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소규모 정수처리장에서 모니터링 자료를 이용한 원수의 망간농도 예측에 관한 연구

Estimation for Raw Water Quality of Manganese Concentrations from Archived Data in Small-scale Water Systems

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Abstract

In small-scale water systems, the measurement of quality of raw water in running water is generally implemented when the quality of water is stable and frequency of measurement is low. However, units such as water temperature and pH, which are easily monitored, are frequently measured. In establishing an improvement plan for a water treatment system, the range of concentration of the target material present in the raw water of the running water provides relevant information. If the concentration of target material can be specified by the quality of water of data items that are measured daily, inverse estimation of the range of concentration is possible as well. In this paper, we took note of manganese in the raw water from Ogasawara-mura, Tokyo, and estimated the manganese concentration in the raw water of the running water for the past five years. Based on the results obtained, we have proposed a manganese removal system, considering the current situation and geographical conditions of Ogasawara-mura.

Key words : raw water quality, manganese, water treatment, correlation analysis, multiple regression analysis.

주제어 : 원수수질, 망간, 정수처리, 상관분석, 중회귀 분석

1. Introduction

Manganese concentrations in raw water for water supplies can be high when sampled from surface sources, such as lakes and marshes, and sub-surface sources such as ground water. Manganese in water exists in an ionic or colloidal state and is known to be absorbed into suspended micro particles and combined with organic matter including humic acid [1]. Manganese is a metal being oxidized slower than iron, and the oxidation rate is reduced at pH 9 or less. Manganese can also react with chlorine during the water treatment process and can cause unwanted tastes, odors, or colorations. Moreover, manganese that remains in running water becomes oxidized and deposited, producing a black tint in the water.

There are various methods of management, such as oxidation or manganese sand used for manganese

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treatment at water treatment plants. When new water treatment systems are proposed in areas where raw water manganese concentrations are high, the treatment method is selected according to the level of raw water manganese concentrations. However, most sites do not conduct water quality measurements except for characteristics that can be easily measured including pH, water temperature, and turbidity. These measurements are often collected when there is little variation in water conditions, but when water quality deteriorates because of heavy rain, plant personnel must allocate their time for the maintenance of uninterrupted water treatment operations, and in many cases water quality measurements are not conducted. Therefore, manganese concentrations during the deterioration of water quality are often uncertain. When changes or new plans for water treatment systems are proposed, estimation of the manganese concentration range is required in the selection of a manganese treatment system.

In light of these issues, the aim of this paper is to estimate over the past five years the concentration levels of manganese in raw water for water supplies at the Ogiura water treatment plant in Ogasawara-village, Tokyo. This facility provides a small-scale water system based on estimation results and establishes the most appropriate manganese treatment system for the target area.

2. Current situation of water treatment

Bonin Island (alias "Chichijima" in Japanese) is a small solitary island, which is a part of Ogasawara-village. It is located in 1,000km south of Tokyo. **Figure 1** shows the geography position of the island. The population of Bonin Island is about 2000 people. The population served by water supply as percent of total population is 100%, and the percentage of sewered population is also 100%.

The water treatment plant that was selected for this study has two mountain streams, four water reservoirs, and two wells as water sources. **Figure 2** shows the place in facilities related to water service.

The maximum quantity of scheduled daily water distribution is 1,100 m^3/day, and the maximum quantity of daily water intake is 1,140 m^3/day. Watershed areas are forests composed of subtropical trees with substantial leaf mold accumulated on the forest floor. Surface water flows down over this

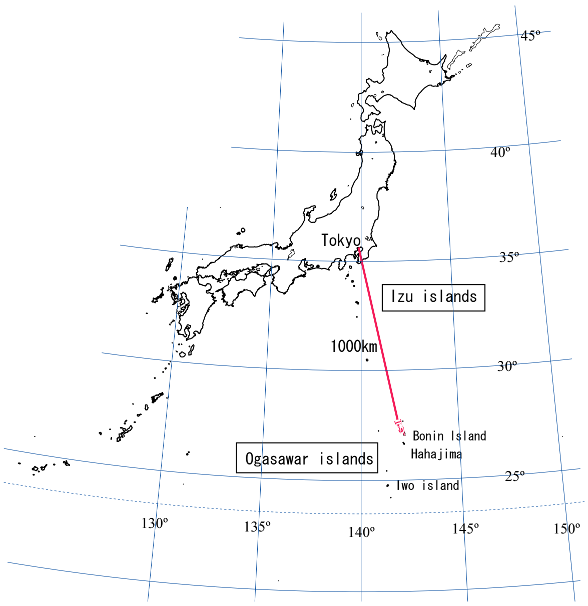

Fig. 1. The geographical location of Bonin Island

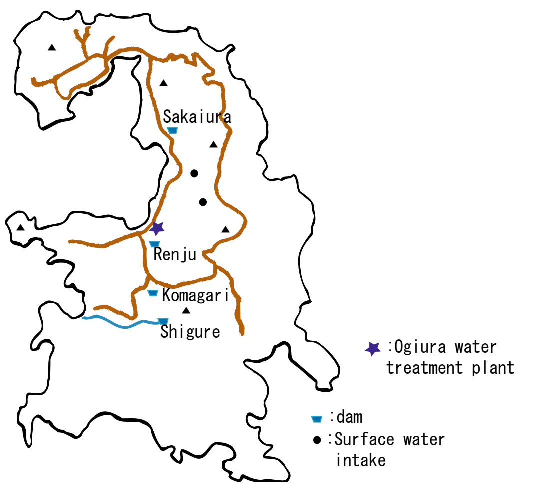

Fig. 2. The place in facilities related to water service in Bonin Island.

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organic matter, including humic acid, into the reservoir, which amasses a high concentration of organic matter. Moreover, Ogasawara Island was originally formed with a type of soil called laterite containing considerable amounts of iron, manganese, and aluminum; therefore, concentrations of these metals in the raw water for water supplies are naturally high. Current purification treatment flow at the purification process center is shown in **Figure 3**, and **Table 1** shows measurement frequency of raw water quality item.

3. Analytical method and data used analytical method

Multiple regression analysis was performed to estimate manganese concentrations.

Multiple regression analysis explains the output results using several input factors representing the relationship between objective variables and explanatory variables with linear combination equation (1) [2].

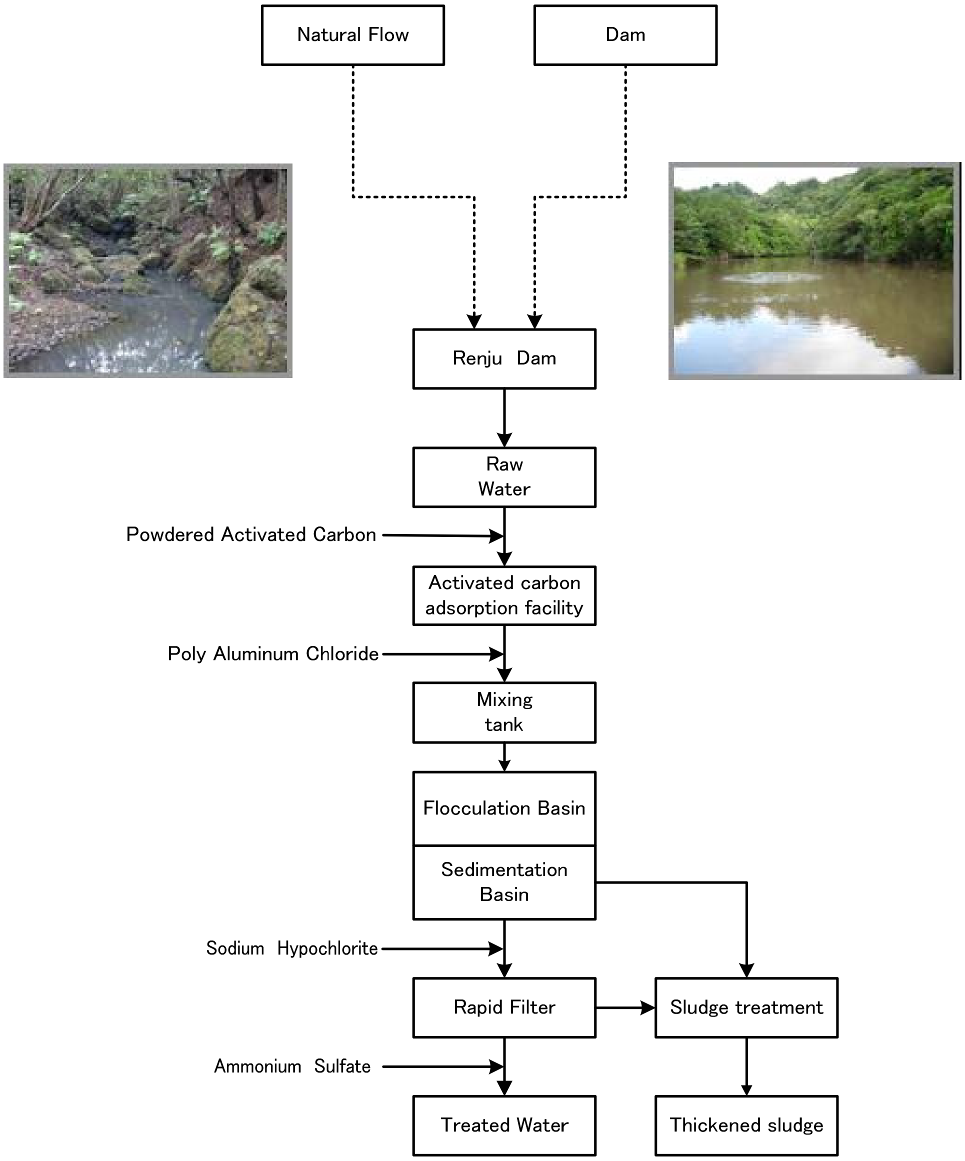

Fig. 3. Water treatment flow of Ogasawara

Table 1. Measurement frequency of raw water quality and Water quality standard for drinking water

Water examination item	measurement frequency			Water quality standard for drinking water in Japan
	Twice a day	once a month	once a year	
water temperature	○	○		—
pH	○	○	○	about 7.5
alkalinity	○	○		—
electric conductivity	○	○		—
taste		○	○	not abnormal
odor		○	○	not abnormal
color*	○	○	○	<5 color units
turbidity*	○	○	○	<2 units
total organic carbon*		○	○	< 3 mg/L
cadmium & cadmium compound			○	< 0.003 mg/L (for amount of cadmium)
mercury & mercury compound			○	< 0.0003 mg/L (for amount of mercury)
selenium & selenium compound			○	< 0.01 mg/L (for amount of selenium)
lead & lead compound			○	< 0.01 mg/L (for amount of lead)
arsenic & arsenic compound			○	< 0.01 mg/L (for amount of arsenic)
hexavalent chromium compound			○	< 0.05 mg/L (for amount of hexavalent chromium)
cyanide ion & cyanogen chloride			○	< 0.01 mg/L (for amount of cyanide)
nitrate nitrogen & nitrite nitrogen			○	< 10 mg/L
fluoride & fluoride compound			○	< 0.8 mg/L (for amount of fluoride)
boron & boron compound			○	< 1.0 mg/L (for amount of boron)
carbon tetrachloride			○	< 0.002 mg/L
1,4-dioxane			○	< 0.05mg/L
cis-1,2-dichloroethylene & *trans*-1,2-dichloroethylene			○	< 0.04 mg/L
dichloromethane			○	< 0.02 mg/L
tetrachloroethylene			○	< 0.01 mg/L
trichloroethylene			○	< 0.03 mg/L
benzene			○	< 0.01 mg/L
zinc & zinc compound			○	< 1.0 mg/L (for amount of zinc)
aluminium & alminium compound*			○	< 0.2 mg/L (for amount of aluminium)
iron & iron compound*		○	○	< 3.0 mg/L (for amount of iron)
copper & copper compound			○	< 1.0 mg/L (for amount of copper)
sodium & sodium compound			○	< 200 mg/L (for amount of sodium)
manganese & manganese compound*		○	○	< 0.05 mg/L (for amount of manganese)
chloride ion*		○	○	< 200 mg/L
hardness*		○	○	< 300 mg/L
evaporated residue*			○	< 500 mg/L
anionic surface active agent			○	< 0.2 mg/L
geosmin*			○	< 0.00001 mg/L
2-methylisoborneol			○	< 0.00001 mg/L
nonionic surface active agent			○	< 0.02 mg/L
phenolic compounds			○	< 0.05 mg/L (for amount of phenol)
standard plate count		○	○	100 or less colonies in test water 1mL
Escherichia coli.		○	○	not detected
coliform bacteria		○		not detected
anaerobic spore-forming bacteria		○		—

*: Water quality item that might reach a value that is larger than Water quality standard for drinking water

$$y = a + b_1x_1 + b_2x_2 + \cdots + b_nx_n \quad \cdots\cdots\cdots\cdots \quad (1)$$

y : objective variables
x_n : explanatory variables
a, b_n : coefficient

The multiple correlation coefficient R can then be represented by the equation (2).

$$R = \frac{\sum_{\alpha=1}^{n}(y_\alpha - \bar{y})(\hat{y}_\alpha - \bar{\hat{y}})}{\sqrt{\sum_{\alpha=1}^{n}(y_\alpha - \bar{y})^2 \sum_{\alpha=1}^{n}(\hat{y}_\alpha - \bar{\hat{y}})^2}} \quad \cdots\cdots\cdots\cdots \quad (2)$$

However, since the multiple correlation coefficient R tends to be overestimated when the number of explanatory variables (p) becomes greater than sample numbers (n), the multiple correlation coefficient adjusted for the degrees of freedom R^* is

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used for comparison in the accuracy of estimation of multiple regression equations with different explanatory variables.

$$R^* = \sqrt{1 - \frac{n-1}{n-p-1}\left(1 - R^2\right)} \quad \cdots\cdots (3)$$

If there is a nonlinear relation between y and x, it is shown by equation (4).

$$\dot{y} = a\, x_1^{b1} \cdot x_2^{b2} \cdot \cdots\cdots \cdot x_n^{bn} \quad \cdots\cdots (4)$$

$\dot{y}$: objective variables(nonlinear)

Equation (5) will be obtained if the logarithm of both sides of equation (4) is taken, and it becomes an expression similar to equation (1) [3,4].

$$\ln\left(\dot{y}\right) = \ln(a) + b_1 \ln(x_1) + b_2 \ln(x_2) + \cdots + b_n \ln(x_n) \quad \cdots\cdots (5)$$

Quality of raw water is measured twice daily for six characteristics, namely water temperature, turbidity, pH, color, alkalinity, and electric conductivity. Other items including TOC, iron, and manganese, dissolved manganese, and dissolved iron are measured once a month. Monthly data (n=57) for five years, from July 2004 to March 2009, were used in deriving the estimation equation of manganese concentration. **Figure 4** shows monthly measured data of manganese. The average manganese concentration in the data used was 0.09 mg/L, with its maximum value 0.27 mg/L and its minimum value 0.02 mg/L. The manganese concentration of the tap water begins measuring in fiscal year 2005 is 0.00~0.02 mg/L. The water quality target value of Ogasawara-mura is 0.005 mg/L, so the tap water quality of manganese is often exceeded.

Explanatory variables used for the estimation equation were the same as the data measurement characteristics (water temperature, turbidity, pH, color, alkalinity, and electric conductivity), and by assigning daily data to the estimation equation obtained by multiple regression analysis, daily data of manganese concentrations for the past five years were estimated. Monthly data of water temperature, turbidity, pH, color, alkalinity, and electric conductivity show **Figure 5** and **6**.

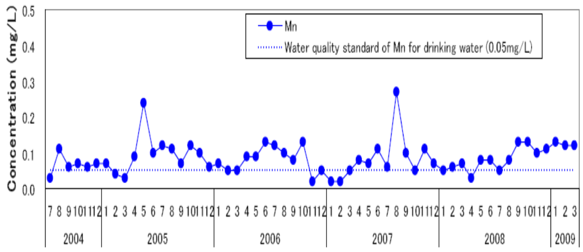

Fig. 4. Monthly data of total manganese

4. Results and discussion

Correlation analysis was implemented for seven characteristics used in estimating the concentration of manganese. Correlation analysis was also provided for logarithmically converted data, taking into account nonlinear relationships. The results are shown in **Table 2.**

Based on the results of correlation analysis, the

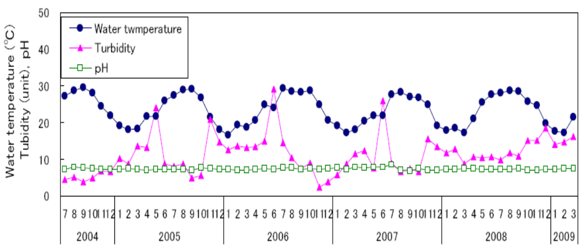

Fig. 5. Monthly data of water temperature, turbidity and pH

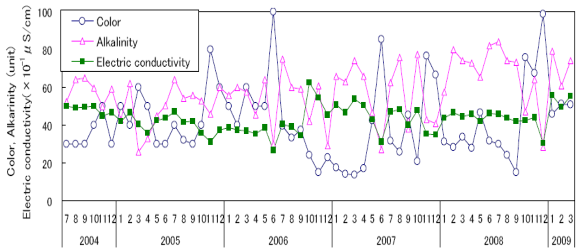

Fig. 6. Monthly data of color, nity, and electric conductivity

Table 2. Result of correlation analysis.

Explanatory variables	Correlation coefficient with manganese	
	Not conversion	Logarithmic conversion
Watr temperature	0.288	0.332
Turbidity	0.374	0.422
Color	0.197	0.370
pH	−0.109	−0.051
Alkalinity	−0.061	−0.098
electric conductivity	−0.093	−0.228

(−57, r_{95}=0.261)

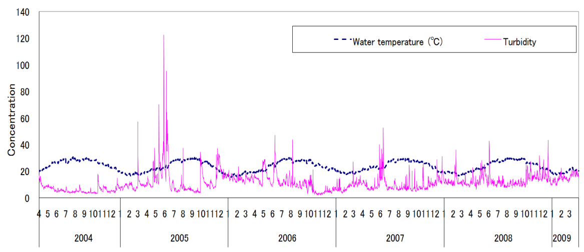

Fig. 7. Daily data of explanatory variables

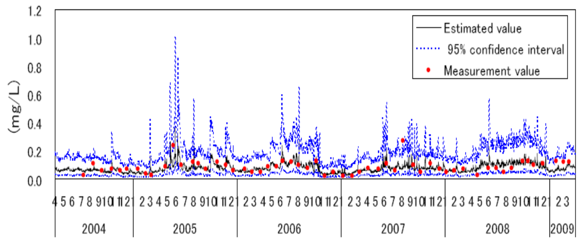

Fig. 8. Estimation of daily data of manganese concentration

objective variable was set as manganese and explanatory variables were set as water temperature, turbidity, color, pH, alkalinity, and electric conductivity. In the light of the correlation between the objective variables and internal correlation, explanatory variables were selected and multiple regression analysis was performed, which derived the following multiple regression equation.

$$y = 9.244\times10^{-5} x_1^{1.645} x_2^{0.667} \quad (6)$$

x_1 = Water temperature,

x_2=Turbidity, R^* = 0.665, (n=57)

With the equation (6), daily data for the past five years were estimated inversely. **Figure 7** shows daily data of water temperature and turbidity as explanatory variables. The results are shown in **Figure 8.**

Moreover, the upper limits of the confidence intervals at 90%, 95%, and 99% were calculated. As for turbidity, which has the highest correlation with manganese concentration, averages of monthly data and daily data were almost identical. However, the ratio of the maximum value and the average value were 2.6 in the monthly data used for the derivation of the estimate equation, but 11.0 in the daily data. This demonstrates that the measurement of manganese concentration was not collected when turbidity was high. When 11.0 (ratio of the maximum value and the average of daily data on turbidity) is multiplied by the average of manganese concentration estimated by daily data, 0.89 mg/L is derived. Estimating on the side of caution in light of high turbidity, the maximum value of 1.02 mg/L at the 95% confidence interval was used as the upper limit of the concentration of manganese in raw water for water supplies. Based on this estimation the authors have proposed a water treatment system for manganese removal.

In introducing a manganese−capable water treatment system, water quality requirements, economic factors, and compatibility with existing water treatment facilities are considered when recommending a treatment system. There are various options to treat manganese including oxidation, treatment with manganese sand, and treatment with microorganisms. An outline of the major manganese treatment methods is shown in **Table 3.**

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Table 3. The major manganese treatment methods. [5-11]

Removal method	processing
Oxidation treatment	Aeration oxidation
	Chlorine oxidation
	Chlorine dioxide
	Ozone oxidation
	Potassium permanganate oxidation
Filtration	Fitration by sand alone
	Filtration by manganese sand
Microbial treatment	Trickling filter method
	Slow filtration

The target water treatment plant continues to use sand that was filled into the rapid filter tower in 1983. Over the years this filter sand has been transformed into manganese sand, therefore it is assumed that manganese is being processed by manganese sand at the plant. However, as shown in Figure 1, this method requires that a chloric agent be injected before filtering, which allows it to exist as free chlorine. For manganese to react with manganese sand, the conditions require an ionic state without oxidization and precipitation; thus, making injection rate control difficult.

The generally accepted removal of manganese is by oxidization and precipitation through addition of oxidizing reagent and separated (solid−liquid) through such methods as coagulating sedimentation and rapid filtering. However, this process presents several difficulties - for example, it actually requires approximately 1.5 − 3 times the theoretical injection rate. Air and chloric agents can be readily used in Chichi−jima, Ogasawara; other oxidizing reagents are inappropriate in terms of safety, operability, and cost given the location of this remote island. During the oxidization process, oxidizing reagents are usually injected before treatment of coagulating sedimentation, but because the target raw water has a high iron concentration, oxidation by air is prone to cause aggregation and minute colloidation of iron. However, minute colloidal iron particles are not captured through aggregation and precipitation treatment or through sand filtering. Moreover, in oxidation using chloric agents, chlorine injection rates should be high - the rate corresponding to the estimated manganese concentration 1.0 mg/L is 1.3 mg/L, and when only dissolved manganese is targeted, the rate required for removal is 0.9 mg/L. Addition of high−concentration chloric agents to raw water with high concentrations of organic matter can produce trihalomethane.

Conversely, treatment with manganese sand requires, if the source water contains a high concentration iron, an prior iron removal process is required so that it will not decrease the manganese treatment capacity. Additionally, as stated above, a disadvantage exists in which the chlorine injection rate control is uncertain.

Treatment methods utilizing microorganisms must manage corrosion from iron bacteria, however, control of microorganisms is crucial in the target area where fluctuations in water quality are great.

It was concluded that, as a treatment corresponding to the estimated manganese concentration of 1.02 mg/L, the optimal method is to remove nearly all the iron and about half of the manganese by oxidation through chloric agents whose concentration is slightly higher than that corresponding iron without pH control, and coagulating sedimentation processes. The remnant manganese is then removed by manganese sand. With this method, the injection rate of chlorine before the treatment of coagulation and sedimentation can remain low and only a part of manganese is oxidized because in low pHs, the manganese is less prone to be oxidized than iron. After the coagulation sedimentation process, almost all manganese will be removed in the filtering process using manganese sand.

5. CONCLUSIONS

In this paper, we targeted a small-scale water system with limited data regarding the quality of raw water in the running water, and based on the relatively few number of manganese measurement data taken when the water quality was stable, we derived an equation to estimate the concentration of manganese with commonly measured water characteristics and estimated the daily concentration of manganese over the past five years. Based on the obtained results, we calculated the concentration range of manganese, and considered concrete manganese removal methods appropriate for the calculated concentration. Based on the estimated manganese concentration, we judged that "oxidation + treatment with manganese sand" illustrates an appropriate, effective, and economic method of manganese removal. Future studies include similar estimations of other material such as iron and organic matter that can affect the smooth operation of water treatment plants as well as to suggest general proposals for water treatment systems based on these results.

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