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Relationship Between TOC, Oxygen Demanding Values and Na, Cl Ion Concentrations in the Sum River and the Wonju Stream Area

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Relationship between the various oxygen demanding values and concentrations of Na, Cl ions in Sum river and Wonju stream were investigated. r^2 value between TOC and, sodium and chloride ions turn out to be 0.7124 and 0.7237, respectively which implies strong relationship between theses physical data. r^2 values between Na and other oxygen demanding values, such as BOD, COD_{Mn} and COD_{Cr}, showed rather poor relationships. r^2 values between Cl and other oxygen demanding values also provided poor relationships. The r^2 values between Na and Cl ion concentrations were 0.9705. These data means the major source of Na and Cl ion is the ionization of NaCl which might be come from city sewage. As seen on Kim's previous paper, the increase of NaCl concentration is due to the city sewage, and these data implies the major contribution of increasing TOC value in Wonju stream and Sum River can be a city sewage.

Key words: TOC, BOD, COD, Oxygen demanding value

1. Introduction

TOC, BOD and CODs have been used as a classical ruler of water contamination. TOC stands for 'Total Organic Carbon' and this value should be very related to BOD and COD values since the latter values are obtained by oxidation of organic compounds in water, mainly. However, the difference of oxidation method and potential results in difference of BOD, COD values.[1)]

We assumed that the water contamination by alkylylphenol and bisphenol A[2)] in Wonju stream and Sum river can be mainly due to the city sewage. We investigated this hypothesis and the results are quite satisfactory. As seen on Kim's paper,[3)] the total sums of nonylphenol and bisphenol A (SNB) are very closely related to the concentration sodium ion which might be derived from NaCl of city sewage.

This result was fascinate enough for us to make another assumption which the major organic contamination of Wonju stream and Sum river could be city sewage. If this assumption is correct, the TOC, BOD or COD values should be increased directly proportionally to the increase of sodium and chloride ion concentrations but not to the other ions.

Water samples from 12 different sites of Wonju stream and Sum river area were obtained at dry season of May 2002.[4)] Na, Mg, K, Ca, Pb, Hg ions and Cl, SO_4, PO_4 ions were selected for cation and anion respectively, and the concentrations were determined. TOC, BOD, COD_{Mn} and COD_{Cr} values were also carefully measured.

Sum river is one of a branch of upper area of south Han river. The water of Sum river is eventually reached to Paldang which has been used for drinking water source of Seoul - national capital with more than 10 million population. Wonju stream penetrate Wonu city then passed thru cultural area and factory area as well. From a glance view, Wonju stream considered to have various contaminating source but indeed, benomyl - one of the most popular pesticide - was not detected over MDL. According to the nature of the factories in Wonju area, organic contaminating material is not expected to

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be released a lot to Wonju stream. These information leads us to eliminate cultural and factory areas as a major organic contaminating source. Naturally it concludes to that the major organic contaminating source of Wonju steam might be a city sewage.

Alkylphenols are generated from the decomposition of surfactants and mainly found in city sewage. Our previous results reported that the concentration of the sodium ion is very proportionally varied upon the concentration of alkylphenols. This indicated the major source of NaCl can be a city sewage also. If our assumption - major organic contamination source is city sewage - is correct, the concentration of Na or Cl should be increased on proportion to the TOC value.[5)]

2. Materials and Methods

2.1. Sampling

Water samples from 12 different sites of Wonju stream and Sum river area were obtained at dry season of May 2002 (Fig. 1). Sum river is one of a branch of upper area of south Han river. Amber bottles for water sample were washed with distilled water and methanol sequentially then dried before use. All the sampling bottle was equipped with polytetrafluoroethylene (PTEE) lined screw cap to minimize the cross contamination.

Water samples for cation were obtained under the regulation of U.S. EPA's "Sampling and Analysis Methods". Since our major purpose of the research is investigation of relationship between ionic species (cations, anions) and TOC or oxygen demanding values, repeating experiment with rainy season sample which can be easily diluted by the rain was not performed.

2.2 Reagents and Apparatus

Benomyl was analyzed by LC/MS-TOF (Waters, Me690/Micromass, LCT) with μBondapak C18 as a analytical column.

Cationic analysis was performed with ICP-MS (Varian, Ultramass) and Mercury analyzer (Cetac, M-6000A), and anions were analyzed by ion Chromatograph (Metrohm, 761 Compact IC). TOC was analyzed by Dohrmann (Phoenix 8000) and BOD, CODs were determined under the regulation of US EPA methods.

All the standard reagents materials for analysis were purchased from TCI (Japan), Sigma-Aldrich or Inorganic Venture company. The purity of those reagents are guaranteed over 97% or equivalent. Pesticide grade methanol and methylene chloride were used and purchased from J. T. Baker. All the other used solvents were also pesticide grade. The purity of nitrogen gas for blowing was over 99.999% to minimize the contamination.

2.3. Sample preparation and Analysis

2.3.1. Benomyl

To 2 L of erlenmeyer flask, 1 L of aqueous sample

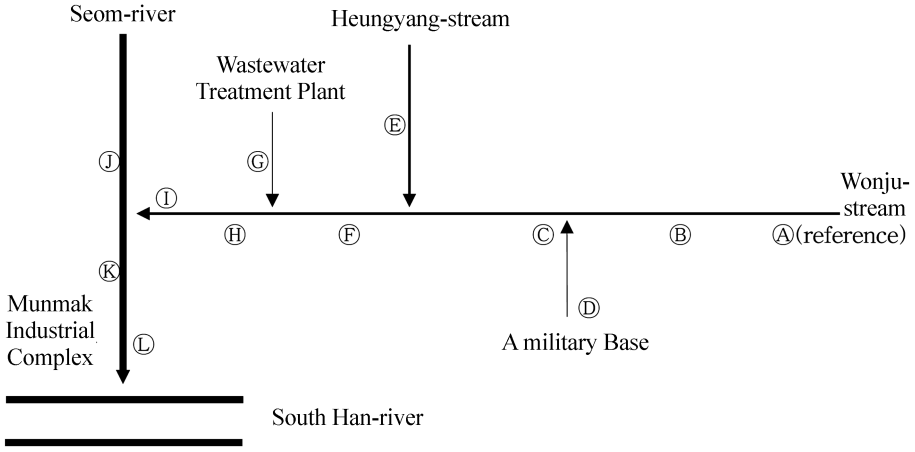

Fig. 1. Sampling sites, in the Sum river and the Wonju stream.

was placed, then treated with 1:1 sulfuric acid to adjust the pH below 2. The resulting sample was stirred for 3 hours at room temperature then added saturated NaOH solution to increase the pH around 6. The sample was transferred to 2 L separatory funnel and extracted with 80 mL of methylene chloride. Repeat extraction two more times and the all the combined organic layer was dried over anhydrous sodium sulfate then concentrated to 1 mL by Kunderna-Danish (K-D) concentrator. Cool down the K-D concentrator and washed with 5 mL of methanol then concentrated to 0.5 mL final volume by nitrogen blowing. These pre-treated samples were analyzed by LC/MS-TOF SIM(Selected Ion Monitoring).[6)]

3. Results and Discussion

The analysis were performed under the methods and regulation of Japan SPEED 98 or U.S. EPA.

The 12 samples were collected from upper area of Wonju stream thru downward to the merging point to the Sum river, and from Sum river merging point thru to the South Han river merging point. Benomyl[7)] was analyzed from 8 samples which were collected from the sites located contamination source nearby. Anionic and cationic chemical species were analyzed from all 12 samples. Since benomyl was not detected at any site, we assumed that the agricultural contamination effect is not great enough. The sample obtained from the most upper ares of the stream was selected for a background concentration. The background concentration of Na and Cl ions were 2.76 and 2.86 mg/L, respectively (Table 1).

The relationship between sodium ion concentration and BOD, TOC and CODs (Table 2) were depicted (Fig. 2). The correlation value (r^2 value) between sodium ion and BOD was not good enough (r^2=0.3433). The r^2 values between sodium ion and TOC, CODMn and COD_{Cr} showed relatively good lineality with 0.7124, 0.6446 and 0.6817, respectively. Since we assumed that the major part of organic contamination and NaCl are influxed from city sewage, it is well understandable that the r^2 value of TOC showed best linearity to the concentration of sodium ion. The COD values are also dependable to the concentration of organic species in

Table 1. Concentrations of ionic species.

		A	B	C	D	E	F	G	H	I	J	K	L
cation	Hg*	0.06	0.05	0.05	0.05	0.10	0.04	0.03	0.10	0.09	0.08	0.05	0.10
	Pb*	0.18	0.44	0.26	0.59	0.25	0.53	0.45	0.24	1.01	0.37	0.78	0.38
	Ca**	6.62	26.60	36.01	28.75	21.96	21.30	12.64	26.37	26.63	16.63	12.93	21.14
	K**	6.91	10.02	5.45	9.39	8.75	10.63	17.25	10.59	11.01	2.58	16.85	10.61
	Mg**	1.87	3.65	5.81	3.60	2.70	2.44	1.75	4.59	4.84	2.48	1.84	2.41
	Na**	2.76	15.96	21.13	19.10	12.42	24.48	27.13	45.25	47.73	13.01	24.02	24.51
anion	Cl**	2.86	16.27	30.46	26.09	18.05	24.02	34.07	60.31	62.96	16.00	31.04	33.40
	SO_4**	6.27	13.64	20.60	16.45	10.58	17.32	12.08	23.05	23.11	8.98	11.65	14.44
	PO_4**	ND	ND	ND	ND	ND	ND	1.66	2.62	4.35	ND	2.11	1.00

*: unit=ug/L, **: unit=mg/L

Table 2. Physical data of sampling sites.

	A	B	C	D	E	F	G	H	I	J	K	L
Temp.(°C)	9.60	12.50	18.60	19.10	17.40	16.00	15.20	16.60	20.20	19.10	20.60	17.50
pH	8.98	7.53	8.12	8.56	8.75	7.71	7.14	7.30	8.19	8.52	8.26	8.83
DO	11.92	10.89	10.90	10.67	13.30	9.24	8.76	8.91	11.56	11.01	10.65	13.58
BOD	0.32	1.10	3.77	4.79	3.33	4.14	11.11	6.40	5.93	1.75	7.96	2.69
TOC	0.75	1.93	4.51	4,44	2.95	4.04	9.13	8.85	10.16	2.80	9.49	4.71
COD_{Mn}	1.40	3.50	7.20	7.21	5.70	7.60	10.80	9.80	12.20	4.60	12.50	8.30
COD_{Cr}	3.60	4.03	11.66	9.40	6.75	8.56	17.05	16.41	17.78	7.38	16.86	10.20

unit=mg/L

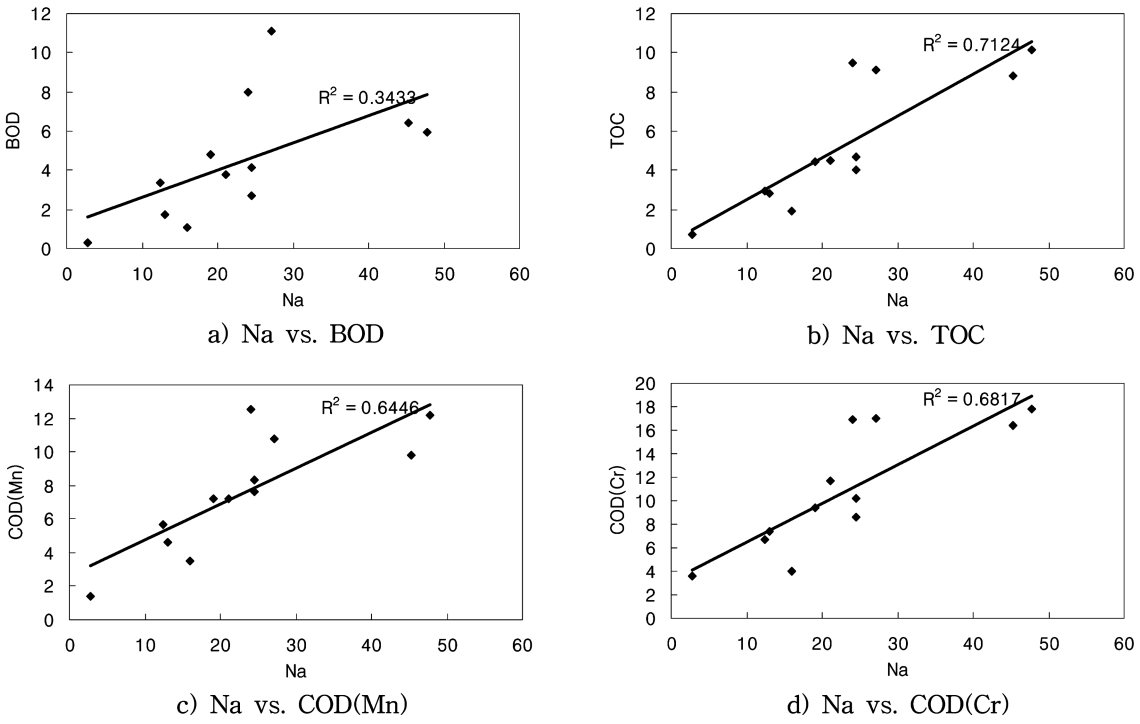

Fig. 2. Concentration of Na ion vs. BOD, TOC and CODs.

water. Actually organic compounds give major contribution to the COD value. However, the organic compounds which are very resistant to oxidizing reagents can reduce the COD values, and the portion of oxidation resisting chemicals in total organic compound is not either regulated or predictable at each sampling sites. The amount of easily oxidizing inorganic compounds can also be considered as a error although it effects a little to the value. BOD values are obtained from the result of biological degradation of organic compounds. These results are very sensitive to the nature of the organic compounds. Therefore, the BOD values are much more inconsistent to the amount of the organic species than COD values. Sodium chloride is ionized to sodium and chloride ions in aqueous phase. The r^2 value between sodium and chloride ions is very close to 1 (0.9705) which means the major contribution for the concentration of Na and Cl is NaCl salt (Fig. 3).

As expected from these data, the r^2 value between TOC and Cl is similar to that of between Na and TOC. It shows good linearity (r^2=0.7237). The linearity

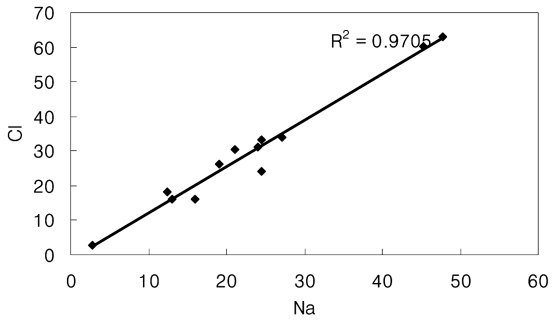

Fig. 3. Concentration of Na vs. Cl ions. (dimension=ng/L)

between TOC and the other inorganic ions was not good. r^2 values lie below 0.5 regardless cation or anion.

4. Conclusion

TOC and CODs in Wonju stream and Sum river were increased linearly in proportion to the concentration of Na or Cl ions. Particularly, TOC shows better linearity to the Na and Cl ions than COD. BOD shows no linearity to the Na and Cl concentrations. No detecton

of benomyl - popular pesticide - means the agricultural contaminating source was not greatly effect on TOC and CODs.

According to the result, we may use the Na or Cl ion concentration as a rough estimation of COD or TOC value in the water. But this result is strictly applicable only to Sum river and Wonju stream and it is necessary to generalize this assumption by broadening the research to the nationwide water system.

Acknowledgements

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