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Characteristic Occurrence Patterns of Micropollutants and their Removal Efficiencies in Industrial Wastewater Treatment Plants

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Content

Sample preparation

Previous U.S.EPA methods have provided several analytical methods of each class of the target compounds in this study (*e.g.*, method 528 for Phenols, 610 for PAHs, 524.2 for ClBzs). Therefore, to perform multi-residue analysis, we used the modified U.S.EPA methods[1] for the analysis of 1,4-dioxane, ClBzs, phenol, ClPhs, and PAHs. Twenty milliliters of wastewater adjusted to pH 2 with sulfuric acid for 1,4-dioxane were extracted with 50 mL of methylene chloride (MC, Ultra residue analysis, J.T. Baker, USA) twice after spiking with internal standards (10 ng of 1,4-dioxane-d_8, Fluka, Switzerland). Another 500 mL of wastewater adjusted to pH 2 with sulfuric acid for the other target compounds comprising ClBzs, phenol, ClPhs, and PAHs were extracted with 75 mL of MC twice after spiking with internal standards [10 ng of 1,4-dichlorobenzene-d_4, 10 ng of phenol-d_5, 10 ng of 2-chlorophenol-d_4, 50 ng of mixture of PAH internals (*i.e.*, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}, AccuStandard inc., USA)]. Extracts were adjusted to 20 mL with TurvoVap II (Zymark, USA) and mixed with 30 mL of 2 M of K_2CO_3 (Wako, Japan). After this step, phenol and ClPhs were partitioned into K_2CO_3 layer (top layer) and ClBzs and PAHs were in MC layer (bottom layer). Bottom layer were collected and evaporated for instrumental analysis and acetylation procedure with 0.5 mL of acetic anhydride was performed for residual top layer. After acetylation for 5 minutes, 40 mL of MC were added and extracted twice. All 3 kinds of extracts (*i.e.*, 1,4-dioxane extract, ClBzs and PAHs extract, and phenol and ClPhs extract) were evaporated with TurvoVap II (Zymark) until 1 mL and concentrated to 0.5 mL with nitrogen evaporator after spiking with recovery standard (10 ng of *p*-terphenyl-d_{14}; AccuStandard inc.). Two microliters of 1,4-dioxane sample, 12 ClBzs and 16 PAHs sample, and phenol and 19 ClPhs sample were injected to GC/MSD (Agilent 6890 GC/5973 MSD, USA) and quantified, respectively. For PCDD/Fs analysis,[1] 2 L of wastewater was extracted with 200 mL toluene (Ultra residue analysis, J.T. Baker) after spiking with internal standards (1 ng of EPA-1613LCS, Wellington Laboratories Inc., Canada). After evaporating to 1–2 mL in a rotary evaporator (Buchi, Switzerland), the residues were transferred to n-hexane (Ultra residue analysis, J.T. Baker) and adjusted to a volume of 1 mL with nitrogen evaporator. Samples were cleaned-up on a multi-layer silica gel (70–230 mesh, Neutral, Merck, Germany) column [from top to bottom: sodium sulfate, silica-sulfuric acid (8 g, 44% of H_2SO_4), silica (2 g), silica-sodium hydroxide (4 g, 30% of NaOH), silica, and sodium sulfate]. The eluates were cleaned up on an activated neutral alumina (70–230 mesh, Neutral, Merck) column with successive portions of 3% MC in n-hexane and 50% MC in n-hexane. The second fraction was concentrated to less than 1 mL with rotary evaporator (Buchi), and evaporated at room temperature to dryness. The residue was dissolved with n-nonane (Pesticide residue analysis, Fluka) and adjusted to 20 μL after spiking with $^{13}C_{12}$-labelled 1,2,3,4-TCDD and 1,2,3,7,8,9-HxCDD (1 ng of EPA-1613ISS, Wellington Laboratories Inc.) as recovery standards. Seventeen toxic PCDD/Fs isomers as well as homologues from tetra-CDDs/Fs and octa-CDD/F were assessed. The detailed compounds investigated were tabulated in Table S1.

Instrumental analysis

All compounds except PCDD/Fs were analyzed by GC-MSD(Agilent 6890 GC/5973 MSD) with a HP-5MS column (60 m long, 0.32 mm i.d., 0.25 μm film thickness, J&W Scientific, USA). PCDD/Fs were analyzed by gas-chromatography/high-resolution-mass-spectrometry (GC/HRMS) on a Agilent 6890 gas chromatographer using a Jeol JMS-700T high resolution mass spectrometer equipped with DB-5MS column (60 m, 0.32 mm i.d., 0.25 μm film thickness, J&W Scientific, USA). The temperature programs of the GC were as follows: (1) for 1,4-dioxane, initial hold at 35°C for 5 min, increase at 6°C·min^{-1} to 140°C, hold for 0 min, then increase at 20°C·min^{-1} to 300°C, hold for 5 min; (2) for ClBzs and PAHs, initial hold at 40°C for 5 min, increase at 10°C·min^{-1} to 100°C, hold for 0 min, then increase at 5°C·min^{-1} to 310°C, hold for 10 min; (3) for Phenol and ClPhs, initial hold at 40°C for 5 min, increase at 15°C·min^{-1} to 100°C, hold for 0 min, 4°C ·min^{-1} to 200°C, hold for 0 min, then increase at 10°C ·min^{-1} to 300°C, hold for 5 min. (4) for PCDD/Fs, initial hold at 140°C for 4 min, increase at 15°C ·min^{-1} to 220°C, hold for 0 min, 1.5C ·min^{-1} to 240°C, hold for 2 min, then increase at 4°C ·min^{-1} to

310°C, hold for 6 min. One μL of each sample was injected at temperatures of 200°C, 280°C, 250°C, and 300°C for 1,4-dioxane, ClBzs and PAHs, phenol and ClPhs, and PCDD/Fs, respectively. The electron impact (EI)-MSD was operated and the ionization energy was 70 eV for the target compounds analysis except PCDD/Fs. The HRMS for PCDD/Fs analysis was operated under positive EI conditions (38 eV) with a resolution of 10,000 mass-to-charge ratio (m/z). Data were collected in selected ion monitoring (SIM) mode.

Quality assurance and quality control (QA/QC)

In wastewater sample extraction, the recoveries of the internal standards as surrogate standards, which were spiked into the samples before extraction, were assessed and ranged from 50 to 120% [1,4-dioxane-d_8, 68 - 92%; phenol-d_5, 71 - 88%; 2-chlorophenol-d_4, 80 - 105%; 1,4-dichlorobenzene-d_4, 69 - 98%; PAHs (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, perylene-d_{12}), 52 - 110%; $^{13}C_{12}$-PCDD/Fs, 50 - 120%]. Procedure blank samples using distilled water were analyzed with samples to check for blank contamination during the sample treatment and none of the target compounds were detected. Limits of detection were evaluated as three times of signal-to-noise ratio and were calculated for each sample. Average detection limits were 0.35 μg/L for 1,4-dioxane, 0.01 μg/L for phenol, 0.01 μg/L for ClPhs, 0.01 μg/L for ClBzs, 0.05 μg/L for PAHs, and 0.1 pg/L for PCDD/Fs. The amounts below LOD values were represented as "Not detected: ND". To check instrumental stability (*i.e.*, sensitivity variation and calibration check), a quality control standard [*i.e.*, middle stage of calibration standards (CS), normally CS3] was analyzed after every ten samples were injected into the instrument.

Statistical analysis

To investigate the similarities of the distribution patterns of the target compounds, statistical tool comprising correlation (CA), principle component (PCA), and hierarchical cluster (HCA) analyses have been applied as useful method.[2,3] The concentration of each target compound was standardized by dividing with the highest concentration of target compound in each sample.[2,3] The standardized target compounds compositions were used as raw data for statistical analysis. In the case of non-detected compounds, the concentration was given a value of 10% of detection limit of each compound.[4] All kinds of statistical treatments (*i.e.*, correlation, principle component, and hierarchical cluster analyses) were performed for all target compounds according to their classes. The same results were obtained when applying these three methods on each data set. Therefore, one of the statistical results which can be more easily explained (*e.g.*, correlation result for phenol and ClPhs, hierarchical cluster result for PAHs, PCA result for PCDD/Fs) were selected.

Table S1. Concentration levels of micropollutants in the 9 WWTPs.

Compound	**SS**, Influent(*)→AS(*)→CCR(*)→SF→Effluent→(*)				**CS**, Influent(*)→CCR(*)→AS(*)→SF→Effluent→(*)			
	Influent	AS	CCR	Effluent	Influent	CCR	AS	Effluent
1,4-Dioxane (ng/L)	20.80	22.40	18.60	18.20	6.40	5.85	0.73	0.76
ClBzs (ng/L)								
MonoClBz	0.02	ND	0.02	0.02	ND	ND	ND	ND
1,3-DiClBz	0.19	0.02	0.02	0.04	0.03	0.02	0.01	0.01
1,4-DiClBz	0.09	0.01	0.01	0.01	0.01	0.01	0.01	0.01
1,2-DiClBz	0.02	0.01	0.01	0.03	0.01	0.01	ND	ND
1,2,4-TriClBz	0.03	ND	ND	0.01	0.03	0.02	0.01	0.01
1,3,5-TriClBz	0.02	0.02	0.01	0.02	0.13	0.10	0.02	0.02
1,2,3-TriClBz	ND	ND	ND	ND	ND	ND	ND	ND
1,2,3,5/1,2,4,5-TetraClBz	0.01	0.01	ND	0.01	0.05	0.05	0.01	0.01
1,2,3,4-TetraClBz	0.01	ND	ND	ND	0.12	0.11	0.01	0.01
PentaClBz	0.02	0.02	0.01	0.02	0.09	0.08	0.01	0.01
HexaClBz	0.02	0.01	ND	ND	ND	ND	ND	ND
ΣClBzs	0.42	0.09	0.10	0.15	0.46	0.41	0.06	0.07
Phenol (ng/L)	20.40	1.06	0.76	0.69	ND	ND	ND	0.02
ClPhs (ng/L)								
2-MonoClPh	0.08	0.01	0.01	0.01	0.02	0.01	0.04	0.04
3/4-MonoClPh	4.98	0.19	0.11	0.07	0.18	0.16	0.08	0.05
2,4/2,5-DiClPh	0.03	0.03	0.01	0.02	0.07	0.06	0.01	ND
2,3,-DiClPh	0.08	0.01	ND	ND	0.07	0.05	0.01	0.01
2,6-DiClPh	0.05	0.04	0.02	0.03	ND	ND	ND	ND

3,5-DiClPh	ND	ND	ND	ND	ND	ND	ND	ND
3,4-DiClPh	0.02	0.01	0.01	0.01	0.57	0.57	0.06	ND
2,3,5-TriClPh	0.05	0.04	0.04	0.03	0.01	ND	ND	ND
2,4,6-TriClPh	0.33	0.23	0.18	0.16	ND	ND	ND	ND
2,4,5-TriClPh	0.01	0.06	0.04	0.03	0.04	0.04	ND	ND
2,3,4-TriClPh	0.03	0.04	ND	ND	0.02	0.02	ND	ND
2,3,6-TriClPh	0.01	ND	ND	ND	0.02	0.02	0.02	0.02
3,4,5-TriClPh	0.01	ND	ND	ND	0.45	0.50	0.04	ND
2,3,4,5/2,3,4,6-TetraClPh	0.51	ND	ND	ND	0.03	0.04	0.01	ND
2,3,5,6-TetraClPh	3.76	0.03	0.08	0.04	0.27	0.36	0.02	ND
PentaClPh	ND	ND	ND	ND	ND	ND	ND	ND
ΣClPhs	9.95	0.69	0.50	0.40	1.74	1.82	0.28	0.11
PAHs (ng/L)								
Naphthalene	19.10	0.14	0.23	0.07	0.20	0.23	0.14	0.15
Acenaphthylene	1.43	ND	ND	ND	ND	ND	ND	ND
Acenaphthene	0.76	ND	ND	ND	ND	ND	ND	ND
Fluorene	2.57	ND	ND	0.11	ND	ND	ND	ND
Phenanthrene	4.29	ND	ND	ND	0.06	0.06	ND	ND
Anthracene	1.38	ND	ND	ND	ND	ND	ND	ND
Fluoranthene	2.00	ND	ND	ND	ND	ND	ND	ND
Pyrene	1.37	ND	ND	ND	0.13	0.12	0.09	0.07
Benzo[*a*]anthracene	0.23	0.15	ND	ND	0.39	0.36	ND	ND
Chrysene	0.18	ND	ND	ND	ND	ND	ND	ND
Benzo[*b*]fluoranthene	0.13	0.10	ND	ND	ND	ND	ND	ND
Benzo[*k*]fluoranthene	0.11	0.11	ND	ND	ND	ND	ND	ND
Benzo[*a*]pyrene	0.16	ND	ND	ND	ND	ND	ND	ND
Indeno[*1,2,3-cd*]pyrene	0.18	ND	ND	ND	ND	ND	ND	ND
Dibenzo[*a,h*]anthracene	0.06	ND	ND	ND	ND	ND	ND	0.06
Benzo[*g,h,i*]perylene	0.18	ND	ND	ND	ND	ND	ND	ND
ΣPAHs	34.13	0.50	0.23	0.18	0.78	0.77	0.23	0.28

PCDD/Fs (pg/L)	Influent	Effluent	Influent	Effluent
2,3,7,8-TCDF	ND	ND	8.8	ND
1,2,3,7,8-PeCDF	2.1	ND	13.7	ND
2,3,4,7,8-PeCDF	3.2	ND	24.2	ND
1,2,3,4,7,8-HxCDF	ND	ND	22.7	ND
1,2,3,6,7,8-HxCDF	ND	ND	25.2	1.1
2,3,4,6,7,8-HxCDF	ND	ND	28.9	ND
1,2,3,7,8,9-HxCDF	ND	ND	10.5	ND
1,2,3,4,6,7,8-HpCDF	ND	ND	71.5	2.1
1,2,3,4,7,8,9-HpCDF	ND	ND	6.4	ND
OCDF	ND	ND	25.0	ND
2,3,7,8-TCDD	ND	ND	ND	ND
1,2,3,7,8-PeCDD	ND	ND	ND	ND
1,2,3,4,7,8-HxCDD	ND	ND	4.4	ND
1,2,3,6,7,8-HxCDD	ND	ND	7.7	ND

1,2,3,7,8,9-HxCDD	ND	ND	2.9	ND
1,2,3,4,6,7,8-HpCDD	1.1	ND	28.7	1.7
OCDD	9.7	ND	25.9	3.3
Σ_{17}PCDD/Fs	16.1	ND	306.5	8.2
ΣPCDD/Fs	78.5	0.1	1250.3	16.9

Compound	**UG**, Influent(*)→CCR(*)→AS(*)→AC→Effluent→(*)				**NC**, Influent(*)→AS →Effluent→(*)		**GJ**, Influent(*)→DAF/CCR →Effluent→(*)	
	Influent	CCR	AS	Effluent	Influent	Effluent	Influent	Effluent
1,4-Dioxane (ng/L)	23.16	17.23	15.50	2.85	6.30	0.97	1.14	2.47
ClBzs (ng/L)								
MonoClBz	ND	ND	ND	ND	0.01	0.02	0.01	0.02
1,3-DiClBz	0.34	0.11	ND	ND	ND	ND	ND	0.02
1,4-DiClBz	ND	ND	ND	ND	ND	ND	0.01	ND
1,2-DiClBz	0.01	0.01	ND	ND	ND	ND	0.03	ND
1,2,4-TriClBz	0.29	0.16	0.02	ND	0.01	ND	ND	0.02
1,3,5-TriClBz	0.54	0.22	0.02	0.02	0.02	0.01	0.03	0.02
1,2,3-TriClBz	0.02	ND	ND	ND	ND	ND	ND	ND
1,2,3,5/1,2,4,5-TetraClBz	0.36	0.25	ND	ND	ND	ND	ND	ND
1,2,3,4-TetraClBz	0.05	0.01	0.01	ND	ND	ND	ND	ND
PentaClBz	0.06	0.05	0.01	ND	ND	ND	ND	ND
HexaClBz	ND	ND	ND	ND	ND	ND	ND	ND
ΣClBzs	1.67	0.81	0.05	0.02	0.04	0.03	0.08	0.07
Phenol (ng/L)	5.06	0.47	0.41	0.38	16.22	0.54	16.52	0.29
ClPhs (ng/L)								
2-MonoClPh	0.09	0.02	0.01	0.01	ND	0.01	0.01	ND
3/4-MonoClPh	0.08	0.08	0.09	0.02	ND	ND	ND	0.03
2,4/2,5-DiClPh	0.10	0.02	0.02	0.01	ND	0.04	0.01	0.02
2,3,-DiClPh	0.06	0.02	0.02	ND	0.03	ND	0.02	0.02
2,6-DiClPh	0.08	ND	ND	ND	ND	ND	0.01	0.01
3,5-DiClPh	ND	ND	ND	ND	ND	ND	ND	0.12
3,4-DiClPh	ND	ND	ND	ND	ND	ND	ND	0.03
2,3,5-TriClPh	0.11	0.03	0.03	ND	ND	ND	0.01	0.02
2,4,6-TriClPh	ND	ND	ND	ND	ND	ND	0.05	0.09
2,4,5-TriClPh	0.04	ND	ND	ND	ND	ND	ND	ND
2,3,4-TriClPh	0.02	0.01	0.01	ND	ND		ND	ND
2,3,6-TriClPh	ND	ND	ND	ND	ND	ND	ND	ND
3,4,5-TriClPh	ND	ND	ND	ND	ND	ND	ND	0.31
2,3,4,5/2,3,4,6-TetraClPh	0.11	0.05	0.05	ND	ND	ND	0.02	0.01
2,3,5,6-TetraClPh	0.01	0.01	ND	ND	ND	ND	0.07	0.05
PentaClPh	ND	ND	ND	ND	ND	ND	ND	ND
ΣClPhs	0.69	0.22	0.23	0.03	0.03	0.05	0.20	0.70
PAHs (ng/L)								
Naphthalene	1.27	0.24	0.14	0.16	0.84	0.12	0.50	0.12

Acenaphthylene	1.96	ND	ND	ND	ND	ND	ND	ND
Acenaphthene	22.43	ND	ND	ND	ND	ND	0.05	ND
Fluorene	36.27	4.60	ND	ND	ND	ND	ND	ND
Phenanthrene	61.46	ND	ND	ND	0.78	0.05	ND	ND
Anthracene	29.55	ND	ND	ND	ND	ND	ND	ND
Fluoranthene	90.59	ND	ND	ND	ND	ND	ND	ND
Pyrene	58.25	0.05	0.05	ND	ND	ND	ND	ND
Benzo[*a*]anthracene	5.28	ND	ND	ND	ND	ND	ND	ND
Chrysene	1.82	ND	ND	ND	ND	ND	ND	ND
Benzo[*b*]fluoranthene	0.64	ND	ND	ND	ND	ND	ND	ND
Benzo[*k*]fluoranthene	0.91	ND	ND	ND	ND	ND	ND	ND
Benzo[*a*]pyrene	0.91	ND	ND	ND	ND	ND	ND	ND
Indeno[*1,2,3-cd*]pyrene	0.08	ND	ND	ND	ND	ND	ND	ND
Dibenzo[*a,h*]anthracene	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[*g,h,i*]perylene	ND	ND	ND	ND	ND	ND	ND	ND
ΣPAHs	311.41	4.89	0.19	0.16	1.62	0.17	0.55	0.12
PCDD/Fs (pg/L)	Influent		Effluent		Influent	Effluent	Influent	Effluent
2,3,7,8-TCDF		ND		ND	17.7	14.5	7.7	10.4
1,2,3,7,8-PeCDF		1.4		ND	10.2	8.1	6.5	6.3
2,3,4,7,8-PeCDF		ND		ND	2.6	6.4	0.8	2.0
1,2,3,4,7,8-HxCDF		2.6		ND	1.2	3.1	1.4	1.0
1,2,3,6,7,8-HxCDF		1.4		ND	ND	0.9	1.5	1.0
2,3,4,6,7,8-HxCDF		0.9		ND	ND	ND	ND	ND
1,2,3,7,8,9-HxCDF		1.0		ND	ND	ND	ND	ND
1,2,3,4,6,7,8-HpCDF		2.4		1.1	0.8	ND	6.4	ND
1,2,3,4,7,8,9-HpCDF		ND		ND	ND	ND	ND	ND
OCDF		2.1		ND	ND	ND	26.6	ND
2,3,7,8-TCDD		ND		ND	ND	ND	ND	7.7
1,2,3,7,8-PeCDD		ND		ND	ND	ND	ND	ND
1,2,3,4,7,8-HxCDD		ND		ND	ND	ND	ND	ND
1,2,3,6,7,8-HxCDD		ND		ND	ND	ND	ND	ND
1,2,3,7,8,9-HxCDD		ND		ND	ND	ND	ND	ND
1,2,3,4,6,7,8-HpCDD		ND		1.9	1.5	1.9	2.0	2.3
OCDD		5.0		3.6	5.3	2.3	4.5	4.3
Σ_{17}PCDD/Fs		16.7		6.7	39.3	37.2	57.4	35.0
ΣPCDD/Fs		20.7		10.9	124.3	105.0	115.8	80.0

Compound	**DS**, Influent(*)→AS(*)→CCR →Effluent→(*)			**DA**, Influent(*)→CCR(*)→RBC→Effluent→(*)		
	Influent	AS	Effluent	Influent	CCR	Effluent
1,4-Dioxane (ng/L)	6.27	11.72	12.19	4.04	3.50	3.15
ClBzs (ng/L)						
MonoClBz	0.04	0.02	0.02	0.01	0.01	0.01
1,3-DiClBz	0.02	0.01	0.01	ND	ND	ND
1,4-DiClBz	0.01	ND	ND	ND	ND	ND

1,2-DiClBz	0.11	0.03	0.03	0.01	ND	ND
1,2,4-TriClBz	0.01	0.01	0.01	ND	ND	ND
1,3,5-TriClBz	0.14	0.18	0.17	0.02	0.02	0.02
1,2,3-TriClBz	0.03	0.01	0.01	ND	ND	ND
1,2,3,5/1,2,4,5-TetraClBz	ND	ND	ND	ND	ND	ND
1,2,3,4-TetraClBz	ND	ND	ND	ND	ND	ND
PentaClBz	ND	ND	ND	ND	ND	ND
HexaClBz	ND	ND		ND	ND	ND
ΣClBzs	0.36	0.26	0.24	0.04	0.03	0.03
Phenol (ng/L)	10.83	0.44	0.39	1.90	0.75	0.65
ClPhs (ng/L)						
2-MonoClPh	0.59	0.03	0.02	0.04	0.03	0.03
3/4-MonoClPh	0.06	0.03	0.02	0.06	0.04	0.04
2,4/2,5-DiClPh	0.02	0.01	0.01	0.01	0.01	ND
2,3,-DiClPh	0.03	0.01	0.01	0.01	0.01	0.01
2,6-DiClPh	0.03	0.01	0.01	0.01	0.01	0.01
3,5-DiClPh	0.06	0.03	0.03	0.02	0.02	0.02
3,4-DiClPh	0.03	ND	0.03	0.04	0.03	ND
2,3,5-TriClPh	0.06	0.04	0.03	ND	ND	ND
2,4,6-TriClPh	0.13	0.13	0.13	0.05	0.04	0.02
2,4,5-TriClPh	ND	ND	ND	0.01	0.01	ND
2,3,4-TriClPh	0.60	0.01	ND	0.01	ND	ND
2,3,6-TriClPh	ND	ND	ND	ND	ND	0.01
3,4,5-TriClPh	0.01	ND	0.19	ND	ND	ND
2,3,4,5/2,3,4,6-TetraClPh	0.16	0.06	0.09	ND	ND	ND
2,3,5,6-TetraClPh	0.80	0.59	0.61	0.05	0.04	0.01
PentaClPh	0.07	ND	ND	ND	ND	ND
ΣClPhs	2.62	0.94	1.19	0.30	0.22	0.15
PAHs (ng/L)						
Naphthalene	0.43	0.11	0.11	0.18	0.09	0.15
Acenaphthylene	ND	ND	ND	ND	ND	ND
Acenaphthene	0.10	ND	ND	ND	ND	ND
Fluorene	ND	ND	ND	ND	ND	ND
Phenanthrene	0.70	0.37	0.33	0.18	0.02	0.07
Anthracene	0.12	ND	ND	0.04	ND	ND
Fluoranthene	ND	ND	ND	0.22	0.03	0.11
Pyrene	ND	ND	ND	0.57	0.07	0.24
Benzo[*a*]anthracene	ND	ND	ND	0.07	ND	ND
Chrysene	ND	ND	ND	0.12	0.02	0.06
Benzo[*b*]fluoranthene	ND	ND	ND	ND	ND	ND
Benzo[*k*]fluoranthene	ND	ND	ND	ND	ND	ND
Benzo[*a*]pyrene	ND	ND	ND	0.05	ND	ND
Indeno[*1,2,3-cd*]pyrene	ND	ND	ND	0.05	ND	ND

Dibenzo[*a,h*]anthracene	ND	ND	ND	ND	ND	ND
Benzo[*g,h,i*]perylene	ND	ND	ND	0.08	0.02	ND
ΣPAHs	1.35	0.48	0.44	1.56	0.24	0.63
PCDD/Fs (pg/L)	Influent		Effluent	Influent		Effluent
2,3,7,8-TCDF	9.4		13.8	12.6		10.5
1,2,3,7,8-PeCDF	7.3		8.5	7.8		7.5
2,3,4,7,8-PeCDF	0.9		2.6	3.7		2.4
1,2,3,4,7,8-HxCDF	1.2		1.4	1.9		1.7
1,2,3,6,7,8-HxCDF	ND		1.4	0.6		1.7
2,3,4,6,7,8-HxCDF	ND		ND	ND		ND
1,2,3,7,8,9-HxCDF	ND		ND	ND		ND
1,2,3,4,6,7,8-HpCDF	1.3		ND	0.9		0.5
1,2,3,4,7,8,9-HpCDF	ND		ND	ND		ND
OCDF	ND		ND	0.8		ND
2,3,7,8-TCDD	ND		ND	ND		ND
1,2,3,7,8-PeCDD	ND		ND	ND		ND
1,2,3,4,7,8-HxCDD	ND		ND	ND		ND
1,2,3,6,7,8-HxCDD	ND		ND	ND		ND
1,2,3,7,8,9-HxCDD	ND		ND	ND		ND
1,2,3,4,6,7,8-HpCDD	1.5		1.3	1.3		1.2
OCDD	7.0		1.8	3.5		2.5
Σ_{17}PCDD/Fs	28.5		30.8	33.1		28.0
ΣPCDD/Fs	126.7		101.1	103.3		93.1

Compound	**SP**, Influent(*)→AS(*)→CCR→Effluent→(*)			**YS**, Influent(*)→CCR(*)→AS→Effluent→(*)		
	Influent	AS	Effluent	Influent	CCR	Effluent
1,4-Dioxane (ng/L)	9.81	11.99	11.37	6.44	6.98	7.16
ClBzs (ng/L)						
MonoClBz	ND	ND	ND	ND	ND	ND
1,3-DiClBz	0.02	0.01	0.01	ND	0.01	0.01
1,4-DiClBz	0.01	0.01	0.01	ND	ND	ND
1,2-DiClBz	0.18	0.02	0.02	0.02	0.02	ND
1,2,4-TriClBz	0.01	0.02	0.02	0.02	ND	ND
1,3,5-TriClBz	0.02	0.06	0.07	0.01	0.01	0.02
1,2,3-TriClBz	0.01	0.01	0.01	ND	0.04	ND
1,2,3,5/1,2,4,5-TetraClBz	ND	0.03	0.03	0.01	0.01	0.01
1,2,3,4-TetraClBz	ND	0.06	0.07	ND	ND	ND
PentaClBz	ND	0.02	0.03	ND	0.01	ND
HexaClBz	ND	ND	ND	ND	ND	ND
ΣClBzs	0.25	0.25	0.27	0.06	0.09	0.03
Phenol (ng/L)	9.90	0.55	0.58	11.16	8.59	0.58
ClPhs (ng/L)						
2-MonoClPh	0.68	0.01	0.01	0.09	0.09	0.02
3/4-MonoClPh	0.99	0.03	0.03	0.06	0.14	0.04

2,4/2,5-DiClPh	0.67	0.16	0.16	0.11	0.20	0.10
2,3,-DiClPh	0.30	0.04	0.03	0.10	0.07	0.01
2,6-DiClPh	ND	ND	ND	0.01	0.02	ND
3,5-DiClPh	ND	ND	ND	ND	ND	ND
3,4-DiClPh	ND	ND	ND	ND	ND	ND
2,3,5-TriClPh	1.06	0.07	0.08	0.04	0.12	0.05
2,4,6-TriClPh	0.03	ND	ND	ND	ND	ND
2,4,5-TriClPh	ND	ND	ND	ND	ND	ND
2,3,4-TriClPh	ND	ND	ND	0.01	0.01	ND
2,3,6-TriClPh	ND	ND	ND	ND	ND	0.01
3,4,5-TriClPh	ND	ND	ND	ND	ND	ND
2,3,4,5/2,3,4,6-TetraClPh	0.14	0.05	0.06	ND	0.01	0.01
2,3,5,6-TetraClPh	0.03	ND	ND	ND	ND	ND
PentaClPh	0.07	0.01	0.01	ND	ND	ND
ΣClPhs	3.96	0.37	0.39	0.42	0.65	0.23
PAHs (ng/L)						
Naphthalene	0.70	0.17	0.21	0.19	0.19	0.12
Acenaphthylene	ND	ND	ND	1.05	0.06	ND
Acenaphthene	ND	ND	ND	ND	ND	ND
Fluorene	ND	ND	ND	3.38	0.46	ND
Phenanthrene	ND	ND	ND	0.09	ND	ND
Anthracene	ND	ND	ND	0.06	ND	ND
Fluoranthene	ND	ND	ND	0.09	ND	ND
Pyrene	ND	ND	ND	0.37	0.09	ND
Benzo[*a*]anthracene	0.16	0.22	0.21	ND	ND	ND
Chrysene	0.20	ND	ND	ND	ND	ND
Benzo[*b*]fluoranthene	ND	ND	ND	0.20	0.06	0.06
Benzo[*k*]fluoranthene	ND	ND	ND	ND	ND	ND
Benzo[*a*]pyrene	ND	ND	ND	0.25	0.07	ND
Indeno[*1,2,3-cd*]pyrene	0.47	ND	ND	0.26	0.08	0.06
Dibenzo[*a,h*]anthracene	0.92	ND	ND	0.39	0.13	0.08
Benzo[*g,h,i*]perylene	0.35	ND	ND	0.13	0.07	0.07
ΣPAHs	2.79	0.39	0.42	6.44	1.21	0.39

PCDD/Fs (pg/L)	Influent	Effluent	Influent	Effluent
2,3,7,8-TCDF	4.7	ND	ND	ND
1,2,3,7,8-PeCDF	23.6	ND	ND	ND
2,3,4,7,8-PeCDF	39.3	ND	ND	ND
1,2,3,4,7,8-HxCDF	25.4	ND	ND	ND
1,2,3,6,7,8-HxCDF	28.4	ND	ND	ND
2,3,4,6,7,8-HxCDF	33.6	ND	ND	ND
1,2,3,7,8,9-HxCDF	ND	ND	ND	ND
1,2,3,4,6,7,8-HpCDF	95.7	1.4	2.0	1.0
1,2,3,4,7,8,9-HpCDF	11.9	ND	ND	ND

OCDF	36.5	ND	ND	ND
2,3,7,8-TCDD	ND	ND	0.4	ND
1,2,3,7,8-PeCDD	11.3	ND	ND	ND
1,2,3,4,7,8-HxCDD	10.6	ND	ND	ND
1,2,3,6,7,8-HxCDD	16.2	ND	ND	ND
1,2,3,7,8,9-HxCDD	12.4	ND	ND	ND
1,2,3,4,6,7,8-HpCDD	77.4	2.6	2.5	1.3
OCDD	69.9	5.0	3.3	4.1
Σ_{17}PCDD/Fs	497.0	8.9	8.1	6.3
ΣPCDD/Fs	1549.6	12.4	8.6	7.6

ND : Not detected; Biological treatment (Activated sludge, AS; Rotating biological contactor, RBC); Chemical treatment (Chemical coagulation reactor, CCR; Dissolved air flotation, DAF); Advanced treatment (Sand filtration, SF; Activated carbon filtration, AC)

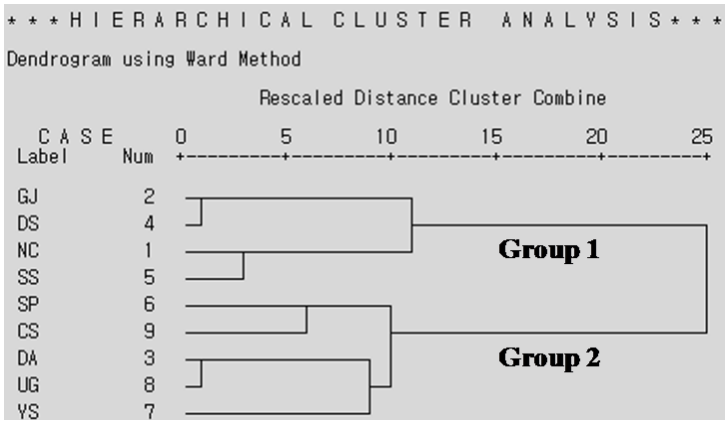

Figure S1. Relationship according to the PAHs compositions of each WWTP

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