Figure 3 | rNV-VLPs, Qβ and MS2 removal by a coagulation–ceramic MF process with alum coagulant at doses of (a) 0.54 mg-Al/L and (b) 1.08 mg-Al/L. Circles, triangles, and diamonds represent rNV-VLPs, Qβ and MS2, respectively. The arrows indicate values greater than those that could be estimated accurately by ELISA.

Comparison of removal performances between PACl and alum

Because the concentration of rNV-VLPs in the MF permeate with the 1.08 mg-Al/L coagulant dose (Figures 2b and 3b) was less than the detection limit of the ELISA kit (approximately 10^8 VLPs/mL), further concentration using a centrifugal filter device (molecular weight cutoff 30,000, regenerated cellulose; Amicon Ultra-15, Millipore Corp.) was performed in the present study to evaluate 4-log removal, as regulated by the U.S. Environmental Protection Agency (USEPA) National Primary Drinking Water Standards (U.S. Environmental Protection Agency 2001). An approximately 10-fold concentration was obtained by the concentration method for rNV-VLPs in the MF permeate.

Figure 4 shows the effect of coagulant type (PACl vs. alum) on the removals of rNV-VLPs, Qβ, and MS2 in the coagulation–ceramic MF process with a 1.08 mg-Al/L coagulant dose. The experiment with PACl achieved >4-log removal of rNV-VLPs regardless of the filtration time, whereas with alum 3.3-log to >3.9-log removals were observed. This means that the experiment with PACl more effectively removed rNV-VLPs than that with alum, and that it satisfied the USEPA requirement of 4-log removal/inactivation. The difference in removal performance between PACl and alum was possibly due to differences in

the characteristics of the aluminium floc particles generated during the coagulation process. Gregory & Dupont (2001) reported that aluminium floc particles formed with PACl are larger, stronger, and more readily separated by the settling process than those formed with alum. In the present study, because the rNV-VLPs were adsorbed to or entrapped in the aluminium floc particles, and settled out from suspension during the settling process or were separated during the MF process, the difference in the characteristics of the aluminium floc particles between PACl and alum may account for the difference in the removal performance for rNV-VLPs of the coagulation–ceramic MF process. Further investigation is needed.
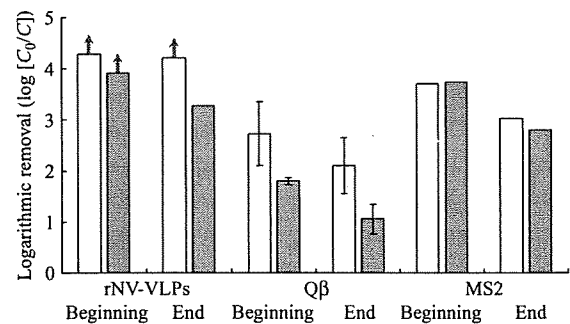

Figure 4 | Effect of coagulant type on the removal of rNV-VLPs Qβ and MS2 at the beginning and end of filtration in a coagulation–ceramic MF process. White and gray columns represent PACl and alum, respectively. The coagulant dose was 1.08 mg-Al/L. The arrows indicate values greater than those that could be estimated accurately by ELISA.

The removal ratios of Qβ and MS2 were smaller than those of rNV-VLPs in the coagulation–ceramic MF process with both aluminium coagulants: the ratio of Qβ was approximately 2-log smaller than that of rNV-VLPs, and the MS2 ratio was approximately 1-log smaller. Accordingly, both bacteriophages have the potential to become appropriate surrogates for native NV in the coagulation–ceramic MF process, with Qβ being the more conservative surrogate of the two. We imagine that the characteristics of rNV-VLPs, Qβ, and MS2 such as surface charge and hydrophobicity affect the removal performance in the coagulation–MF process. Further investigation of differences in surface properties between rNV-VLPs and the two bacteriophages is needed.

Our research group has shown that PACl exhibits virucidal activity during the coagulation process (Shirasaki et al. 2009a,b): an approximately 4-log difference between the total (infectious + inactivated) concentration measured by real-time RT-PCR and the infectious concentration measured by the PFU method was observed during the coagulation process, indicating that some of the bacteriophages were probably inactivated by PACl. Because rNV-VLPs lack RNA, which is necessary for infection and replication in host cells, we cannot discuss the fate of infectivity of NV in the treatment process. If PACl exhibits virucidal activity for native NV as well as for bacteriophages, >4-log removal (including inactivation) of native NV might be easily achieved during the coagulation–ceramic MF process.

CONCLUSIONS

- The removal performance of NV as particles was evaluated by using rNV-VLPs in a coagulation–ceramic MF process.
- Both coagulation type and coagulant dose affected the removal performance of rNV-VLPs: the experiment with a 1.08 mg-Al/L PACl dose achieved high ratios of rNV-VLP removal, >4-log, which satisfies the USEPA requirement of 4-log removal/inactivation.
- The removal ratios of rNV-VLPs were higher than those of Qβ and MS2 in the experiments with the 1.08 mg-Al/L

coagulant dose: the Qβ ratio was approximately 2-log smaller than that of rNV-VLPs, and the MS2 ratio was approximately 1-log smaller. This means that both bacteriophages have the potential to become appropriate surrogates for native NV in the coagulation–ceramic MF process, with Qβ being the more conservative of the two.

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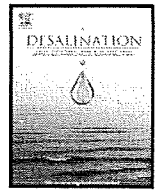
NF membrane fouling by aluminum and iron coagulant residuals after coagulation–MF pretreatment

Koichi Ohno [a,*], Yoshihiko Matsui [a], Masaki Itoh [b,1], Yoshifumi Oguchi [a], Takuya Kondo [a], Yosuke Konno [a], Taku Matsushita [a], Yasumoto Magara [c,2]

[a] Graduate School of Engineering, Hokkaido University, N13W8, Sapporo 060-8628, Japan
[b] Department of Water Supply Engineering, National Institute of Public Health, Saitama, Japan
[c] Center for Environmental Nano and Bio Engineering, Hokkaido University, Sapporo, Japan

ARTICLE INFO

ABSTRACT

The effects of coagulant residuals on fouling of a nanofiltration (NF) membrane were investigated. Experiments were carried out with a laboratory-scale microfiltration (MF)–NF setup and a pilot MF–NF plant. In the laboratory-scale experiments, NF feed water was pretreated with poly-aluminum chloride (PACl) or alum followed by MF. NF membrane permeability declined when the feed water contained residual aluminum at 18 µg/L or more, but not when it was lower than 9 µg/L. When pretreated with ferric chloride, no substantial decline of NF membrane permeability was observed; residual iron did not affect the permeability. When SiO_2 was added to the water before the pretreatment with PACl, the NF membrane permeability declined at about double the speed. Thermodynamic calculations and elemental analysis of foulants recovered from the membranes indicated that the majority of inorganic foulants were compounds composed of aluminum, silicate, and possibly potassium. In the pilot plant, NF feed was pretreated by PACl. Transmembrane pressure for NF doubled over 4.5 months of operation. Although the aluminum concentration in the NF feed was not high (30 µg/L), analysis of membrane foulants revealed excessive accumulation of aluminum and silicate, also suggesting that aluminum residuals caused the membrane fouling by alumino-silicates or aluminum hydroxide.

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1. Introduction

Nanofiltration (NF) is a promising advanced drinking water treatment process that offers an efficient alternative to conventional advanced treatment (ozone-activated carbon) and has the potential to produce potable water of better quality. NF is expected to perform better than conventional advanced treatment in removing natural organic matter, precursors of disinfection by-products [1,2] and trace hazardous chemicals such as pesticides [3] from water; however, NF is still more expensive, and its cost needs to be reduced if it is to be widely accepted.

Membrane fouling leads to a continuous decline in membrane permeability, and fouling mitigation considerably reduces the cost of designing and operating membrane filtration systems. In the case of NF of surface waters, the accumulation of particulate matter severely decreases the permeability of the NF membranes; such particulates must be removed by pretreatment processes such as coagulation, followed by clarification and then multi-media filtration or microfiltration (MF).

Although these pretreatments can alleviate the effect of organic foulants as well as that of particulate, the pretreatment increases coagulant residuals to NF feed and they may precipitate on the membrane surface and reduce membrane permeability. Kim et al. [4] used three types of NF feed: untreated raw water (RAW water), pretreated by in-line coagulation followed by MF (MF water) and pretreated by coagulation, sedimentation and sand filtration (CS water). They found that the order of the ratio of inorganic foulants to the total amounts of foulants was CS water>MF water>RAW water. Gabelich et al. tested reverse osmosis (RO) membrane using feed pretreated with conventional or direct filtration treatment plants. They used either alum or ferric chloride, and also used cationic polymer and chloramines for pretreatment. The tests using alum with RO elements revealed rapid deterioration in specific flux, on the other hand, the specific flux using ferric chloride did not decrease over time [5]. They also suggested that three types of aluminum-based foulants: aluminum silicates, aluminum hydroxides, and aluminum phosphates [6]. Accordingly, both pretreatment methods and types of coagulants may play a crucial role in the control of NF/RO fouling. Application of conventional coagulation, clarification and multi-media filtration can

take advantage of preexisting facilities; however, the processes offset the benefit of small area required for NF membrane process. Pre-coagulated MF would be more advantageous process for pretreatment for NF.

Most of the surface water treatment plants in Japan that have coagulation process currently use aluminum coagulants [7]. During our pilot plant experiment [8], which is also discussed in this study, we found that residual aluminum coagulants in the NF feed might cause the membrane fouling. Therefore, the objective of this study was to investigate the effects of coagulant residuals on NF membrane fouling when NF is applied as an advanced water treatment process of surface or ground water. In laboratory-scale experiments, we used two types of aluminum coagulant: poly-aluminum chloride (PACl) and alum and pretreated by in-line coagulation and ceramic MF. As an alternative coagulant, iron coagulant (ferric chloride) was also used. To clarify the effect of residual coagulants, groundwater that contained low organic matter was used as raw experimental water. To elucidate the effects of SiO_2 on the NF membrane fouling, we added SiO_2 to the raw water in some of the experiments. The results of the pilot scale experiment, in which PACl was used as a coagulant agent, were also presented and discussed.

2. Experimental

2.1. Laboratory-scale experiment

In the laboratory-scale experiment, Hokkaido University ground-water was used as raw experimental water. The average quality of this water was: DOC 0.5 mg/L, EC 450 μS/cm, pH 7.2, Na 29 mg/L, K 9.6 mg/L, Ca 50 mg/L, Mg 15 mg/L, Cl 25 mg/L, SO_4 40 mg/L. Types of coagulants used were PACl (10% Al_2O_3, basicity 52%, Japanese Industrial Standard (JIS) grade), alum (Aluminum Sulfate 14–18 Water, reagent grade, Wako Pure Chemicals, Osaka, Japan) or ferric chloride (Iron (III) Chloride Hexahydrate, reagent grade, Wake Pure Chemicals). The raw water was firstly treated with activated carbon cartridge filter to quench residual chlorine and then pretreated by in-line coagulation followed by MF. The MF filtrate (pH 7.0–7.1) was then pumped at a rate of 1.5 L/h to a flat sheet membrane test cell (filtration area 60 cm², C10-T, Nitto Denko Matex Corp., Tokyo, Japan; Fig. 1) that housed the NF membrane (UTC-60, nominal NaCl rejection 55%, Toray Industries, Inc.). NF was performed at a filtration flux of 2.5 cm/h and a water recovery rate of 10%. The system flow is shown in Fig. 2. We conducted nine experimental runs and their conditions are summarized in Table 1. In all experimental runs, the coagulant
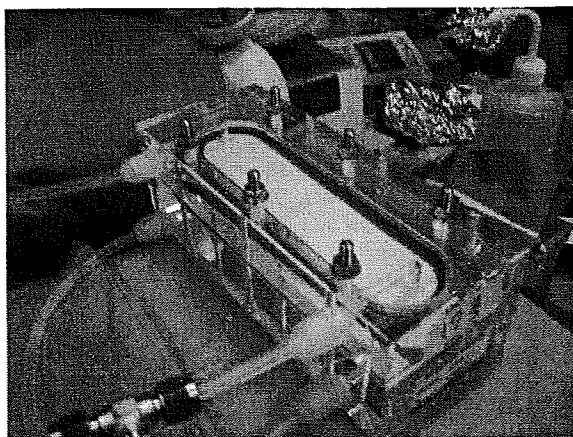

Fig. 1. Flat sheet membrane test cell.

dose was set at 0.04 mM (1.1 mg-Al/L, 2.2 mg-Fe/L). MF was performed with a laboratory-use ceramic membrane (nominal pore size 0.1 μm, membrane area 0.4 m², NGK Insulators, Nagoya, Japan) at very low filtration flux (0.83 cm/h), without periodic hydraulic backwashing; the MF membrane was replaced with a chemically cleaned membrane when the inlet pressure reached 0.05 MPa. After the NF experiments, spent NF membranes were cleaned with 2% citric acid, and the aluminum and iron concentrations in the citric acid drain were analyzed.

After five experimental runs with the laboratory-scale experimental setup, an automatic hydraulic backwash system was introduced to the MF step; the MF was performed at a normal filtration flux (6.25 cm/h), and the MF membrane was hydraulically cleaned by backwash at a pressure of 500 kPa for 10 s every 2 h [9]. MF permeate (pH 6.8–7.0) was introduced to the NF membrane test cell at a filtration flux of 2.08 cm/h, which is slightly lower than the fluxes used for the previous experiments. Runs 6–9 were conducted with this system. Run 6 used PACl as a coagulant, and Run 7 used ferric chloride.

In the next two experimental runs (Runs 8 and 9), SiO_2 was added to the chlorine-quenched groundwater before coagulation with PACl and MF pretreatment. By comparing these results with the results of Run 6, in which the mean silicate concentration was 35 mg-SiO_2/L, we investigated the effect of silicate on the NF membrane fouling. Diluted sodium silicate was added so that the silicate concentration in the NF feed would be approximately 80 mg-SiO_2/L. Sodium silicate is a basic reagent, and thus the pH was adjusted to approximately 7 with hydrochloric acid. After Runs 6, 8, and 9, the spent NF membranes were cleaned sequentially with HCl, NaOH, and citric acid; and then the aluminum, silicate, calcium, and potassium concentrations in the cleaning water were analyzed.

2.2. Pilot MF–NF plant experiment

The pilot plant received water at a rate of 24 m³/h from the outlet of a sedimentation basin of the Ishikawa Water Treatment Plant, Okinawa, Japan, after PACl (basicity 50%, JIS grade) coagulation. In the pilot plant, MF (polyvinylidene fluoride membrane, nominal pore size 0.1 μm; Toray Industries, Inc., Tokyo, Japan) filtrates (pH 6.5–7.3) were transferred to the NF modules (nominal NaCl rejection 55%; polyamide SU-610, Toray Industries, Inc.), which were operated at constant flux (2.5 cm/h) and water recovery rate (95%) by adjustment of the feed pressure. Average quality of MF filtered water was: TOC 0.9 mg/L, EC 185 μS/cm, Na 19 mg/L, Ca 11 mg/L, Cl 27 mg/L, SO_4 14 mg/L, and residual Al was 0.03 mg/L. The 15 NF modules were placed in a multistage array (8, 4, 2, and 1 modules in series), and the water recovery rate of each element was about 13%. Details of the process configuration and operation are given elsewhere [8]. After 4.5 months of system operation, foulants on the NF membrane surface were collected by gentle scraping of the membrane deposits. The foulants were then dried, weighed, combusted for 30 min in a muffle furnace at 550 °C, and then weighed again to obtain the mass of fixed solid. The recovered foulant was analyzed for Al, Ca, Fe, S, and Si.

2.3. Analytical methods

Aluminum and iron concentrations were measured by an inductively coupled plasma-mass spectrometer (ICP-MS; HP-4500; Agilent Technologies, Inc., Palo Alto, CA, USA). Ion concentrations (Na^+, K^+, Mg^+, Ca^+, Cl^-, NO_3^-, SO_4^{2-}) were measured by ion chromatograph (DX-120, Nippon Dionex K.K., Osaka, Japan). SiO_2 was measure by molybdenum yellow colorimetric method. TOC and DOC were measured by TOC-5000A (Shimadzu Corporation, Kyoto, Japan) or Sievers 900 Laboratory TOC analyzer (GE Analytical Instruments, Boulder, CO, USA).
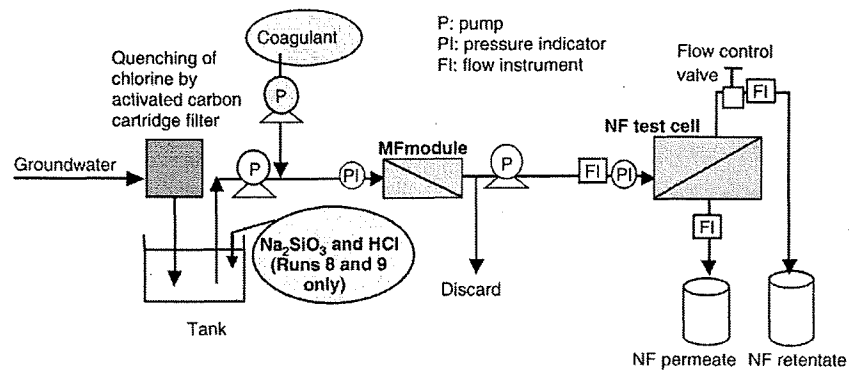
Fig. 2. Experimental setup for laboratory-scale MF–NF experiments.

3. Results and discussion

3.1. Laboratory-scale experiment pretreated with aluminum coagulants (Runs 1–3)

Changes in NF membrane permeability over time in the laboratory-scale experiment with different aluminum coagulants (i.e., PACl and alum) are compared in Fig. 3. Because variation in the initial filtration flux of the pieces of NF membrane sheet used in the NF cross-flow cell was small, nanofilter permeability was evaluated in terms of the dimensionless standardized filtration flux, which is the standardized flux at 1 MPa and 25 °C divided by the standardized flux for pure water, as described by the following equations [10]:

$$J = \frac{Q}{A} \cdot \frac{\alpha}{\Delta P} \qquad (1)$$

where J is standardized filtration flux [m/(h MPa)], Q is filtration rate (m³/h), A is membrane surface area (m²), α is a temperature compensation factor to 25 °C, and ΔP is transmembrane pressure (TMP) (MPa); and

$$J^* = \frac{J}{J_W} \qquad (2)$$

where J^* is dimensionless standardized flux, and J_W is standardized filtration flux for pure water [m/(h MPa)].

After 25 days of operation of the laboratory-scale experiment with PACl coagulant (Run 1) in which MF permeate (NF feed) had a mean aluminum concentration of 20 μg/L, the filtration flux decreased by about 15% (Fig. 3). In an experiment with alum coagulant (Run 2) in which NF feed contained aluminum at a mean concentration of 18 μg/L, the filtration flux again decreased by about 15%. Lower mean

aluminum concentration (8.7 μg/L) in NF feed was observed in another experiment with PACl coagulant (Run 3); we did not change any specific condition of coagulation and MF, and we could not elucidate the reason why we could achieve this lower residual aluminum concentration. In this Run 3, the NF membrane permeability did not change substantially. The percentage rejection of aluminum by NF was more than 85%; most of the aluminum remaining after MF obviously could not permeate the NF membrane and thus had the potential to be deposited on the NF membrane, reducing membrane permeability. However, the aluminum concentrations in the NF retentates were only slightly higher than the concentrations in the corresponding NF feed; more than 98% of the aluminum fed to the NF was discharged with the NF retentate. Therefore, the high rejection ratio of aluminum did not produce a retentate that was highly concentrated in comparison with the feed and did not necessarily result in a high deposition rate on the NF membrane.

3.2. Laboratory-scale experiment with iron coagulant pretreatment (Runs 4 and 5)

Unlike Runs 1 and 2, Runs 4 and 5 did not show a large change in nanofilter permeability (Fig. 4). Mean iron concentrations in the NF feed after the ferric chloride coagulation and MF pretreatments in Runs 4 and 5 were 10 and 18 μg/L, respectively, and the aluminum concentration in the NF feeds was less than 2 μg/L. The percentage rejection of iron by NF was 60–90%, which was not as high as that of aluminum. These results suggest that the concentration of residual aluminum after coagulation influenced NF fouling more strongly than did the residual iron concentration.

Table 1
Laboratory-scale experimental conditions and mean concentrations of residual coagulant in NF feed water.

Run	Type of coagulant	Automatic backwash system in MF and filtration flux (cm/h)	SiO₂ was added to be ~80 mg/L	Mean concentration of residual coagulant in NF feed water	NF filtration flux (cm/h)
1	PACl	No (0.83)		20 μg-Al/L	2.5
2	Alum	No		18 μg-Al/L	2.5
3	PACl	No		8.7 μg-Al/L	2.5
4	FeCl₃	No		10 μg-Fe/L	2.5
5	FeCl₃	No		18 μg-Fe/L	2.5
6	PACl	Yes (6.25)		40 μg-Al/L	2.08
7	FeCl₃	Yes		8.6 μg-Fe/L	2.08
8	PACl	Yes	Yes	103 μg-Al/L	2.08
9	PACl	Yes	Yes	85 μg-Al/L	2.08

Fig. 3. Time dependence of dimensionless standardized flux (standardized flux/standardized flux for pure water) for NF after coagulation and MF in the laboratory-scale experiment (Runs 1–3).
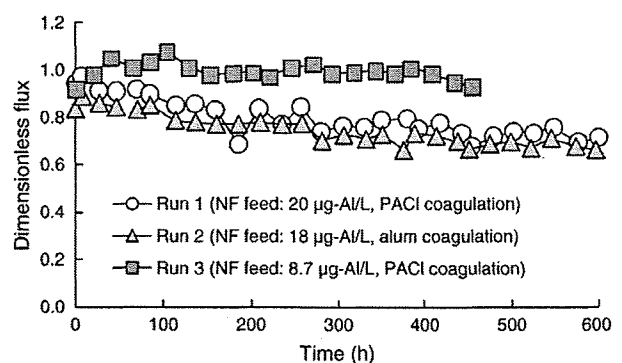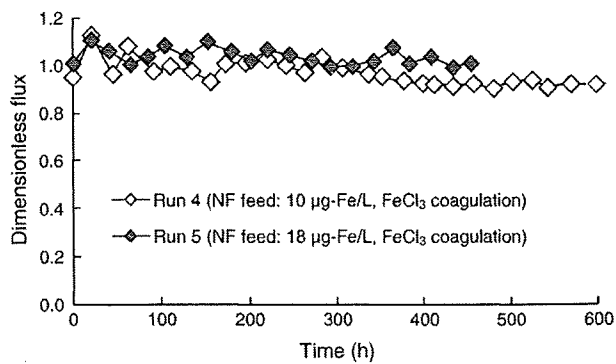
Fig. 4. Time dependence of dimensionless standardized flux (standardized flux/ standardized flux for pure water) for NF after coagulation and MF in the laboratory-scale experiment (Runs 4 and 5).
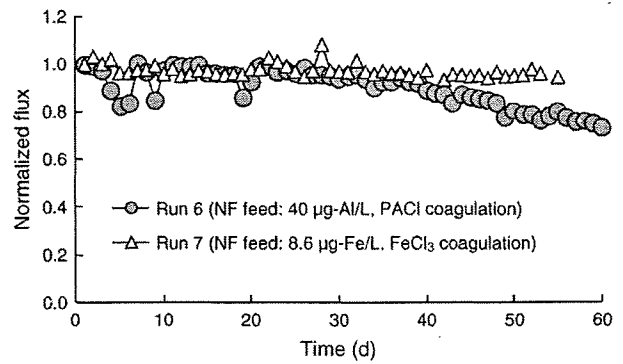

Fig. 5. Time dependence of normalized flux (standardized flux/first day standardized flux) for NF after coagulation and MF in the laboratory-scale experiment (Runs 6 and 7).

Table 2 summarizes the masses of aluminum and iron eluted from the spent NF membranes by citric acid. The membranes used in Runs 1 and 2, which showed larger permeability declines, contained more aluminum (3.6 and 4.0 mg/m²-membrane surface) than the others. The amount of iron eluted from the spent membranes was similar to the amount of aluminum (Table 2), but unlike the mass of aluminum, the mass of iron was not obviously correlated with membrane permeability decline (Figs. 3 and 4).

3.3. Laboratory-scale experiment with backwashing in the MF step

3.3.1. Comparison of aluminum and iron coagulation (Runs 6 and 7)

An automatic backwash was introduced to the MF step after Run 5, and this alteration permitted MF at a normal filtration flux. Under this altered condition, experimental runs with PACl coagulant (Run 6) and ferric chloride (Run 7) were performed. Nanofilter permeability declined during Run 6 (Fig. 5). In this run, the NF feed contained residual aluminum of 40 µg/L in average, and the membrane permeability declined by 25% after 60 days (1440 h) of operation. The permeability declined at lower rates in this run than in Runs 1 and 2; this result was probably due to the fact that the filtration flux (2.08 cm/h) was lower than in Runs 1 and 2 (2.5 cm/h). In the experiment with ferric chloride (Run 7), no substantial decline in NF membrane permeability was observed; this result was the same as those for Runs 4 and 5.

3.3.2. Effect of SiO₂ addition (Runs 6, 8 and 9)

When SiO_2 was added to the water before the pretreatment by coagulation with PACl and MF (Runs 8 and 9), the NF membrane permeability declined at about double the speed observed for Run 6 (Fig. 6). The pH in Run 8 was not strictly controlled (the pH of the NF feed water fluctuated between 6.6 and 7.5). Aluminum is more soluble at alkaline pH than at neutral pH [11], and therefore the mean aluminum concentration in the NF feed was as high as 103 µg/L. In Run 9, the pH was controlled more strictly (6.7–7.0 over the course of the run); nevertheless, the mean aluminum concentration was also rather high (85 µg/L) in this run. This higher residual aluminum may

have been due to the effect of excess silicate. Lartiges et al. [12] reported that flocculation of colloidal silica with polymerized aluminum begins with the formation of negatively charged alumino-silicate sites. Duan and Gregory [13,14] investigated the interaction of aluminum coagulants with silica and found that a small amount of dissolved silica can improve coagulation by affecting the charge-neutralizing behavior of hydrolyzed aluminum species, but silica coagulation is inhibited as the amount of silica is increased, as a result of the increasing negative charge of the particles.

To explore further the effect of a large amount of silicate on the faster decline of NF membrane permeability, we cleaned the spent membrane sequentially with HCl, NaOH, and citric acid after the experimental runs. Results after chemical cleaning with HCl are shown in Table 3; aluminum and silicate were recovered in molar ratios of 1:0.49 (Run 6), 1:1.52 (Run 8), and 1:1.78 (Run 9). These results suggest that aluminum and silicate were major inorganic foulants of the nanofilter.

We calculated the aluminum solubility diagram for the NF feed solution used in Runs 6, 8, and 9 (Fig. 7) with Geochemist's Workbench (ver. 6, RockWare, Inc., Golden, CO, USA). The major difference in the feed water quality of these runs was silicate concentration. The aluminum concentration in the NF feed water exceeded the upper solubility limit in the case of gibbsite ($Al(OH)_3$), pyrophyllite ($AlSi_2O_5OH$), and kaolinite ($Al_2Si_2O_5(OH)_4$), that is, an aluminum compound and two compounds containing both aluminum and silicate. Furthermore, changing the silicate concentration from 40 to 80 mg-SiO_2/L led to a large decrease in the solubility of pyrophyllite and kaolinite (from dotted line to solid line), although the solubility of gibbsite did not change. This result implies that more aluminum silicate compounds may have deposited on the NF membrane as the amount of silicate in the feed water increased. Therefore,

Table 2
NF membrane foulants in the laboratory-scale MF–NF experiment in Runs 1–5.

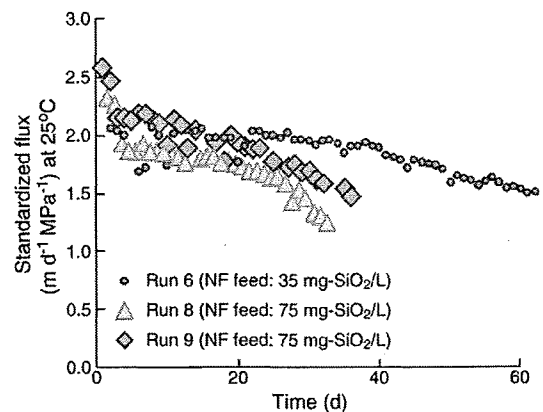|	Coagulant	Foulant	
		Al (mg/m²)	Fe (mg/m²)
Run 1	PACl	3.6	2.5
Run 2	Alum	4.0	1.7
Run 3	PACl	1.8	2.1
Run 4	FeCl₃	0.2	3.3
Run 5	FeCl₃	1.2	1.8

Fig. 6. Changes in standardized flux for NF after coagulation and MF in the laboratory-scale experiment (Runs 6, 8, and 9).

Table 3
Molar ratio of Si and K to Al recovered by cleaning with HCl.

	Mean Si concentration in NF feed water (mg-SiO₂/L)	Si/Al (mol/mol)	K/Al (mol/mol)
Run 6	35	0.49	0.48
Run 8	75	1.52	1.02
Run 9	77	1.78	0.70

the silicate concentration could play a major role in NF membrane fouling, even though the rejection rate of silicate itself was not high: the rejection percentages of silicate were only 10–20% in both the pilot plant and laboratory experiments.

Calcium was not detected on the spent membrane from Run 6 but was detected in Runs 8 and 9. In these runs, calcium was detected in the NaOH cleaning solution, which suggests that calcium fouled the NF membrane in combination with organic substances. In contrast, potassium was largely detected in the HCl and citric acid cleaning solutions. The molar ratios of aluminum to potassium in the HCl cleaning solution were 1:0.48 (Run 6), 1:1.02 (Run 8), and 1:0.70 (Run 9) (Table 3). The thermodynamic calculation (Geochemist's Workbench) also suggests that the aluminum concentration in the NF feed water was higher than the solubility of mordenite-K ($K_2Al_2Si_{10}O_{24} \cdot 7H_2O$) (Fig. 7), and in some calculations, clinoptilolite-K ($K_6Al_6Si_{30}O_{72}$) also appeared as a candidate foulant (data not shown). These two minerals are siliceous zeolites [15,16], and the chemical formulas of natural zeolites are very complicated; not only potassium but also other cations, including sodium, calcium, and magnesium, are incorporated into the zeolites because zeolites have ion-exchange properties [17]. The foulants in the other experiments were not analyzed for potassium (because we did not consider potassium as a potential foulant when the research started) and other cations except calcium; we therefore could not elucidate further the effects of these cations.

3.4. Pilot MF–NF plant experiment

The permeability of the first stage modules in the multistage array of nanofilters declined with operation time (Fig. 8). Although no severe membrane fouling was expected for the first stage module, TMP doubled and the permeability (represented by standardized filtration flux at 25 °C and 1 MPa) was reduced to 1/3 the original permeability over 4.5 months of operation. The mean silt density index of the NF feed water was 2.25 (minimum 1.0, maximum 3.2), which suggests an absence of severe fouling by particulate matter. Gabelich et al. [18] recently reported that aluminum residuals, most
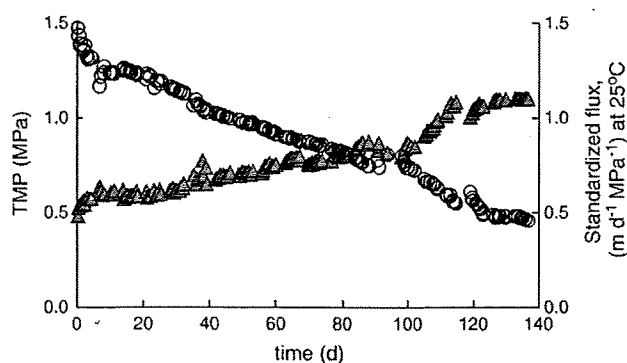
Fig. 8. Water permeability for the first stage of the multistage array in the NF pilot plant. Triangles, transmembrane pressure (TMP); circles, permeability represented by standardized filtration flux at 25 °C and 1 MPa of TMP.

notably from alum coagulation, cause colloidal fouling of RO membranes through interaction with the ambient silica to form aluminum silicate. They suggested that keeping the aluminum concentration at <50 μg/L would result in stable RO membrane performance. The aluminum concentration in the NF influent of our experiment was below this suggested limit (mean 30 μg/L, minimum 10 μg/L, maximum 47 μg/L).

Collection of the membrane deposits was followed by combustion at 550 °C, and we recovered remaining foulants (regarded as ash) at a rate of 330 mg/m²-membrane surface. We conducted elemental analysis of this ash for Al, Ca, Fe, S, SiO₂ and their concentrations were 46, 0.33, 2.5, 3.9, and 30 mg/m², respectively. This excessive accumulation of aluminum and silicate also suggests that aluminum residuals probably caused the membrane fouling by forming alumino-silicates or aluminum hydroxide.

4. Conclusion

Residual aluminum in the NF feed water greatly increased the decline of NF membrane permeability both in a pilot MF–NF plant experiment and in laboratory-scale MF–NF experiments when aluminum coagulants were used in the pretreatment process. On the contrary, there was no substantial decline in NF membrane permeability in the laboratory-scale experiments when ferric chloride was used as a coagulant. In the laboratory-scale experiments with aluminum coagulants, NF membrane permeability declined when the feed water contained residual aluminum at 18 μg/L or more, but not when the aluminum concentration was lower than about 9 μg/L. Therefore, the control of residual aluminum in the pretreatment processes of NF is crucial for mitigation of severe fouling of the NF membrane. The silicate concentration in the NF feed water also greatly increased NF membrane fouling, and other cations, especially potassium, may have been incorporated in the foulants in the form of zeolites.

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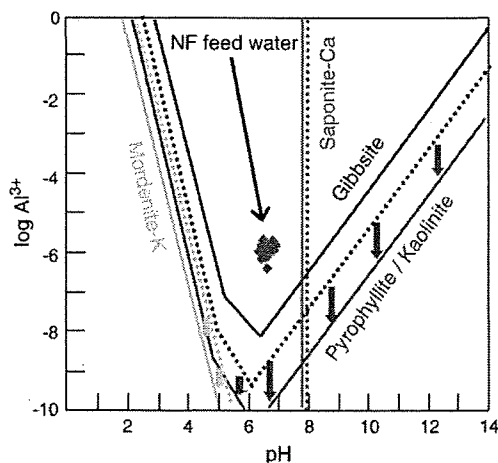

Fig. 7. Solubility diagram for aluminum at 25 °C: dotted lines, solubility diagram for the NF feed solution in Run 6 (40 mg-SiO₂/L); solid lines, Runs 8 and 9 (80 mg-SiO₂/L).

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Plant capacity affects some basic indices of treated water quality: multivariate statistical analysis of drinking water treatment plants in Japan

Koichi Ohno, Emi Kadota, Yoshihiko Matsui, Yoshimi Kondo,
Taku Matsushita and Yasumoto Magara

ABSTRACT

The quality of treated water produced by a drinking water treatment plant (DWTP) is affected by many factors. Relative impacts of various factors that affect the following treated water quality indices—turbidity, color, aluminum concentration and aggregate organic constituents—were investigated. Multivariate statistical analysis based on Hayashi's Quantification Theory Type 1 was performed on a dataset comprised of statistics on raw and treated water quality collected from thousands of DWTPs throughout Japan. Explanatory factors were the source of the raw water, water treatment process employed, plant capacity, total plant capacity of the water supplier (TCWS), raw water quality and pH of treated water. The statistical analyses mainly revealed that not only did obvious factors such as raw water quality affect treated water quality, but also more obscure factors such as plant capacity and TCWS. The results also imply that the larger the water supplier a DWTP of a given size belongs to, the higher the quality of treated water will be.

Key words | aluminum, color, quantification theory, TOC, turbidity

Koichi Ohno (corresponding author)
Emi Kadota
Yoshihiko Matsui
Yoshimi Kondo
Taku Matsushita
Department of Socio-Environmental Engineering,
Hokkaido University,
N13W8,
Sapporo 060-8628,
Japan
Tel./Fax:+81 11 706 7282
Email: ohnok@eng.hokudai.ac.jp

Yasumoto Magara
Center for Environmental Nano and Bio
  Engineering,
Hokkaido University,
N13W8,
Sapporo 060-8628,
Japan

INTRODUCTION

The coverage of the water supply system in Japan has reached a high level, serving over 97% of its population (JWWA 2007a). Concurrently, drinking water treatment technologies have advanced. However, treated water quality fluctuates within a drinking water treatment plant (DWTP), and it also varies among DWTPs. Treated water quality may be affected by various factors such as raw water quality. The effects of raw water quality on the performance of drinking water treatment processes have been widely investigated: they include the effects of pH on coagulation process (Qin et al. 2006) and on floc formation and granular media filtration (Gregory & Carlson 2003). The effects of types and dose of coagulants as well as pH during coagulation on natural organic matter removal and residual aluminum were also investigated (Yan et al. 2008). There may be, however, other factors that affect treated water

quality. Trained DWTP operators comprehend the characteristics of raw water as well as the treatment system of their own DWTP, and can appropriately operate the system and control treated water quality despite fluctuations in raw water quality. It may be difficult, however, for them to predict the effects on the treated water quality of changing the raw water source or the application of a new treatment process. That is to say, treated water quality is probably affected not only by explicit factors that can be studied relatively easily by plant operators, such as raw water quality, but also by implicit factors that are invisible to plant operators, including treatment processes and raw water sources. The effects of these factors remain uncertain unless performance is compared among DWTPs.

The size of a DWTP and the scale of a water supplier may also be factors that affect treated water quality.

WHO (2004) pointed out in its drinking water quality guidelines for aluminum: "Small facilities (e.g., those serving fewer than 10,000 people) might experience some difficulties in attaining this level (0.1 mg/L aluminum), because the small size of the plant provides little buffering for fluctuation in operation; moreover, such facilities often have little resources and limited access to the expertise needed to solve specific operational problems". It has also been pointed out that the lack of appropriately trained operators and the low numbers of personnel in small-scale operations may lead to insufficient management of water quality and finance (NRC 1997; Ogasawara 2008).

In the present study, we aimed to elucidate and discuss what factors affect treated water quality, and by how much. Multivariate statistical analysis was conducted with the data from *Statistics on Water Supply* (*Suidou Toukei* in Japanese), the annually published report containing data on treated water in Japan. The report contains data on both raw and treated water quality of DWTPs nationwide, as well as their facility data, such as plant capacity and treatment process employed.

Multiple regression analysis is the most commonly applied method of multivariate statistical analysis. Standard multiple regression analysis requires the use of quantitative data. However, factors that affect treated water quality are not always quantitative; qualitative factors such as the water treatment process employed may also have an impact. Therefore, Hayashi's Quantification Theory (Hayashi 1950, 1952) was employed as the multivariate statistical analysis method. Employing this theory, the effects of qualitative explanatory items can be quantified. Furthermore, this theory does not require a linear relationship between explanatory and response variables by categorizing the explanatory variables. For example, pH does not linearly affect the performance of coagulation; near-neutral pH is more preferable than extremely acidic or basic pH in the case of general drinking water treatment. Therefore, by categorizing the quantitative variables that are not normally distributed, like pH, the theory can quantify the effects of such quantitative variables.

Five indices on treated water quality; turbidity, color, potassium permanganate ($KMnO_4$) consumption, total organic carbon (TOC) and aluminum concentration were treated as the response variables. These variables were selected because we focused on the solid–liquid separation performance of DWTPs in this study. Turbidity and color are the basic indicators of the performance. Aluminum is used as a coagulant in almost all DWTPs in Japan, and control of residual aluminum in treated water is crucial because high residual aluminum in treated water indicates inadequate coagulation. $KMnO_4$ consumption is an indicator of aggregate organic constituents in drinking water, with a measurement method similar to that of chemical oxygen demand using $KMnO_4$ as the oxidizing agent (JWWA 2001); $KMnO_4$ consumption was a drinking water quality standard unique to Japan until its replacement by TOC in the current standard, which took effect in fiscal year (FY) 2004. Therefore, multiple regression analysis on TOC with the data of FY 2004 and 2005 was also performed. We investigated which of the explanatory items may affect the five treated water quality indices.

METHODS

Statistical data source

Statistics on Water Supply of FY 2001–2005 (JWWA 2003, 2004, 2005, 2006, 2007b) were used. The statistics include data on the quality and quantity of both raw and treated water from thousands of DWTPs in Japan. Treated water quality of the indices applied in this study was measured at a treated water reservoir or a distribution reservoir at each DWTP. There are many DWTPs where only chlorination is performed as a drinking water treatment process. These DWTPs are generally very small and located in rural areas, but they are large in number. The data from these DWTPs were excluded because our focus was the performance of solid–liquid separation processes. The data of FY 2001–2005 were compiled into a single dataset; each single-year dataset was also analyzed separately.

Multivariate statistical analysis

Hayashi's Quantification Theory Type 1 (HQTT1; Hayashi 1952) was applied as the method of multivariate analysis. This method is equivalent to multiple regression

analysis using dummy (0/1) variables. Both qualitative and quantitative explanatory items were categorized as shown in Table 1. Explanatory items were the source of the raw water, water treatment process, plant capacity (DWTP size), total plant capacity of the water supplier (TCWS), raw water quality defined in terms of the response variables (except aluminum) and pH of treated water. Water treatment process is actually an aggregate item; each treatment process shown in Table 1 is regarded as an

independent explanatory item. We assigned dummy variables, which consisted of negative (0) or positive (1) responses, for every subcategory; the subcategories were treated as explanatory variables (x). The response variables (y) were quantitative treated water quality indices and included turbidity (Japanese Turbidity Unit; JTU), color (Japanese Color Unit; JCU), $KMnO_4$ consumption (mg $KMnO_4$/L), TOC (mg C/L) and aluminum concentration (mg/L). The unit of JTU is similar to Nephelometric

Table 1 | Response variables (y), explanatory items and subcategories as explanatory variables (x)

Response variables (y)	Explanatory items		Subcategories (x) and their descriptions
Turbidity (Japanese turbidity unit; JTU)	Source of raw water		Surface water[a]
			Lake water[b]
Color (Japanese color unit; JCU)			Groundwater[c]
	Drinking water treatment process	Granular activated carbon[d]	Employed (1)
$KMnO_4$ consumption (mg $KMnO_4$/L)			Not employed (0)
		Powdered activated carbon	1/0
TOC (mg C/L)		Ozonation	1/0
Aluminum (mg/L)		Biological treatment	1/0
		Membrane filtration	1/0
		Slow filtration	1/0
		Rapid filtration	1/0
	Plant capacity (m³/d) (DWTP size)		<500
			500–1,000
			1,000–2,000
			2,000–5,000
			5,000–10,000
			10,000–20,000
			20,000–50,000
			>50,000
	Total plant capacity of the water supplier (TCWS) (m³/d)		<1,000
			1,000–2,000
			2,000–5,000
			5,000–10,000
			10,000–50,000
			50,000–100,000
			>100,000
	Raw water quality		Depends[e]
	pH of treated water		<6.75
			6.75–7.00
			7.00–7.25
			7.25–7.50
			7.50–7.75
			>7.75

[a]Includes water discharged from dams and lakes.
[b]Includes water collected directly from dams.
[c]Includes riverbed water.
[d]Includes biological activated carbon filtration.
[e]Range and division of the subcategories of the raw water quality item depend on the response variable. This item was not employed for aluminum because only a small number of DWTPs reported aluminum concentration in raw water.

Table 2 | Basic statistics and Japanese drinking water quality standard values for the response variables

Response variable	Measurement unit	Years of the dataset (FY)	Number of cases (*N*)	Treated water quality Mean	Standard deviation	Standard value until FY 2004	Standard value after FY 2004[*]
Turbidity	JTU	2001–2005	11,918	0.09	0.12	2	2
Color	JCU	2001–2005	11,987	0.61	0.56	5	5
KMnO$_4$ consumption	mg KMnO$_4$/L	2001–2004	10,782	1.26	0.78	10	–
TOC	mg C/L	2004–2005	2,376	0.61	0.39	–	5
Aluminum	mg/L	2001–2005	7,389	0.03	0.04	0.2[†]	0.2

[*]The Japanese drinking water quality standard was revised for FY 2004.
[†]It was not a legally binding standard value, but a complementary guideline value.

Turbidity Units (NTU), but the standard substance is not formazin but mixed polystyrene particles. Regarding the unit of JCU, 1 JCU corresponds to the color of a standard solution that contains 1 mg/L of platinum and 0.5 mg/L of cobalt. The annual mean value of each treated water quality index was input as the response variable for each DWTP. There are cases where the annual mean value of a certain water quality index in a DWTP was lower than the quantification limit. In these cases, we substituted the 50% value of the quantification limit.

Basic statistics and Japanese drinking water quality standard values for these indices are summarized in Table 2. The number of cases (*N*) of TOC and aluminum are smaller than those of other water quality indices. This is because they were newly incorporated into the drinking water quality standard in FY 2004; measurement and reporting of TOC and aluminum has become obligatory since then. Standard deviation is similar to or higher than the mean value for some water quality indices, which

implies the distribution shape of the data is not a normal distribution and is skewed because the values of these water quality indices cannot be lower than zero.

The multiple regression models for predicting the response variables can be described as follows:

$$\hat{Y} = C + \sum_{i}\sum_{j} b_{i,j} X_{i,j} \tag{1}$$

where $\hat{Y}$ is a predicted value of a response variable, C is a constant, $b_{i,j}$ is a partial regression coefficient and $X_{i,j}$ is a categorized dummy (0/1) variable for the *i*th item in the *j*th subcategory. The kinds of explanatory items and their subcategories are described in Table 1. In this study, there are five water quality indices treated as response variables, and five independent regression models are used.

In HQTT1, the sum of dummy variables in each explanatory item must be 1. In this case, variables within an explanatory item contain redundant information. For example, when an item has k subcategories and the

Table 3 | Ranges of partial regression coefficients for each explanatory item

Explanatory items	Response variables/partial regression coefficients Turbidity (JTU)	Color (JCU)	KMnO$_4$ consumption (mg KMnO$_4$/L)	TOC (mg C/L)	Aluminum (mg/L)
Source of raw water	0.010	0.152	0.175	0.104	0.003
Water treatment process[*]	0.045	0.434	0.404	0.076	0.025
Plant capacity (DWTP size)	0.040	0.224	0.196	0.097	0.008
Total plant capacity of the water supplier (TCWS)	0.044	0.194	0.236	0.126	0.014
Raw water quality	0.051	0.681	1.822	0.753	
pH of treated water	0.043	0.295	0.083	0.077	0.020

[*]The water treatment process item is not a single item but an aggregated one, and thus the magnitude of the range should not be directly compared with other explanatory items.
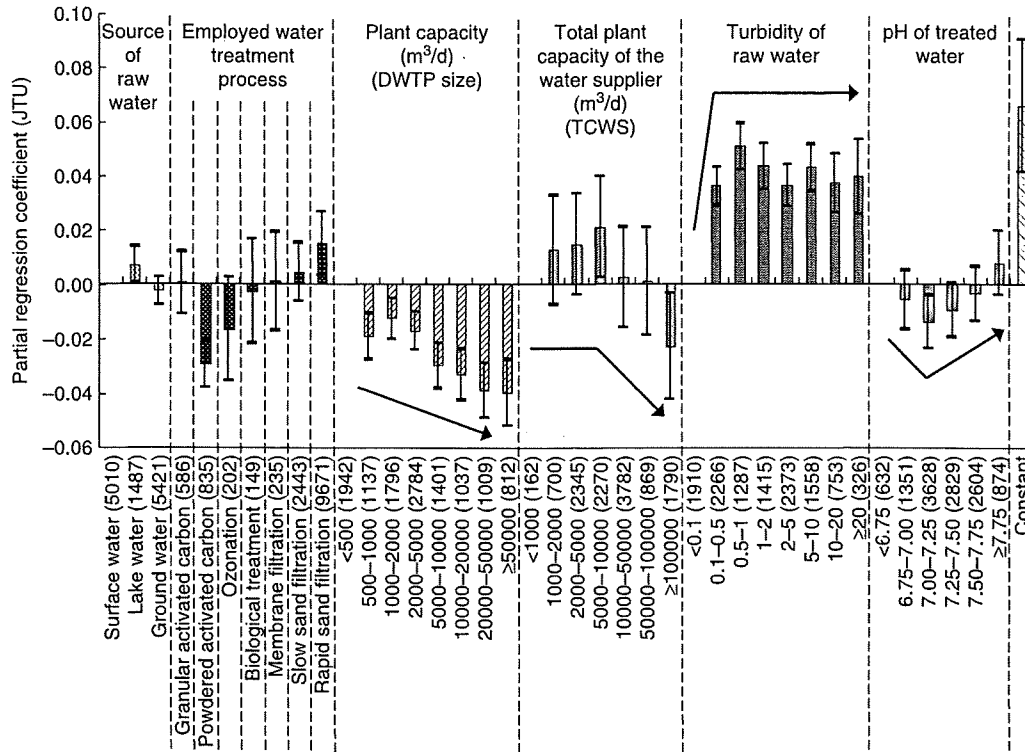
Figure 1 | Partial regression coefficients for the turbidity of treated water. Vertical line segments with attached bars indicate 95% confidence intervals. Subcategories where no bar is shown indicate the arbitrarily selected standard (zero value) for each explanatory item. Values in parentheses give the number of DWTPs belonging to each subcategory. Arrows indicate the tendency with increase of the explanatory variables. An arrow pointing obliquely upward, for example, indicates that turbidity increases with increase of the explanatory variable. If an arrowed line is horizontal, there is no significant change of turbidity with increase of the explanatory variable. The tendency changes where the slope of an arrowed line changes. Detailed description of the tendency is given in the text.

value 0 is assigned to $k - 1$ subcategories, the value 1 is consequently assigned to the remaining subcategory. To avoid this kind of redundancy, one subcategory in each item should be deleted. The deleted subcategory can be arbitrarily determined, and we principally deleted the first subcategory. The deleted subcategory becomes the standard for partial regression coefficients in that item, meaning that the partial regression coefficient of the deleted subcategory becomes 0. Thus, the other subcategories within the same item can be compared by the magnitude of each partial regression coefficient. For the items describing treatment processes, we assigned the dummy variables as employed (1) and not employed (0); that is, each treatment process was treated as an independent explanatory item.

The SPSS 14.0J (SPSS Japan Inc., Tokyo, Japan) software package was used for statistical analysis.

We did not observe any multicollinearity problems in the regression analysis. The highest absolute value of correlation coefficient between two independent explanatory variables was 0.65, the correlation between plant capacity and TCWS. This correlation was not high enough to cause multicollinearity.

RESULTS AND DISCUSSION

The determination coefficients (R^2) for the multiple regression analyses of each response variable were 0.066 (turbidity), 0.13 (color), 0.38 (KMnO$_4$ consumption), 0.40 (TOC) and 0.069 (aluminum). The coefficients are not high, except for KMnO$_4$ consumption and TOC; therefore, the regression model is unlikely to be appropriate for
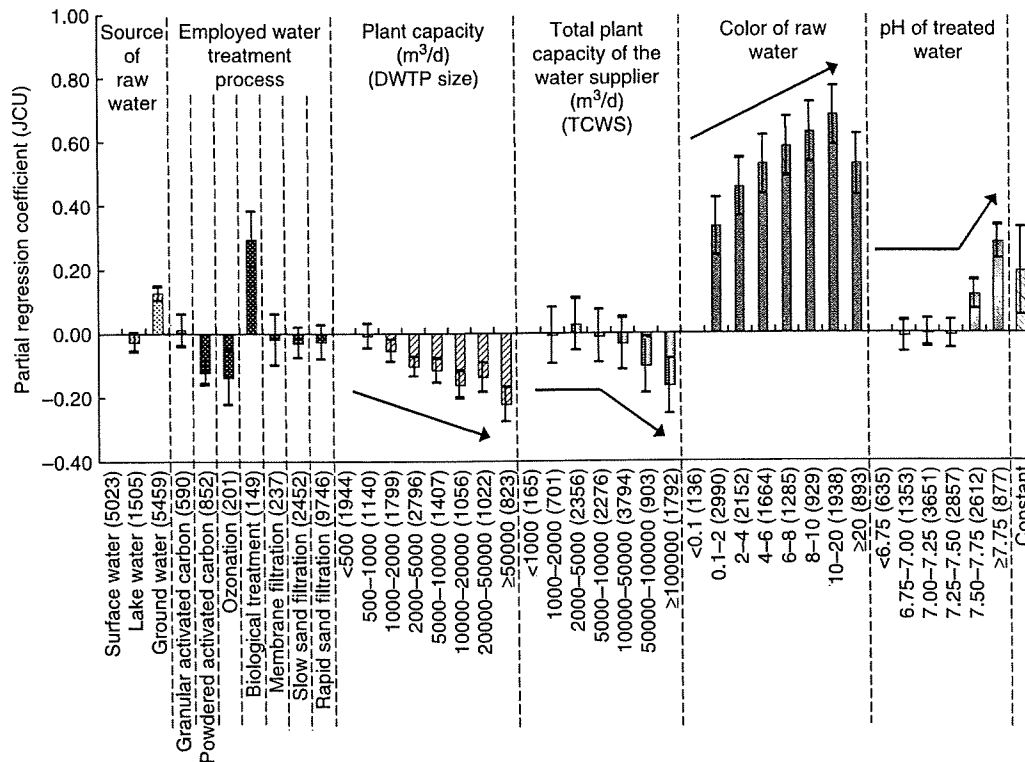
Figure 2 | Partial regression coefficients for color of treated water.

the quantitative prediction of treated water quality. Instead, we can clarify the dominant factors affecting the treated water quality by comparing partial regression coefficients. To compare the magnitude of the effect on treated water quality among explanatory items, we obtained the range of partial regression coefficients of each explanatory item by calculating the difference between the maximum and the minimum values within the same explanatory item (Table 3).

In general, the following tendencies were observed by comparing the magnitude of the ranges among explanatory items within the same response variable (water quality index). Raw water quality had quite a large effect on all of the treated water quality indices, except for aluminum, which was not included in the dataset in this study. Plant capacity and TCWS had a moderate impact on all the indices. The pH of treated water had a large impact on aluminum and also a moderate impact on turbidity and color. Each treated water quality index is, however, likely to have specific characteristics. Hereafter, we discuss the results for each water quality index individually.

Turbidity

Turbidity in raw water had the largest impact on the turbidity of treated water (Figure 1, Table 3). However, these variables did not exhibit any quasi-linear relationship; lower turbidity was observed only when the raw water turbidity was less than 0.1 JTU. TCWS had the second largest impact. The plant capacity also appeared to be quite influential; the larger the plant capacity, the lower the treated water turbidity a DWTP achieved, especially when the plant capacity was larger than $1,000 \, m^3/d$. TCWS does not appear to have a quasi-linear relationship to turbidity, but when we divide the subcategories of TCWS into two parts, $> 10,000$ and $< 10,000 \, m^3/d$, it is obvious that larger DWTPs achieve lower turbidity in treated water. As mentioned above, multicollinearity was not observed in the analyses; therefore, it can be said that, among DWTPs of equal capacity, the larger the water supplier a DWTP belongs to, the better the treated water quality that is obtained, especially in the case TCWS $> 10,000 \, m^3/d$.
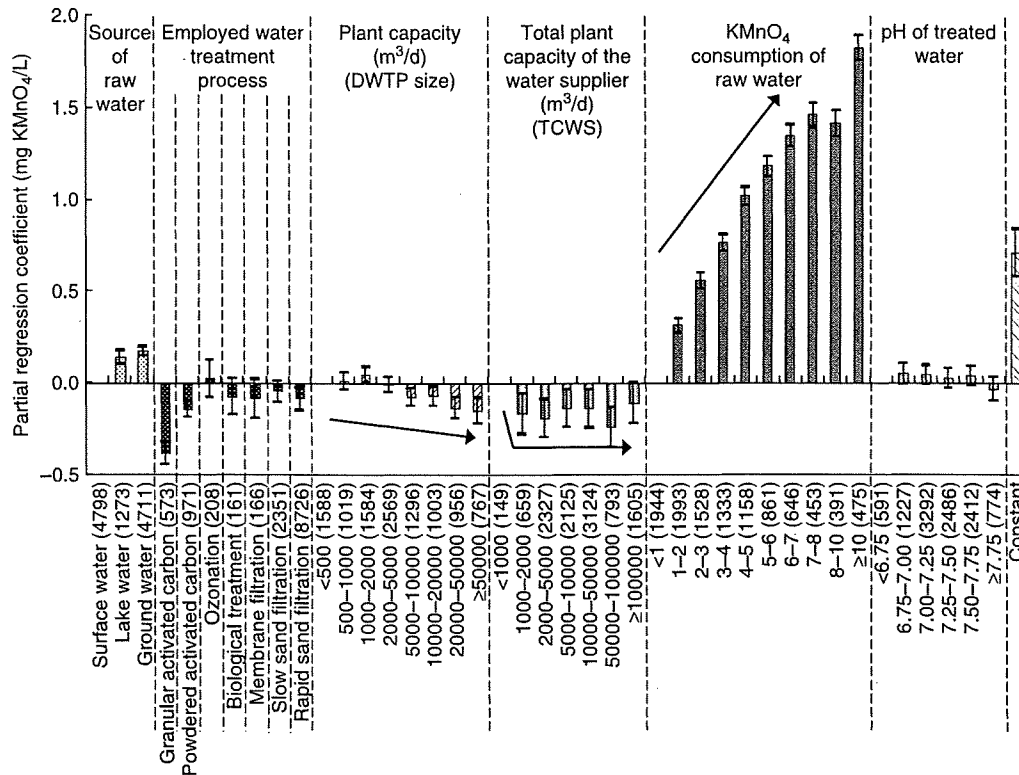
Figure 3 | Partial regression coefficients for KMnO4 consumption of treated water.

Both plant capacity and TCWS had a range of partial regression coefficients of about 0.04 (Table 3); that is, turbidity may differ by up to 0.04 JTU depending on the capacity of the DWTP and that of the water supplier. This may be a large dependence, considering that the mean treated water turbidity is 0.09 JTU (Table 2).

Having treated water at a pH of about 7 can lower the turbidity; turbidity is higher at both lower and higher pH levels. Coagulation of clay particles by use of aluminum coagulant is best performed at a pH of approximately 7 (Tambo 1980). Therefore, a pH of about 7 was the most appropriate for removing turbidity, although the removal ability also depends on other factors such as organic substances in raw water. The statistical result on the effect of pH is consistent with the coagulation theory.

Among water treatment processes, powdered activated carbon (PAC) was the best for lowering treated water turbidity. Because the partial regression coefficient of PAC

is approximately − 0.03, a turbidity decrease of 0.03 JTU is expected when PAC is employed. On the other hand, granular activated carbon (GAC) was found to be ineffective for lowering turbidity. Rapid sand filtration appears to cause increased turbidity in treated water, but the actual correlation lies between relatively high raw water turbidity and the choice of rapid sand filtration as a treatment technique. That is to say, when the water source is high in turbidity, rapid sand filtration is more likely to be chosen as the water treatment process, compared to slow sand filtration.

Color

Color in raw water had the greatest impact on the color of treated water (Figure 2, Table 3). A quasi-linear relationship between the color of raw and treated water was observed, unlike in the case of turbidity. The lower the color of the raw
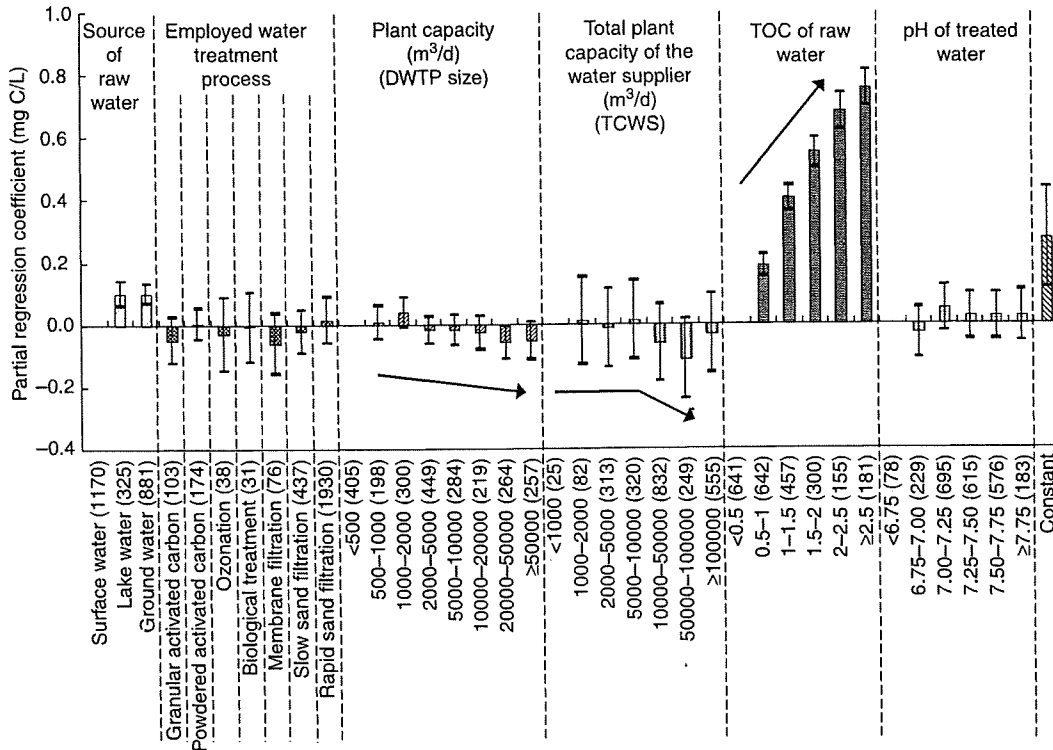
Figure 4 | Partial regression coefficients for TOC of treated water.

water, the lower that of the treated water, except when the color of the raw water was above 20 JCU. The color of the treated water was still much affected by the quality of the raw water despite advances in water treatment processes.

PAC and ozonation processes lowered color by about 0.1 JCU, whereas biological treatment was associated with increased color of about 0.3 JCU. One possible explanation for this increase is that the color of raw water is relatively high at DWTPs that use biological treatment processes because they are regarded as successful in removing organic matter but not in removing color. Another possible explanation is that organic substances produced by bacteria interfere with coagulation. This effect is further discussed in the section discussing aluminum.

GAC appeared to be ineffective in reducing color although PAC was effective. It may be due to the combined effects of the GAC process. Basically, GAC is an adsorption process. However, biological activity may also occur in GAC filters with time. It is because many microorganisms in water are attracted to particle surfaces, and they are also

attracted to GAC particles (MWH 2005). As mentioned above, the adsorption process such as PAC could reduce the color, but a biological process increased the color. Since the GAC process is a mixture of an adsorption and biological process, a clear tendency could not be observed.

Similar to the case with turbidity, lower color is achieved as plant capacity increases and also as TCWS increases. This relationship between the color and the TCWS means that, even if a DWTP is small, lower treated water color can be. achieved in the case that the DWTP belongs to a large water supplier.

Treated water color increased when the pH was higher than 7.5. According to coagulation theory, colored substances have a high negative charge on their surfaces and can be best removed in a pH range of 5–6 because positively charged aluminum ions predominate at a pH of about 5 (Binnie et al. 2002). This pH value is relatively low compared to the optimal pH for the removal of turbidity. Our result by statistical analysis of real DWTPs corresponds to the coagulation theory.
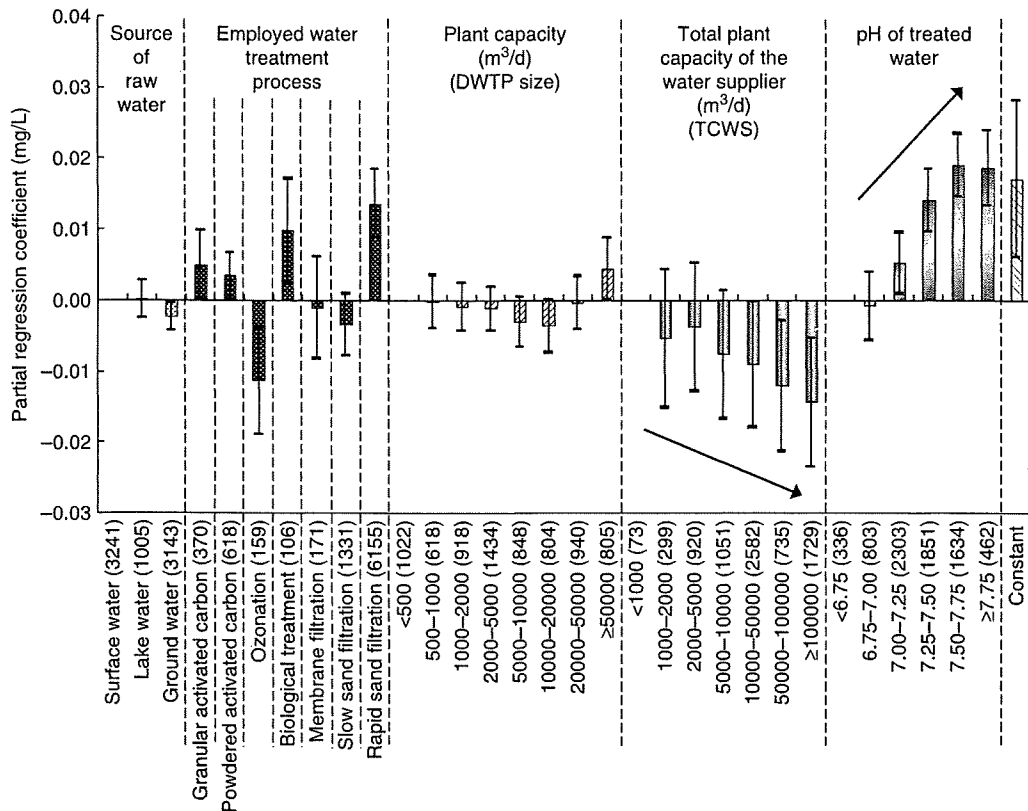
Figure 5 | Partial regression coefficients for aluminum of treated water.

KMnO₄ consumption

As was the case with turbidity and color, KMnO₄ consumption of raw water had the greatest impact on that of treated water (Figure 3). In the case of KMnO₄ consumption, the raw water quality had a much larger range of partial regression coefficients than other explanatory items (Table 3). A quasi-linear relationship is observed between KMnO₄ consumption in raw and in treated water. From these results and the relatively high R^2 value (0.38) mentioned previously, KMnO₄ consumption of treated water can be said to be determined, to a considerable degree, by the raw water quality. Although the values of other partial regression coefficients are small, larger DWTPs had lower KMnO₄ consumption. In addition, GAC and PAC processes reduce the KMnO₄ consumption. However, the partial regression coefficients of GAC and PAC are quite small compared to that of raw water KMnO₄ consumption, implying that the use of GAC and PAC for the reduction of KMnO₄ consumption is not very effective. TCWS higher than $1,000\,m^3/d$ may slightly reduce the KMnO₄ consumption; pH was found to have no relationship with KMnO₄ consumption.

TOC

Almost the same tendency was observed for treated water TOC as was observed for KMnO₄ consumption (Figure 4, Table 3). Treated water TOC is affected almost only by raw water TOC. The larger the DWTP and TCWS are, the lower the treated water TOC tends to be; these trends are similar to but smaller than those observed for KMnO₄ consumption. Unlike the case for KMnO₄ consumption, GAC and PAC appear to have little impact on treated water TOC. This suggests that there is organic matter that can be indicated by TOC but not by KMnO₄ consumption. However, there is a possibility that a small number of

Table 4 | Summary of the results[*]

Response variables	Source of raw water	Drinking water treatment process							Plant capacity (DWTP size)	Total plant capacity of the water supplier (TCWS)	Raw water quality	pH of treated water
		GAC	PAC	Ozonation	Biological treatment	Membrane filtration	Slow filtration	Rapid filtration				
Turbidity (Figure 1)	Slightly higher turbidity with lake water	↗						↖	↗	↗	Lower only when raw water turbidity < 0.1 ↑	pH ≈ 7 is optimal
Color (Figure 2)	Higher color with groundwater	↗	↗		↖				↗	↗	↖	Increases when pH > 7.5 ↖
KMnO₄ consumption (Figure 3)	Lower KMnO₄ with surface water	↗	↗						Small impact ↗	Lower when TCWS > 1,000 (m³/d) ↑	Large impact ↖	
TOC (Figure 4)	Lower TOC with surface water								Small impact ↗	↗	Large impact ↖	
Aluminum (Figure 5)	Slightly lower aluminum with groundwater			↗	↖			↖		↗	Insufficient data	Large impact ↖

[*]Direction of arrows correspond to the Figures 1–5. An arrow pointing upward, for example, means the value of the treated water quality index increases, i.e. the quality deteriorates, as the value of the explanatory item is higher or when the drinking water treatment process is employed. Blank sections indicate negligible impacts on treated water quality.

cases in the dataset ($N = 2,376$; Table 2) compared to other water quality indices may cause the statistically insignificant impact of GAC and PAC. Further data accumulation is necessary to clarify this effect.

Aluminum

The aluminum concentration in treated water was mainly influenced by treated water pH, TCWS, rapid sand filtration, ozonation and biological treatment (Figure 5). Higher treated water pH corresponded to higher aluminum concentration in treated water. This result agrees with solubility data for aluminum; aluminum has minimum solubility at about pH 6.2 at 25°C (MWH 2005). TCWS had a quasi-linear relationship with treated water aluminum, which suggests that aluminum was better controlled by larger water suppliers.

The ozonation treatment process seemed to decrease aluminum concentration although the results of statistical analysis using the single-year datasets were not stable. Ozonation was effective in the datasets of FY 2002 and 2003, but not in those of FY 2001, 2004 and 2005 (data not shown). Biological treatment and rapid sand filtration increased aluminum concentration in treated water. Biological treatment is an advanced drinking water treatment process; the aerobic treatment especially removes ammonium nitrogen, musty odor and algae (JWWA 2000). There are two plausible explanations for the undesired influence of biological treatment on the residual aluminum. One is that the raw water of DWTPs applying biological treatment may contain a lot of dissolved organic matter that binds easily to aluminum and keeps it in a soluble form. Another explanation is that the biological treatment itself may release such dissolved organic matter into the water. It is known that algogenic organic matter (AOM), especially extracellular organic matter (EOM), forms complexes with coagulant species and disturbs flocculation (Bernhardt *et al.* 1985). Intracellular organic matter (IOM) and EOM reduce coagulation efficiency (Takaara *et al.* 2007). Furthermore, some of the proteins isolated from IOM and EOM have a high affinity with aluminum hydrate, meaning that these proteins are able to form complex compounds with aluminum (Takaara *et al.* 2005; Pivokonsky *et al.* 2006). Therefore, this AOM may chelate aluminum coagulants,

which then remain in treated water as dissolved residual aluminum. For the same reason that AOM interferes with coagulation, the biological treatment might increase the color of treated water as discussed above.

CONCLUSION

The results of our statistical analyses are summarized in Table 4. The following results were obtained:

1. The larger the plant capacity is, the better the treated water quality is in terms of turbidity, color, $KMnO_4$ consumption and TOC.
2. The larger the water supplier is, the better the treated water quality is in terms of turbidity, color, $KMnO_4$ consumption and aluminum concentration.
3. Raw water quality has the greatest impact on all treated water quality indices except aluminum. This result implies that treated water quality still depends on raw water quality despite advances in water treatment technology.
4. Treated water pH has the greatest impact on aluminum and some impact on turbidity and color. Treated water with pH > 7 gives more residual aluminum, pH ≈ 7 gives the lowest turbidity and pH > 7.5 increases color.
5. The PAC water treatment process is very effective in reducing turbidity and color. Both PAC and GAC are effective in reducing $KMnO_4$ consumption, but they do not affect TOC. Treated water color and aluminum are higher in DWTPs with biological treatment as compared to DWTPs in which biological treatment is not employed.

Some of these results are in accordance with practical and theoretical understanding. On the other hand, some inherent factors, which cannot be revealed through individual DWTP experiences, also affect treated water quality. These factors include plant capacity and TCWS. The results imply that the larger the water supplier a DWTP of a given size belongs to, the higher the quality of treated water will be. Therefore, we suggest that it is a good strategy for small DWTPs to garner the cooperation of large water suppliers, especially regarding water treatment expertise and experience, to improve treated water quality.