Manganese treatment to reduce black water occurrence in the water supply

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ABSTRACT

26 multi-regional water treatment plants (WTPs) were investigated, to determine the characteristics of manganese (Mn) concentration and removal in Korea. Mn concentrations of raw water in most WTPs were higher than the drinking water standard (i.e., 0.05 mg/L); thus, proper removal of Mn at the WTPs is needed. Mn concentration was generally higher in lakes than rivers due to seasonal lake turnovers. The Mn concentrations of treated water at 26 WTPs in 2012 were less than 0.05 mg/L, due to strict law enforcement and water treatment processes optimization. However, before 2010, those concentrations were more than 0.05 mg/L, which could have led to an accumulation of Mn oxides in the distribution system. This could be one of the main reasons for black water occurrence. Therefore, regular monitoring of Mn concentration in the distribution system, flushing, and proper Mn removal at WTPs are needed, to supply clean and palatable tap water.

Keywords: Black water, Granular media filtration, Manganese removal, MOCM (manganese oxide coated media), Water treatment.

1. Introduction

Controversies on the detection of microorganisms in Korean tap water led in 2002 to the promulgation of a Treatment Technique (TT) for virus and protozoa. Currently, under TT rules, most filtered water turbidities are less than 0.3 NTU. Despite strict rules and upgraded water treatment processes, trust in tap water quality is very low in Korea; the percentage of drinking water directly from the tap is less than 2% [1].

Based on the Korean government survey in 2012, the first reason for the distrust of tap water was vague mental anxiety (i.e., 25.2%). The next was improper water quality management in the distribution system. 11.7% of the distrust of tap water originated from colored water (e.g., red or black water) occurrence, and 7.3% from particulate matters. In contrast with the high quality of filtered water, trust in tap water quality is very low, due to unsuitable management in the distribution system. Therefore, enhancement of water quality in the distribution system is very important to improve trust in tap water. Colored water occurrence and particulate matter problems, which dominate 19% of the reasons for the distrust in tap water in Korea, can be attributed to untreated soluble iron, manganese (Mn), and corrosion of pipes [1].

Mn is an abundant transition metal of the earth's crust, of which it comprises approximately 0.1% [2, 3]. This mineral is primarily associated with aesthetic problems, such as the discoloration of water, unpleasant taste of water, and staining of plumbing fixtures and laundry; however, the presence of Mn in tap water is not known to cause health problems. The presence of discolored drinking water due to Mn can mitigate customer confidence [4]. At the same time, deposited insoluble Mn in water transmission pipes can cause increased turbidity, and reduced flow.

Mn can have various colors, depending on its oxidation state. Mn^{4+} is insoluble, and has a brown-black color; while Mn^{2+} is soluble, and has a pale pink color [5]. Aqueous Mn^{2+} is the dominant form of Mn in anoxic waters. It can be found by the reduction that takes place in the presence of metal-reducing bacteria under anaerobic or low oxidation conditions at the sediment/water interface [3, 6]. Oxidation of Mn^{2+} can thermodynamically lead to three different insoluble $MnO_x(s)$ (e.g., MnO_2, Mn_2O_3, and Mn_3O_4) with the predominant form being MnO_2 [6].

From 2011, Korea strengthened its drinking water standard for Mn from 0.3 mg/L to 0.05 mg/L. USEPA sets a secondary maximum contaminant level for Mn of 0.05 mg/L; and European Directive 98/83/CE also sets a Mn concentration level of 0.05 mg/L [1, 7, 8].

Reduction of Mn to this level is no guarantee that the operator will not receive black water complaints. Consumer complaints were reported with Mn concentration as low as 0.02 mg/L. While removal of Mn to 0.02 mg/L is a positive step, removal to 0.01

mg/L is an ideal step for the maintenance of the transmission system in clean condition. In Japan, the drinking water standard of Mn is 0.05 mg/L, which is the same as those of U.S. and Korea; while the guideline for Mn for the water management goal is 0.01 mg/L. Mn concentration is maintained at less than 0.01 mg/L at most water treatment plants (WTPs) in Japan [1, 5, 7, 9-12].

The predominant form of Mn in surface water is soluble Mn^{+2}, while insoluble Mn^{+3} and Mn^{+4} also exist. Insoluble Mn can be relatively easily removed at the conventional water treatment processes composed of coagulation, sedimentation and granular media filtration, while soluble Mn is hardly removed. Therefore additional treatment and/or processes are needed to remove soluble Mn at WTPs.

Several different treatment technologies of chemical and biological oxidation, adsorption by natural minerals or modified minerals, lime softening, and ion-exchange have been employed to remove Mn^{2+} from drinking water supplies [6, 13-15]. Oxidation of soluble Mn^{2+} by strong oxidizing chemicals (e.g., ozone and potassium permanganate) and precipitation of $MnO_x(s)$ can be applied at WTPs; but many conventional WTPs have used adsorption of soluble Mn^{2+} onto Mn oxide (e.g., $MnO_2(s)$) coated media (MOCM), and its subsequent oxidation by free chlorine to $MnO_x(s)$, for the regeneration of MOCM [8, 16]. In this case, common filter media are sand and/or anthracite. MOCM can also eliminate metals, such as lead, copper, arsenic and copper [17, 18].

Soluble Mn removal in the MOCM filter is dependent on the solution pH, concentration of oxidant, temperature, $MnO_2(s)$ surface concentration, and time available for the reaction. The chemistry of Mn oxidation is much more complex and not fully understood; but soluble Mn removal mechanism by MOCM is suggested as [19, 20]

$$Mn^{2+} + MnO_2(s) \rightarrow MnO_2(s) - Mn^{2+}$$
$$MnO_2(s) - Mn^{2+} + HOCl + H_2O \rightarrow 2MnO_2(s) + 3H^+ + Cl^-$$
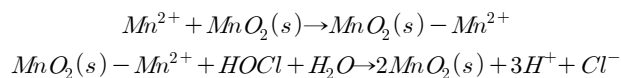
Mn^{2+} can be adsorbed onto the media surface, and forms $MnO_2(s)-Mn^{2+}$. This species is inert, and the surface that Mn^{2+} is attached to loses its adsorption capacity. Therefore, regeneration of the exhausted MOCM by oxidizing agents is needed, to restore the adsorption capacity.

The major objectives of this research were to: (1) investigate the characteristics of Mn concentration in raw water by seasons and types of source; (2) evaluate the Mn removal efficiency in water treatment processes; and (3) investigate the filter media depth and diameter of MOCM as a function of the duration of filtration for high Mn concentration of raw water.

2. Materials and Methods

2.1. Water Treatment Plants

To investigate the characteristics of Mn removal at WTPs in Korea, 26 multi-regional WTPs were investigated, as shown in Fig. 1. Mn concentration of raw and treated water, Mn removal characteristics, and properties of MOCM at WTPs were analyzed.
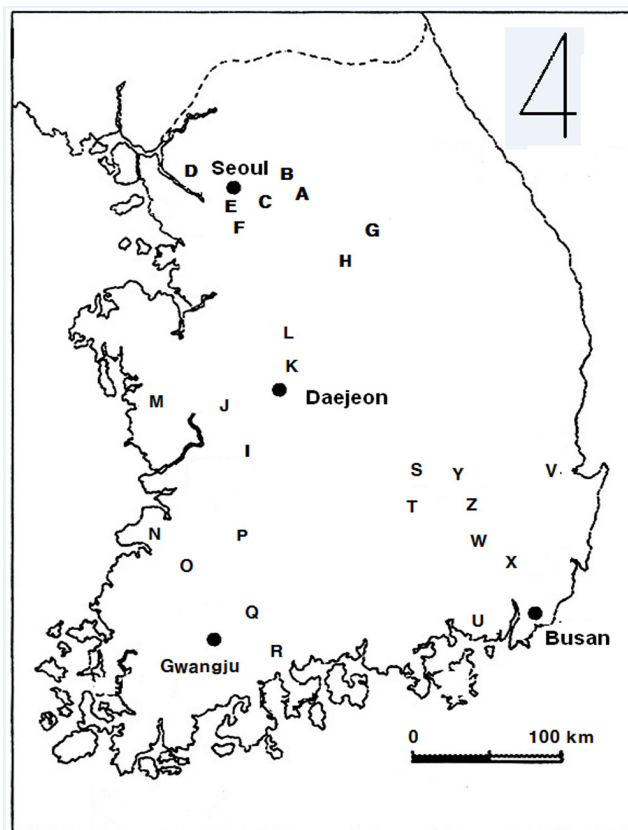

Fig. 1. Location of water treatment plants.

All of the 26 WTPs investigated treated surface water. WTPs G, O, R, S, and T in Fig. 1 took raw water from rivers, while the other 21 WTPs took it from lakes. All WTPs, except D, F, and T, adopted conventional water treatment processes, including rapid granular media (e.g., sand and/or anthracite) filtration. WTPs D and T, which took raw water from Paldang lake and Nakong River respectively, adopted GAC adsorber, after rapid filtration. WTP F, which took raw water from Paldang lake, had retrofitted a sand filter to a GAC filter-adsorber (FA) to remove natural organic matter as well as preformed disinfection by-products.

MOCS was obtained from WTP N, where sand had been coated with Mn oxides during 7 years of filter operation. Booahn WTP was an 87,000 m^3/d plant that used polyaluminum chloride coagulation, sedimentation, and rapid sand filtration, followed by chlorination. Prechlorination was continuously implemented before coagulation, and residual free chlorine concentration of the filter influent was around 1.0 mg/L. The concentration of Mn in raw water was higher during winter than summer, due to lake turnover. The average (± standard deviation) concentration of Mn in the raw water at WTP N during this research was 0.188 (± 0.163) mg/L.

2.2. Analytical Methods

Mn concentration can be analyzed, using various experimental apparatuses. AA (SpectraAA-22; Varian, USA) and ICP (Optima 3000XL; PerkinElmer, USA) were used throughout the research.

In most of the experiments, ICP was used; and sometimes, AA was used for higher Mn concentration.

To measure the surface-extractable Mn content of MOCM as a function of filter depth, duration of filtration, and influence of backwashing, 4 g of medium was put into 100 mL of 0.5% nitric acid and 250 mg of hydroxylamine sulfate for the reduction of surface oxides, as documented by Knocke et al. [19]. The resulting solutions were then analyzed for Mn content. The amount of extracted Mn was used as a relative index of the amount of surface Mn oxide coating present for filter media. Change of filter media depth as a function of filtration duration was also measured.

3. Results and Discussion

3.1. Manganese Concentration in Raw Water

Fig. 2 shows the Mn concentration of raw water at 26 WTPs for 3 years (Jan. 2010 to Dec. 2012), based on weekly or monthly test results. In general, Mn concentrations of raw water significantly depend on the geological characteristics of watersheds.

In 23 WTPs, Mn concentration of raw water was above the drinking water standards (i.e., 0.05 mg/L). The maximum Mn concentration of WTP Y, which took raw water from Woonmoon lake, was 0.978 mg/L during the investigated period, which was 19.6 times the Korean drinking water standard.

In addition, WTPs H, N, Y, and Z had maximum concentrations of more than 10 times that of the drinking water standard, and all 4 WTPs took raw water from lakes or reservoirs. Comparisons of Mn concentrations of different sources elucidated that raw water from lakes showed higher concentration of Mn than rivers. This can be attributed to seasonal lake turnover by water temperature change, which led to the rise of reduced Mn ions (i.e., Mn^{2+}) to the surface of the lake [21]. Those reduced Mn ions hardly precipitate at the lake even after oxidation with air. Even at a pH of 9.5, it takes about 1 h of detention time for Mn^{2+} to oxidize, which suggests that oxidation with air is not a practical method [6]. Therefore, during the lake turnover period, raw water with elevated concentration of Mn^{2+} can flow into the WTPs.
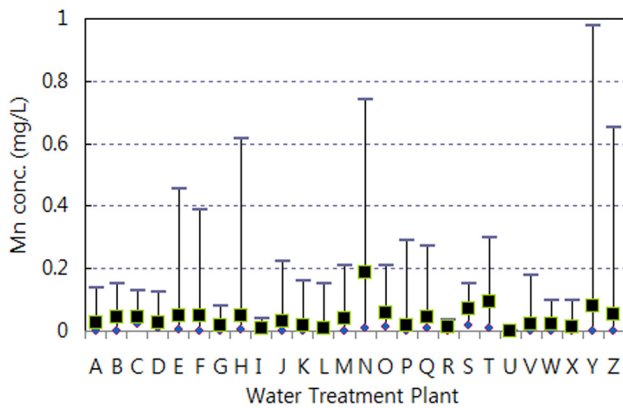
Fig. 2. Mn concentration in raw water at WTPs (maximum, average, and minimum). Location of WTPs can be found in Fig. 2 (maximum, average, and minimum).

Figs. 3(A) and 3(B) show Mn concentrations of raw water at WTPs N and Y, which took raw water from Booahn and Woonmoon lakes, respectively. Both WTPs took raw water between the surface and 10 m subsurface of the lake. The Mn concentrations of both lakes show similar trends: high concentration in fall and winter (i.e., Oct.-Dec.), and low concentration in summer (June-Aug.). On the other hand, the duration of high Mn concentration in Woonmoon lake was less than 1 month; while that of Booahn was consistently high, except in August. Soluble Mn can be effectively removed through adsorption by well maintained MOCM, under incessant high Mn inflow. However, it can be hard to sufficiently
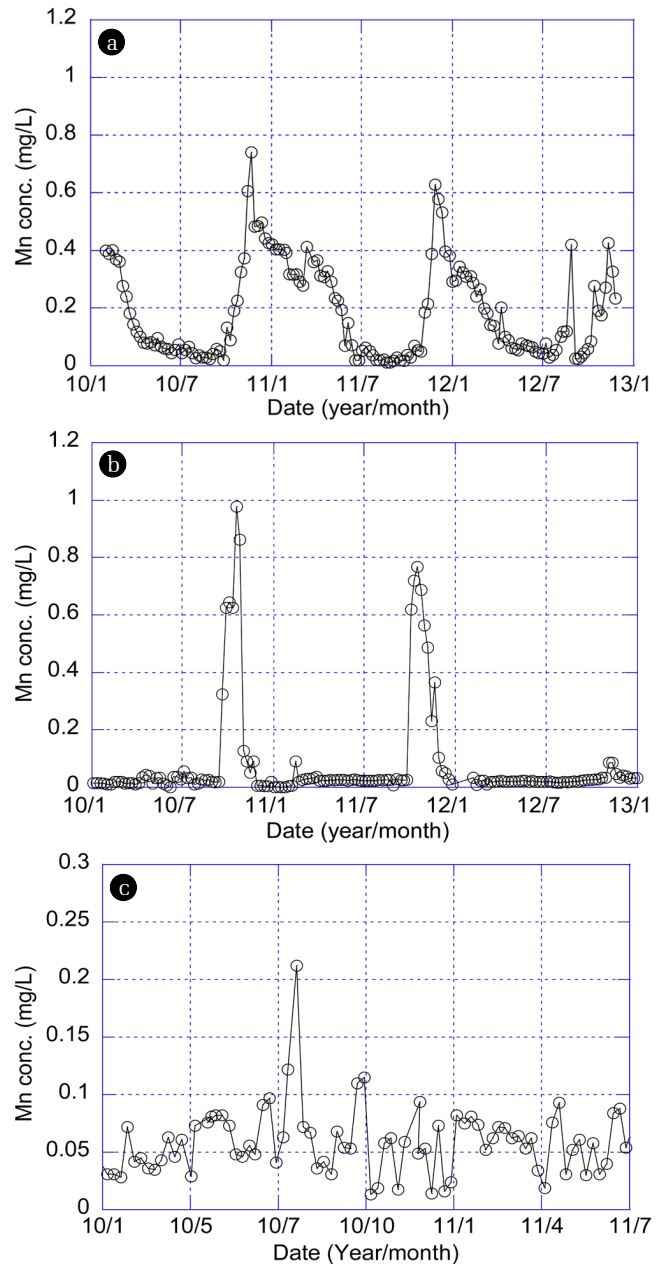
Fig. 3. (A) Mn concentration in Booahn lake, (B) Woonmun lake and (C) Sumjin river (2010.1-2012.12 and 2010.1-2011.7).

remove soluble Mn under short duration of high Mn concentration in raw water, due to the slow conversion of filter media to MOCM.

Fig. 3 (C) presents the Mn of raw water at WTP O, which took raw water from the lower Sumjin river. Unlike other lakes, which showed high Mn concentration during fall and winter, higher concentration was noticed during summer. This can be attributed to the intense flush during the rainy season (i.e., June to Aug.) of the upper lakes, which had high Mn concentration.

The monthly Mn concentration from different levels (i.e., upper, middle and lower) of Milyang lake is shown in Fig. 4(A). Unlike Fig. 3, higher Mn concentration was noticed in spring (i.e., Apr. to May) regardless of lake depth. The average concentrations of the upper, middle, and lower layers were 0.0327, 0.0507, and 0.0625 mg/L, respectively, which means the Mn concentration of the upper layer was 52%, compared to that of the lower layer. A similar trend was noticed in most measurements, though in 2007 fall, the Mn concentration of the lower layer was relatively higher, compared to that of the middle and upper layer. Milyang lake was built in 2000 as a result of dam construction; thus, differences of Mn concentration between the upper and lower layers were insignificant, presumably due to slight build up of Mn sediments at the bottom of the lake.

Fig. 4 (B) shows the relationship between lake levels and average Mn concentrations of the upper, middle, and lower layers of the lake. Milyang dam has a bottom and top elevation of 150 m and 210 m, respectively, making a possible lake depth of 60 m. Based

on a 3 year survey, the maximum and minimum lake depths were 52.0 m and 32.1 m, respectively, and the average was 41.8 m. The ratio of the maximum and minimum lake level was 1.62. In Milyang lake, seasonal changes of the lake levels, as well as turnovers, seem to have influenced the Mn concentrations.

3.2. Manganese Concentration in Treated Water

Fig. 5 shows the Mn concentration of treated water. All WTPs met the drinking water standard of Mn, which has been 0.05 mg/L since 2011. However, an increase of Mn removal efficiency at many WTPs is needed to meet more stringent regulations such as the Japanese water quality management goal (i.e., 0.01 mg/L).

Insufficiently removed Mn at WTPs can react with residual free chlorine in the distribution system, which in turn changes into insoluble Mn (e.g., $MnO_2(s)$), which then sticks to water pipes as black sediment. This can cause black water occurrence under sudden hydraulic changes, such as velocity increase. Therefore, an increase of soluble Mn removal at WTPs, as well as regular flushing in the distribution system, is needed to minimize black water occurrence.

The average Mn removal in all 26 WTPs was 93.5%. In general, more than 95% Mn removal can be achieved through properly operated MOCM filtration. However, soluble Mn removal can significantly decrease through immature MOCM filters. Therefore, proper operation of MOCM should be implemented, based on regular monitoring of the Mn concentration of raw and treated water.

The highest Mn concentrations of raw and treated water were noticed at WTP Y, which took raw water from Woonmoon lake. However, WTP N, which had the second highest Mn concentration in raw water, showed relatively low Mn concentration in treated water (i.e., 17th), which suggested that Mn in raw water was efficiently removed by MOCM at the WTP.

The correlation between Mn concentrations of raw and treated water under proper treatment at the WTPs is known to be weak. However, the Mn concentration of raw water can directly influence the concentration of treated water, when porous filter media (e.g., sand or anthracite) are not fully converted to MOCM, or when proper operation of MOCM (e.g., insufficient regeneration) is not implemented [21]. At WTP Q, higher Mn concentration of treated water was noticed under relatively low Mn concentration of raw waters as shown in Fig. 2 and Fig. 5. This can be attributed to
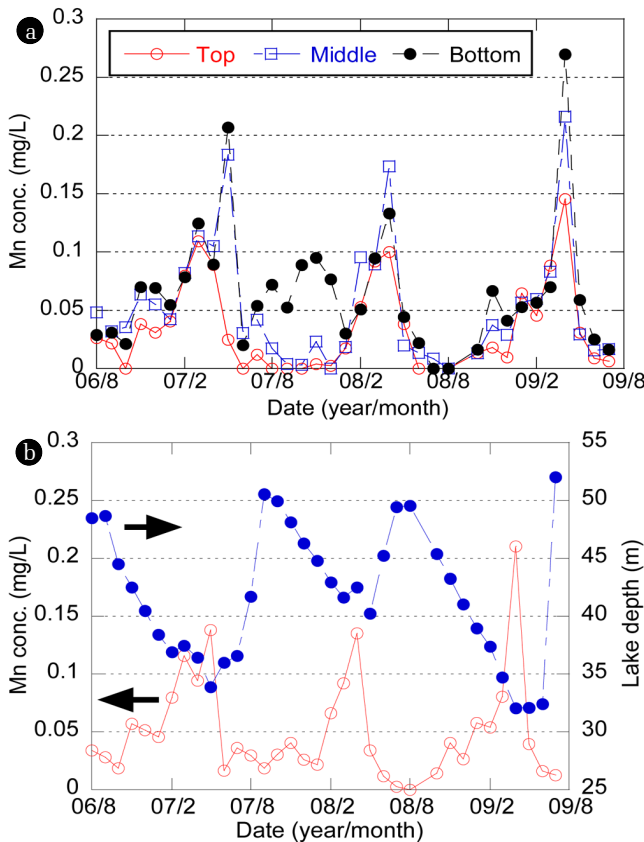
Fig. 4. (A) Mn concentration vs. lake level and (B) depth in Milyang lake (2006.8-2009.7).
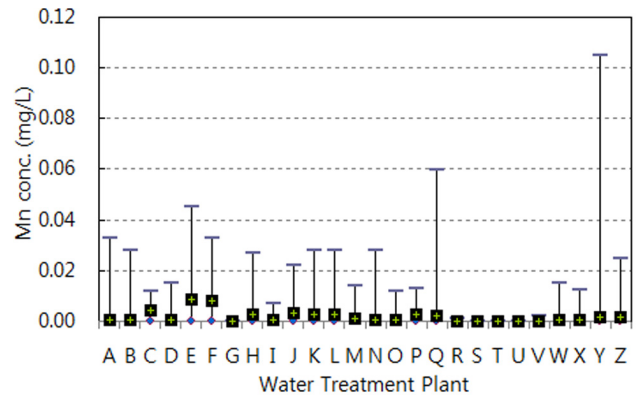
Fig. 5. Mn concentration of treated water at WTPs (maximum, average, and minimum) (2010-2012).
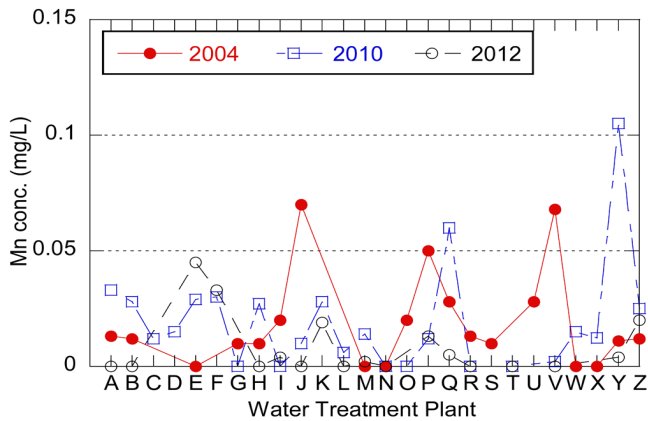
Fig. 6. Maximum Mn concentration of treated water at WTPs.

the types and operational modes of filters, optimization of pre-treatment processes, and oxidation status of Mn in raw water.

Fig. 6 shows the annual maximum Mn concentrations of treated water in 2004, 2010, and 2012 at the 26 WTPs. While the averages of the annual maximum concentrations of the 26 WTPs for 2004 and 2010 were 0.0188 and 0.0193 mg/L respectively, that of 2012 was 0.0081 mg/L. The Mn concentration of treated water in 2012 was almost half of the maximum concentrations of 2004 and 2010, due to optimization of the water treatment processes for the removal of Mn, according to the tightened water quality standards from 2011. The Mn concentrations of 3 WTPs in 2004, and 2 WTPs in 2010 exceeded 0.05 mg/L; therefore, some of the untreated Mn was supplied through water pipes, which in turn, deposed in the distribution system as sediment. These untreated Mn oxides might flow out of the tap as a form of black particulates.

3.3. Operational Characteristics of MOCM

All WTPs except F, which retrofitted its sand filter to carbon filter-adsorber, adopted rapid filtration systems, which used sand and/or anthracite filter media to remove particles. No WTPs installed MOCM or greensand, to remove soluble Mn at the stage of construction. Conventional sand and anthracite were gradually turned into MOCM by the coating of Mn oxides, under high concentration of Mn inflow.

The Mn concentrations of raw water at WTP N, which took raw water from Booahn lake, were 0.741 (maximum) mg/L, 0.011 mg/L (minimum), and 0.188±0.163 (average ± standard deviation) mg/L. However, the Mn concentrations of filtered water at WTP N were 0.028 (maximum) mg/L, 0.000 mg/L (minimum), and 0.0007±0.04 (average ± standard deviation) mg/L; and the overall removal efficiency in the filtration system by MOCM was 99.64 %.

Fig. 7 shows the mass of Mn oxide accumulation as a result of 6 years of operation at WTP N. Filter media were collected for every 5 cm interval, and the mass of Mn oxides was investigated before and after backwashing. In MOCM filtration, the diameter of filter media kept increasing, as the Mn oxides accumulated on the surface of the filter media. The mass of Mn of the filter media increased rapidly from 2003 to 2005. It then increased gradually, partially due to the increase of flow shear with the increase of filter media diameter, as Mn oxide accumulated.
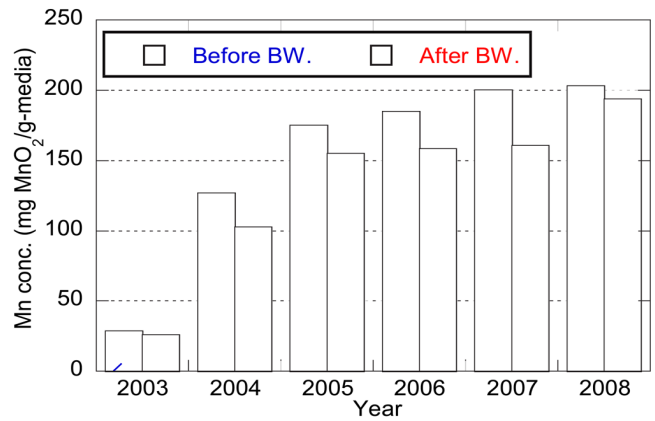

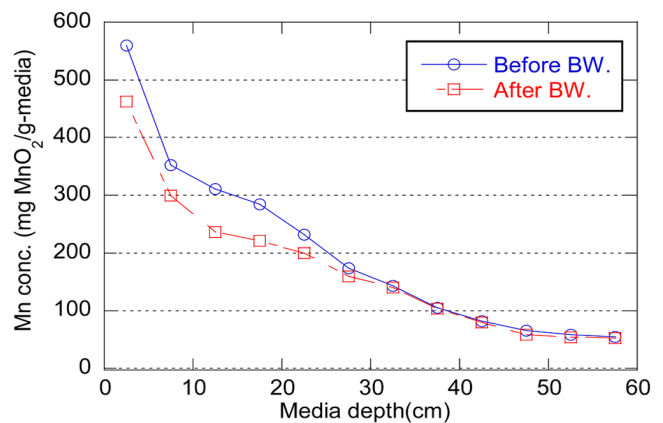**Fig. 7.** Mn oxide concentration vs. backwashing (BW.) effect at N WTP.

Fig. 8. Mn oxide concentration vs. filter depth at N WTP before and after backwashing (BW.).

The mass of Mn oxide as a function of filter depth at WTP N is shown in Fig. 8. It is known that the adsorption of Mn by MOCM is rapid. Therefore, more mass of Mn was noticed at the top of filter, and it gradually decreased with the increase of filter depth. The commercial MOCS has at least 4 mg $MnO_2(s)$ per unit gram of filter media (i.e., 2.53 mg Mn/g media) [5]; while the MOCS used during this research had an average of 201.6 mg $MnO_2(s)$ /g of media, which was high, compared to a similar research [22].

A comparison of filter depth in the 2010 and 2011 results in Table 1 shows that the filter depth increased by 1.35 cm (1.99%) during one year. In the calculation of change in filter depth, the result of number 6 was excluded, because some MOCM of the filter was sent to another WTP that had trouble with the removal of dissolved Mn. Filter bed medium is commonly lost after repeated filter washings; rapid sand filters generally lose 1 to 2% of the total bed depth, annually [23]. However, the filter depth at WTP N showed an increase, due to an accumulation of Mn oxides on the surface of the sand filter. Meanwhile, the filter depth of number 3 decreased, though there was no intentional removal of MOCM. This was presumably caused by an excessive backwash rate and/or leakage of the filter media through the underdrain system, and so on.

It was shown that the filter depth and media progressively increased, as the normal filter bed medium converted to MOCM.

Table 1. Filter Depth Survey Results at NWTP

Filter No.	Filter side	Filter depth (cm)		Loss rate (%) (A-B)/B×100
		Year 2009 (A)	Year 2010 (B)	
1	Left	70.2	70.2	0
	Right	68.7	68.7	0
2	Left	75.3	76.0	-0.9
	Right	74.5	77.6	-4.2
3	Left	78.7	75.5	4.3
	Right	76.8	76.0	1.1
4	Left	72.6	71.9	0.9
	Right	71.9	72.6	-0.9
5	Left	71.0	70.3	1.0
	Right	66.5	70.1	-5.4
6	Left	78.5	72.8	7.4
	Right	79.5	76.9	3.3
7	Left	81.9	81.9	0
	Right	78.4	78.4	0
8	Left	68.6	78.8	-14.9
	Right	71.2	77.3	-8.6

One of the main functions of a filter is to remove particles. Therefore, a proper ratio of filter depth (L) over filter media diameter (d) (i.e., L/d) should be observed [23, 24]. To maintain proper particulates removal, as well as dissolved Mn removal, regular replacement of excessive MOCM with fresh filter medium, and removal of excessive Mn coating by chemical treatment, can be recommended.

4. Conclusions

The Mn concentrations of raw and treated water, and characteristics of MOCM operation were investigated for 26 multi-regional WTPs in Korea. The results of this research have yielded the following conclusions.

1) The Mn concentration of raw water was above the drinking water standard (i.e., 0.05 mg/L) in 23 WTPs. Therefore, proper treatment should be implemented to remove it. Higher Mn concentrations and recurrent trends were noticed at WTPs that took raw water from lakes rather than rivers, due to seasonal lake turnover.

2) The Mn concentrations of treated water in 2012 were less than the drinking water standard, yet they exceeded the Japanese water quality management goal (i.e., 0.01 mg/L). Thus, more Mn should be removed through water treatment processes. The standard for Mn was 0.3 mg/L until 2010, and during that time, the Mn in treated water was more than 0.05 mg/L. Therefore, there was a possibility of black water occurrence, due to the accumulation of untreated Mn oxides in the distribution system.

3) The mass of Mn oxide that coated the filter media kept growing during the period of filtration at WTP N, which had high concentration of influent Mn. More accumulation of Mn oxide was noticed at the top layer. Subsequently, accumulation gradually increased at the lower layer.

4) The filter depth and media diameter kept growing at WTP

N, as the removed dissolved Mn gradually coated the surface of the filter media. As a filter has to remove particulate matters, as well as soluble Mn, more effort has to be implemented to maintain a proper ratio between filter depth and filter media.

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