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Assessment of Polluting Situation of Han River Water Basing on Anions Determination by Ion Chromatography

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This paper brings together information on the water quality functioning of Han River and some other springs of it. Recently, Han River represents a surface water supply resource of Seoul and marvelous riverine areas for restaurants as well as illegal fishing. The environment of the river therefore impacted by that discharge source of nutrient and other industrial wastes. In order to evaluate man- made and natural effects on water quality, anion variables have been analysed in water samples collected every month from four springs of Han River. In this paper, a large amount of samples from four springs were taken and analytically determined with ion chromatography and Ecotest. Measured values of ammonia, nitrate, nitrite, phosphate and COD showed that could exist a relation between the concentration ratio of chloride to sulfate (Cl/S- salt ratio) and polluted level of each sampling area. Series of test with periodically monthly river water samples have been also carried out to classify this ratio regarded as a polluting indicator at the first consideration. Further studies and statistic data are needed to verify this parameter.

Key words: Han River, ion chromatography, anions, water pollution, chloride, sulfate.

1. Introduction

River basins generally constitute areas with a high population density owing to favorable living conditions such as the availability of fertile land, water for irrigation, industrial, drinking or fishing purposes and efficient means of transportation. Rivers play an important role in assimilating or carrying off industrial and municipal wastewater, manure discharges and runoff from agricultural fields, roadways, streets, which are responsible for river pollution (Stroomberg et al., 1995; Ward and Eliot, 1995). Rivers also constitute the main water resources in inland areas for drinking irrigation and industrial purposes; thus, it is an essence for effective and efficient water management to have reliable information of water quality.

The discharge of industrial and municipal wastewater can be regarded as a constant and major polluting source, but not so the blooming of the population on both sides of the river. Although flow in the river is functioning for moderation and distribution, pollution at different branches is variable due to their geological and habitant characteristic. Topography of area have fairly strong effect on flow rate and hence on the concentration of pollutants in the water. The release of traces of elements or acidic water from high slope hills and rock mountains on both sides of the river could also result in the increase of pollutants and toxic effects. Moreover, the fishing activities of minor inhabitants might cause the degradation of wide life habitat or water quality.

Environmental and conservation issues need to be placed within the context of social and economic uses of the river by the community and therefore requires the perceptions of local residents, landowners, the water industry and other stake holders to be taken into account. Environmental analysis and assessment has an important role to play in the decision marking

process. Statistical data is required to understand the water quality, hydrological, and ecological functioning of a highly complicated environmental system and in producing models to explore how water quality might change in response to social, economic, legislative and environmental drivers. Furthermore, that work may provide a yardstick to determine how important these drivers are in relation to other factors such as development activities of the residents and their influence on environment.

In this paper, analytical results are presented of Han river general characteristic through a number of water samples taken in mid of March. The objective of this study was to evaluate the status of pollution of river water via a parameter so called "salt ratio" of chloride-sulfate (Cl/S: CS) and the relation between pollution level of water and that ratio.

2. Experimental

2.1 Reagents

All chemicals used were of analytical grade quality. The double distillated water was filtered through an ultra pure apparatus, Mili- Q plus with conductivity at 18.2 MΩ

Seri of anion standard solution was prepared by dilution stock solution 1000 mg/l provided by Dionex. Eluant was prepared by dissolving 1.6958 g Na_2CO_3 and 0.168 g $NaHCO_3$ in 2000 L of ultra pure water. Regenerant was prepared by dropping 2, 8 ml sulfuric acid 98% into 1000 ml ultra pure water, then fill to mark of 2000 ml vessel.

With COD and ammonia determination, test kit named "Ecotest" was used. Analytes were determined by color intensity and comparison with standard color.

2.2 Apparatus

Fig. 1 shows a schematic representation of the instrumental operation. Details of the operating conditions are given in Table 1. The measurements

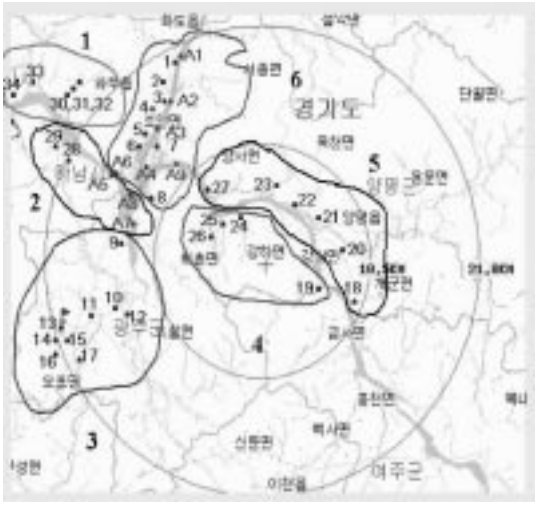

Fig. 1. The Han river sampling points and areas in March

Table 1. The condition of ion exchange chromatography

Analysis Column:	Ion pack AS14A (Dionex)
Suppressor:	AMMS® III (Dionex)
Eluent:	8mM Na_2CO_3 & 0.1mM $NaHCO_3$ (under nitrogen)
Regenerant:	28mM H_2SO_4 98%
Injection volume:	10 µl (loop), manual injection
Conductivity detector:	DS5 Detection Stabilizer (Dionex)

were carried out by a Dionex DX-80 system. The sulfuric acid for the chemical suppression and eluent were delivered from two transparently plastic vessels.

3. Results and discussion

3.1 Sampling location

In the paper, all data and statistical analysis are presented. Measured values for nitrate, nitrites, phosphate, ammonia and COD showed a definite variability during the pollution map drawing. Possible trends include spatial trends, in which the concentrations vary along the length of the river, and temporal trends, meaning a variation in concentrations through time at a single monitoring site. Therefore, all the sampling sites are divided into six areas basing on the local topography as

Table 2. The characteristic of surface water from six sampling areas of the Han River water in March

Area on map	COD (ppm)			NH_4-N (ppm)			NO_3-N (ppm)			NO_2-N (ppm)			PO_4-P (ppm)			Cl (ppm)			SO_4-S (ppm)		
	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean
1	30.0	1.0	12.8	8.00	0.60	3.44	5.92	0.00	1.72	2.09	0.00	0.71	4.44	0.00	1.38	36.16	20.25	26.91	8.14	4.45	6.38
2	15.0	1.0	7.2	0.07	0.05	0.05	1.91	0.87	1.25	0.26	0.00	0.12	0.4	0.00	0.1	40.61	6.00	21.79	12.39	4.89	7.58
3	9.0	5.0	6.3	10.00	0.05	3.37	15.80	0.56	3.54	6.22	0.00	0.73	1.21	0.00	0.32	97.50	13.58	26.91	21.03	3.42	6.38
4	1.0	1.0	1.0	0.01	0.03	0.02	2.34	0.59	1.39	0.00	0.00	0.00	0.00	0.00	0.00	12.26	3.68	6.76	5.10	2.09	3.08
5	4.0	1.0	1.5	2.00	0.00	0.55	1.61	1.00	1.29	0.10	0.00	0.04	0.84	0.00	0.19	18.15	4.34	9.99	4.08	2.25	2.87
6	5.0	1.0	1.4	1.00	0.05	0.14	2.16	1.01	1.30	0.09	0.00	0.01	0.13	0.00	0.01	10.72	4.03	5.39	5.67	1.92	1.81

well as inhabitant dwelling and activity.

3.2 Analytical results

Over 43 analytical tests including several chemical parameters were conducted in the monitoring study. The results conducted in the study indicated that NO_3- N, NO_2- N, PO_4- P concentration in and 43 sampling sites of four springs ranged from 0-15 ppm, 0-6 ppm and 0-4 ppm, respectively, besides, COD and NH_4- N are 1-30 ppm and 0-1.5 ppm. Some of checked parameters were in the unusual ranges of contaminated surface water and comparisons between meaningful values of the analytical data show degradation of water quality at some sampling sites. Table 1 summarises briefly the mean values of river water sample at six sampling areas mentioned above.

The major anions present in river water are chloride, sulfate and nitrate (Table 2). These ions result primarily from the dissolution of rocks and minerals or from discharges of municipal or industrial sources. Excessively large concentrations of major ions are objectionable in drinking water because of possible physiological effects, unpalatable mineral tastes, and greater costs because of corrosion or the need for additional treatment (U.S. Environmental Protection Agency, 1986). Sources for sulfate and chloride in the Han River may be related to restaurant services as well as resident activities along and near the river sides or from wastewater-treatment and industrial discharges Additional sources include seepage from ground water affected by the dissolution of marine sediment, concentration by irrigation, and seepage from sewage lagoons, which tend to be enriched in sulfate and chloride. Therefore, a relation between pollution level and the presence of chloride and sulfate at sampling areas might be possible. Normally, these inorganic anions appear to be independent with other anions such as nitrate, nitrite and phosphate... in surface water. They are only closely related to cations which are usually appear in surficial water as sodium,

Table 3. The relation between chloride, sulfate (sulfur) with pollution level of the Han River water

Area on map	Area name	Salt ratio [Cl]/[S]	[Cl]+[S]	COD mean	NH_4-N mean	NO_3-N mean	NO_2-N mean	PO_4-P mean
1	Namyangju city	4.49	33.29	12.8	3.44	1.72	0.71	1.38
2	South Namyangju city	2.09	21.16	7.2	0.05	1.25	0.12	0.1
3	Kyungahn	4.22	55.91	6.3	3.37	3.54	0.73	0.32
4	Southern side of NamHan river	2.19	9.84	1.0	0.02	1.39	0.00	0.00
5	Northern side of Namhan river	3.48	12.87	1.5	0.55	1.29	0.04	0.19
6	Bukhan river	1.81	8.36	1.4	0.14	1.30	0.01	0.01

calcium... However, water samples collected in March 2002 from four springs of Han river showed this assumption that were used to help define the water quality in that part of the study area.

3.3 "Percentage of salt ratio" and "salt level"

The calculation of chloride and sulfate-sulfur concentration at each area showed a relation between salt ratio as well as their sum and other parameters. The highest value of salt ratio and the secondly highest sum of chloride and sulfate-sulfur are responsible for Namyangju city, one of most polluted areas, (Table 3). The assumption is simply derived from the reasons mentioned above. In fact, the data showed relatively match evidences including the mean value of nitrate in Namyangju city. Similarly, the lowest of the formers match with Bukhan river, the cleanest area in this study. This correlation is not the proportional increase of salt ratio or sum with other data of NO_3, NO_2, COD... but the water quality might be classified in concerning with these parameters. Following the idea, the salt ratio of Bukhan and Namyangju city is regarded as reference values for the most unpolluted and polluted level, respectively in scale

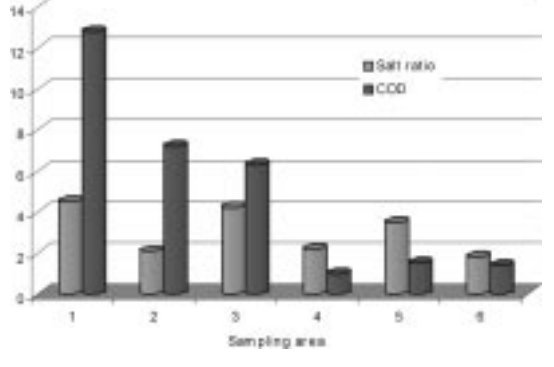

Fig. 2. Relation between salt ratio and mean value of COD at six sampling areas. The numbers on the horizontal axis from 1 to 6 represent for the sampling areas of Namyangju city, Southern Namyangju city, Kyungahn, Southern Namhan river, Northern Namhan river, Bukhan river, respectively.

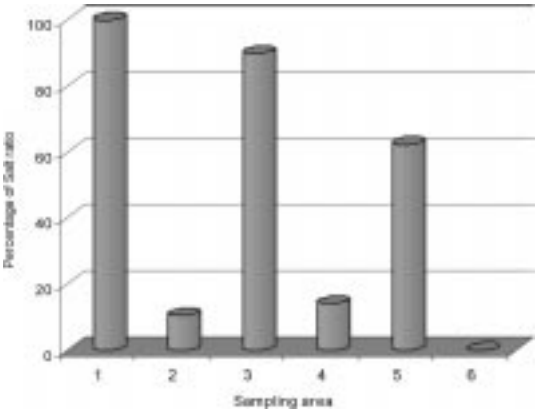

Fig. 3. Classification of water quality at sampling areas in Han river with salt ratio. The numbers on the horizontal axis from 1 to 6 represent for the sampling areas of Namyangju city, Southern Namyangju city, Kyungahn, Southern Namhan river, Northern Namhan river, Bukhan river, respectively.

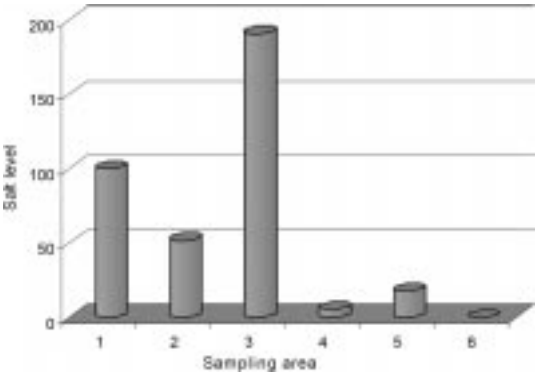

Fig. 4. Classification of water quality at sampling areas in Han river with salt level. The numbers on the horizontal axis from 1 to 6 represent for the sampling areas of Namyangju city, Southern Namyangju city, Kyungahn, Southern Namhan river, Northern Namhan river, Bukhan river, respectively.

from 0-100 (Fig. 3)

The parameter that so- called "percentage of salt ratio" is based on the idea of salt ratio. The verification with the quantity of chloride and sulfur, the result that presented the most polluted area in six, was relatively satisfied. Kyungahn is indicated as the outstanding amount of chloride and sulfate-sulfur (Fig. 4); this is fairly closed to the presentation of salt ratio although the

overwhelming of Namyangju city was reserved. Mean value of nitrate also performed to be the top quantity in Kyungahn. The so-called "salt level" played as a role of parallel parameter in order to confront with the estimation index. Deviation of the second index might be explained with the unequal number of sampling sites in each area and the improper distribution of sample collection. However, the water quality in sampling areas was possible to be initially estimated through these values.

The numbers on the horizontal axis from 1 to 6 represent for the sampling areas of Namyangju city, Southern Namyangju city, Kyungahn, Southern NamHan river, Northern NamHan river, Bukhan river, respectively.

4. Conclusion

The study undertaken aimed to point out the relation between contamination level of Han River water and values of chloride and sulfur as well as differentiate various areas in term of general estimation. Following the "salt ratio" , "percentage of salt ratio" and "salt level" classification, the most polluted area was around Kyungahn and the cleanest one was Bukhan river. Although it is not yet possible to become systematically proper criteria as water references, the correlation of pollution status and these components is obvious. The fact that the sources of surface contamination include industrial, municipal wastewater as well as river -side inhabitant activities added to the discharge into the river caused the gradual degradation of river water.

Since the Han River quality will be increasingly dependent upon by the inhabitants of riverine areas, timely plans should be made by local authorization to reserve this drinking water source.

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