Characterization of microparticles in raw, treated, and distributed waters by means of elemental and particle size analyses

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Abstract
The elemental composition and particle size distribution of suspended particles in raw water, treated water, and distributed water were determined to understand the behavior of particles during the water treatment–distribution process. The weight of suspended particles collected on a 0.6-µm filter was 1.1 times (raw water), 1.4 times (treated water), and 1.5 times (distributed water) that collected on a 2.7-µm filter, suggesting that smaller particles may remain after conventional water treatment. Organic suspended particles were removed less efficiently than inorganic suspended particles. After sand filtration, the Al content in the fixed suspended solids (FSS) markedly increased, indicating that either a small percentage of aluminium floc passed through during sand filtration or dissolved aluminum precipitated after sand filtration. The Mn and Fe concentrations increased after chlorination. The percentages of carbon and nitrogen in the volatile suspended solids (VSS) were roughly the same in the raw, treated, and distributed waters. The carbon/nitrogen/phosphate/VSS ratios indicated that the VSS of the suspended particles consisted of organic matter originating from microorganisms. The major constituents of the FSS in the treated and distributed waters were compounds of Fe, Al, Ca, Mg, and Mn, but these compounds accounted for only 16% or less of the FSS in raw water, indicating the existence of Si compounds. In distribution pipes, the total suspended solids concentration, especially the FSS concentration, was higher than that of water just after treatment. The Fe concentration in distributed water increased, probably due to oxidation and rusting of iron pipes.

Keywords
Distributed water; microparticles; treated water

Introduction
Aquatic suspended particles are extremely heterogeneous with respect to size, density, shape, chemical composition, surface charge, and so on. To understand the behavior of suspended particles during water treatment, the individual particles must be characterized. This information is important for the design of efficient treatment facilities, though bulk parameters such as the mass of suspended matter or turbidity are currently used for that purpose. Particle counters are currently capable of measuring the sizes of microparticles at very low mass concentrations (American Water Works Association, 1999). However, very little is known about the chemical nature of the particles (Gauthier et al., 2001). Because only small quantities of suspended particles can be collected on filters, a flow centrifuge method is usually used to collect large quantities of suspended particles for comprehensive chemical and physical analyses (Burrus et al., 1989). However, newer multi-element analysis techniques, such as ICP-MS, can be carried out with small quantities of suspended particles. Consequently, the chemical nature of microparticles in treated and distributed waters can be analyzed after collection by filtration.

This paper describes recent field studies that examined (1) how the nature of suspended particles changes during water treatment and in water distribution pipes, (2) which fraction of suspended particles may be transported, deposited as sediment, or generated through these processes, and (3) the seasonal variations of the chemical characteristics of suspended particles. This study provides insights into the quantity and chemical nature of suspended matter in raw, treated, and distributed waters.
Sampling sites and methods

Suspended particle sampling and analysis were conducted during 2001 to 2003 at two water treatment plants and their water service areas. Treatment plant A takes raw water from Lake Biwa, the largest lake in Japan. Treatment plant B takes raw water from the Kiso River. Both plants use conventional process trains: aluminium coagulation, sedimentation, sand filtration, and chlorine disinfection. Treatment plant A employs both intermediate chlorination and post-chlorination (i.e. chlorine is added after sedimentation and after sand filtration), whereas chlorine is added only after sedimentation in treatment plant B. Suspended particles were collected from raw water, water after sand filtration (filtered water), and water after post-chlorination (finished water) in treatment plant A, and from raw water, filtered water, and water from the outlet of the service reservoir (finished water) in treatment plant B. In treatment plant A, samples were collected from the end distribution pipe located about 8 km from the plant. Samples in the service area of treatment plant B were collected from three distribution pipes about 7, 11, and 20 km from the plant.

Suspended particles were collected on quartz filters (QM-A, 0.6-µm nominal pore size, Whatman) and glass-fiber filters (GF/D, 2.7-µm nominal pore size, Whatman) using an 8-line filtration system. Quartz filters were selected because of their negligible metal content; the glass-fiber filters were used for comparison of collection efficiencies. The quartz filters were available only with the 0.6-µm nominal pore size. Prior to collection, filters were rinsed with 0.1 mol l⁻¹ nitric acid and precombusted at 550°C in a muffle furnace. Organic membrane filters were not used because of their interference with carbon and nitrogen analyses.

The total volume filtered for each line was calculated by integrating the filtered flow rate over the elapsed time. The amount of water filtered was about 5–10 L for raw water and 100–500 L for the other waters. Following filtration, the filters were transferred to a crucible, dried at 105°C, and stored in a desiccator until analysis. Gravimetric analyses were conducted by weighing the filters after drying at 105°C and after combustion in a muffle furnace at 550°C, which provided the total suspended solids (TSS) and volatile suspended solids (VSS) concentrations. The fixed suspended solids (FSS) concentration was calculated by subtracting VSS from TSS (Standard Methods for the Examination of Water and Wastewater, 1998).

Elemental analysis was conducted by digesting the suspended particles retained on the filter with repeated additions of nitric acid and hydrogen peroxide (United States Environmental Protection Agency, 1999) and analyzing the resulting solution by ICP-MS (7500i, Agilent). The 7500i ICP-MS instrument is capable of simultaneously detecting 19 elements (B, Na, Mg, Al, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Sr, Mo, Cd, Ba, Hg, Pb), but only 8 elements (Mg, Al, Ca, Mn, Fe, Cu, Zn, Pb) were actually detected. The other 11 elements were below their detection limits. The total carbon and nitrogen contents were determined with an NC analyzer (Sumigraph NC-800, Sumika Chemical Analysis Service, Osaka, Japan); the organic carbon content was determined with a TOC analyzer (TOC-5000, Shimadzu) equipped with a solid-sample module (SSM-5000A, Shimadzu). Phosphate was determined by the ascorbic acid method after decomposition in potassium persulfate solution (Standard Methods for the Examination of Water and Wastewater, 1998). In addition to performing the elemental and gravimetric analyses of the suspended particles, we conducted on-site particle size distribution analyses by using a portable particle counter (VersaCount, Hiac/Royco). The particles were counted for the following size ranges: 2–5, 5–10, 10–15, 15–20, 20–25, 25–50, and 50–100 µm.

Results and discussion

Size distribution of microparticles

The particle size distributions for the raw waters were almost the same, and the particle size distribution did not vary much from raw water to end distribution-pipe water (Figure 1).
Particles in the range 2–5 µm dominated, and more than 80% of the particles were 10 µm or smaller.

Untreated and treated water were filtered with two different pore size filters (QM-A filter, 0.6-µm nominal pore size; GF/D filter, 2.7-µm nominal pore size) and the sizes of the particles retained by the filters were compared. The manufacturer’s catalog claims that the QM-A filter retains 99.999% of 0.6-µm particles in the air under an aspiration speed of 5 cm/s and that the GF/D filter retains 98% of 2.7-µm particles in water by filtration. The collection efficiencies for particles with sizes less than the nominal pore size are not reported in the catalog. The collection efficiency, however, is expected to vary with particle concentration, filtration volume, and filtration velocity. Although we did not derive the exact collection efficiency, the QM-A filter, as expected, collected more small particles than the GF/D filter. The weight of suspended particles collected on the QM-A filter was 1.1 times (raw water), 1.4 times (chlorinated water), and 1.5 times (distributed water) that collected on the GF/D filter (Figure 2). This result suggests that the percentage of total filtered particles having a nominal size of 0.6–2.7 µm was about 9% in raw water but >28% in chlorinated waters. Therefore, smaller particles may tend to remain after conventional water treatment. When the size distribution data (see Figure 1) were converted to a volume basis, however, the percentage of total filtered particles having a size of 2–5 µm was <10% whereas the percentage of total filtered particles having a size of 5–100 µm was >90%.

Figure 1  Size distribution of particles. Sampling dates: treatment plant A, 18 Dec 2002; treatment plant B, 11 Dec 2002

Figure 2  Average concentrations of suspended solids on the QM-A and GF/D filters. Treatment plant A. Sampling dates: 23 Oct 2002, 18 Dec 2002, 8 Jan 2003, and 5 Feb 2003
study is needed to evaluate the size distribution of the suspended particles. The VSS/FSS ratios of the particles collected on the QM-A and GF/D filters were almost the same, suggesting that there was not a large difference in organic content between the large particles (retained by the 2.7-µm filter) and the small particles (retained by the 0.6-µm filter).

**Seasonal variation of the microparticles in raw water**

In treatment plant A, the TSS concentration in raw water varied from 1.0 to 3.2 mg/L and was highest in winter (Figure 3). Because wind speed is strongest in winter in this region, and the intake of treatment plant A is in shallow water, resuspension of sediment probably occurred. The percentages of VSS and carbon were 35% and 15% on average, but in summer, these percentages increased to 48% and 20%, respectively. Almost 100% of the carbon was organic carbon; inorganic carbon was not measured. We attribute the summertime increases in the VSS and carbon contents to algal blooms in the summer.

**Changes during the treatment–distribution process**

The TSS concentration in the raw water of treatment plant B was higher than that of treatment plant A (Figure 4). This difference was attributed to the concentrations of FSS, probably consisting of clay and silt particles. These results are consistent with the general understanding that lake waters contain relatively few suspended inorganic particles because these particles easily settle due to their large specific gravity (Ebise and Inoue, 1991).

![Figure 3](https://iwaponline.com/wst/article-pdf/50/12/71/419414/71.pdf)  
Figure 3  Seasonal changes of suspended solids in the raw water of treatment plant A (QM-A filter): (a) concentration; (b) percentage

![Figure 4](https://iwaponline.com/wst/article-pdf/50/12/71/419414/71.pdf)  
Figure 4  Change in suspended solids concentration during the water treatment-distribution process.  
After sand filtration, of course, the TSS concentration drastically decreased from a value on the order of mg/L in raw water to a value on the order of µg/L in filtered water (Figure 4). The TSS removal efficiency was 99.6% in both treatment plants. The VSS/TSS ratio for filtered water was 0.82 for treatment plant A and 0.70 for treatment plant B (Figure 5). These values were much higher than those for the raw waters, indicating that organic suspended particles were removed less efficiently than inorganic suspended particles. For finished waters, a large difference was observed between the treatment plants. For treatment plant A, where chlorine was added after sand filtration, the TSS concentration in finished water was 3.4 times the TSS concentration in filtered water. The increase in FSS could be due to the oxidation–precipitation of iron and manganese by chlorine, as described later. The reason why VSS increased after chlorination is not clear, but iron and manganese precipitates might adsorb or entrap dissolved organic matter. For treatment plant B, where chlorine was added only before sand filtration, the TSS concentration did not increase from filtered water to finished water. The TSS concentration, especially the FSS concentration, in the distribution pipes was higher than those in treated water.

The percentages of carbon and nitrogen in the VSS were roughly the same in the raw, filtrated, finished, and distributed waters (Figure 6). The organic carbon content measured with a TOC analyzer was almost equal to the total carbon content. Therefore, the carbon in the suspended particles was mostly organic carbon, and the fraction of inorganic carbon was marginally low. The average C/N ratio of suspended particles in raw water was 6.4 by weight and was almost equal to the Redfield C/N ratio (5.7) calculated for average organic matter having the empirical formula (CH2O)106(NH3)16H3PO4 (Richards et al., 1965). Therefore, the nitrogen should be mostly organic nitrogen. The average C/P ratio was 60, higher than the Redfield C/P ratio (41), but close to 69, the value obtained for seston such as bacteria, algae, and their detritus (Aizaki and Otsuki, 1987). The carbon/VSS ratio was about 40%, similar to the value obtained for algae (Takamura et al., 1981) or seston (Socol et al., 1999). These results indicate that the VSS of all suspended particles was composed of organic matter originating from microorganisms.

Fe, Al, Ca, Mg, and Mn were detected at levels greater than 1 mg/g-TSS (Figures 7 and 8). Among these elements, Fe was detected at the highest level in raw water and distributed water, followed by Al, Zn, Cu, and Pb which were detected at very low levels (<1 mg/g-TSS). The percentage of mineral elements in the FSS was <10% in the raw waters and 30%–60% in the filtered, finished, and distributed waters. When the elements were assumed to be present as FeO(OH), Al(OH)₃, CaCO₃, MgCO₃, and MnO₂, these mineral elements accounted for all of the FSS in filtered, finished, and distributed waters. For the
raw waters, however, these compounds accounted for no more than 16% of the FSS, indicating the existence of Si compounds.

After sand filtration, the Al content of the FSS markedly increased from 2% to 40% in treatment plant A and from 2% to 23% in treatment plant B (Figure 7). Polyaluminium chloride was used as a coagulant in these treatment plants, so it is possible that a small percentage of aluminium floc passed through during sand filtration or that dissolved...
aluminium precipitated after sand filtration. In treatment plant A, the Mn and Fe concentrations increased from filtered water to finished water, probably due to oxidation–precipitation during post-chlorination. In treatment plant B, however, the Fe and Mn concentrations did not increase because chlorine was added before sand filtration; oxidized and precipitated Fe and Mn could then be eliminated by sand filtration. The Fe concentration in both distribution systems increased, probably due to oxidation and rusting of iron pipes.

Conclusions

1. The constituents of suspended particles changed after water treatment. The percentages of volatile suspended solids (VSS), carbon, and nitrogen in the suspended particles, all of which indicated organic suspended particles, were greater after water treatment than before water treatment. Inorganic suspended particles were removed more efficiently than organic suspended particles. The difference in weight of suspended particles retained by 0.6 and 2.7 µm filters suggested that smaller particles may remain after conventional water treatment. The increase in the Al content of the fixed suspended solids (FSS) after sand filtration indicated that either a small percentage of aluminium floc passed through during sand filtration or dissolved aluminium precipitated after sand filtration. The Mn and Fe concentrations increased after chlorination because of oxidation–precipitation of dissolved Mn and Fe.

2. The carbon in the suspended particles was mostly organic carbon, and the fraction of inorganic carbon was very low. The percentages of carbon and nitrogen in the VSS were roughly the same in the raw, filtrated, finished, and distributed waters. The carbon/nitrogen/phosphate/VSS ratios indicated that the VSS of suspended particles consisted of organic matter originating from microorganisms. Major constituents of the FSS in filtered, finished, and distributed waters were compounds of Fe, Al, Ca, Mg, and Mn, but these compounds accounted for only 16% or less of the FSS in raw water, indicating the existence of Si compounds.

3. In distribution pipes, the total suspended solids (TSS) concentration, especially the FSS concentration, was higher than that just after water treatment. The Fe concentration of distributed water increased in both distribution systems, probably due to the oxidation and rusting of iron pipes.

4. The percentage of VSS and organic carbon in the lake water was almost constant except during summer, whereas the TSS concentration varied from 1 to 3.2 mg/L. The summertime increases in carbon and nitrogen contents were attributed to the algal bloom in summer. The FSS/TSS ratio was lower in the lake water than in the river water.

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References


