IDENTIFICATION OF ECO-TOXICOLOGICAL SUBSTANCES IN INDUSTRIAL EFFLUENT USING THE ACUTE TOXICITY TEST AND STATISTICAL ANALYSIS

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Introduction

At present, 43 pollutants in industrial effluent are regulated by discharge standards in Korea. In particular, a whole effluent toxicity testing was implemented to assess the toxicity of unknown chemicals for the aquatic ecosystem protection and to promote the water quality management plan focused on receptors, dating from 2011. To do this, the acute toxicity test using *Daphnia magna* was adopted, and fish and algae will be added in the future.

Industrial effluent has a variety of chemicals such as heavy metals with a wide range of concentrations. Therefore, a comprehensive management scheme is required to prevent water pollution due to industrial activities and investigate the fate and transport of toxic substances in the aquatic environment.

About 1,918 points were designated as part of the national water quality monitoring network for rivers, lakes, industrial drainages, etc., from 1978 in Korea. In particular, 11 industrial drainages sites in 8 out of 100 industrial complexes in the Gyeonggi province have been periodically monitored. In this study, the effluent from Banwol, one of the largest industrial complexes in Korea, was sampled and analyzed for water quality and acute toxicity using *Daphnia magna* to identify eco-toxicological substances and propose a management plan.

Materials and Methods

The Banwol industrial complex, located in Ansan city, Gyeonggi province, has about 5,000 plants comprised of mechanical plants (35.9%), electrical plants (27.6%), petroleum chemical plants (9.9%). etc., as of 2011. The wastewater of the Banwol industrial complex is conveyed to the Ansan city wastewater treatment plant after pretreatments at each plant. Figure 1 shows the target area status and sampling sites. B-l and B-2 are outlets of industrial drainages and B-3 is an effluent outlet of the Ansan WWTP operating a modified A/O process, one of the advanced biological treatments. The WWTP treats 300,800 ton/d including the sewage of Ansan city (122,185 ton/d, 40.6% of total) and the effluent of the Banwol industrial complex (178,615 ton/d, 59.4% of total). Samples were taken four times in March, April, July and September, 2011 and analyzed for acute toxicity using *Daphnia magna* and also for pH, DO, EC, BOD, COD, SS, T-P, T-P, F, and heavy metal (Cd, Pb, Cr, Cr^{+6}, As, Hg, Cu, Mn, Zn, Fe) according to Korean standard methods. Subsequently, statistical analyses, correlation and regression tests, were performed to characterize the water quality and identify the eco-toxicological factors in the effluent.

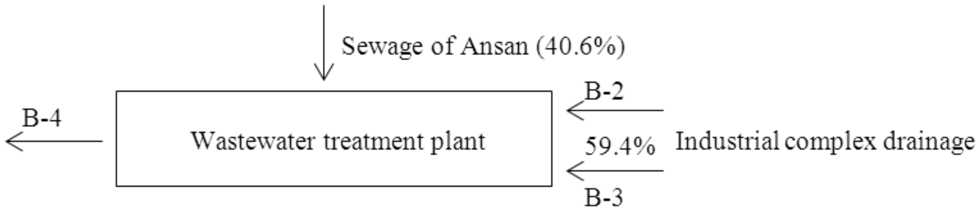

Figure 1 Target site status and sampling sites

Results and Discussion

Table 1 shows the water quality and acute toxicity to *Daphnia magna* in each site. The B-2 site showed high concentrations in which Cu exceeded not only the discharge standard, 3 mg/L, in April but also both Cu and Zn were much higher than those of the US criteria maximum concentration (CMC)[1], i.e. Cu 0.015~0.028 mg/L and Zn 0.102~0.178 mg/L, respectively, and the toxicity ranged 5.5~22.7 TU.

Table 1 Water quality parameters and acute toxicity of industrial drainages (unit: mg/L)

Parameter	B-2				B-3				B-4			
	1st	2nd	3rd	4th	1st	2nd	3rd	4th	1st	2nd	3rd	4th
pH	6.4	6.1	7.0	8.2	7.2	7.0	7.4	7.9	6.8	6.3	7.0	8.1
DO	5.7	5.2	3.6	2.0	4.2	6.0	3.0	1.7	7.2	6.7	5.2	4.6
BOD	95.1	133.2	57.5	161.1	223.7	33.4	10.2	1294	3.1	0.8	1.2	1.1
COD	80.8	108.9	37.1	61.3	124	80.9	9.3	232	10.6	9.3	6.7	8.0
SS	30	58	24	72	58	25	7.3	20	2.3	1.3	0.7	0.3
EC (μs/㎝)	1193	602	735	710	3300	2336	827	1344	768	740	708	585
T-N	11.092	9.044	7.459	5.707	28.031	34.242	6.522	15.821	4.807	5.355	5.145	6.947
T-P	0.611	0.695	0.351	0.465	0.588	0.762	0.174	0.447	0.409	0.474	0.131	0.409
Cu	1.03	4.33	0.824	1.395	0.045	0.596	0.029	0.023	0.008	0.009	0.021	N.D.
Mn	0.554	0.744	0.468	0.597	0.800	0.81	0.519	0.558	0.086	0.107	0.123	0.045
Zn	2.107	2.465	2.216	4.081	0.281	0.205	0.159	0.145	0.069	0.051	0.053	0.043
Cr	0.02	0.08	0.02	0.07	0.02	0.02	N.D.	0.01	N.D.	N.D.	0.02	N.D.
Fe	0.77	1.56	1.53	0.11	1.81	0.85	0.7	0.57	0.04	0.06	0.13	N.D.
F	0.74	0.73	0.68	1.00	0.41	0.56	0.38	0.66	0.49	0.6	0.48	0.62
Hardness	215	195	110	160	235	240	185	220	115	85	105	110
EC_{50} (%)	18.3	8.3	12.1	4.4	58	35.4	>100	>100	>100	>100	>100	>100
TU	5.5	12	8.3	22.7	1.7	2.8	0	0.4	0	0	0	0

These high Cu and Zn concentrations could be attributed to the mechanical and electronic manufacturing plants upstream which have increased in number continuously from 2005. The toxicity values of Cu to *Daphnia magna* have been known to be 0.026~0.036 mg/L and 0.021~0.146 mg/L for 24hr EC_{50} and 48hr EC_{50}, respectively[2]. Although the toxicity of heavy metals depends upon various factors such as hardness[2] etc., they probably caused the relatively high toxicity at the B-2 site. On the other hand, the B-3 site was characterized by high concentrations of organic matters (BOD) and nutrients (T-N, T-P). However, it showed much lower concentrations of Cu and Zn than those of B-2 and the toxicity ranged from 0~2.8 TU. At the B-4 site, the effluent of the Ansan WWTP, demonstrated stable water quality satisfying discharge standards, as can be seen in Table 1. Pollutants including heavy metals significantly decreased to have no toxicity at the B-4 site. Several studies have demonstrated different results in terms of the toxicity after WWTP, that is, some found a reduction while others found an increase. However, this study showed that the WWTP played an important role in removing eco-toxicity as well as pollutants. Therefore, it was necessary to identify the eco-toxicological substances in various types of industrial effluents and find a measure to control them.

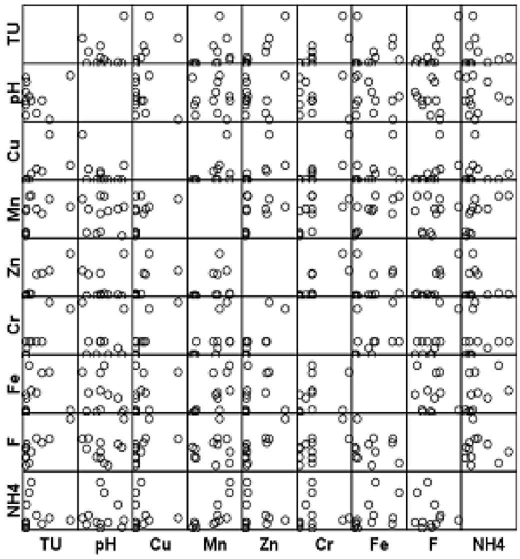

Figure 2 Scatter-plot of water quality parameters and acute toxicity (TU) of the Banwol industrial drainage

Statistical analyses were performed to investigate the relationship between water quality parameters and toxicity. Figure 2 is a scatter plot graph showing approximate correlations among water quality parameters. Correlation analysis indicates that Zn, Cr, F and Cu in the effluent showed strong positive correlations with eco-toxicity values. Therefore, stepwise multiple regression analysis was performed to find the quantitative relation between Zn, Cr, F, Cu and toxicity. The eco-toxicity value, TU was assigned as a dependent variable and Zn, Cr, F, Cu were independent variables. The analysis resulted in a simple regression equation between Zn and toxicity because the other independent variables except Zn were eliminated during the selection process. However, while Zn, Cr, and F had very strong correlations with toxicity, Cr and F were not selected in the regression equation. This may be explained by the fact that the Cr and F concentrations were lower than the US criteria maximum concentration and their toxicities would change according to the speciation profile and water environment[4,5]. The equation was shown to satisfy the assumptions and conditions through the F test, T-test and Durbin-Watson test and was highly reliable (R^2=0.926). This equation meant that a Zn concentration of 1 mg/L increased eco-toxicity by 4.884 TU and that the Zn concentration should be managed to be less than 0.285 mg/L to keep the eco-toxicity (TU) to less than 1 (see Table 2)

Table 2 Regression equation between acute toxicity (TU) and water quality in the Banwol site (No of samples: 12)

Regression equation	F-test	T-test	Durbin-Watson	R^2
TU = 4.884 × Zn(mg/L) - 0.391	0.000	0.000	1.804	0.926

In conclusion, the removal of Zn, Cr, F, and Cu by a proper treatment is required in the Banwol industrial complex in order to control eco-toxic chemicals. In particular, because Zn was identified as a major eco-toxicological substance in the effluent, it will be possible to set a discharging standard for eco-toxicity management using the obtained equation.

Acknowledgements

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