池貝隆宏	流域の環境負荷評価のための農薬流出推定	環境情報科学論文集	**20**	31-36	2006
Matsui Y., Narita K., Inoue T. and Matsushita T	Precise Data Sets on Farming and Pesticide Properties Verify a diffuse Pollution Hydrological Model for Predicting Pesticide Concentration	10th Specialised Conference on Diffuse Pollution and Sustainable Basin Management			2006
鴨志田公洋, 小坂浩司, 浅見真理, 相澤貴子	塩素処理における有機りん系農薬の類型別反応性とオキソン体への変換について	水環境学会誌（掲載予定）			
Kunikane, S	Application of "Water safety Plan" to drinking water quality management in Japan.	Proceedings of the Japan-U.S Gavernmental Conference on Drinking Water Quality Management and Wastewater Control,			Okinawa January 2007
Ema M, Fujii S, Ikka T, Matsumoto M, Hirose A, Kamata E	Early pregnancy failure induced by dibutyltin dichloride in mice	Environ Toxicol	22	44-52	2007
Ema M, Fujii S, Matsumoto M, Hirose A, Kamata E	Prenatal developmental toxicity study of basic rubber accelerator, 1,3-di-o-tolylguanidine, in rats	Reprod Toxicol	22	672-678	2006
Ema M, Fukui Y, Aoyama H, Fujiwara M, Fuji J, Inouye M, Iwase T, Kihara T, Oi A, Otani H, Shinomiya M, Sugioka K, Yamano T, Yamashita KH, Tanimura T	Comments from the Developmental Neurotoxicology Committee of the Japanese Teratology Society on the OECD Guideline for the Testing of Chemicals, Proposal for a New Guideline 426, Developmental Neurotoxicity Study, Draft Document (October 2006 version), and on the Draft Document of the Retrospective Performance Assessment of the Draft Test Guideline 426 on Developmental Neurotoxicity	Cong Anom (in press)			

Ema M, Fukunishi K, Matsumoto M, Hirose A, Kamata E, Ihara T	Developmental toxicity of dibutyltin dichloride in cynomolgus monkeys	Reprod Toxicol	23	12-19	2007
Ema M, Ito Y, Matsumoto M, Hirose A, Kamata E	Combined repeated dose and reproductive/developmental toxicity study of rubber accelerator, N,N-dicyclohexyl-2- benzothiazolesulfenamide, in rats	Drug Chem Toxicol	30 (in press)		
Hasegawa R, Hirata-Koizumi M, Dourson M, Parker A, Hirose A, Kamata E, Ema M	Pediatric Susceptibility to 18 Industrial Chemicals: A Comparative Analysis with Older Experimental Animals	Regul Toxicol Pharmacol	47	Epub ahead of print PMID : 17157422	2006 Dec 6
江馬　眞	OECDの高生産量化学物質安全性点検プログラムとその手順	化学生物総合管理学会誌	2	83-103	2006
江馬　眞	生殖発生毒性試験の役割	産科と婦人科	74(3) 特集・妊娠と薬	309-315	2007
高橋美加、松本真理子、川原和三、菅野誠一郎、菅谷芳雄、広瀬明彦、鎌田栄一、江馬　眞	OECD化学物質対策の動向（第9報）－第17回OECD高生産量化学物質初期評価会議（2003年アローナ）	化学生物総合管理学会誌	2	163-175	2006
高橋美加、松本真理子、川原和三、菅野誠一郎、菅谷芳雄、広瀬明彦、鎌田栄一、江馬　眞	OECD化学物質対策の動向（第10報）－第18回OECD高生産量化学物質初期評価会議（2004年パリ）	化学生物総合管理学会誌	2	286-301	2006
高橋美加、松本真理子、河原和三、菅野誠一郎、菅谷芳雄、広瀬明彦、鎌田栄一、江馬　眞	OECD化学物質対策の動向（第11報）—第19回OECD高生産量化学物質初期評価会議（2004ベルリン）	国立医薬品食品衛生研究所報告	124	62-68	2006
松本真理子、川原和三、菅谷芳雄、江馬　眞	OECD高生産量化学物質点検プログラム：第２１回初期評価会議概要	化学生物総合管理学会誌	2	135-146	2006
松本真理子、日下部哲也、川原和三、菅谷芳雄、江馬　眞	OECD高生産量化学物質点検プログラム：第22回初期評価会議概要	化学生物総合管理学会誌	2	302-312	2006

研究成果の刊行物・別刷

Estimation of geographical variation of cancer risks in drinking water in Japan

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Abstract The cancer risks posed by ten substances in raw and purified water were estimated for each municipality in Japan to compare risks between raw and purified water, and inter-municipality. Water concentrations were estimated by use of statistical data. Assigning cancer unit risks to each substance and applying the assumption of additive toxicological effects to multiple carcinogens, total cancer risks of the waters were estimated. As a result, the geometric means of total cancer risks in raw and purified water were 1.16×10^{-5} and 2.18×10^{-5}, respectively. In raw water, the contribution ratio of arsenic to total cancer risk accounted for 97%. In purified water, that of four trihalomethanes (THMs) accounted for 54%.
The increase of total cancer risks in purified water was due to THMs. In regard to the geographical variation, the relationship between population size and total cancer risks were investigated. The result was that there were higher cancer risks in the big cities with the population more than a million both in raw and purified water. One plausible reason for the higher risks in purified water in the big cities is a larger chlorination dose due to the huge water supply areas. The reason for the increase in raw water remained unclear.
Keywords Arsenic; cancer risk; drinking water; geographical variation; trihalomethane; water purification

Introduction

Drinking water quality issues, especially the issues on adverse health effects, have been one of the great concerns both of water works and water consumers. Although statistical data on drinking water quality have been provided by Japan Water Works Association (JWWA) for a long time, the data are merely a number of concentrations of substances, and thus it is very difficult for people to understand. Recently, Geographical Information System (GIS) has been widely applied as one of the new tools for visualization and spatial analyses. Integration of statistical water quality data and GIS may clarify the geographical characteristics of raw and purified water quality.

In this study, we focus on the carcinogenic substances in drinking water in Japan. Ten carcinogenic substances were selected for evaluation and the concentrations of these substances both in raw and purified water were estimated by the municipality unit. Applying the oral cancer unit risk for each substance and the assumption of additive toxicological effects to multiple carcinogens, total cancer risks of the waters were estimated by the municipality unit, and nationwide maps regarding the total cancer risks in raw and purified water were drawn with GIS. Furthermore, the characteristics and geographical variation of cancer risks were analyzed by use of drawn maps and statistical methods. The differences in substances contributing to the total cancer risks between raw and purified water, and the relationship between population size and total cancer risks were discussed.

Methods

Selection of target substances and assignment of their cancer unit risks

Chemical substances for the estimation of cancer risks were selected based on the following conditions. First, the substances that were in the Japanese Drinking Water Quality

Standard of 2001 were chosen. Although the new Standard was amended in 2004, statistical water quality data for 2004 were not yet available. Therefore, carcinogenic substances such as haloacetic acids and bromate, which were newly introduced in the Standard, were not included in this study. Second condition was that the substances should be carcinogenic or suspected to be carcinogenic. Third was that the substances should have oral unit risks as carcinogen in the Integrated Risk Information System (IRIS) by the United States Environmental Protection Agency (US-EPA). Consequently, ten substances were chosen for the analysis in this study. The names of the substances and oral unit risks assigned in this study, and Standard Values of Japanese Drinking Water Quality as of 2001 are shown in Table 1.

The term 'oral unit risk' is defined as the upper-bound excess lifetime cancer risk estimated to result from continuous exposure to an agent at a concentration of 1 mg/L in water (US-EPA, 2005) and expressed as the probability of developing tumors. The unit risks used in this study were mainly quoted from IRIS database (US-EPA, 2005). The unit risks of several substances were presented as several discrete values or a range of values. In this case, the geometric mean (G-mean) of the several unit risks or that of the maximum and the minimum values was used. The unit risk of chloroform is an exception. The oral unit risk of chloroform is not applicable in IRIS as of 2005 because EPA relies on a nonlinear dose-response approach and the use of margin-of-exposure analysis for cancer risk, for chloroform is not expected to produce rodent tumors via a mutagenic mode of action (US-EPA, 2005). Nonetheless, it was considered to be very useful to estimate and compare the extent of cancer risks of chloroform as one of trihalomethanes (THMs). Therefore, the unit risk of 1.8×10^{-4} (per mg/L) for chloroform, which had formerly been applied by IRIS, was used in this study. It should be noted that the quantitative cancer risk of chloroform might cause the overestimation of total cancer risk in this study.

Procedures to estimate the total cancer risks by the municipality unit

Concentrations of target substances in raw and purified water in each water purification plant. Statistics on water supply ("*Suidou Toukei*" in Japanese) were used as water quality and quantity database. The statistics have been edited by JWWA every year and consist of the data of water utilities which have more than 5000 design population served. Therefore, data of the smaller water utilities are not included in the statistics and were omitted in this study.

The statistics published in 2003 (JWWA, 2003), which describe the data of the fiscal year 2001, were mainly used in this study. The statistics include the data on

Table 1 Substances and oral unit risks assigned in this study, and Standard Values of Japanese Drinking Water Quality (2001)

Substances (CAS No.)	Oral unit risks assigned in this study (per mg/L)	Standard Values of Japanese Drinking Water Quality as of 2001 (mg/L)
1,2-Dichloroethane (107-06-2)	2.6×10^{-3}	0.004
1,3-Dichloropropene (542-75-6)	1.8×10^{-3}	0.002
Dichloromethane (75-09-2)	2.1×10^{-4}	0.02
Arsenic, inorganic (7440-38-2)	5×10^{-2}	0.01
Benzene (71-43-2)	8.4×10^{-4}	0.01
Carbon tetrachloride (56-23-5)	3.7×10^{-3}	0.002
Chloroform (67-66-3)	1.8×10^{-4}	0.06
Bromodichloromethane (75-27-4)	1.8×10^{-3}	0.03
Dibromochloromethane (124-48-1)	2.4×10^{-3}	0.1
Bromoform (75-25-2)	2.3×10^{-4}	0.09

concentrations of the target substances in raw and purified water measured in each water purification plant. Frequency of measurements is generally varied from monthly to yearly depending on the level of concentrations of substances in raw water, or some other unspecific reasons by the water purification plant. In this study, the annual average concentration of target substances was used because cancer is a chronic effect, and hence cancer risk is not directly concerned with the maximum concentration but with the average one. When the average concentration is below the limit of determination, which is normally 10% of the standard value, 10% of the determination limit was assigned except for THMs. For THMs, 0 was assigned as raw water concentration and 50% of the determination limit was assigned as purified water concentration. The reasons for this assumption are that there are generally no THMs in raw water, and there must be some THMs in purified water because chlorination is legally required in Japan.

Furthermore, there were some cases where a concentration was abnormal value and suspected to be an error such as a typo. In those cases, the average concentration of the fiscal year 2000 (JWWA, 2002) and 2002 (JWWA, 2004) was assigned instead of the abnormal value of the year 2001.

Calculation of representative concentrations of target substances in each municipality. If there are multiple water purification plants in a municipality, the representative concentrations in the municipality should be calculated in order to create the cancer risk maps by the municipality unit. Using the daily average volume of purified water as weighting function, the weighted average concentrations of the water purification plants in the municipality were calculated for each target substance and assigned as the representative concentrations of the municipality.

Estimation of the total cancer risks in each municipality. Total cancer risk in a municipality was estimated using equation 1.

$$\text{Total cancer risk} = \sum_i UR_i \times C_i \qquad (1)$$

where UR_i is the oral unit risk of substance i, and C_i is the representative concentration of substance i in a municipality.

In estimating the total cancer risks, the following two assumptions were adopted. One was that arsenic both in raw and purified water was in inorganic form. This may be valid except in some special cases. The other was that the cancer risks of multiple substances were additive in terms of toxicological effects. This seems valid for the substances which have the similar mode of action to develop tumors, but it does not necessarily seem valid for the substances which have the different mode of action. The validity of the assumption has been a controversial issue for toxicologists and beyond the compass of this study.

Mapping and statistical analyses

Based on the total cancer risks estimated by the municipality unit, nationwide cancer risk maps of raw and purified water were drawn. As a GIS tool for drawing maps, Arc View 8.2 software (ESRI, USA) was used. Furthermore, some statistical analyses were implemented in order to investigate the characteristics of spatial distribution of cancer risks in municipalities. As tools for statistical analyses, Statistica software (Statsoft, Inc., USA) was mainly used.

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Results and discussion

Estimation and mapping the nationwide cancer risks by the municipality unit

The total cancer risk maps of raw and purified water were drawn by the municipality unit. As an example, drawn maps of the northern and eastern part of Japan are shown in Figure 1. It should be noted that the original maps are nationwide and colorized, and thus it is easier to distinguish a difference. Drawing the maps such as Figure 1 can facilitate understanding of the characteristics in terms of water quality. For example, the differences in cancer risks between raw and purified water in the same municipality can be understood easily.

Seeing Figure 1, it is suggested that the total cancer risks of purified water become larger than those of raw water in many municipalities. To examine this, statistical analyses were carried out. Figure 2 shows the box and whisker plot of the total cancer risks in logarithmic scale. The large variations can be seen in the total cancers risks among municipalities in Figure 2, the lognormal distribution was applied as the distribution type instead of the normal distribution. Therefore, G-mean and geometric standard deviation were calculated and indicated in Table 2 with median values. As a result, G-mean of the total cancer risks were 1.16×10^{-5} in raw water and 2.18×10^{-5} in purified water. Furthermore, medians in raw and purified water were 5.34×10^{-6} and 2.13×10^{-5}, respectively. Therefore, the result that the total cancer risk in the purified water was larger than that in raw water was obtained by comparison of G-mean and also of median. Reasons for this will be further discussed later.

One more thing to be mentioned here is the large difference between the median and the G-mean of total cancer risks in raw water. As shown in Figure 2, median, 25th percentile and 1st percentile in raw water were all in similar values. This is deeply associated with the lower determination limit of arsenic. In almost all municipalities, the lower determination limit of arsenic is 0.001 mg/L, and when the average arsenic concentration of the municipality is lower than the limit, 10% of this value was substituted as arsenic concentration in the municipality in accordance with the assumption in this study.
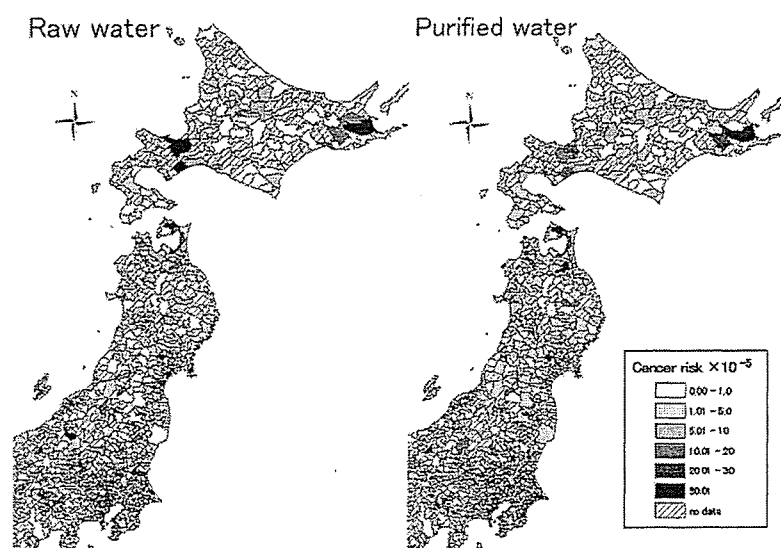

Figure 1 Total cancer risk maps of raw and purified water drawn by municipality unit (example of the northern and eastern part of Japan)
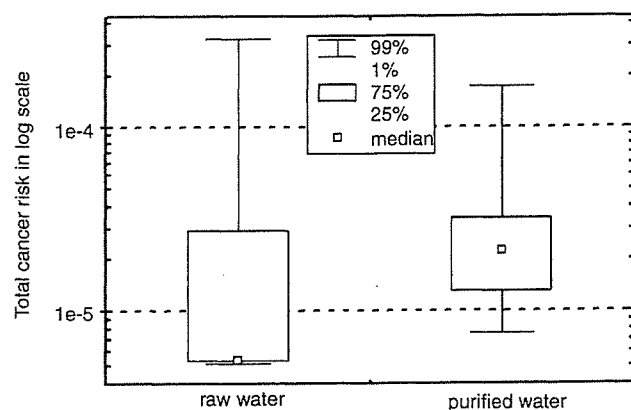
Figure 2 Box and whisker plot of total cancer risks (in log scale)

In this case, 5×10^{-6} was calculated as the cancer risk posed by arsenic. This value is almost the same as the median of total cancer risks in raw water. Therefore, it can be said that total cancer risks in raw water in more than half of the municipalities are over-estimated because of the determination limit of arsenic.

Contribution of each substance to the total cancer risk

Contribution ratio of each substance to the total cancer risk is shown in Figure 3 (raw water) and Figure 4 (purified water). This was calculated on the basis of the G-mean of cancer risk of each substance, therefore the variability among municipalities was not taken into account in this section. The contribution of arsenic was the largest both in raw and purified water, and it accounted for 97% and 44%, respectively. The main cause for this is that the cancer risk compared to the Standard value (5×10^{-4}), is quite high. However, it should not be concluded that we must remove much more arsenic in the water purification processes. There are several reasons for this. First, the oral unit risk of arsenic is estimated on the basis of the data of skin cancer (US-EPA, 2005). The lethality of skin cancer is relatively low compared to the cancer of many other parts, and thus the risks in units of mortality rate may be different even if the cancer risks are the same. Secondly, there may be some overestimation in the cancer risks of arsenic because of the aforementioned problem on the determination limit. Thirdly, the treatment achievability and the cost-efficiency should also be considered in establishing a standard. In terms of the treatability of arsenic, the G-means of cancer risks posed by arsenic in raw and purified water are 1.15×10^{-5} and 7.54×10^{-6}, respectively. Therefore, arsenic could be removed well during the water purification processes in many municipalities, for the least arsenic cancer risk estimated in this study is 5×10^{-6} because of the determination limit. Kang *et al.* (2003) mentions that arsenic can be removed by coagulation.

Table 2 Statistical indicators on the total cancer risks estimated

	Number of municipalities (*n*)	Median	Geometric mean (G-mean)	Geometric Standard Deviation (GSD)
Raw water	1992	5.34×10^{-6}	1.16×10^{-5}	3.18
Purified water	2119	2.13×10^{-5}	2.18×10^{-5}	2.10

Raw water
G-mean of total cancer risks = 1.16×10^{-5}

Benzene
0.8%

others
2.6%

Carbon
tetrachloride
0.6%

Arsenic
97.4%

1,2- Dichloroethane
0.7%

Dichloro-
methane
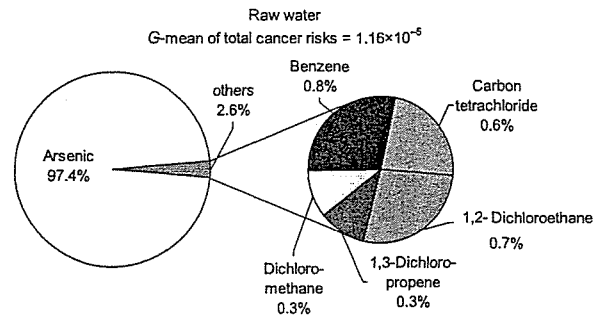0.3%

1,3-Dichloro-
propene
0.3%

Figure 3 Contribution ratio of substances to the total cancer risk of raw water

As for purified water, the cancer risks posed by 4 THMs (chloroform, bromodichloro-methane, dibromochloromethane and bromoform) accounted for 54% of the total risk. THMs are produced as a result of chlorination. Although G-mean of cancer risks of the THMs is about the level of 10^{-5} and not so high, the optimization of chlorination dose should be further developed to reduce THMs production.

Cancer risks in relation to the population size

Figure 5 shows the G-mean of total cancer risk in relation to the population size of municipalities. The big cities with the population more than a million had higher risks both in raw and purified water than the smaller municipalities. In the case of raw water, arsenic concentrations were higher in the big cities. The reason for this was not apparent and should be further investigated, although there are some big cities that have a natural arsenic contamination source in the upstream. For purified water, concentrations of the total THMs were higher in the big cities. This may be because the raw water quality is worse in the big cities with respect to THMs formation potential. Furthermore, it should be noted that the concentrations of chloroform and bromodichloromethane were relatively higher in the big cities, however, those of dibromo- chloromethane and bromoform were similar to that in the smaller municipalities. One plausible reason for this is a larger chlorination dose in the big cities due to their huge water supply areas, but it is also uncertain and should be further investigated.
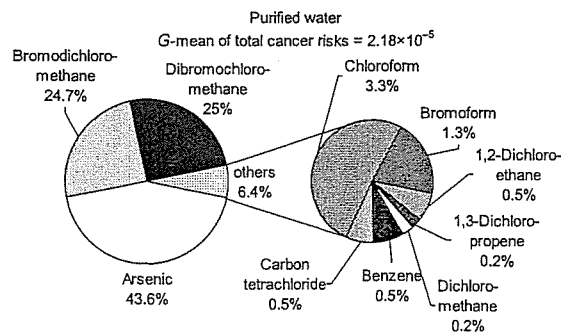
Purified water
G-mean of total cancer risks = 2.18×10^{-5}

Bromodichloro-
methane
24.7%

Dibromochloro-
methane
25%

Chloroform
3.3%

Bromoform
1.3%

others
6.4%

1,2-Dichloro-
ethane
0.5%

1,3-Dichloro-
propene
0.2%

Arsenic
43.6%

Carbon
tetrachloride
0.5%

Benzene
0.5%

Dichloro-
methane
0.2%

Figure 4 Contribution ratio of substances to the total cancer risk of purified water
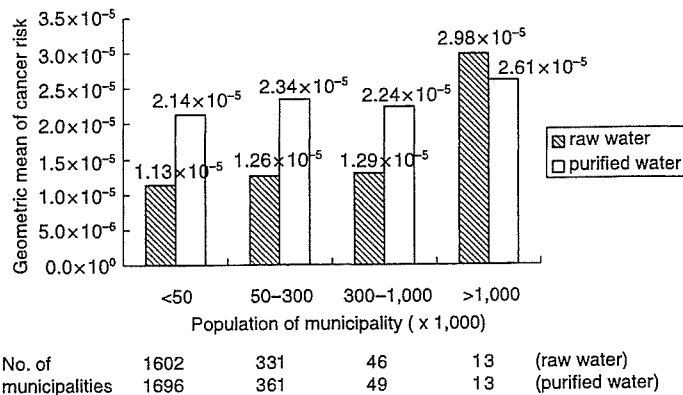
Figure 5 Total cancer risks in relation to the population size of municipalities

The table under the figure:

| No. of | 1602 | 331 | 46 | 13 | (raw water) |
| municipalities | 1696 | 361 | 49 | 13 | (purified water) |

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Conclusions

The total cancer risks of raw and purified water by the municipality unit were estimated by use of statistical water quality data and GIS. As a result, the total cancer risks of purified water were larger than that of raw water. This was mainly because of the THMs produced in the chlorination process. In raw water, arsenic has almost all of the contribution to total cancer risks, but it can be removed well during a water purification processes such as coagulation. As for the population size, the big cities with the population more than a million had higher cancer risks both in raw and purified water than the smaller municipalities.

Although there may be another carcinogenic substances that have large risks, they could not be included in this study. However, we can revise the estimation result when their unit risks and concentration data become available. Finally, an integrated analysis of statistical drinking water quality data and GIS may be one of the new methods to help the comprehensive understanding of drinking water quality and this may lead to improvements in the drinking water quality.

Acknowledgements

References

JWWA (2002). *Suidou toukei (Statistics on water supply)*. Japan Water Works Association, vol. 83, [in Japanese].

JWWA (2003). *Suidou toukei (Statistics on water supply)*. Japan Water Works Association, vol. 84. [in Japanese].

JWWA (2004). *Suidou toukei (Statistics on water supply)*, Japan Water Works Association, vol. 85. [in Japanese].

Kang, M., Chen, H., Sato, Y., Kamei, T. and Magara, Y. (2003). Rapid and economical indicator for evaluating arsenic removal with minimum aluminum residual during coagulation process. *Water Res.*, 37, 4599–4604.

US-EPA (2005). *Web site (Integrated Risk Information System)*, United States Environmental Protection Agency, USA. http://www.epa.gov/iris/.

Development of evaluation methods to introduce a nanofiltration membrane process in drinking water treatment

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Abstract The objective of this study was to develop a new prediction method for evaluating performance of full-scale nanofiltration (NF) pilot plant by using small-scale pilot plants. Operating experiments using both multistage array pilot plant and two small-scale pilot plants in parallel had been conducted for about a year. From this experiment, it was revealed that data obtained from small-scale pilot plants could predict the performance of multistage pilot plant from the viewpoint of flux and rejection. In other words, both permeate water quantity of multistage pilot plant without noticeable fouling caused by aluminium from coagulant and permeate water quality of multistage pilot plant could be estimated.

Keywords Aluminium; multistage array; nanofiltration; prediction method; small-scale

Introduction

Recently, there are a water shortage areas in Japan. The water resources for these areas, for example, stream water and reservoir water, are polluted by household effluent or farming effluent or eutrophication. These waters are used for drinking water in these areas. The drinking water will have a musty smell and taste and contain higher amounts of disinfection by-products. In order to solve these problems many drinking water treatment plants have introduced advanced drinking water treatment processes such as ozone oxidation and activated carbon adsorption. These processes have good treatment performance to decrease dissolved organic matter. Recent amendment of WHO drinking water quality guidelines and Japanese drinking water quality standards require stringent treatment to comply with disinfection by-products guidelines or standards. However, there are many problems to be solved in these processes. In the ozone oxidation process, reacting the bromide ion with ozone generated bromate which is extremely carcinogenic. In biological activated carbon adsorption, there is leakage of nuisance microorganisms, which grow through this process. Additionally, it is impossible for ozone oxidation and activated carbon adsorption to remove hazardous metals such as arsenic and antimony and inorganic substances such as calcium that cause hard water. Therefore, the nanofiltration (NF) process is an alternative advanced drinking water treatment process to solve the existing problem for drinking water treatment. However, there is little experience using NF process for advanced drinking water treatment in Japan. For this reason, experiments with the pilot plant must be implemented for about 6–12 months before introducing it to drinking water treatment plants, so more energy, money and time have to be spent if full-scale pilot plant is to be constructed for the experiment. Therefore, in order to easily introduce the NF process, it is desired to establish simple methods for performance evaluation by using small-scale plants without constructing a full-scale pilot plant. In a previous study, the possibility of simulating downstream elements of

multistage NF plant by using a small-scale plant with returning concentrate water to feed water and concentrating feed water quality was shown (Itoh and Magara, 2004).

In this study, multistage array pilot plant and two small-scale pilot plants were installed and operated in parallel, and then performance of the multistage plant was predicted by using data obtained from small-scale plants.

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Method

Equipment

A schematic diagram of the multistage array pilot plant is shown in Figure 1. The multistage plant consisted of 8-4-2-1 typed vessel array from upstream and each vessel contains five membrane elements (total membrane elements installed were 75). The water recovery ratio of the multistage plant was up to 95% and total permeate flow rate was 315 m^3/d. A schematic diagram of the small-scale plant is shown in Figure 2. The small-scale plant consisted of two membrane elements which were connected in series and could operate by returning a portion of concentrate water to feed water. Two small-scale pilot plants were used.

In order to compare performance of the multistage plant with the small-scale plant, a partition was installed in the product tube of one vessel of first stage and the fourth stage. The partition was set between second and third element in the first stage, and between the third and fourth element in the fourth stage to collect permeate samples from two membrane elements (hatched elements in Figure 1). The performances of hatched elements in Figure 1 were compared with that of small-scale plants.

The membrane element used in this study was SU-610 (Toray, Japan, spiral wound module, nominal NaCl rejection: 55%, membrane surface: 7 m^2). The water into NF system of this experiment was obtained from Ishikawa drinking water treatment plant in Okinawa after coagulation and sedimentation by PACl (polyaluminium chloride), and pretreated by microfitration (MF, Toray, Japan, nominal pore size: 0.1 μm) to remove particulate matter before entering NF system. Water quality item of pretreated water by MF is shown in Table 1. FI value, which is fouling index for reverse osmosis (RO) system, of MF filtered water was measured during experimental period every week. These values were always no more than 3, therefore this MF filtered water was seemed to be adaptable enough for NF system.
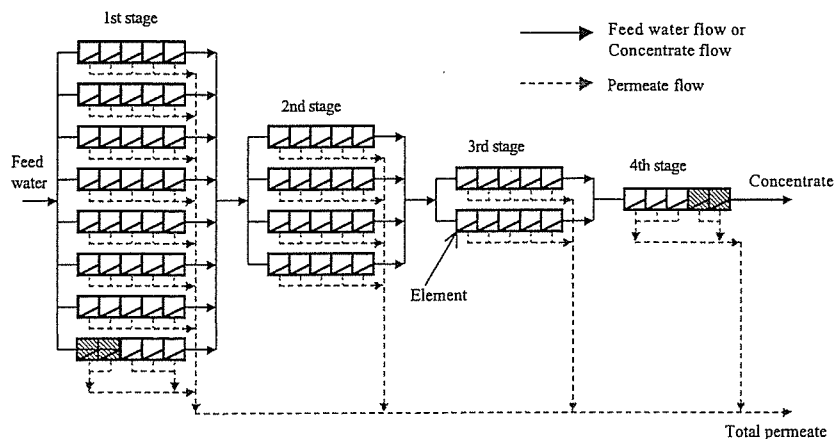

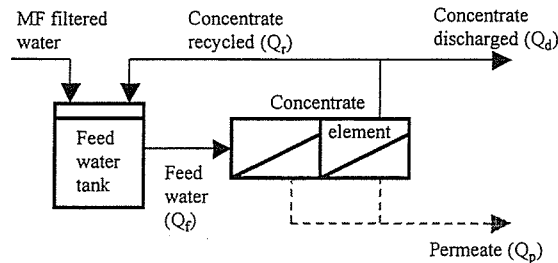**Figure 1** Schematic diagram of the multistage array pilot plant

Figure 2 Schematic diagram of the small-scale pilot plant

Experimental procedure

The operating condition of the multistage plant were as following; vessel array: 8-4-2-1, water recovery ratio of system r_S (r_S = total permeate flow rate/feed water flow rate): 95%, average permeate flux of each stage: 0.6m/d. So as to keep permeate flux constant, transmembrane pressure was controlled at each stage. Before the continuous operation, this plant was operated at the above operating condition. As a result, the fourth stage's flux had decreased rapidly and permeate flow rate had become nearly zero in a day. Therefore, in order to perform NF plant without noticeable flux decline, acid addition was implemented. In RUN1, acid addition was introduced at second stage feed water and pH value of fourth stage feed water was adjusted about to 5. In RUN2, acid addition was introduced at first stage feed water and pH value of first stage feed water was adjusted about 4.

The operating condition of small-scale plants is shown in Table 2. One small-scale plant simulated first and second elements of first stage, the other simulated fourth and fifth elements of the fourth stage. These flow rate conditions were decided by flow rate calculation result obtained from assuming that the water recovery ratio of each element within a vessel was constant. By making this assumption, permeate flow rate of any two elements could be calculated simply. It was normally impossible to measure permeate flow rate of two elements within a vessel, however in this study, it was possible to measure this permeate flow rate by the partition installed in the product tube. These cal-culated permeate flow rates were almost the same as measured values. In the fourth stage's simulating small-scale plant, by returning a portion of concentrate water to feed water, the water recovery of the system was also set the same as target elements of multi-stage plant in order to reach water quality of feed water to that of target elements of multistage plant. Acid addition was also implemented in small-scale plants in order to agree pH value of small-scale plant with that of target elements of multistage plant.

In the operating conditions mentioned above, multistage plant and small-scale plants in parallel had been operated continuously in both RUN1 and RUN2 for about three months. Before RUN2 was started, chemical cleaning using alkaline solution (pH10, sodium hydroxide solution) and acidic solution (pH2, hydrochloric acid solution) was implemented in both multistage plant and small-scale plants in order to remove foulant inside the NF plants, which accumulated during operation RUN1.

Table 1 Water quality of MF filtered water

Item	Conc.	Item	Conc.
E.C. (μS/cm)	185	SiO_2 (mg/L)	12.7
Na (mg/L)	18.6	Al (mg/L)	0.0297
Ca (mg/L)	10.6	Mn (mg/L)	0.0151
Cl^- (mg/L)	27.3	TOC (mg/L)	0.927
SO_4^{2-} (mg/L)	13.6	E260 (1/cm)	0.014

Table 2 Flow rate conditions of small-scale pilot plants

Simulating elements	1st stage's 1,2 elements	4th stage's 4,5 elements
Feed water (m^3/d);Q_f	41.5	23.4
Permeate (m^3/d);Q_p	10.2	6.4
Recycled (m^3/d);Q_r	0	16.6
Discharged (m^3/d);Q_d	31.3	0.4
Flux (m/d)	0.73	0.46
Element recovery (%);r_e	24.7	27.6
System recovery (%);r_s	24.7	94.9

Measured item

In the multistage plant, permeate flow rates of upstream of first stage's partition and downstream of fourth stage's partition, transmembrane pressures and feed water temperatures of first and fourth stages were measured. In small-scale plants, permeate flow rates, transmembrane pressures and feed water temperatures of both upstream simulating plant and downstream simulating plant were measured. These items were measured automatically and stored in the computer once per hour. By using these data, fluxes at 25 °C and 1 MPa of both plants were calculated and flux changes of multistage plant were compared with that of small-scale plants.

Waters were sampled every week and measured following items: pH value, electric conductivity (E.C.), sodium (Na), calcium (Ca), chloride ion (Cl$^-$), sulfate ion (SO$_4^{2-}$), silicate (SiO$_2$), aluminium (Al), manganese (Mn), total organic carbon (TOC), ultraviolet absorbance at 260 nm (E260). Sampling waters of multistage plant were feed water, permeate and concentrate of each stage, permeate of upstream of first stage's partition, permeate of downstream of fourth stage's partition and total permeate. Sampling waters of small-scale pilot plant were feed water, permeate and concentrate of both upstream simulating plant and downstream simulating plant. By using concentration data obtained from the small-scale plant, substance rejection was calculated every sampling, and average rejection of all sampling times was calculated. Then, by using rejection data of small-scale plant and the equation that was formulated by rejection's definition, water recovery's definition and flow rate mass balance, substance concentrations of both permeate and concentrate of multistage plant were calculated, and then measured values were compared with calculated values.

Results and discussion

Water quantity prediction

Figure 3 shows flux changes in time in the upstream elements of multistage plant and small-scale plant in RUN1. The upstream elements were the first and second elements of the first stage of multistage plant. For the first three weeks, fluxes of both plants were almost the same. After that, however, flux decline rate of the small-scale plant was greater than that of the multistage plant. This reason was that the third to Fifth elements fouled faster than the first and second elements in the multistage plant. In this way, permeate flow rate obtained from first and second elements of the multistage plant was faster than the predicted flow rate for the small-scale plant. Therefore, differences of flux change between both plants had appeared.

Figure 4 shows the flux changes in time of downstream elements of the multistage plant and the small-scale plant in RUN1. The downstream elements were the fourth and fifth elements of the fourth stage of the multistage plant. Flux of the small-scale plant was greater than that of the multistage plant for almost all the operating periods. This was
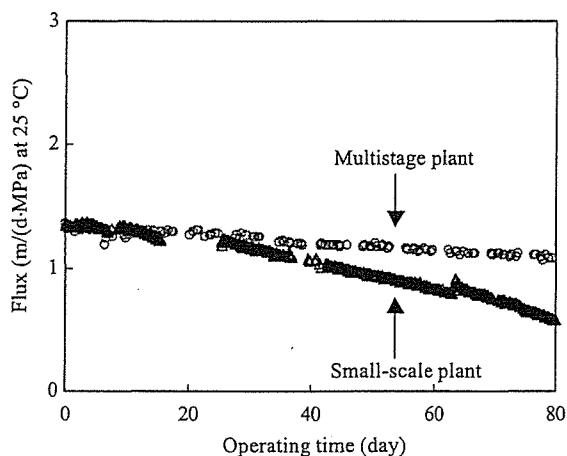
Figure 3 Flux change of upstream elements in RUN1

due to insufficient acid addition. Furthermore, due to the shortage of acid, the flux of the multistage plant decreased rapidly many times. By adding sufficient acid, flux recovered the setting value.

In order to reveal the differences of flux decline rate between the multistage plant and the small-scale plant, foulant was investigated. In the previous study (Nishimura et al, 2004), it was revealed that calcium was one of the foulants for NF system, so Langelier's index (LI), the differences between actual pH value and the theoretical pH value (the pH value when calcium carbonate is not solved and not precipitated in equilibrium) was calculated in order to investigate the occurrance of calcium scale. However, LI is a minus value for all the operating times, so it was revealed that calcium scale did not occur. Next, the relationship between pH value and dissolved aluminium concentration was investigated. Aluminium is also known as one of the foulants for NF system. Figure 5 shows the relationship between pH value and aluminium concentration. As shown in this figure, aluminium concentrations were all in precipitate zone at 1st stage because of no acid addition. At the fourth stage, aluminium concentrations were almost in precipitate
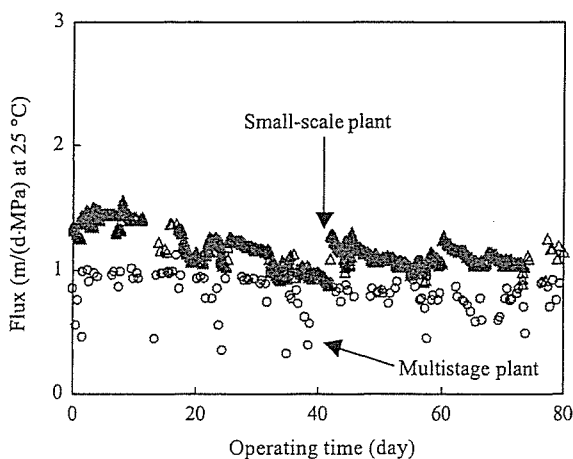
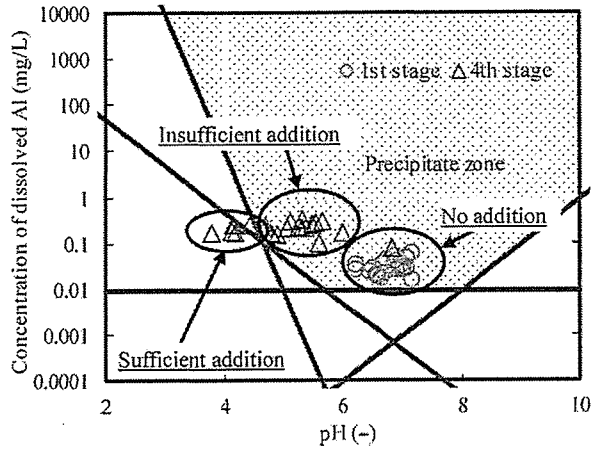Figure 4 Flux change of downstream elements in RUN1

Figure 5 Relationship between pH and Al in RUN1

zone because of insufficient addition. It was revealed that aluminium precipitated at both first and fourth stages. Therefore, it was decided to implement acid addition at first stage feed water and to add more amount of acid. In RUN2, experiment was carried out in this acid adding condition.

Figure 6 shows flux changes in time in upstream elements of the multistage plant and the small-scale plant in RUN2. Except the first 20 days, flux changes of small-scale plant showed good agreement with that of multistage plant. During the first 20 days, the acid addition pump of small-scale plant was not working properly, so adjusting pH was not appropriate, and thereby flux of small-scale plant decreased more significantly than that of the multistage plant. Finally, it was revealed that flux decline rates of both plants could be the same by controlling aluminium fouling by adding acid into the first stage feed water.

Figure 7 shows flux changes in time in downstream elements of both plants in RUN2. Except two occasions of rapid flux declines, flux changes of both plants were almost the
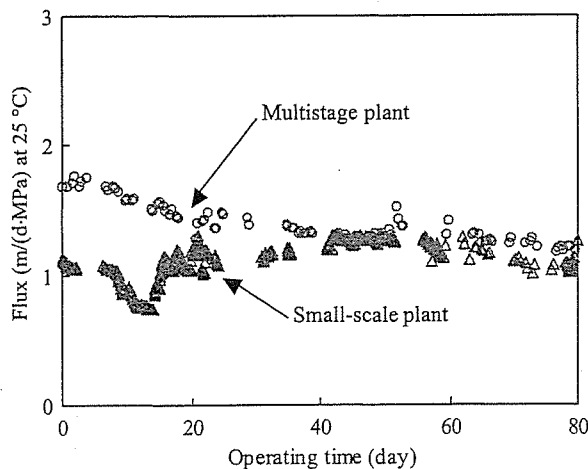

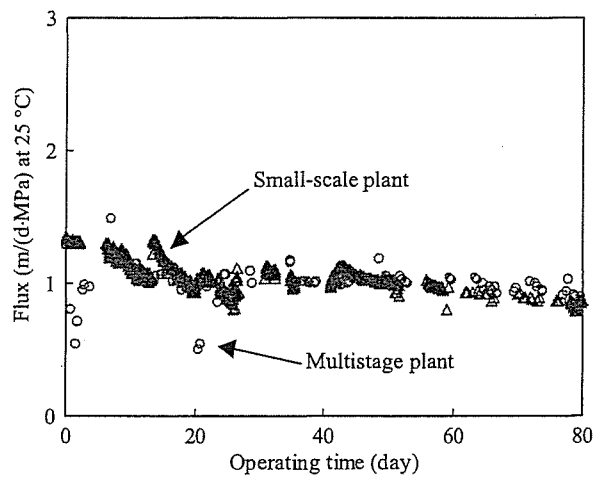**Figure 6** Flux change of upstream elements in RUN2

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Figure 7 Flux change of downstream elements in RUN2

same. These rapid flux declines happened because of shortage of acid addition. By adding more amount of acid and properly adjusting the pH value, flux recovered to the setting value. Also, flux decline rates of both plants could be the same by controlling aluminium fouling in the fourth stage.

Next, the relationship between pH and aluminium was also investigated in RUN2 in order to check whether aluminium was the main foulant. Figure 8 shows the relationship between pH value and aluminium concentration in RUN2. As shown in this figure, aluminium concentrations of MF filtered water were in precipitate zone, but in the first and fourth stage feed waters aluminium concentrations were all out of the precipitate zone. Therefore, the significant flux decline was not observed in RUN2. Comparing the results in RUN1 and RUN2, the aluminium concentrations were almost the same and this concentration was not so high compared to the water quality standard value, which was 0.2 mg/L. However, severe fouling occurred when acid addition was insufficient. Therefore, it may be better to use ferric coagulants instead of aluminium coagulants for the pretreatment of NF in order to avoid excessive acid addition.
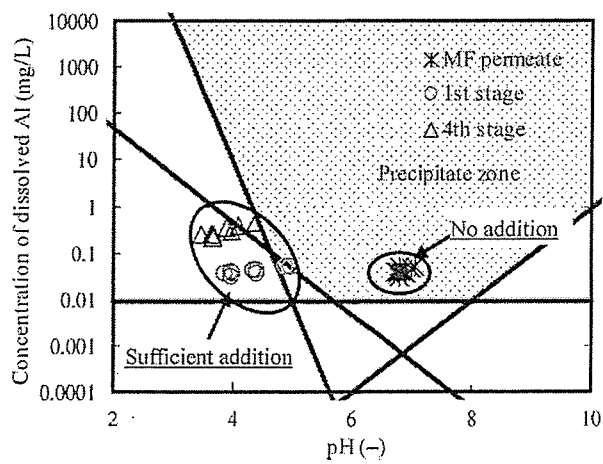

Figure 8 Relationship between pH and Al in RUN2

From water quantity prediction results, it was revealed that without significant flux decline, flux changes of multistage plant were the same as those for small-scale plant. In other words it was possible to trace fouling pattern of full-scale plant by using small-scale plant.

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Water quality prediction

Figures 9 and 10 indicates simulation results of total organic carbon concentrations (TOC) in RUN1 and RUN2, respectively. As shown in these figures, calculated values were the same as measured values in both RUN1 and RUN2. In the other water quality parameter, the same results were also obtained. Therefore, it was possible to predict water quality of multistage plant by using rejection data obtained from small-scale plant regardless of fouling occurrence.
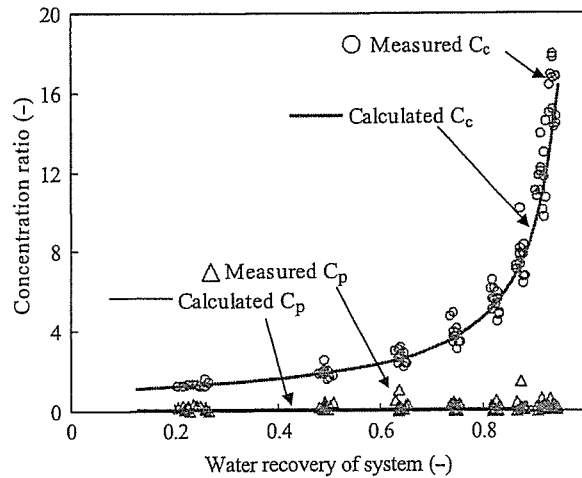

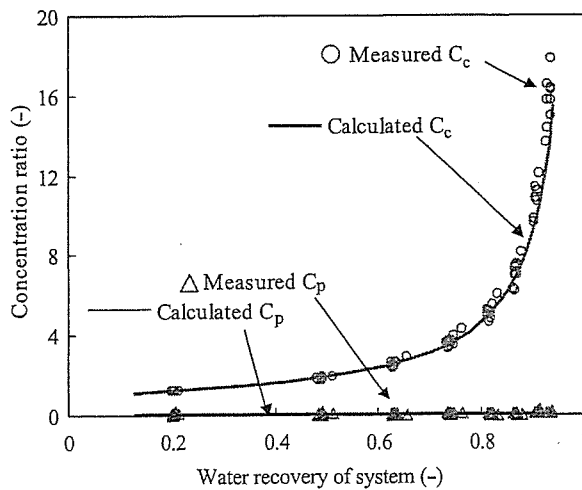**Figure 9** Measured and calculated TOC concentration in RUN1

Figure 10 Measured and calculated TOC concentration in RUN2

Conclusion

In this study, multistage array pilot plant and two small-scale pilot plants were installed and operated for about a year. The following was revealed. First, permeate flux changes of multistage plant can be predicted by flux data obtained from small-scale plant without noticeable fouling. Prime foulant of NF was aluminium from PACl. Secondly, substances concentration of permeate and concentrate of the multistage plant can be predicted by rejection data obtained from the small-scale plant. Thereby, it was revealed that data obtained from the small-scale plant can estimate the performance of the full-scale plant, so introducing NF plant to drinking water treatment plant becomes easier.

In a further study by using ferric coagulant in pretreatment, possibility of operating these NF plants for a longer time without noticeable flux decline and getting better operation results will be investigated.

References

Itoh, M. and Magara, Y. (2004). Accelerated fouling test of NF membrane and foulant characteristics using small-scale pilot plant. *Preprints of Water Environment-Membrane Technology, Conference, Seoul, Korea, June 2004*, 971–977.

Nishimura, K., Ohgai, T., Kang, M., Kamei, T., Ohno, K. and Magara, Y. (2004). Comprehensive analysis of fouling and treatability for the management of NF. *Preprints of Water Environment-Membrane Technology, Conference, Seoul, Korea, June 2004*, 341–348.

安全で低環境負荷の浄水処理をめざして

水道原水を考慮した浄水処理*

眞 柄 泰 基**

はじめに

広島県公営企業部が所管する送水隧道(すいどう)の崩落事故が8月25日に発生し,その影響を受けて受水団体である呉市および江田島市の約3万2,000世帯が断水の影響を受けるとともに,工業用水も断水した。その修復には3週間程度と長期間かかるものと推定され,種々の問題を提起した。

この隧道は1965年に供用開始されたものであるが,点検を含めて維持管理事業を行うためには給水停止が伴うことから,利水者との調整が取れなかったことから点検作業が行われてこなかったとされている。しかし,隧道自体の劣化によるものではなく,隧道上部の岩盤が崩落して隧道内に落下したのが原因とされており,維持管理業務が行われていたとしても,このような事故を予見することは困難であったかもしれない。しかし,この事故によって多くの市民の日常生活に支障をきたしたばかりでなく,事業所用水を含めてさまざまな社会活動に深刻な影響を与えた。

阪神淡路大震災で水道水の供給が停止したことによって,社会活動に深刻な影響を与えたことの教訓,すなわち社会活動や日常生活に必要な水は水道以外にない。したがって,水道は止められないということである。それ

は,水道の普及率が約97%に達し,実質的に水道法の目的である公衆衛生の向上と生活環境の改善という目的は達成されるに至っていることの証左でもある。

2001年度末における水道資産は約37兆円であり,送配水施設が約23兆円,浄水施設は約5兆円,そのほかの施設が8兆円の構成となっている。この37兆円の資産により,年間約3.2兆円の水道料金収入があり,水道事業体職員が約6万7,000人,関連民間企業等で24万9,000人の雇用効果をあげている。

しかし,このような状況であっても水道料金の一般家庭の可分所得に占める割合はわずか0.7%であることや,施設更新のための積立留保金が十分でないことなどにより,施設の適切な更新や維持管理を困難にしている。水道事業が公設・公営原則であり,水道料金の設定が地方議会の議決事項となっているため,財政的にきわめて厳しい状態にならない限り,料金改定ができないのが原因であると考えられる。そのため,持続性を求められる社会基盤施設としての水道に必要な投資が先送りされているという問題が顕在化しつつある。

広島県の例ばかりでなく,経年化施設の維持管理や更新が適切に行われ難い状況を考慮