toxic metals in effluents from industrial wastewater treatment plants (WWTPs) raise water pollution issues through the direct discharge of

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effluents to watersheds [3–5] because these contaminants in the effluents can cause serious problems to the ecosystems and public health due to their toxicity, long persistence, and bioaccumulation in the aquatic food chain [6,7].

The Ministry of Environment, Korea is regulating 25 hazardous chemicals and toxic metals (i.e. non-conventional pollutants) in effluents from individual industrial dischargers (i.e. indirect dischargers) as effluent limits which are similar to the Pretreatment Program for industrial users controlled by National Pollutant Discharge Elimination System in the United States. Those 25 non-conventional pollutants include copper, lead, arsenic, selenium, mercury, cyanide, phenols, organic phosphorous, hexavalent chrome, cadmium, polychlorinated biphenyl (PCB), benzene, carbon tetrachloride, dichloromethane, 1,1-dichloroethylene, 1,2-dichloroehane, chloroform, trichloroethylene (TCE), tetrachloroethylene (or perchloroethylene, (PCE)), 1,4-dioxane, bis-2(ethylhexyl)phthalate(DEHP), bromoform, vinyl chloride, acrylonitrile, and acrylamide. Effluents from indirect dischargers flow into industrial WWTPs or publicly owned treatment works (POTWs) as influents, which are generally located in the same industrial complex.

The Ministry of Environment, Korea, though, is not regulating those hazardous chemicals and toxic metals in effluents from POTWs, yet regulating seven conventional pollutants including biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS), total nitrogen, total phosphorus, total coliforms, and toxicity unit [8]. When indirect dischargers observe the effluent limits, there is no issue regarding the non-conventional contaminants in effluents from WWTPs or POTWs. However, if indirect dischargers are intentionally or unintentionally violating the regulations, WWTPs or POTWs cannot systematically control the issues because they do not have regulatory authority for the non-conventional pollutants.

Despite corporative efforts of the government and municipalities on industrial wastewater management for indirect dischargers, occurrence events of those non-conventional pollutants above the limits have been reported in effluents from WWTPs and POTWs [2,8]. This could be concerns considering the dilution

Table 1
Characteristics of industrial wastewater treatments surveyed

Plant no.	Capacity (m^3/d)	Current loading (m^3/d)	Main treatment process
1	12,500	6,616	Activated sludge process
2	14,000	8,750	Sequencing batch reactor
3	23,000	7,413	Activated sludge process
4	13,000	3,287	Activated sludge process
5	70,000	56,227	Biological nutrient removal process
6	35,000	20,510	Activated sludge process
7	20,000	9,724	Activated sludge process
8	30,000	5,060	Activated sludge process
9	60,000	52,155	Activated sludge process
10	31,000	21,255	Activated sludge process
11	11,000	6,737	Activated sludge process
12	16,000	4,990	Chemical coagulation and sedimentation
13	3,500	2,449	Activated sludge process
14	63,000	23,997	Biological nutrient removal process
15	47,000	44,929	Activated sludge process
16	75,000	60,428	Activated sludge process, Fenton, biological activated carbon filter
17	55,000	55,841	Activated sludge process, Fenton, biological activated carbon filter
18	65,000	35,402	Biological nutrient removal process
19	70,000	45,129	Biological nutrient removal process
20	5,000	2,839	Contact oxidation
21	4,600	2,649	Chemical coagulation and sedimentation
22	80,000	41,466	Activated sludge process, chemical coagulation, sand filter
23	28,000	18,872	Membrane bioreactor
24	115,000	89,966	Biological nutrient removal process
25	30,000	9,989	Sequence batch reactor
26	40,700	19,599	Activated sludge process
27	27,000	9,592	Activated sludge process

effects when effluents from indirect dischargers flow into WWTPs or POTWs. Therefore, a regulatory program to address the non-conventional pollutants from indirect dischargers through WWTPs to water bodies needs to be established. As a first step to establish the regulatory program, we investigated the occurrence and removal of hazardous chemicals and toxic metals in influents and effluents of 27 industrial WWTPs in Korea for better understanding of the fate of those contaminants through the systems.

2. Materials and methods

2.1. Sampling campaign

Twenty-seven WWTPs in Korea with capacities more than 2,000 m^3/d were selected for sampling campaign. Table 1 summarizes capacities and treatment processes of the WWTPs surveyed. Treatment capacity of the WWTPs ranged from 3,500 to 115,000 m^3/d. Main treatment trains of the WWTPs were biological treatment processes and physicochemical plus biological treatment processes. All the WWTPs were partially or fully receiving industrial wastewater and located in national industrial complex throughout the country. Raw (influents) and treated (effluents) wastewaters were collected from each WWTP in July through September, 2012, basically three times (once each month) at each WWTP. Seasonal variations were not concerned in this study. Staff members at each utility collected samples and immediately delivered the samples to authorized laboratories for analysis.

2.2. Analytical methods

Among 25 non-conventional pollutants regulated (effluents limits) for indirect dischargers, 22 hazardous chemicals and toxic metals were analyzed for this study, excluding vinyl chloride, acrylonitrile, and acrylamide. Vinyl chloride, acrylonitrile, and acrylamide were excluded because they were barely detected. All the samples were analyzed in authorized laboratories according to the *Korea Standard Methods for the Examination of Water and Wastewater*, which is on the basis of *Standard Methods* [9,10]. Table 2 summarizes analytical methods for hazardous chemicals and toxic metals monitored. Basically volatile organic compounds were analyzed by gas chromatograph-mass spectrometry, and toxic metals were analyzed by inductively coupled plasma. Other water quality parameters such as pH, BOD, COD, SS, total nitrogen,

Table 2
Summary of analytical methods for water pollutants monitored

Pollutant	Analytical method	Standard method no.
Copper	Inductively coupled plasma	3120 B
Lead		3120 B
Arsenic		3120 B
Selenium		3120 B
Cadmium		3120 B
Mercury	Cold-vapor atomic absorption spectrometry	3112 B
Phenols	UV–visible spectrometry	ES 04365.1*
Cyanide	Ion selective electrode method	ES 04353.2*
Organic phosphorous	Liquid–liquid extraction/gas chromatography	6321 B
Hexavalent chromium	Atomic absorption spectrometry	3110
Polychlorinated biphenyl	Gas chromatography	2720 C
Benzene	Purge and trap gas chromatography/mass spectrometric	6232 C
Carbon tetrachloride		6232 C
Dichloromethane	Purge and trap gas chromatography	6232 D
1,1-dichloroethylene		6232 D
1,2-dichloroethane		6232 D
Chloroform		6232 D
Trichloroethylene		6232 D
Tetrachloroethylene		6232 D
1,4-dioxane	Liquid–liquid extraction gas chromatography/mass spectrometry	6410 B
Bis-2(ethylhexyl)phthalate		6410 B
Bromoform	Headspace-gas chromatography/mass spectrometry	ES 04602.1*

*Korea standard methods for the examination of water and wastewater.

total phosphorus, and DOC were also measured according to *Standard Methods* [10].

3. Results and discussion

3.1. Occurrence of hazardous chemicals and toxic metals

Table 3 summarizes monitoring results of hazardous chemicals and toxic metals in influents of the WWTPs, presenting average, minimum, 25th percentile, median, 75th percentile, and maximum values. Most of 22 hazardous chemicals and toxic metals were detected in influents of the WWTPs except for PCB. Some of the compounds (Cd, bromoform) were present at trace levels, while others were dispersed in a broad range of concentrations.

Concentrations of the hazardous chemicals and toxic metals in the influents were mostly detected below the effluent limits for indirect dischargers in industrial complex (pretreatment program). However, levels of benzene, mercury, 1,1-dichloroethylene, and arsenic in some of the samples exceeded the effluent limits. Maximum concentrations of benzene, mercury, 1,1-dichloroethylene, and arsenic were respectively 5.7, 4.2, 1.9, and 1.4 times higher than the effluent limits for indirect dischargers in industrial complex. The actual concentrations of those pollutants in effluents from the indirect dischargers were potentially much higher than concentrations detected in the influents to WWTPs considering the dilution effect. The dilution factors were calculated by dividing the total amount of influent to each WWTP by the total amount of effluents from all the indirect dischargers in the industrial complex, which were containing a specific pollutant, and were over 20 for all the industrial complexes surveyed. These results implicated that some indirect dischargers in the complex violated effluent limits for the pretreatment program.

Number of samples exceeded the limits were two for each benzene and mercury, three for 1,1-dichloroethylene, and one for arsenic. In case of 1,1-dichloroethylene, the concentrations of most samples were low

Table 3
Concentration ranges of hazardous water pollutants in influents to 27 WWTPs ($n = 81$ for each pollutant)

Pollutant	Effluent limit* (mg/L)	Concentration (mg/L) Minimum	25th percentile	Median	75th percentile	Maximum	Detection limit (mg/L)
Copper	3	ND	0.023	0.067	0.141	1.306	0.002
Lead	0.5	ND	ND	ND	0.109	0.31	0.002
Arsenic	0.25	ND	ND	ND	0.012	0.348	0.006
Mercury	0.005	ND	ND	ND	0.001	0.021	0.0005
Cyanide	1	ND	0.01	0.014	0.03	0.4	0.01
Organic phosphorous	1	ND	ND	ND	0.003	0.018	0.0005
Hexavalent chromium	0.5	ND	ND	0.04	0.08	0.19	0.01
Cadmium	0.1	ND	ND	ND	ND	0.006	0.002
Tetrachloroethylene	0.1	ND	ND	ND	0.005	0.023	0.001
Trichloroethylene	0.3	ND	ND	0.001	0.005	0.025	0.001
Phenols	5	ND	0.011	0.024	0.065	2.09	0.005
Polychlorinated biphenyl	0.003	ND	ND	ND	ND	ND	0.0005
Selenium	1	ND	ND	ND	0.041	0.293	0.03
Benzene	0.1	ND	ND	ND	0.003	0.568	0.002
Carbon tetrachloride	0.08	ND	ND	ND	0.033	0.059	0.001
Dichloromethane	0.2	ND	ND	0.005	0.014	0.117	0.001
1,1-dichloroethylene	0.6	ND	ND	0.002	0.009	1.134	0.001
1,2-dichloroehane	0.3	ND	ND	ND	0.019	0.134	0.001
Chloroform	0.8	ND	0.001	0.004	0.01	0.14	0.001
1,4-dioxane	4	ND	ND	ND	0.004	0.315	0.001
Bis-2(ethylhexyl) phthalate	0.8	0.003	0.006	0.011	0.017	0.07	0.001
Bromoform	0.3	0.001	0.001	0.001	0.001	0.001	0.002

*Effluent limits of each pollutant for indirect dischargers in industrial complex (pretreatment program), Korea.

(75th percentile = 0.009 mg/L). However, three samples from the same industrial complex exceeded the limit. Therefore, WWTPs in the industrial complex may need to pay attention to the industrial users (indirect dischargers) using 1,1-dichloroethylene during manufacturing processes.

Table 4 summarizes monitoring results of hazardous chemicals and toxic metals in effluents of the WWTPs, presenting average, minimum, 25th percentile, median, 75th percentile, and maximum values. Concentrations of organic phosphorous, hexavalent chromium, cadmium, PCB, and carbon tetrachloride in all the effluent samples were below the detection limits. Concentrations of 22 hazardous chemicals and toxic metals in the influents were detected below the effluent limits for indirect dischargers in industrial complex although levels of mercury, selenium, arsenic, lead were respectively 3.2, 2.1, 1.4, and 1.1 times higher than the effluent limits for indirect dischargers in "clean" area.

3.2. Removals of hazardous chemicals and toxic metals

Phase transfer such as diffusion of volatile organic compounds to the air and adsorption of chemicals and metals onto activated sludge are technically not treatment, but in this study we counted them to quantify "removal" of pollutants. Fig. 1 presents removal rates of hazardous chemicals and toxic metals in 27 WWTPs surveyed. They are cumulative data from three sampling campaigns. Neither treatment processes nor conventional pollutants exhibited significant correlation with non-conventional pollutants, possibly due to complexity of operations in full scale plants.

Volatile organic compounds such as TCE and PCE were readily removed through the WWTPs as we expected. Overall, removal rates of all the volatile organic compounds surveyed were over 70% on average. In general, removal rates of volatile organic compounds are inversely proportional to water solubility of the compounds and proportional to the air to water ratios [11]. However, no strong correlation between Henry's constants of the compounds and removal rates was observed in this study, possibly due to complexity of operations in full scale plants. Fig. 2 presents concentrations of TCE in influents and effluents of 27 WWTPs surveyed as an example for volatile organic compounds. As shown in Fig. 2, in most cases TCE was not detected in effluents of the WWTPs.

In a similar manner to volatile organic compounds, most of metals were removed over 60% on average in the WWTPs (Fig. 1). Toxic metals can be adsorbed by

Table 4
Concentration ranges of hazardous water pollutants in effluents from 27 WWTPs ($n = 81$ for each pollutant)

	Concentration (mg/L)				
Pollutants	Minimum	25th percentile	Median	75th percentile	Maximum
Copper	ND	0.005	0.019	0.072	0.174
Lead	ND	ND	ND	ND	0.11
Arsenic	ND	ND	ND	0.001	0.069
Mercury	ND	ND	ND	ND	0.003
Cyanide	ND	ND	0.005	0.014	0.04
Organic phosphorous	ND	ND	ND	ND	ND
Hexavalent chrome	ND	ND	ND	ND	ND
Cadmium	ND	ND	ND	ND	ND
Tetrachloroethylene	ND	ND	ND	ND	0.002
Trichloroethylene	ND	ND	ND	ND	0.002
Phenols	ND	ND	0.001	0.012	0.131
Polychlorinated biphenyl	ND	ND	ND	ND	ND
Selenium	ND	ND	ND	ND	0.214
Benzene	ND	ND	ND	ND	0.002
Carbon tetrachloride	ND	ND	ND	ND	ND
Dichloromethane	ND	ND	ND	0.001	0.012
1,1-dichloroethylene	ND	ND	ND	ND	0.012
1,2-dichloroehane	ND	ND	ND	0.002	0.044
Chloroform	ND	ND	0.002	0.007	0.084
1,4-dioxane	ND	ND	ND	0.002	0.043
Bis-2(ethylhexyl)phthalate	0.003	0.003	0.003	0.006	0.012
Bromoform	0.001	0.001	0.001	0.002	0.004

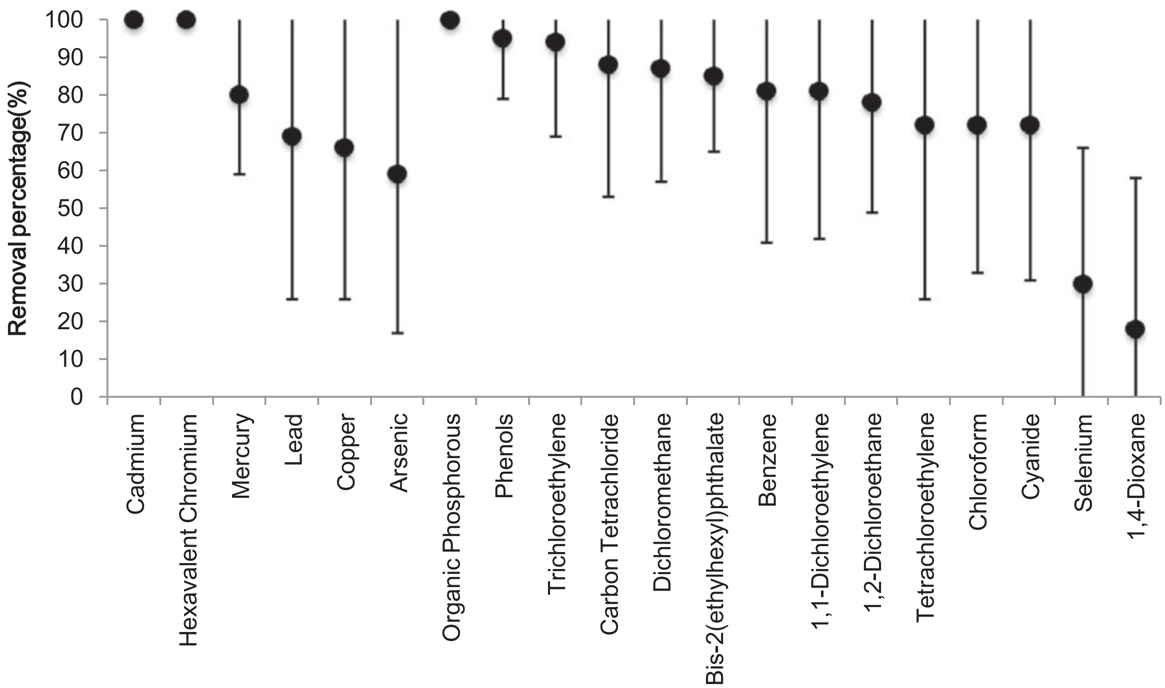

Fig. 1. Removal efficiencies of hazardous pollutants in 27 industrial WWTPs.
(●: average, ⌶: standard deviation).

carboxylic and amino groups of sludge surfaces [12,13]. Some of the compounds (Hg, Cd, Cr^{6+}) in effluents were present at trace levels and sometimes under the detection limits, while others were observed in a broad range of concentrations. Fig. 3 presents concentrations of copper in influents and effluents of 27 WWTPs surveyed as an example for toxic metals. Copper was removed >65% in most WWTPs.

Another chemical frequently detected was DEHP, which is widely used as a plasticizer in manufacturing of articles made of PVC due to his suitable properties and the low cost [14]. Fig. 4 presents concentrations of

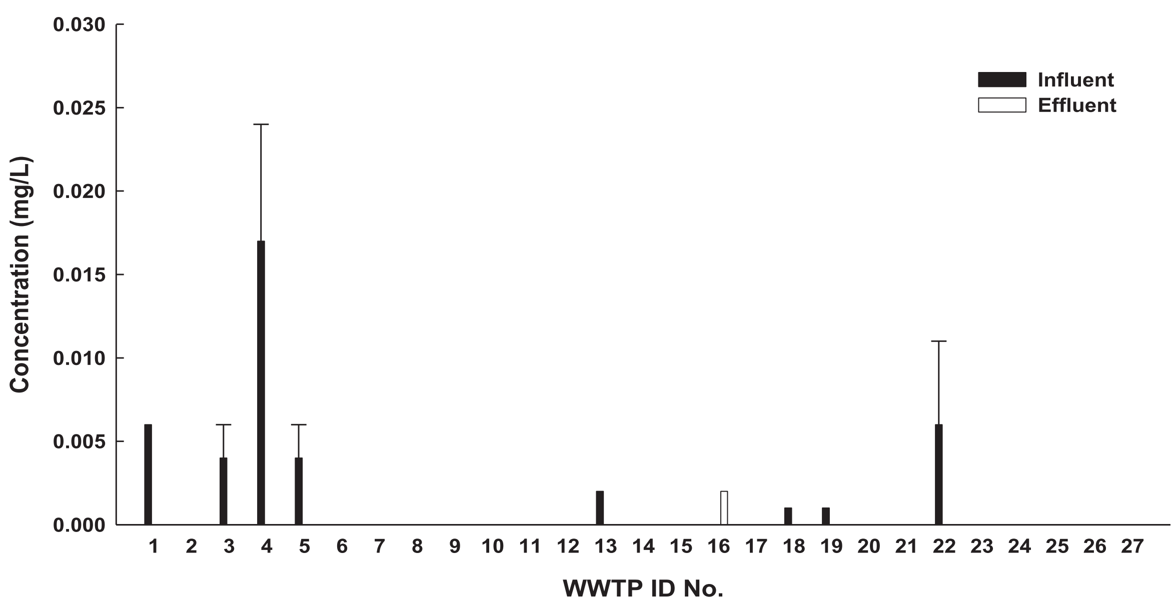

Fig. 2. Concentrations of TCE in influents and effluents of 27 WWTPs.
(Bar: average, ⌶: standard deviation).

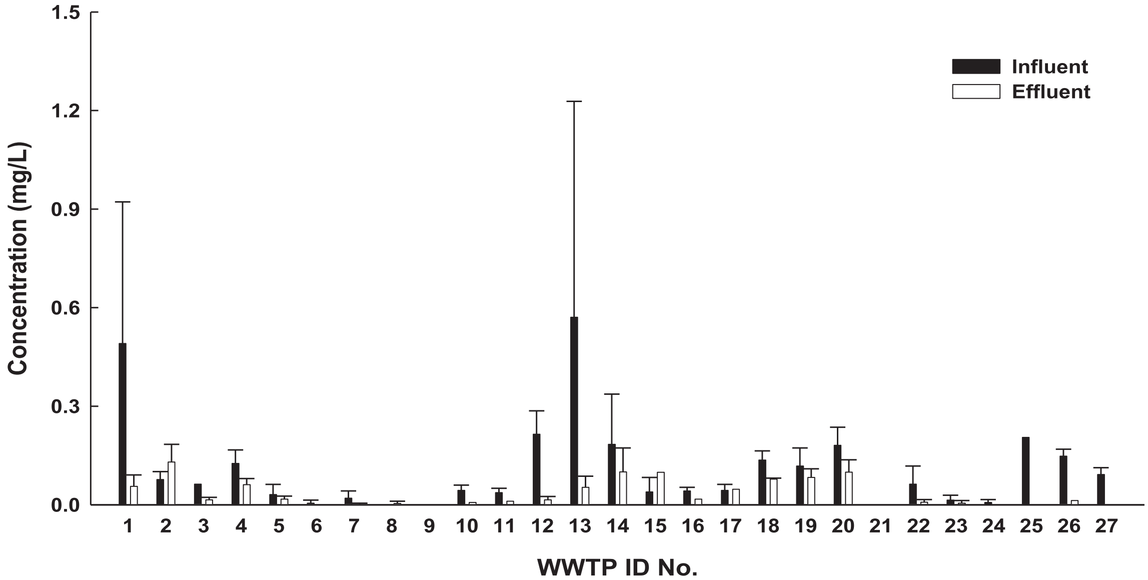

Fig. 3. Concentrations of copper in influents and effluents of 27 WWTPs.
(Bar: average, ⊥: standard deviation).

DEHP in influents and effluents of 27 WWTPs surveyed. DEHP was detected nine of 27 WWTPs, and the removal rates were over 85% on average. The major mechanisms of DEHP removal was possibly biodegradation and adsorption by sludge due to its high hydrophobicity ($pK_{ow} = 7.6$) [15–17].

Removal rates of selenium and 1,4-dioxane were lower than other chemicals and metals. Selenium was detected at 6 of 27 WWTPs, and removal rate was 30% on average. Selenium can cause hair and hoof loss and white muscle disease in animals, and treatment of selenium has been a notable challenge to biological treatment systems [18]. Advanced treatment technologies such as nanofiltration may be required for further treatment [19]. Removal of 1,4-dioxane was 18% on average because 1,4-dioxane could be

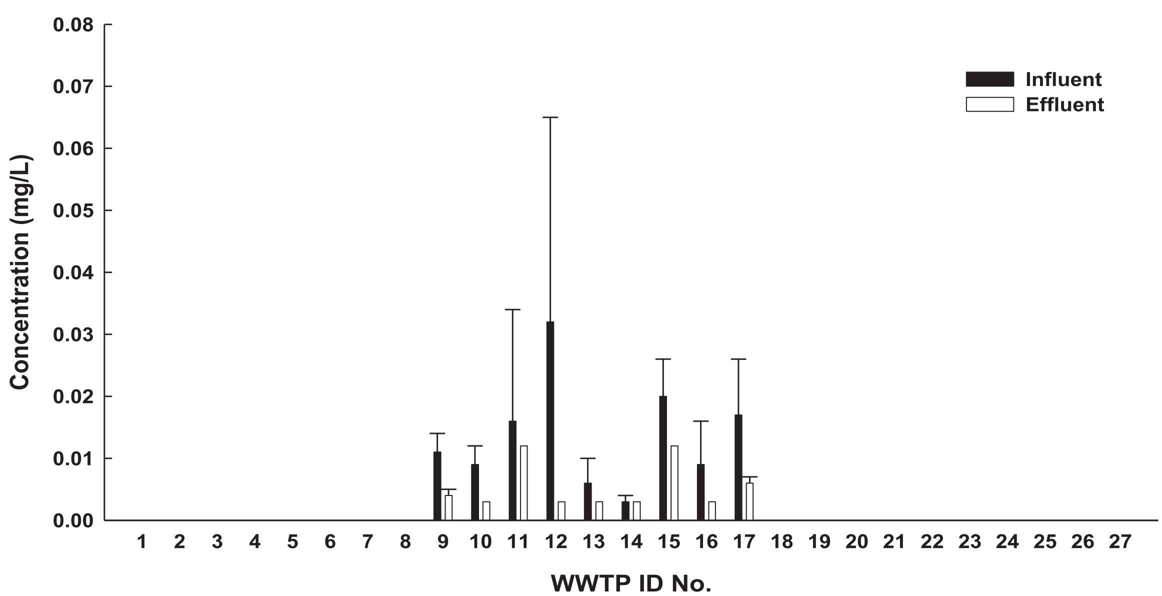

Fig. 4. Concentrations of DEHP in influents and effluents of 27 WWTPs.
(Bar: average, ⊥: standard deviation).

re-desorbed into water after absorption by sludge [20]. However, it was detected at only two of 27 WWTPs. Therefore, it may be more efficient to manage concerning non-conventional pollutants at each WWTPs rather than establishing a universal limits for all WWTPs. For this implementation, database of information on the manufacturing processes, materials, chemicals and products should be updated.

4. Conclusions

Hazardous chemicals and toxic metals in influents and effluents of 27 industrial WWTPs in Korea were surveyed to investigate the occurrence and the removal of those non-conventional pollutants through the WWTPs. Some of the compounds (Cd, bromoform) were present at trace levels while others were dispersed in a broad range of concentrations. Concentrations of benzene, mercury, 1,1-dichloroethylene, and arsenic in influents to WWTPs were relatively high (i.e. above the effluent limits for indirect dischargers in industrial complex). Considering phase transfer such as diffusion of volatile organic compounds to the air and adsorption of chemicals and metals onto activated sludge, removal rates of all the volatile organic compounds were over 70% on average, but no strong correlation between Henry's constants of the compounds and removal rates was observed in this study. Most of metals were removed over 60% on average in the WWTPs. Neither treatment processes nor conventional pollutants exhibited significant correlation with non-conventional pollutants, possibly due to complexity of operations in full scale plants. Further study is required to differentiate mass transfer and "actual" removal. Removal rates of selenium and 1,4-dioxane were lower than other chemicals and metals. However, selenium and 1,4-dioxane were respectively detected at 6 and 2 of 27 WWTPs. Therefore, it may be more efficient to manage concerning non-conventional pollutants at each WWTPs rather than establishing a universal limits for all WWTPs.

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