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Author(s)	NAGASAWA, Mikio; TERAGUCHI, Teruaki
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Natural Purification of the Nishiyoge River*

Mikio NAGASAWA AND Teruaki TERAGUCHI

Faculty of Liberal Arts and Sciences

In recent years, water pollution of this river has aggravated while doing a great deal of damage to city water supply and become a serious social problem. The largest factor contributing to water pollution is organic waste water discharged from pig farms, followed by waste waters from poultry farms, domestic sewage, and industrial waste water. Clarification of natural purification of rivers is very important for rational treatment of city sewage and industrial waste water. The magnitude of natural purification was estimated from the value of the coefficient of natural purification K.

Water Pollution of the Nishiyoge River

The authors previously reported¹⁾ on water pollution of the Nishiyoge River. The Nishiyoge River is a small river with total length of about 14 km and average rate of flow 0.3-0.6 m³/sec and flows northward from Lake Sayama formed by

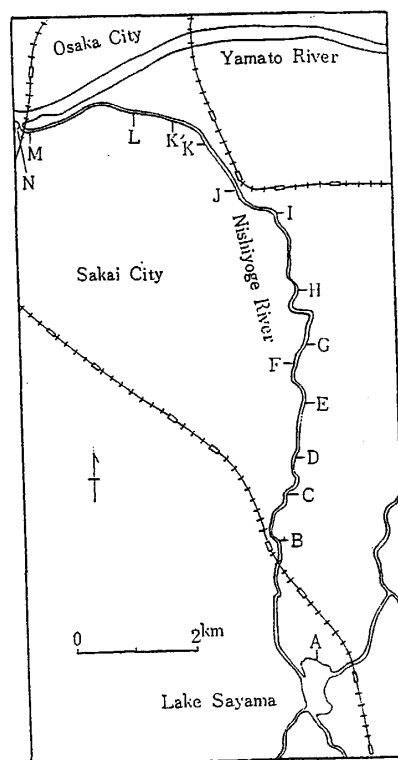


Fig. 1. Map of the Nishiyoge River showing the location of stations.

* This paper constitutes Part II of a series entitled "Water Pollution in Small Rivers."

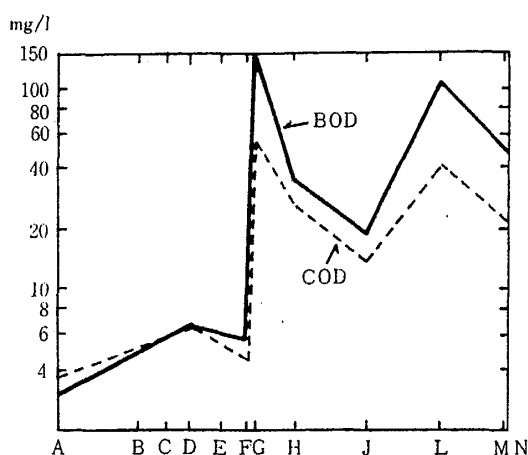


Fig. 2. Graph showing increase in BOD and COD with drift of the Nishiyoge River. Average data during the period of July-Nov. 1969.

damming up the Amano River and the Mitsuya River. The Nishiyoge River and observation stations A, B, C, ... N are shown in Fig. 1. Also, the changes in BOD and COD with drift are shown in Fig. 2. It can be seen that peaks are present at station G and station L, and at the end of flow, both are about 20 times larger than at the beginning. The degree of saturation of dissolved oxygen is below 50% at station L and frequently zero was measured at station M. That is, water pollution of the Nishiyoge River is due chiefly to domestic animal waste water flowing in at station G and station L.

The Significance of Natural Purification and Phelps Equation

The Significance of Natural Purification. As can be seen from changes in BOD and COD in Fig. 2, the water quality is highly polluted by domestic animal waste water flowing in at station G. BOD and COD become lower as the river flows downstream and it can be seen that these have become considerably lower at station J which is 3.4 km downstream of station G and at station K which is 5 km downstream. Also, the values at station M which is 2 km downstream of station L, the next pollution source, have decreased considerably. Numerous other dissolved substances also indicate similar changes. Needless to say, this is due to the natural purification of the river.

Natural purification refers to the process of purification of polluted water with passage of time in the natural condition, that is without receiving artificial water treatment. Now, if natural purification can be defined as reduction in concentration of pollutant at a specified point, simply dilution at that point with clear water can also be called natural purification. However, other factors which are important in the reduction of concentration of pollutant are change into non-polluting substance by chemical and biochemical changes, precipitation and adsorption to the river bed and escape into the atmosphere of volatile substances.

Clarification of natural purification of rivers is very important for rational treatment of city sewage and industrial waste water, prevention of water pollution scientifically and high degree of water utilization.

Application of Phelps Equation. It is considered that change in concentration with passage of time of organic pollutant present in rivers normally conforms to PHELPS equation.

$$C_B = C_A 10^{-Kt} \dots\dots\dots (1)$$

Eq. (1) is applicable when water flows downstream at a constant rate of flow but it is not applicable when a large amount of water goes in or out between A and B. HANYA et al. used²⁾ the following equation for such cases.

$$Q_A C_A = Q_B C_B 10^{-Kt_B} + q_1 c_1 10^{-Kt_1} + q_2 c_2 10^{-Kt_2} + \dots\dots\dots q_n c_n 10^{-Kt_n} \dots\dots\dots (2)$$

Also, TAMBO and MORI took the sum of deoxygenation constant k and coefficient due to precipitation and adsorption k' as \bar{K} , took this as the purification velocity constant or natural purification constant and used the following equation.

$$Q_{im} = M = M_0 e^{-\bar{K}t} \dots\dots\dots (3)$$

The authors investigated natural purification with COD and BOD between station G-J and station L-M as indices and have found that ① waste which flows in between these is small scale domestic sewage and consequently, each section can be considered as being a steady state, ② the rate of flow at the respective observation stations between station G and J, and station L and M are occasionally the same and ③ the concentration of chlorides among components which are determined simultaneously and which do not self-decrease is almost the same between station G and J, and station L and M, as explained below. In view of this, Eq. (1) was used as it is because it was assumed that each section can be considered as a closed system of equal rate of flow. And, the magnitude of natural purification was estimated from the value of the coefficient of natural purification K .

Method of Investigation

Investigation stations. As mentioned above, the largest polluting sources of the Nishiyoge River are station G and station L. In view of this, experiments were carried out between station G which is 6.1 km and station J which is 9.5 km, and also between station L which is 11.9 km and station M which is 13.9 km from the water source of Lake Sayama.

Time of Investigation and Determination Items. Sampling and analysis of water were carried out at 4 hour intervals at station G and station J for 16 days from December 14, 1969. Determinations were made on COD, chloride, and sulfate. Sampling and analysis of water were carried out at 4 hour intervals at station L and station M for 28 days from March 26, 1970. Determinations were made on BOD, COD, residue on evaporation and electrical conductance. Necessary investigations were also carried out at other times.

Flow Time. The correlation coefficient of index substances (COD value, etc.) at an arbitrary time t at station G and station L, and $t + \Delta t$ at station J and station M was obtained. The time when the correlation coefficient is the maximum was taken the flow time.

Selection of Pollution Indices. Generally BOD is used as the index of pollution in investigation of natural purification of rivers. However, some opinions have been expressed recently to the effect that, depending on the conditions, COD is more suitable as the index. The authors used BOD and COD as indices and at the same time, determined sulfate and residue on evaporation as inorganic components which indicate self-decrease. Electrical conductance was also measured and used as

reference.

Method of Analysis. Water was sampled and the temperature measured at each investigation station, ① pH measured by colorimetry and electrical conductance measured with a portable conductivity meter in the field but measurements were also made with a pH meter and conductivity meter provided in the laboratory in order to assure accuracy. ② Dissolved oxygen was measured by sampling the water with a 100 ml injection syringe and analyzing by the azide modification of iodometric method.⁴⁾ ③ COD was obtained by the acidic oxidation method using potassium permanganate and heating for 15 minutes in boiling water but basic oxidation method was also used. ④ BOD₅ was determined by the 5 day dilution method at 20°C, ⑤ sulfate by the barium sulfate gravimetric method, ⑥ chloride by the Mohr argentometric method and mercuric nitrate method and ⑦ residue on evaporation was obtained from the total residue.

Estimation of the Coefficient of Natural Purification From Measured COD and BOD.

Measurement of COD Between Station G-J. The measurement results of COD at station G and station J are shown in Fig. 3. The range of fluctuation at station G is large as it is 10 - 100 ppm; it is minimum at 6 hours; and maximum at 18 hours. It is clear from this that waste water is discharged from the swinery at this time. The range of fluctuation at station J is 10 - 30 ppm and it is clear from this that there is a time lag of about 4 hours. The flow time t was obtained by the abovementioned method and this was 0.188 day. The COD value after this flow time was obtained and this was

$$K=1.52 \text{ (1/day)}$$

from Eq. (1).

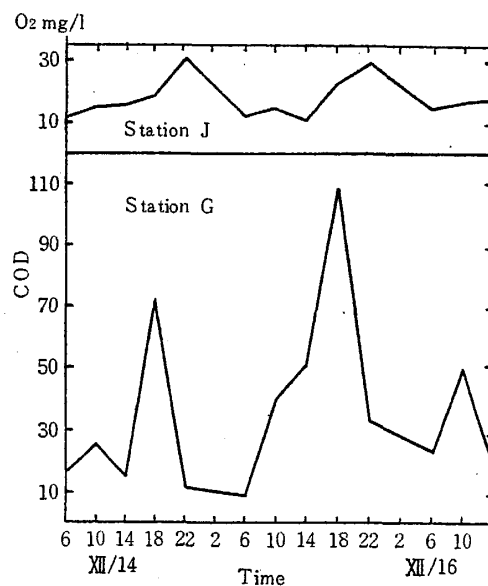


Fig. 3. Time-lapse variation of COD at station G and station J on Dec. 1969.

Measurement of COD and BOD Between Station L-M. Similarly, the fluctuations in COD and BOD between station L-M are shown in Fig. 4. BOD at station L indicated a minimum of about 110 ppm at 22 hours, a maximum of 310 - 330

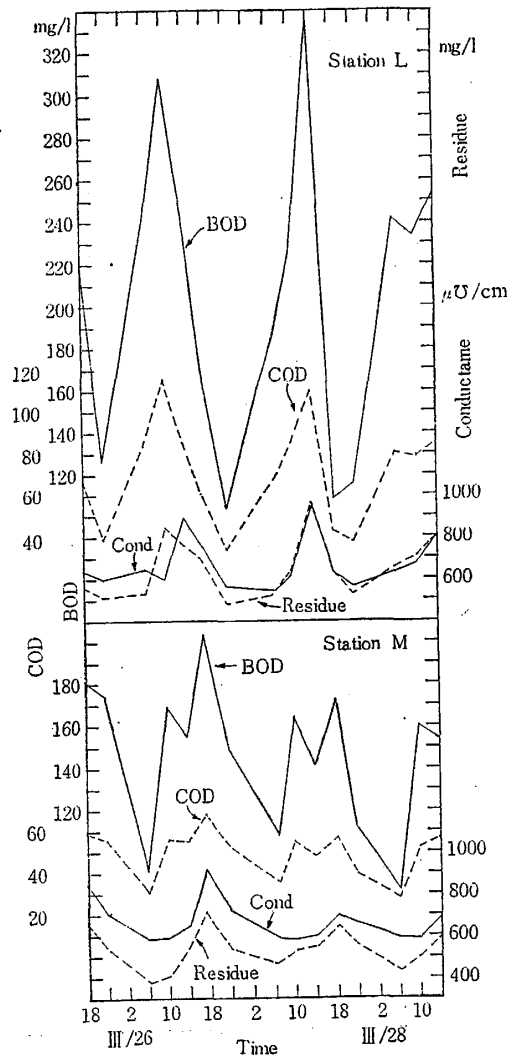


Fig. 4. Time-lapse variation of COD, BOD, residue on evaporation and conductance at station L and station M on Mar. 1970.

ppm at about 14 hours; and at station M, the peak becomes lower from 90 to 200 ppm. The maximum lags 18 hours and the minimum 6 hours. COD indicates similar fluctuation but it is between 30 - 110 ppm at station L and 30 - 70 ppm at station M. Correlation coefficient was obtained in a similar method as mentioned above and the flow time obtained. COD was 0.28 (day), and BOD 0.25 (day). From Eq. (1), $K_{\text{COD}}=0.53$ (1/day) and $K_{\text{BOD}}=0.57$ (1/day).

Also, it can be seen in the figure that the time lag of peak was 8 hours, from 10 hours to 18 hours, on March 26th and 4 hours, from 14 hours to 18 hours, on March 27th. This tendency is exactly the same for residue on evaporation and electrical conductance. Consequently, the flow time becomes the average value of both by this method. Although these values are somewhat questionable, it was decided to use them.

Measurement of Deoxygenation Constant

$\text{BOD}_1\text{-BOD}_7$ were measured by the slope method⁶⁾ and the deoxygenation constant k and first stage BOD were obtained. The values shown in Table 1 were

Table 1 The Values of K, k and k'

	Stations	K (1/day)	k (1/day)	k' (1/day)	Date
BOD	L-M	0.57			Mar. '70
	L		0.19		Mar. '70
	M		0.21		Mar. '70
	G		0.21		Nov. '69
	L		0.19		July '70
	L		0.20		July '70
	L ^{a)}			0.35	July '70
	L ^{b)}			0.14	July '70
COD	G-J	1.52			Nov. '69
	L-M	0.53			Mar. '70
	L ^{c)}			0.05 ₅	Mar. '70
	M ^{c)}			0.07	Mar. '70
	L ^{a)}			0.10	July '70
	L ^{b)}			0.04	July '70

a) Supernatant liquid after it was left standing at 20°C.

b) Air blown in by bubbling continuously at room temperature of 25-32°C.

c) Supernatant liquid after it was left standing at room temperature.

obtained at measurement stations G, L and M. k is a constant value of about 0.20 irrespective of the measurement station and season.

Estimation of Coefficient of Decrease From Laboratory Experiment

The coefficient of natural purification obtained from laboratory experiment was taken as the coefficient of decrease k' . k' was obtained and this was compared with K.

Coefficient of Decrease With Respect to BOD. The sample taken at station L on July 13, 1970 was used. Water was sampled at intervals of 24 hours for 1 - 7 days and BOD₅ was measured for the 3 kinds of samples of (a) supernatant liquid after it was left standing at 20°C, (b) air blown in by bubbling continuously at room temperature of 25 - 32°C and (c) (a) stirred when sampled, and k' was obtained from Fig. 5. As a result, k'_{BOD} values of 0.35 (1/day) at (a), 0.14 at (b) and 0.14 at (c) were obtained.

Coefficient of Decrease With Respect to COD. The coefficient of decrease with COD as the index obtained by using the same sample was 0.10 at (a), 0.04 at (b) and also 0.04 at (c). Also, k' measured with samples from station L and station M obtained on March 26, 1970 was 0.06 at station L and 0.07 at station M for supernatant liquids obtained by standing at room temperature. At any rate, the value of k'_{COD} is small and is almost linear. KOYAMA and TAMBO⁷⁾ carried out similar experiment and has reported that reduction in COD could not be observed in the range of the experiment and was almost constant. It was therefore decided not to use k' of COD as an index.

In Case of (a). Suspended solid decreases rapidly between 1 - 7 days and becomes zero on the 4th day. The degree of saturation of DO which was 30% decreased rapidly and became 0.1-0.4% by the 4th day. It began to increase again

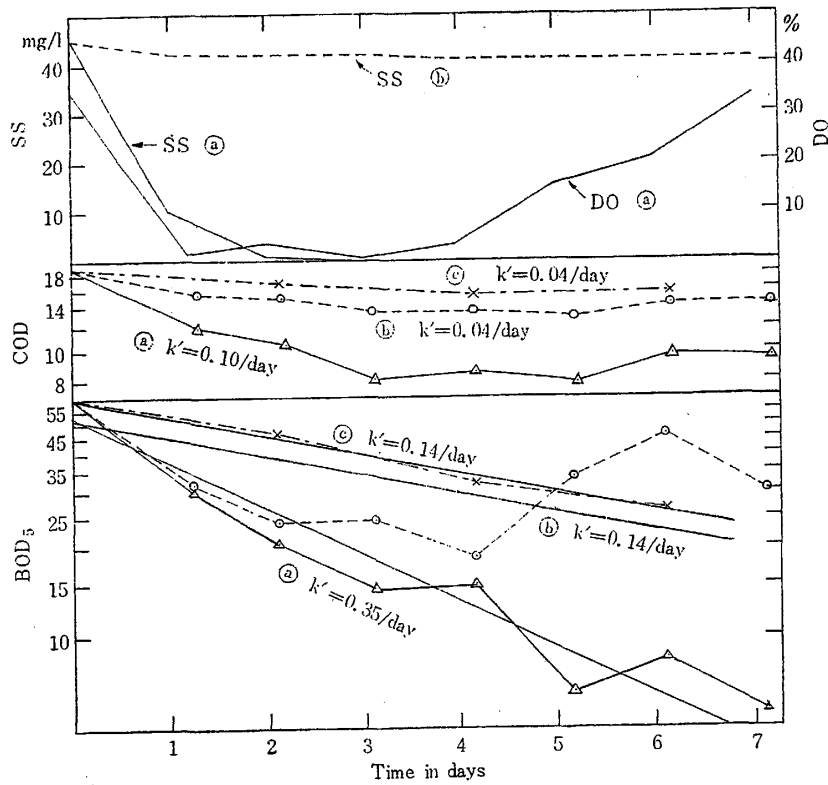


Fig. 5. Relation between suspended solid dissolved, oxygen and coefficient of decrease with BOD and COD.
 (a) Supernatant liquid after it was left standing at 20°C.
 (b) Air blown in by bubbling continuously at room temperature of 25-32°C.
 (c) (a) stirred when sampled.

Table 2 Coefficient of Natural Purification, K, of Several Rivers in Japan

Rivers	K (1/day)	t (day)	Date	Analysts	Indication
Honmyo R.	0.82~8.96	0.208~0.052	Oct.-Dec. 1962	Yamaguchi and Eida, 1963	BOD
Ishikari R. (Mid-stream)	1.20		June-Oct. 1959	Tambo and Mori, 1961	"
"	0.58		Nov. 1959	"	"
Ishikari R. (Kamuikotan-Fukagawa)	0.26~0.38		Janu. 1958	Horasawa, 1959	"
Kiso R. (nearby Ōi)	0.24	0.81		Tanabe, 1955	"
Nishiyoge R. (Down stream)	0.57	0.25	March 1970	Nagasawa and Teraguchi, 1970	"
"	0.53	0.28	"	"	COD
Nishiyoge R. (Mid-stream)	1.52	0.19	Nov. 1969	"	"
Oga R.	1.84	0.12		Tanabe, 1955	BOD
Sagami R. (Down stream)	0.32	0.29		Suishitsu-odakuboshikyogikai, 1956	"
Tama R.	0.33~0.58		July-Aug. 1964	Hanya et al, 1967	COD
Yodo R. (nearby Kammaki)	1.55	0.21		Tanabe, 1955	BOD
Yodo R. (Hirakata-Torigai)	0.75	0.1	Dec. 1958	Iwai et al, 1960	"

from the 5th day and exceeded 30% on the 7th day.

In Case of (b). Suspended solid was almost linear and BOD₅ value was only larger than that of (a) on the 4th day but it began to increase from the 5th day. As a result, k' value becomes small as it was 0.14. k' value of (c) is 0.14 and is approximately the same as that of (b).

That is, the fact that the k' values of (b) and (c) are approximately the same confirms TAMBO's opinion that k' value differs with season but there is almost no change at the experimental temperature. Also, as there was almost no difference as a result of bubbling air, the largest cause of the difference in k' value is whether the sample has been left standing or stirred. Suspended solid settles rapidly during the time the sample is left standing and a large amount of oxygen is consumed for decomposition of organic substances. Consequently, DO is present in trace quantity up to the 4th day and then the balance begins to shift toward the excess side from the 5th day. Sample which has been stirred at room temperature indicates almost the same tendency up to the 4th day as the quantity of oxygen demand for microorganisms to act is constant and the presence of an excess of oxygen does not have such a large effect. BOD₅ increases from the 5th day as separate production of organic compounds starts by decomposition of the suspended solid and the kind of substance to be decomposed changes. It is believed that the condition in an actual river is between (a) and (b) and is closer to (b). Consequently, a value between 0.35 and 0.14 for k' is probably more realistic.

A summary of the above results are given in Table 1.

Now, let us consider $K=0.57$ and $k=0.20$ for BOD. The k value is not a value for BOD₅ but for BOD₁-BOD₇. Consequently, it is not suitable to compare both as they are but as the k value is a value resulting from pure biochemical reaction, it is confirmed that the purification effect by precipitation and adsorption of pollutant to the river bed is considerably large. If a value between 0.35 and 0.14 is assumed to be suitable for k' value, it can be considered that it is approximately the same as the k value.

Change in Inorganic Salts and Coefficient of Natural Purification

When estimating the coefficient of natural purification, determination of chloride is carried out with the same sample. Chloride becomes an index for substances which do not indicate self-decrease as it does not receive almost any biochemical effect, chemical change or the effect of precipitation and adsorption.

Change Between Station G-J. Fig. 6 shows the change in chloride between station G and station J. A curve which resembles that of COD in Fig. 3 is obtained. That is, the peak of station G is at 18 hours and that of station J at 22 hours. Such lag in peak is understandable but there is no decrease at station J and rather, there is a tendency of some increase. The values of chloride with flow time of 0.208 day interval are $C_G = 465.7$ ppm, $C_J = 491.4$ ppm and $K = -0.259$.

The change in sulfate measured at the same time is shown in Fig. 6. $K = 1.22$ at flow time of 0.292 day. The ratio of the portion of decrease of sulfate due to precipitation and adsorption and that due to redox reaction is not known but it can be seen that it differs from chloride as decrease is very fast. The rate of decrease is 66.5%. The rate of decrease of sulfate is 63% when the rate of decrease of chloride 105.5% is taken as 100%. As the rate of decrease of COD is 52%, it becomes 49.3% when calculated by the same method. Consequently, K becomes 1.63 and is slightly larger than 1.52 when natural purification is expressed as the rate of

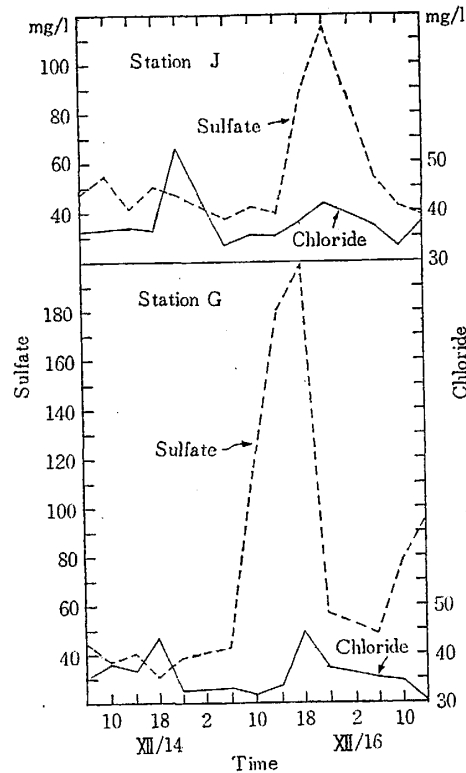


Fig. 6. Time-lapse variation of chloride and sulfate at station G and station J on Dec. 1969.

decrease of COD on the basis of chloride.

Change Between Station L-M. Similarly, the change in chloride of station L and station M was investigated. $C_L = 907.3$ ppm, $C_M = 857.6$ ppm and rate of decrease becomes 94.5% when flow time is 0.25 day. This was an increase of 5% between station G-J but is a decrease of 5% between station L-M. At any rate, it can be said that the chloride quantity of both is the same if measurement error is taken into consideration.

The residue on evaporation and electrical conductance were investigated by the same procedure. Both indicated similar curves as those of COD and BOD (Fig. 4). In case of residue on evaporation, $K = 0.274$ at $t = 0.241$ (day). The ratio of reduction of suspended solid in the amount of reduction of C_M is large. In case of electrical conductance, $K = -0.03$ at $t = 0.171$ (day). This increases slightly at station M. The peaks of COD and residue on evaporation are the same and only the peak of electrical conductance differs. Consequently, the flow time of electrical conductance becomes small and indicates a variety of changes with drift.

Discussion and Summary

The purification process of organic pollutant present in rivers differs with its properties and concentration, kind of water utilization of the river, and the biological and chemical properties of the river. The natural purification of the Nishiyoge River was investigated by the magnitude of coefficient of natural purification K . The observation stations investigated were between station G and station J, and station L and station M. It was found that maximum pollution source is present at station G and

station L.

K value was obtained by using Phelps equation as it is on the assumption that rate of flow was constant and there was almost no change at station G and station J, and station L and station M in the concentration of chloride in the dissolved components in which there is no self-decrease, the rate of flow which was measured occasionally was the same and there was very little inflow and outflow along the way. Flow time was decided by obtaining the correlation coefficient between the concentrations of COD and BOD indices.

The values obtained were $K_{\text{COD}} = 1.52$ between station G-J and $K_{\text{COD}} = 0.53$ and $K_{\text{BOD}} = 0.57$ between station L-M. The K value between station G-J was about 3 times larger in spite of the fact that measurements were made when the water temperature was low. The values were $K_{\text{COD}} = 0.94$ and $K_{\text{BOD}} = 1.60$ between station L-M August 1970 and indicates that the K value becomes higher the higher the water temperature. Also, the K values are generally higher near the pollution source. K values of our country's rivers obtained by other investigators are shown in Table 2. The feature of the K values of our country's rivers is that they are higher than those of the Ohio River. It is said that the reason for this is that there is active movement of water and consequently there is more opportunity of contacting air.

Also, the deoxygenation constant k obtained by the slope method from measurements of $\text{BOD}_1\text{-BOD}_7$ was 0.21 at station G, 0.21 at station M and 0.19, 0.19 and 0.20 at station L. It was 0.19-0.21 without any relation with the observation station and water temperature. It was found that in natural purification, the physical effects of precipitation and adsorption were about 2 times larger than the biochemical effect.

Also, coefficient of decrease k' was obtained for the 3 kinds of conditions. k'_{COD} was small and cannot be used as index. k'_{BOD} gave values of 0.35 and 0.14 but it is believed that an average value between these is more realistic. Consequently, k' and k becomes almost equal.

Acknowledgement

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