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The evaluation method based on the concentration of salinity and sulfate by ion chromatography on surface water

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Normally, abundant inorganic anions such as chloride and sulfate…ect have not being considered in the general assessment of surficial water quality while they coexist with other spices in various forms. However, there obviously exists the correlation between the presence of these anions and water property and so the water pollution level in water environment. The index of pollution (IP) is based on the so-called "salt ratio" between concentrations of chloride and sulfate as sulfur ($[Cl^-]$/ $[SO_4^{2-}$-S]) could be used as the parameter of contamination level of water by human activities. In case of Han River, an important water supply source, the performance of COD, Cl, SO_4 and Cl/ S ratio indicated the feasibility of using this new parameter in water evaluation after samples had been periodically collected and tested with ion chromatography and test kit. The result showed the correlation between contamination level and salt ratio. Water quality of area was regarded to be clean in case salt ratio less than 2, otherwise, to be more polluted in term of general evaluation.

Key words:choride, sulfate, salt ratio, IC, pollution, monitoring

1. Introduction

In the age of industrialization and modernization, the concern over regional and national quality issues regarding inorganic anions for rivers, lakes and seawater have being increased. Many of the river basins are locations of intensive farming and so the issues of nutrient pollution from agriculture to aquifer sources and stream runoff and the changing patterns of agriculture and fertilizer usage.[1] Increasing population pressure has compounded the water contamination by increasing nutrient loads to surface water and rivers and by decreasing nutrient dilution potential by increasing water abstraction for drinking water, farming and reservoir use.[2] There are the abundance of pollutants in surface water such as nitrogenous, phosphorous compounds, chloride, sulfate, heavy metals, organic compounds and POPs (primary organic pollutants like PCBs, organochloride, pesticides in fertilizer, ect…) These substances coexist and perform their influence on the others in aquatic environment. The levels of inorganic anions could contaminate the ground water as well as the source of drinking water. Therefore, the correlation between contamination levels of inorganic anions and their possibility Unfortunately, the contents as well as roles of chloride and sulfate were neglected due to their obvious presence and consistency while they still have positions of certain relations.

In the simultaneous determination of water samples from various sites on the river with the analytical method for natural water, seven widely present inorganic anions as well as COD were determined by ion chromatography and test kit, respectively. The results represented the ratio of chloride ñ sulfate as sulfur ($[Cl^-]$/ $[SO_4^{2-}$ -S]) that so ñcalled "salt ratio" of each sampling site varied with concentrations of other contaminant factors such as nitrate and COD. Hence,

this ratio was expected to use as an index of pollution (IP) in assessment of surface or ground water quality. The present study will review the level of pollution in aspect of IP from the samples collected at Paldang water reservoir in April 2002.

2. Experimental

2.1 Sampling

The water samples were collected at 54 sites of the river and river streams and stored in plastic sampling bottles. The measurement with IC was directly implemented by filtration through 0.45 μm PVDF filter tip from 2 ml syringe.

2.2 Reagents for ion chromatography

Deionized ultra pure distilled water produced by Milipore Milli-Q reagent system with conductivity of 18.2 MΩ cm was used to prepare eluent and regent. Sodium carbonate and sodium bicarbonate (Kanto, Tokyo Japan) of reagent grade were used as the eluents.

All the anion standards were prepared using analytical grade reagents (Kanto, Tokyo, Japan and Samchun, Korea).

2.3 Instrumentation and experimental conditions

The chromatography was performed using Dionex DX -80 ion chromatography with 10 μl loop. The system components consisted of one IonPac® AG14A anion guard column (3×30mm) and IonPac® AS14A (3×150mm) separator column are used for simultaneous separation of anions. The eluent delivered to the column at isocratic flow rate of 2ml.min^{-1} was prepared at concentration of 8mM Na_2CO_3 and 0.1mM $NaHCO_3$. The regenerant was the solution of 28mM H_2SO_4 98%. The ion chromatographic parameters were summarized in Table 1.

2.4 Operational

The sample was loaded through a 2ml plastic syringe to the loop. After injection, the separation occurred on an anion exchange chromatography column (AS14A).

Table 1. The chromatographic condition

Eluent	8mM Na_2CO_3 & 0.1mM $NaHCO_3$ (under nitrogen)
Regenerant	28mM H_2SO_4 98%
Flow rate	2ml.min^{-1}
Separation column	Ion pack AS14A (Dionex) 3×150mm
Guard column	IonPac® AG14A (Dionex) 3×30mm
Injection volume	10 μl loop
Detector	DS5 Detection Stabilizer (Dionex)

On this high capacity column, carbonate/ bicarbonate eluent the anion such as chloride and sulfate were separated along with other ones within 12 minutes. Conductivity detection is sensitive enough for the concentration range of these anions

2.5 Ecotest-test kit

The test kit was based on the color comparison method to determine COD of each sample. The specific color of sample after adding reagents was developed then compared with reference color band. The concentration of analyte was dependent on the intensity of the color. This was a fast and convenient field test for environmental samples.

3. Results and Discussion

3.1 River water analysis

Water samples were obtained from 54 sites along the river branches as well as its streams in and around Seoul. The anion contamination levels were almost not severe in comparison with the mandatory Korea Drinking Water Norm (fluoride: 1.5 mg/L, chloride: 250 mg/L, nitrate: 10 mg/L, sulfate: 200 mg/L), however there were some exceeded concentrations of contaminants at several sites. The chloride to sulfate-sulfur ratio had been considered before hand in order to assess the intrusion level of sea salt. In this study, the ratio was expected to be a parameter that indicates the contamination level of river water. The contents of chloride and sulfate might be explained by the runoff of agriculture and rock mountain, the intrusion of sea as well as industrial discharge. The calculation of salt ratio

Table 2. The calculation of salt ratio and parameters at sampling sites

Parameter \ Site	Bukhan River (1)	Kyungahn (2)	South Kyungahn (3)	South Han River (4)	Han River (5)
Mean value of COD	1.31	5.5	3.8	2.5	7.7
Mean value of Cl^-	5.67	25.7	40.86	8.68	16.29
Mean value of SO_4^{2-}-S	3.4	6.78	8.94	4.01	5.22
($[Cl^-]$/ $[SO_4^{2-}$-S])	1.67	3.79	4.57	2.16	3.24

and its correlation was shown in Table 2.

The average levels of chloride and sulfate were relatively high in most of the samples. Table 2 showed the lowest level of mean COD at Bukhan River area (1.31 mg/l) and the highest at Han River and Kyungahn area (7.7 mg/l and 5.5 mg/l). The corresponding salt ratios of these areas simultaneously presented interesting values indicating the correlation among them. It was seen that the high concentration of chloride over sulfate was possible to partly characterize the quality of water. The plentiful appearance of such as anions chloride as well as sulfate could be the consequence of water contamination involving not only in themselves but also the other spices. Therefore, the salt ratio was considered and in fact the satisfaction could be reached with the collected data. In the study,

Fig. 1. The correlation of chloride, sulfate, salt ratio and COD at sampling sites.

the general sampling site was divided following the river branch and the features of river location. At five areas investigated, we were seen in case salt ratio less than 2 (1.67 at Bukhan River), the water contamination was moderate in term of COD and some other parameters. Otherwise, higher pollution level of water seemed to be recognized as salt ratio above 2 (3.79, 3.24 at Kyungahn and Han River area, respectively). This was represented in Fig. 1.

4. Conclusion

Sampling work of river water covered a large area of Han River had been investigated in April 2002. Inorganic contaminant anions (F^-, Cl^-, NO_2^-, NO_3^-, PO_4^{-3} and SO_4^{-2}) and COD were chemically determined by ion chromatography and test kit named Ecotest, respectively. The results represented a relation between the chloride to sulfate- sulfur ratio ($[Cl^-]/[SO_4^{2-}\text{-S}]$) so called "salt ratio" and pollution level of water. The data showed that in case of salt ratio was less than 2, water at that area was regarded to be clean; on the other hand, polluted areas were where the salt ratio appeared above 2. The number and framework of this study may insufficient enough to widely apply in environmental assessment but this work was expected to contribute a meaningful idea into water monitoring and evaluation.

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