

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.

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

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.

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.

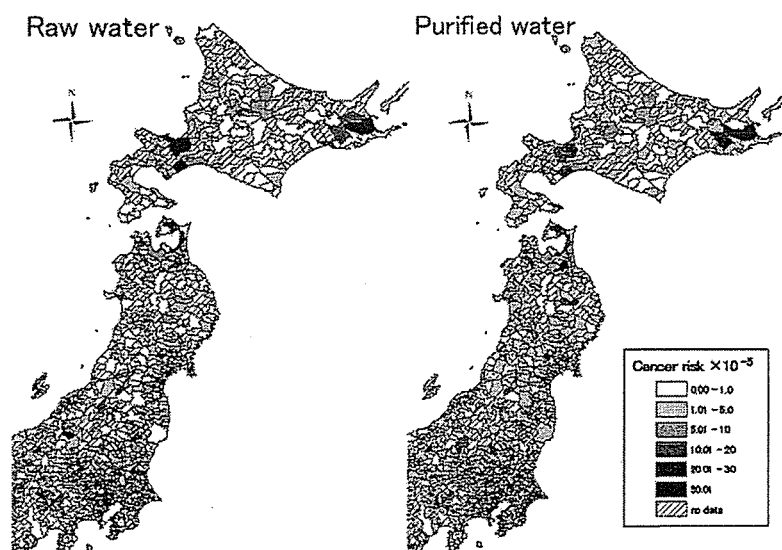


Figure 1 Total cancer risk maps of raw and purified water drawn by municipality unit (example of the northern and eastern part of Japan)

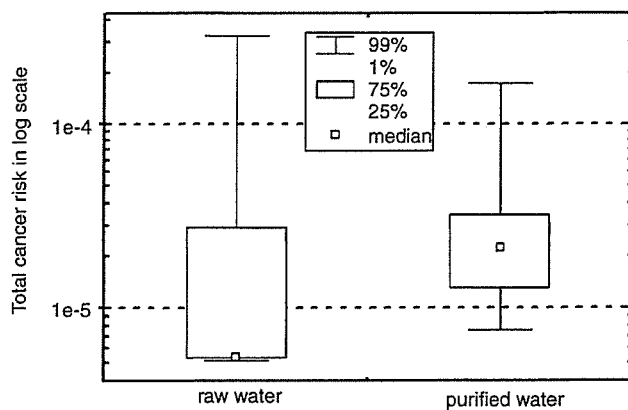


Figure 2 Box and whisker plot of total cancer risks (in log scale)

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 (<i>n</i>) | Median | Geometric mean (<i>G</i> -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 |

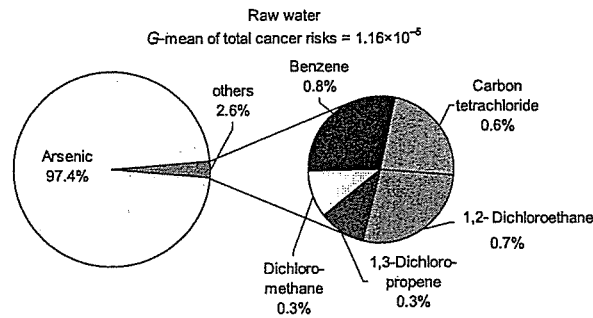


Figure 3 Contribution ratio of substances to the total cancer risk of raw water

As for purified water, the cancer risks posed by 4 THMs (chloroform, bromodichloromethane, 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.

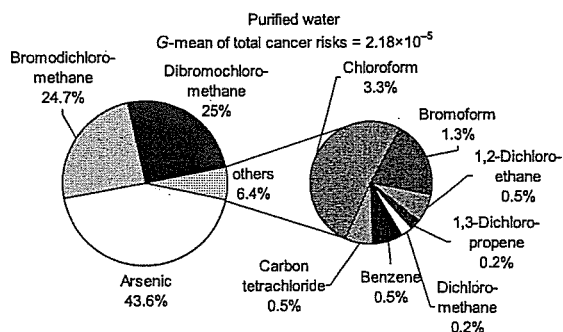


Figure 4 Contribution ratio of substances to the total cancer risk of purified water

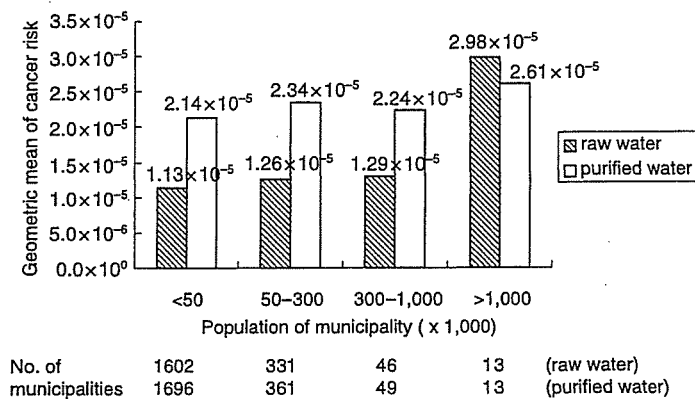


Figure 5 Total cancer risks in relation to the population size of municipalities

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

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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.

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 m³/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 m²). 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 microfiltration (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.

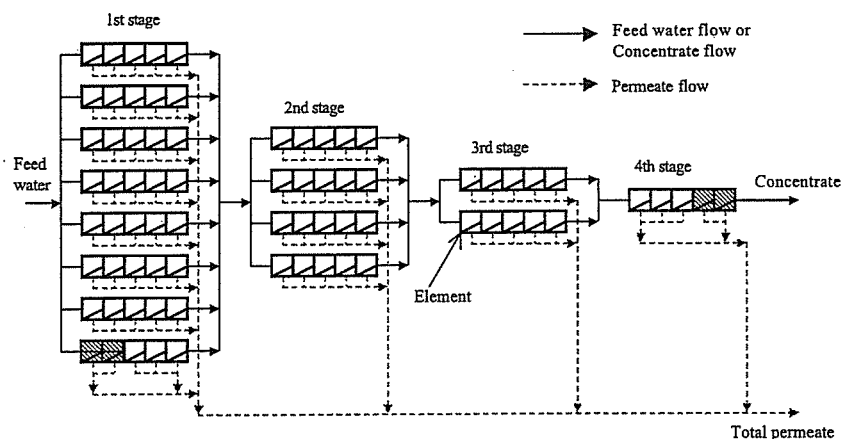


Figure 1 Schematic diagram of the multistage array pilot plant

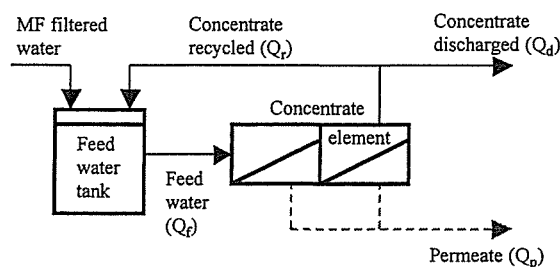


Figure 2 Schematic diagram of the small-scale pilot plant

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 ($r_s = \text{total permeate flow rate/feed water flow rate}$): 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 calculated 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 multistage 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. ($\mu\text{S}/\text{cm}$) | 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 (SO₄²⁻), silicate (SiO₂), 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

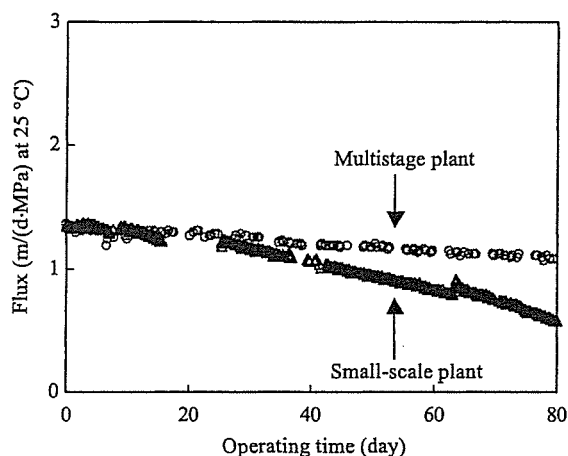


Figure 3 Flux change of upstream elements in RUN1

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 occurrence 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

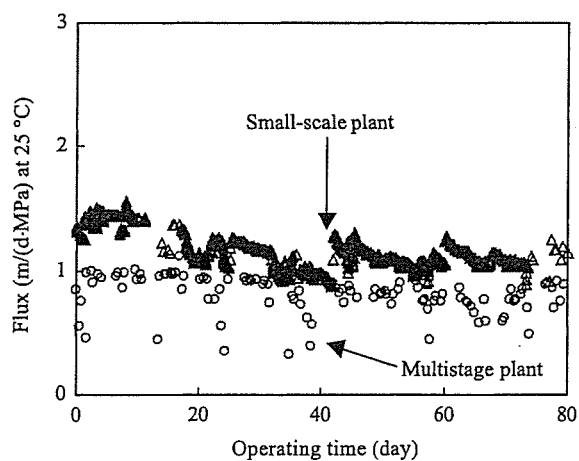


Figure 4 Flux change of downstream elements in RUN1

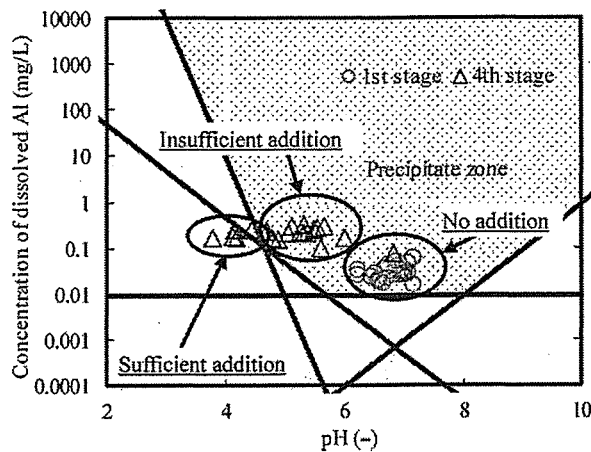


Figure 5 Relationship between pH and Al in RUN1

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

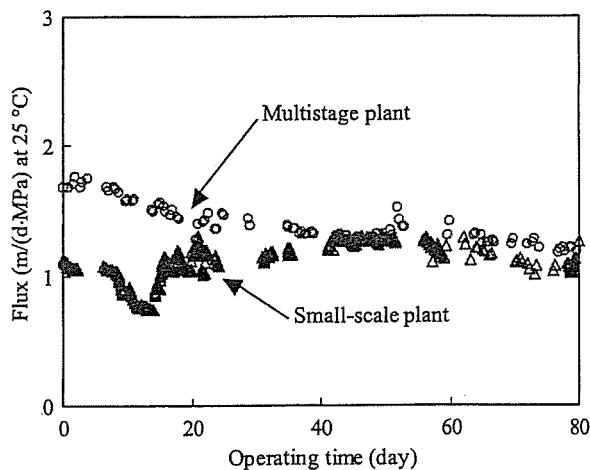


Figure 6 Flux change of upstream elements in RUN2

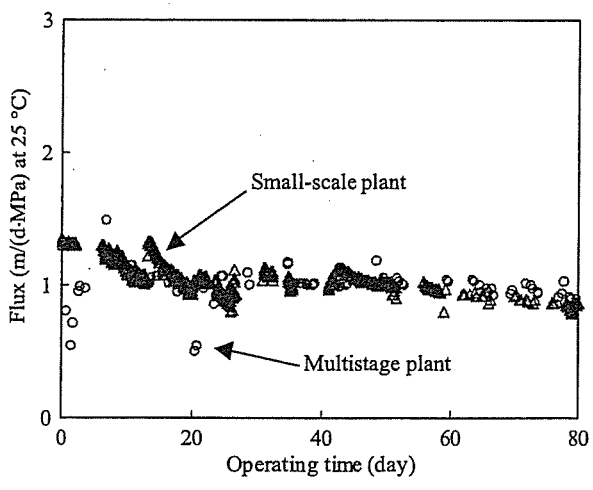


Figure 7 Flux change of downstream elements in RUN2

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.

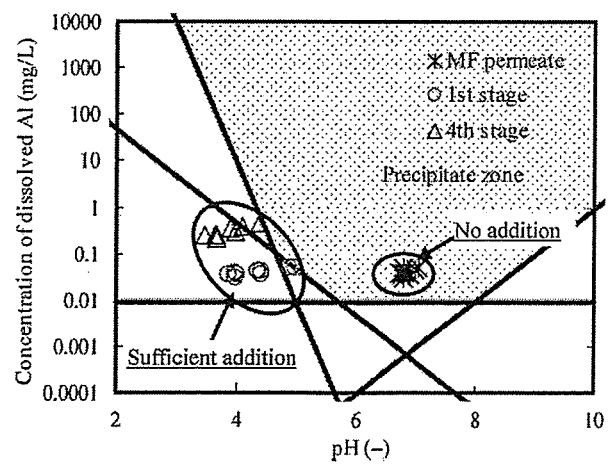


Figure 8 Relationship between pH and Al in RUN2

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.

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.

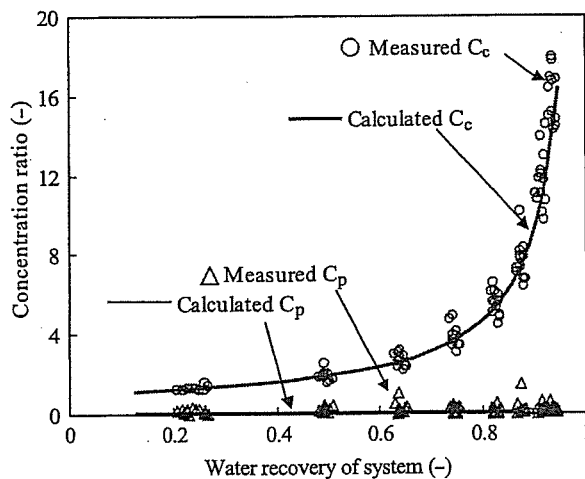


Figure 9 Measured and calculated TOC concentration in RUN1

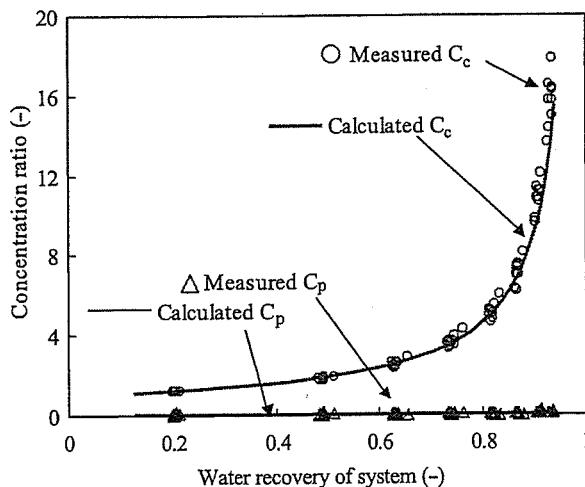


Figure 10 Measured and calculated TOC concentration in RUN2

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.

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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

* Water Purification System in Consideration of Water Quality

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キーワード ①水道水の発がんリスク ②水道原水 ③結合塩素処理 ④水道事業ガイドライン

すると、管路施設ばかりでなく浄水施設についても、どこかで給水停止をせざるを得ない事態を招くと憂慮せざるを得ない。現に、クリプトスポリジウムによる感染症の発生や塩素注入管理が不適切のため感染症が発生して給水停止を実施せざるを得ない事態が発生している。

1965年の年間給水量は約70億 m^3 /年であり、河川の自流水が約55億 m^3 、その他の水源が30億 m^3 であった。水道普及率の向上とともに年間給水量が増加するにつれて、水道水源の構成が大きく異なるようになっていく。すなわち、地盤沈下対策のために地下水取水量の増加は少なく、河川自流水および伏流水の占める割合が低下し、それを補うようにダム・湖沼等新規に開発された水資源施設からの取水が増加している。しかし、湖沼等停滞水域の環境基準の達成率は40%台に留まっており、植物プランクトン等の影響を受

けた水源となっている。しかも、ダムから直接取水して浄水施設まで導水している水道事業者が少ないため、流域から排出される排水や農業排水等非点源負荷の影響を強く受けていることになる。

さらに、化学物質のリスク管理が強化されることに従って水質基準が強化されることに伴い、浄水施設の高度化を図らなければならない。

1. 浄水施設の高度化とは

水質基準項目のうち、発がん性の観点から基準が定められている項目について、水道原水および水道水についてそれぞれの発がんリスクを求め、それらの総和をもって水道原水および水道水の発がんリスクとし、それらの値を首都圏の地方自治体別に示すと図1のようになる。さらに、水道水の発がん物質の構成を示すと図2のようになる。

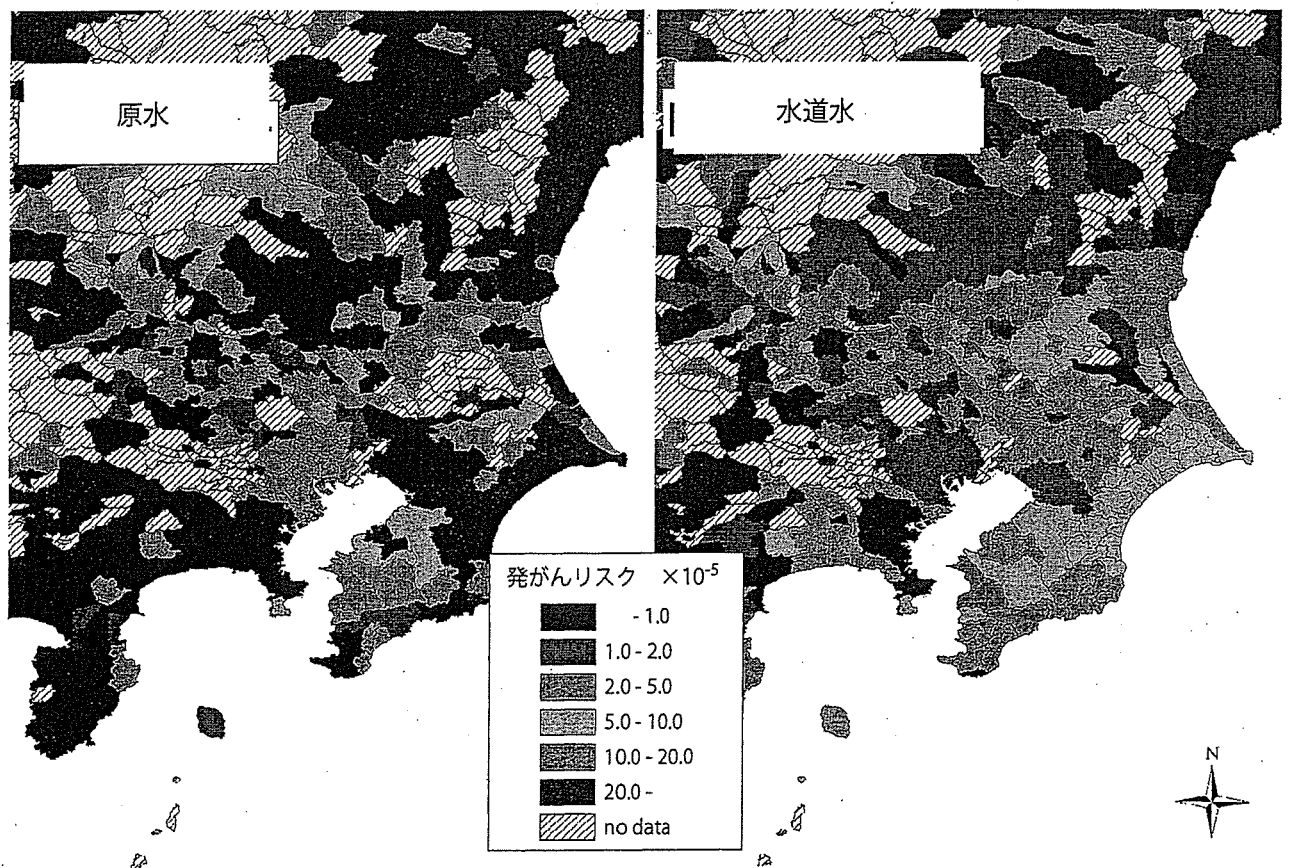


図1 首都圏の水道原水および水道水の発がんリスク分布

水道水の発がんリスクは、個々の発がん物質のリスクレベルを 10^{-5} として水質基準が定められているが、 10^{-4} オーダーの水道原水が存在している。さらに、その発がんリスクは消毒副生成物による寄与が高い。これは、塩素消毒によって発がん性を有するハロゲン化消毒副生成物が生成するためである。浄水処理によって、消毒副生成物の前駆物質の一部は除去されているので、浄水処理によって発がんリスクは低下していることは確かであ

る¹⁾。
水道原水としての公共用水域や地下水の状況、既存の水道施設の水質制御能力を考えたとき、良質で、違和感がなく、利便性障害の少ない水道水を利用できるようにするためには、浄水処理施設をレダントで、まさにマルチバリアーとしての機能を持たせたものとしなければならない。たとえば、今後の浄水処理のフローを選択要件との関係から示すと図3のようになろう。

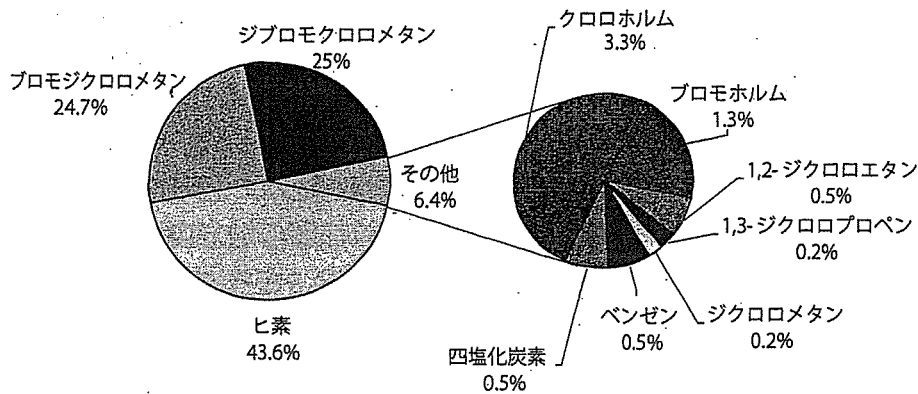


図2 水道水の発がんリスクの構成

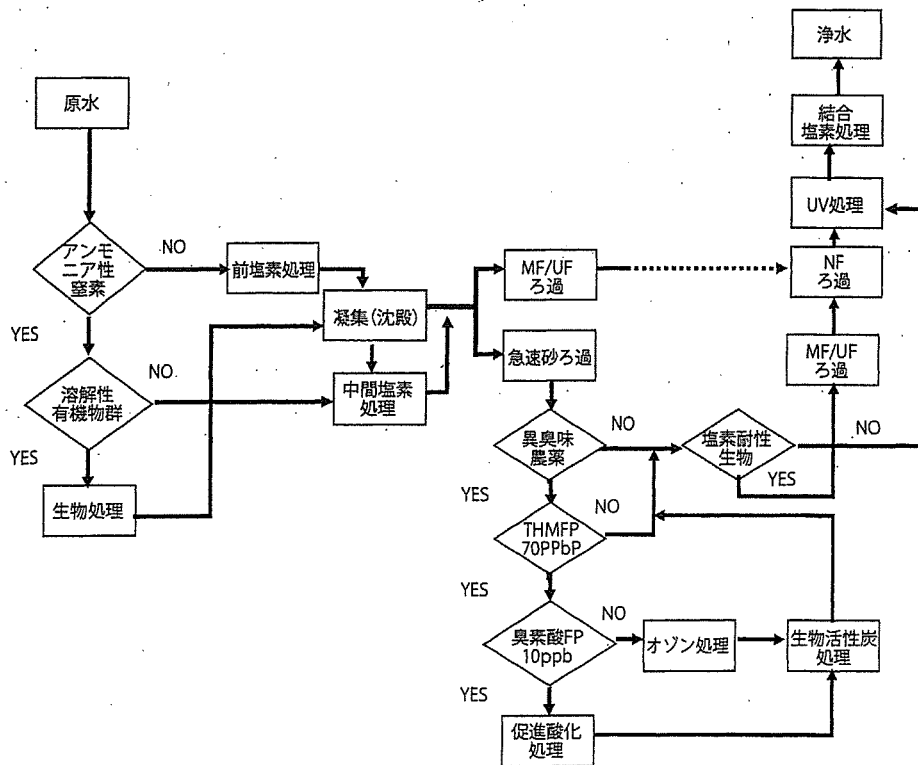


図3 浄水処理システムの構成

WHO飲料水水質ガイドラインが示しているように、水道は感染症対策としての意義がもっとも高い。また、ダム等停滞水域では貧酸素状態が生じると鉄やマンガンのような還元性無機物質が存在するようになり、それらの対策として浄水システム内は酸化条件にしなければならない。塩素等の酸化剤が用いられているが、塩素消費量のもっとも高い還元物質はアンモニア性窒素であり、その濃度変動が大きい場合には酸化反応条件の制御が困難になる。

また、アンモニア性窒素が高い原水では溶解性有機物質も多く、これらの溶解性有機物質は凝集剤として汎用されているアルミ系凝集剤と錯体を形成するなどして凝集反応を阻害する。この錯体となったアルミは浄水に残留することから利便上の障害を生むことがある。このような汚濁した原水では生物処理により、アンモニアや溶解性有機物を可能な限り低減化することが必要となる。なお、アルミ系凝集剤に比べて鉄系凝集剤は溶解性有機物の除去性が高いこと等から、鉄系凝集剤に転換する利点は大きいと考える。

濁質成分を除去する固液分離プロセスとしての凝集沈殿砂ろ過プロセスにおいて、ヒ素のような有害無機物質を除去するために、酸化剤の存在が必要であるため、塩素のような酸化剤を用いた酸化処理が必要になる。凝集沈殿砂ろ過プロセスに代わるMF/UFろ過は、クリプトスポリジウム等耐塩素性生物やピコプランクトンを完璧に分離できる技術であり、汎用浄水技術として扱われるべきものと考えられる。

砂ろ過やMF/UFろ過は固液分離処理プロセスであり、溶解性有機物質についてはその処理効果を実質的に期待することができない。植物プランクトン等が生産するジオスミンや2-MIBのような異臭物質は活性汚泥法等の生物処理でも生産されることから、水資源を繰り返し利用している水域での障害が発

生する可能性が高い。農薬類は季節的に使用されているため、農薬使用時の水道原水中での濃度は高く、慢性影響の観点から健康影響リスク管理目標が設定されているものの、毎年使用されるものであるから季節的な変動を考慮して制御する必要がある。

水道水の発がんリスクは消毒副生成物の寄与が高いことから、消毒副生成物の生成能が高い水道原水では、その前駆物質であるフミン等溶解性有機物をオゾン・活性炭吸着処理によって除去しなければならない。水道原水中に臭化物イオンが存在するとオゾンにより発がん性の強い臭素酸が生成するため、このような場合には臭素酸が生成しないような促進酸化処理が適用されることになる。

異臭味、農薬、消毒副生成物、臭素酸等溶解性の有機物質や浄水処理過程で生成する副生成物を制御するためには、オゾン・活性炭吸着といった高度浄水処理システムを導入しなければならない。しかし、それらの代替システムとして、ナノろ過(NF)膜をベースにした水処理システムが導入される可能性が非常に高い。とくに欧州各国では、蒸発残留物などに起因する水処理上の課題が山積している国際河川ラインを水源とする国々を中心に、オゾン・活性炭からナノろ過膜処理へと転換しつつある。

NF膜ろ過は海水の淡水化で用いられている逆浸透膜の特性とUF膜ろ過の特性を兼ね備えている膜を用いた処理技術であり、一つのプロセスで溶解性有機物も無機イオンも除去できる。運転管理もMF/UF膜ろ過と同様に簡易で自動制御が可能であることから、人的資源の限界がある小規模な浄水場から導入されていくものと考えられるが、大規模な浄水場でもオゾン・活性炭吸着を補完する高度浄水処理施設として導入されるものと考えられる。NF膜ろ過はペットボトル水の生産工程にも利用されており、さらには中国の一部で整備されている給水拠点でNF膜ろ過処理し

た直飲水道水と常用水道水を供給する二元水道でも利用され、水道のような公共サービスでも適用可能なコストに耐えられるレベルに達している技術である。このようなことから、さらに技術革新が期待できる技術である。

感染性生物対策で今後とも有効なのは塩素処理であることは確かである。しかしながら、塩素剤は反応性の高い酸化剤であるため、水道原水中の有機物を低分子化して、生物資化性の高い有機物(AOC)を生成し給配水系での細菌の再増殖や、トリハロメタンやハロ酢酸等の健康影響リスクを有する有機物を生成する。また、塩素特有の臭気は水道水の不快感の原因にもなる。

ダムで貯留され植物プランクトンによる有機物質を含んだ水道原水の占める割合が高くなり、さらに河川上中流部の公共下水道等生活排水処理施設整備の遅れから、生活雑排水の影響を受けた水道原水ということになると、必然的に塩素消費物質が多くなり、塩素注入制御の困難さが高まる。結果的には、残留塩素濃度が高くなり水道水の快適性が損なわれ、同時に塩素消毒副生成物の濃度も高くなる。

このようなことから、浄水システム内で感染性微生物に対して十分なバリアーを構築した上で、給配水系でのリスク管理と塩素臭に対する違和感がない消毒技術として結合塩素処理が導入されることになる。遊離塩素処理を原則としている米国においてすら、ヨーロッパ諸国と同じように結合塩素処理に転換したり、転換することを決定した大都市水道も存在するようになってきている。

おわりに

水道の運営基盤の強化を図るために給水にかかるコストを低減化するとしても限界があり、公平で適正な費用負担を求めつつサービ

ス水準の向上をめざさなければならない。水道施設の更新を含めて水道事業を再活性化するためには、より効率的な事業運営を展開することが求められる。ISO/WD24512の附属文書として扱われることとなっている日本水道協会規格である「水道事業ガイドライン」は、水道事業サービスの実態をできるだけ定量的に評価できる137の指標を規格として示している。指標についての規格であり、規格に基づいてたとえば水質基準適合率という値が求められたとしても、いくら値であれば適正、的確に水道事業が展開されていると評価できるものではない。

しかし、その指標を用いることで、水道水の発がんリスクのみを他の水道事業体と比較するのではなく、そのリスクの背景となっている水源、浄水コスト、人的資源、水道料金等の各種指標と合わせて比較することが可能となったのである。すなわち、自己評価するためのツールが規格となったのである。

つまり水道水の水質は、水質基準というナショナルミニマムは満たしているが、詳細に見ていくと地域的には大きな差異があり、その原因が何であるかを明らかにすることが可能となったのである。このようなツールを活用することによって、レダントな浄水技術を、これまでと同じように浄水施設で適用するか、あるいはブロックや給水拠点で適用することによって、上質な水道水と水質基準を満たす水道水を供給する多元水道の意義が明らかになるものと考えられる。

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Estrogenic activities of chemicals related to food contact plastics and rubbers tested by the yeast two-hybrid assay

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Abstract

Food contact plastics and rubbers possibly contain many kinds of chemicals such as monomers, oligomers, additives, degradation products of polymers and additives, and impurities. Among them, bisphenol A, nonylphenol, benzylbutyl phthalate, styrene oligomers and hydroxylated benzophenones have been reported to possess estrogenic activities. In this study, other chemicals related to food contact plastics and rubbers, and their metabolites induced by the S9-mixture were tested for their estrogenic activities using the yeast two-hybrid assay. Among the 150 chemicals, 10 chemicals such as bis(4-hydroxyphenyl) methane, 4-cyclohexylphenol, 4-phenylphenol, 4,4'-isopropylidenediphenol alkylphosphite, two type of styrenated phenol (including mono type), tris(nonylphenyl) phosphite, 2,2'-dihydroxy-4-methoxybenzophenone, 2-hydroxy-4-methoxybenzophenone and 2,4-diphenyl-4-methyl-1-pentene, their metabolites and the metabolites of 6 other chemicals, such as 2-(phenylmethyl) phenol, styrenated phenol (di and tri type), 1-(*N*-phenylamino)naphthalene, 4-*tert*-butylphenylsalicylate, nonylphenol ethoxylates and 2-methyl-6-*tert*-butylphenol, displayed estrogenic activities. All of them contained a phenol group in their chemical structures or formed one easily by hydrolysis or metabolism. However, most of the chemicals related to food contact plastics and rubbers, and their metabolites did not show any estrogenicity.

Keywords: Estrogenic activity, food contact plastics, rubbers, yeast two-hybrid assay, 2-(phenylmethyl) phenol, 4,4'-isopropylidenediphenol alkyl(C₁₂-C₁₅) phosphite, 1-(*N*-phenylamino) naphthalene, styrenated phenol, tris(nonylphenyl) phosphite, 4-*tert*-butylphenylsalicylate, 2,4-diphenyl-4-methyl-1-pentene, 2-methyl-6-*tert*-butylphenol

Introduction

Food contact plastics and rubbers may contain many kinds of chemicals such as free monomers, oligomers, additives, degradation products of polymers and additives, and impurities. Among these substances, several are recognized as endocrine disruptors that have estrogenic activities. Bisphenol A, a monomer for polycarbonate resin and epoxy resin, has been reported to have an estrogenic activity in ovariectomized rats (Dodds and Lawson 1938), in MCF-7 human breast-cancer cells (Krishnan et al. 1993) and in the rat uterine-cytoplasm fraction (Olea et al. 1996), and another report has shown that the prostatic weight of the male offspring was increased 6 months after birth (Nagel et al. 1997). Nonylphenol is well-known for its estrogenic activity in MCF-7 cells and in ovariectomized rats after

release from a polystyrene test tube (Soto et al. 1991), and it was also determined in several kinds of food contact plastics which originated from the degradation of tris(nonylphenyl) phosphite or tris(mono and/or dinonylphenyl) phosphite used as an antioxidant (Kawamura et al. 1999, 2000). Benzylbutyl phthalate, a plasticizer used for polyvinyl chloride, has been reported to have a weak binding property against the estrogen receptors in MCF-7 (Jobling et al. 1995). Styrene dimers and trimers have been found in polystyrene products (Kawamura et al. 1998a) and also in instant noodles where they had migrated from the polystyrene cup (Kawamura et al. 1998b). Their estrogenic activity in a yeast two-hybrid assay, MCF-7 assay and competitive binding assay have been reported (Nishihara et al. 2000; Ohyama et al. 2001). UV stabilizers, 2-hydroxy-4-methoxybenzophenone have also been reported