Application of membrane processes in fractionation of elements in river water

N. Wu, Y. Wyart, J. Rose, B. Angeletti and P. Moulin

ABSTRACT

The influence of wastewater treatment plant (WWTP) effluents from one microelectronic industrial zone on element concentrations and partitioning in river water was investigated. The stepwise membrane filtration is used to distinguish different size fractions including large particulate (>18 μm), particulate (0.2–18 μm), colloidal/nanoparticle (10 kDa–0.2 μm) and truly dissolved fractions (<10 kDa) in river water samples and WWTP effluents. Results demonstrated that anthropogenic inputs (WWTP effluents and industrial area) had an important influence on concentrations and partitioning of some elements in river water. Mass balance results showed that membrane filtration processes could realize a good fractionation for many elements (good recoveries) in water samples. Flux decline during 0.2 μm and 10 kDa filtrations were analyzed, and corresponding fouling mechanisms are discussed.

Key words | colloids, fouling, membrane filtration, nanoparticles, surface water

INTRODUCTION

Metal contamination in aquatic environments is one of the most common and persistent environmental issues (Ren et al. 2010). However, with the rapid development of many state-of-the-art technologies (e.g. semiconductor and nanotechnology industries), a few specific common or uncommon elements used in these industries could be released into receiving waters via sewage effluents, despite treatment before discharge (Chen 2006; Hsu et al. 2011). Elements can be released not only as soluble fractions but also under particulate and nanoparticulate state (O’Brien & Cummins 2010). For example, the polish suspension used in chemical and mechanical polishing (CMP) processes normally consists of large quantities of Si and/or Ce nanoparticles (Hu et al. 2005; Testa et al. 2011). Other elements like V, Se, Sr, and U are also widely used in microelectronic industries (Meek et al. 2001; Allsopp et al. 2007; Nag & Haglund 2008; Matar et al. 2011). However, knowledge of the exposure concentrations and fates of these elements in receiving waters is lacking (Hsu et al. 2011; Neal et al. 2011), especially for the elements associated with colloidal/nanoparticle fractions. These small particles play an important role in processes such as contaminant speciation, transport and bioavailability, due to their small sizes (1 nm–0.2 μm) and large surface areas (Lead & Wilkinson 2006; Wigginton et al. 2007).

Since natural aquatic colloids and nanoparticles are complex mixtures of different phases, the sample fractionation is often required prior to analysis (Baalousha & Lead 2007). Among a wide number of techniques for sample fractionation, membrane filtration processes are now receiving more attention due to their advantages of simple operation, low cost, high efficiency, high volume, low sample perturbation and environmental friendliness (Tiede et al. 2008), as well as a wide separation range (from about 0.1 nm to 2–3 μm). In traditional analysis of natural water, the simple two-phase fractionation (Doucet et al. 2005) by commonly used 0.45 or 0.2 μm membranes neglects the colloidal and sub-colloidal fractions; therefore more studies employed the stepwise membrane filtration.
to achieve different size fractions (Doucet et al. 2004; Pokrovsky et al. 2010; Ren et al. 2010).

In this paper, elements associated with colloidal/nano-particle fractions in a natural aquatic environment were studied. The industrial zone (IZ) of Rousset–Peynier, France, known as ‘Silicon Valley of Provence’ was selected because a large number of companies in the field of micro-electronics, nanotechnology and surface treatment of components (wafer polishing) are located there. In this area, industrial effluents are treated by specific wastewater treatment plants (WWTPs) of the industrial zone after recycling and treatment at each site, before they are discharged into the Arc river. Although few studies have tested the effectiveness of WWTPs for the treatment and removal of nanoparticles, it has been proved that some nanoparticles could escape from WWTPs and enter receiving waters via effluents (Kiser et al. 2009; Ganesh et al. 2010; Westerhoff et al. 2011). Hence, WWTP effluents of the IZ, and surface water samples from upstream and downstream of the effluent outlet to the Arc river were analyzed to investigate the influence of anthropological sources (IZ site) on river water by distinguishing ‘background’ geogenic sources from anthropological sources. In laboratory scale, filter cartridges (18 μm) and membranes with decreasing pore size or molecular weight cut-off (WCO) (0.2 μm and 10 kDa) were used to distinguish large particulate (>18 μm), particulate (0.2–18 μm), colloidal/nanoparticle (10 kDa–0.2 μm) and truly dissolved fractions (<10 kDa) for water samples. The fouling mechanisms of membranes during fractionation processes are also discussed.

MATERIALS AND METHODS

Sampling sites

Water samples were collected from the industrial zone (IZ) of Rousset–Peynier in France (April 2011). As depicted in Figure 1, the WWTP effluent of IZ, defined as ‘outlet’, was collected right before its release into the Arc river, and the other two surface water samples were taken from the Arc river upstream and downstream of the effluent outlet. About 10 L water samples were collected from each site. For each site, one sample was investigated.

Fractionation processes

The schematic layout of the sample preparation protocol is given in Figure 2. Raw water was firstly filtered by Rigimesh® sintered metal mesh filter cartridges (MBS1001RK, Pall) with a pore size of 18 μm in order to remove large particles. The outlet from the cartridge was collected as feed water. Then a two-step dead-end filtration was immediately undertaken by using a 0.22 μm polyethersulfone membrane (GPWP09050, Millipore) which was cut into an appropriate size (diameter of 76 mm) to fit the filtration cell, and a 10 kDa regenerated cellulose (RC) membrane (PLGC07610, Millipore). In this two-step dead-end filtration, the MWCO/pore sizes of two membranes were selected to further distinguish particulate (0.2–18 μm), colloidal/nanoparticle (10 kDa–0.2 μm) and truly dissolved fractions (<10 kDa) for water samples. Before the filtrations, the membranes were cleaned in sequence by distilled water, citric acid solution (pH = 4), distilled water, NaOH solution (pH = 8), and finally distilled water again. The permeabilities (T = 20 °C) of the clean
membranes were 4.281 ± 234 L h⁻¹ m⁻² bar⁻¹ for 0.22 μm membrane, and 157 ± 7 L h⁻¹ m⁻² bar⁻¹ for 10 kDa membrane, respectively.

The stepwise filtration system was composed of an air-pressurized feed tank connected to an Amicon 8400 stirred filtration cell (Millipore Corporation, Bedford, MA, USA) with a volume of 400 mL and an effective filtration area of 41.8 cm². Each filtration cell was stirred at 250 rpm using a speed-adjustable plate stirrer (HC502) to prevent concentration polarization at the sample surface. Transmembrane pressure (TMP) was maintained at 3.5-3.9 bar for both microfiltration (MF) and ultrafiltration (UF). For each dead-end filtration (0.2 μm and 10 kDa), all the retentates and permeates were collected and their volumes were recorded for mass balance analyses. The volume concentration factors ranged from approximately 30 to 20 for different samples.

Moreover, to evaluate the adsorption on the membrane during dead-end filtration, the membrane was quickly rinsed by 10 mL super-pure HNO₃ (15 M, strong acid was chosen here in order to get the best mass balance result) at the end of each filtration run, and nitric acid rinsing solutions (defined as acid 1 and 2 for 0.2 μm and 10 kDa membranes, respectively) were also collected for mass balance analyses. The mass balance for each dead-end filtration process (0.2 μm and 10 kDa) was checked as Equation (1):

\[
(\% \text{ recovery}) = \left( \frac{C_p V_p + C_r V_r + C_a V_a}{C_f V_f} \right) \times 100\%
\]  
(1)

where \(V_f\), \(V_p\), \(V_r\), and \(V_a\) are the volumes of feed, permeate, retentate and acid samples, respectively, and \(C_f\), \(C_p\), \(C_r\) and \(C_a\) are the concentrations of feed, permeate, retentate and acid samples, respectively.

The percentage of each pore size/MWCO fraction was calculated as Equation (2):

\[
P_{<18 \mu m} = \frac{C_f}{C_{raw}} \times 100\%
\]

\[
P_{>18 \mu m} = 100\% - P_{<18 \mu m}
\]

\[
P_{<0.2 \mu m} = \left( \frac{C_{p1} V_{p1}}{C_{p1} V_{p1} + C_{r1} V_{r1} + C_{a1} V_{a1}} \right) \times P_{<18 \mu m}
\]

\[
P_{0.2-18 \mu m} = 100\% - P_{<0.2 \mu m} - P_{>18 \mu m}
\]

\[
P_{<10kDa} = \left( \frac{C_{p2} V_{p2}}{C_{p2} V_{p2} + C_{r2} V_{r2} + C_{a2} V_{a2}} \right) \times P_{<0.2 \mu m}
\]

\[
P_{<10kDa-0.2 \mu m} = 100\% - P_{>18 \mu m} - P_{0.2-18 \mu m} - P_{<10kDa}
\]

(2)

where \(P\) is the percentage (%) of each pore size/MWCO fraction; \(C_{raw}\), \(C_f\), \(C_p\), \(C_r\), \(C_{a1}\), \(C_{a2}\), \(C_{a3}\), and \(C_{a4}\) are the concentrations of raw (unfiltered), feed (<18 μm), permeate 1 (<0.2 μm), retentate 1 (0.2-18 μm), acid 1 (0.2-18 μm), permeate 2 (<10 kDa), retentate 2 (10 kDa-0.2 μm), and acid 2 (10 kDa-0.2 μm) samples, respectively; \(V_{raw}\), \(V_f\), \(V_{p1}\), \(V_{r1}\), \(V_{p2}\), \(V_{r2}\), and \(V_{a2}\) are the volumes of raw, feed, permeate 1, retentate 1, acid 1, permeate 2, retentate 2, and acid 2 samples, respectively.

### Chemical analysis

Water samples for element analyses were stored at 4 °C after acidification with super-pure HNO₃ (15 M). All the samples were analyzed without dilution, except for acid 1 and 2 samples, which were diluted 10-fold before analysis due to high concentrations. Element concentrations were mainly determined by inductively coupled plasma mass spectrometry (ICP-MS, Thermo X Series II). Indium and bismuth were used as internal standards. Accuracy and precision of ICP-MS measurements were checked using certified reference material SLRS-4 (fresh water sample) from the National Research Council of Canada, which was within 5% of the certified values for the elements of interest. The detection limits for most elements ranged from 0.002 to 0.4 μg L⁻¹. The measurement of Si and Fe was performed using inductively coupled plasma atomic emission spectroscopy (HORIBA Jobin-Yvon Ultima-C) with external calibration, which provided a detection limit of 20.69 μg L⁻¹ for Si and 9.72 μg L⁻¹ for Fe. The pH of samples was measured with a microprocessor pH meter (Hanna, pH210), and the conductivity was measured using WTW Cond 3310 handheld conductivity meters (Germany).

### Fouling resistance and models

The Darcy law was used to calculate the total fouling resistance \((R_f)\) (Springer et al. 2015), as shown in Equation (3):

\[
R_f = \frac{\text{TMP}}{\mu_{20 \, \text{c}} \times J} - R_m
\]

(3)

where \(R_f\) is the total (overall) fouling resistance (m⁻¹), \(\text{TMP}\) is transmembrane pressure (Pa), \(\mu_{20 \, \text{c}}\) is the fluid viscosity (Pa·s), \(J\) is the permeate flux at 20 °C (m s⁻¹), \(R_m\) is the intrinsic membrane resistance (m⁻¹) which was calculated from the pure water flux.

The fouling mechanisms were analyzed according to the conventional non-steady-state filtration laws, which describe the dead-end filtration behavior under constant pressure (Hermia 1982), as shown in Equation (4):

\[
\frac{d^2t}{dV^2} = k \left( \frac{dt}{dV} \right)^n
\]

(4)
where $t$ is the filtration time (s), $V$ refers to the filtrate volume ($m^3$), $k$ is the fouling coefficient (variable unit depending on $n$). The exponent $n$ varies with different models of membrane fouling, as follows.

The cake filtration model ($n = 0$) assumes the formation of a deposit or cake on the membrane surface by retaining molecules with sizes greater than the membrane nominal pore sizes ($d_{\text{particle}} > d_{\text{pore}}$). There is a linear relationship between $t/V$ and $V$ during the cake filtration period, as shown in Equation (5) (Lohwacharin & Takizawa 2009):

$$\frac{t}{V} = \frac{k_c}{2} V + \frac{1}{Q_0}$$

where $k_c$ is cake filtration coefficient ($s \cdot m^{-6}$), $Q_0$ is initial permeate flow rate ($m^3 \cdot s^{-1}$).

The intermediate blocking model ($n = 1$) describes the situation whereby particles settle on each other and seal the membrane pore entrances ($d_{\text{particle}} = d_{\text{pore}}$). The corresponding linear form of the intermediate blocking model can be expressed as Equation (6) (Lohwacharin & Takizawa 2009):

$$\frac{1}{Q} = k_i t + \frac{1}{Q_0}$$

where $Q$ is permeate flow rate ($m^3 \cdot s^{-1}$), $k_i$ is intermediate blocking constant ($m^{-5}$).

The standard blocking model ($n = 1.5$) describes the accumulation of particles on the pore walls inside the membrane ($d_{\text{particle}} = d_{\text{pore}}$). The corresponding linear form of the standard blocking model can be expressed as Equation (7) (Lohwacharin & Takizawa 2009):

$$\frac{t}{V} = \frac{k_s}{2} t + \frac{1}{Q_0}$$

where $k_s$ is standard blocking constant ($m^{-3}$).

The complete blocking model ($n = 2$) assumes that particles arriving at the membrane will seal the pores in a mono-layer manner (particles do not accumulate on each other) and prevent any flow through them ($d_{\text{particle}} = d_{\text{pore}}$). The corresponding linear form of the complete blocking model can be expressed as Equation (8) (Lohwacharin & Takizawa 2009):

$$Q = Q_0 - k_b V$$

where $k_b$ is complete blocking constant ($s^{-1}$).

RESULTS AND DISCUSSION

Characteristics of raw water

The main chemical parameters in raw water of different sampling sites are presented in Table 1. The pH values of raw water were near neutral, ranging from 7.9 to 8.1 between the upstream and downstream, while the conductivity values remained constant (865 $\mu$S cm$^{-1}$). For WWTP effluent (outlet), the pH and conductivity was 8.0 and 851 $\mu$S cm$^{-1}$, respectively.

Mass balance

Mass balance calculation is an important check for data quality of the fractionation process. Figure 3 depicts the mass balance recoveries (%) of elements measured in each dead-end filtration process. Elements (Si, V, Se, U, Sr) had good recoveries, normally within the range of 100 $\pm$ 15% in both 0.2 $\mu$m and 10 kDa filtrations for all sampling sites.

For elements (Al, As, Sc and Fe), the mass balance recoveries were not always desirable, and were generally

Table 1 | Main chemical parameters for raw water and different size fractions

<table>
<thead>
<tr>
<th>Sample code</th>
<th>pH</th>
<th>Conductivity ($\mu$S cm$^{-1}$)</th>
<th>Volume (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upstream</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw</td>
<td>8.1</td>
<td>865</td>
<td>–</td>
</tr>
<tr>
<td>Feed</td>
<td>8.1</td>
<td>723</td>
<td>5,988</td>
</tr>
<tr>
<td>Retentate 1</td>
<td>8.2</td>
<td>715</td>
<td>188</td>
</tr>
<tr>
<td>Permeate 1</td>
<td>8.1</td>
<td>720</td>
<td>5,800</td>
</tr>
<tr>
<td>Retentate 2</td>
<td>8.2</td>
<td>738</td>
<td>195</td>
</tr>
<tr>
<td>Permeate 2</td>
<td>8.2</td>
<td>718</td>
<td>4,790</td>
</tr>
<tr>
<td>Acid 1</td>
<td>–</td>
<td>–</td>
<td>100$^a$</td>
</tr>
<tr>
<td>Acid 2</td>
<td>–</td>
<td>–</td>
<td>100$^a$</td>
</tr>
<tr>
<td>Outlet</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw</td>
<td>8.0</td>
<td>851</td>
<td>–</td>
</tr>
<tr>
<td>Feed</td>
<td>7.9</td>
<td>780</td>
<td>6,060</td>
</tr>
<tr>
<td>Retentate 1</td>
<td>8.2</td>
<td>778</td>
<td>220</td>
</tr>
<tr>
<td>Permeate 1</td>
<td>8.2</td>
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<td>5,840</td>
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<tr>
<td>Retentate 2</td>
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<td>185</td>
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<td>3,830</td>
</tr>
<tr>
<td>Acid 1</td>
<td>–</td>
<td>–</td>
<td>100$^a$</td>
</tr>
<tr>
<td>Acid 2</td>
<td>–</td>
<td>–</td>
<td>100$^a$</td>
</tr>
<tr>
<td>Downstream</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw</td>
<td>7.9</td>
<td>865</td>
<td>–</td>
</tr>
<tr>
<td>Feed</td>
<td>8.2</td>
<td>573</td>
<td>3,550</td>
</tr>
<tr>
<td>Retentate 1</td>
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<td>165</td>
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<td>Permeate 1</td>
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<td>3,385</td>
</tr>
<tr>
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<td>168</td>
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<td>564</td>
<td>3,000</td>
</tr>
<tr>
<td>Acid 1</td>
<td>–</td>
<td>–</td>
<td>100$^a$</td>
</tr>
<tr>
<td>Acid 2</td>
<td>–</td>
<td>–</td>
<td>100$^a$</td>
</tr>
</tbody>
</table>

$^a$Acid samples were diluted 10-fold (from 10 mL) prior to chemical analysis.
- Not determined.
within the range of 72–141%, except for Fe (37% during 0.2 \(\mu\)m filtration of water in upstream). This observation implied that a considerable fraction of Fe was retained inside the 0.2 \(\mu\)m membrane. This could be attributed to the pore blocking of membranes (e.g. trapping of Fe compounds inside membranes), and this process seemed to be irreversible (even after the acid rinse). This hypothesis can also explain that the occurrence of incomplete recovery for some elements (e.g. Al, Ti, Sc, Fe) was relatively more frequent during 0.2 \(\mu\)m filtration, compared to 10 kDa filtration. Similarly, the low recovery data of Fe in river water by 0.1 \(\mu\)m filtration (Morrison & Benoit 2004) and in seawater by ultrafiltration (Wen et al. 1996) were also reported. The possible reasons were given as the trapping of colloids or the sorptive interactions between elements and membranes. In the case of As, it can be noted that its recoveries were almost within the range of 100 ± 15%, except for 10 kDa filtration in downstream. In contrast, the recovery efficiencies of Ti were not good. The unexpected recovery values were possibly affected by contamination or analytical uncertainty due to the low concentrations in some size fractions (near the detection limit).

### Element concentrations associated with different fractions

Figure 4 depicts the concentrations of elements Si, Al, Ti, V, Se, U, As, Sr, Sc and Fe associated with different size fractions as follows: raw water (total concentration), feed water (<18 \(\mu\)m), retentate 1 (0.2–18 \(\mu\)m), acid 1 (0.2–18 \(\mu\)m), permeate 1 (<0.2 \(\mu\)m), retentate 2 (10 kDa–0.2 \(\mu\)m), acid 2 (10 kDa–0.2 \(\mu\)m) and permeate 2 (<10 kDa). For raw water, the concentrations of major elements (e.g. Al, Se, U, As and Fe) measured in river water (upstream and downstream) were below accepted concentrations for drinking water (Lenntech n.d.), which clearly indicates that no contamination of the natural system occurred.

### Concentrations of elements (Si, Al and Ti)

The total concentration of Si in outlet was higher than in river samples (upstream and downstream), and the differences in Si concentrations between outlet and river samples were 2.1–2.9-fold. Compared to outlet, the total concentration of Si decreased in the downstream, but was still higher (about 1.4-fold) than that of the upstream. In river
water (upstream and downstream), the dissolved concentrations (<0.2 μm, permeate 1) of Si (1,636–2,687 μg L⁻¹) were generally within the range reported, for example in Severnaya Dvina river (Pokrovsky et al. 2010). To compare ‘dissolved concentrations’ (normally defined as 0.2 μm or 0.45 μm filtrates) from other references, concentrations of permeate 1 were considered. Permeate 2 (10 kDa filtrates) was defined as ‘truly dissolved fractions’ in this study.

The total concentrations of Al (102.20 μg L⁻¹) and Ti (1.229 μg L⁻¹) from outlet were over one order of magnitude higher than upstream (7.73 μg L⁻¹ for Al, 0.070 μg L⁻¹ for Ti). In downstream, the concentrations of Al and Ti decreased (80–83%) compared to outlet, but were still higher (from 2.3- to 3.6-fold) than those of upstream, which could be attributed to high concentrations from outlet. In the case of Al, the dissolved concentrations (permeate 1) in river waters (2.66–4.35 μg L⁻¹) were much lower than those reported in the Amous river in France (69 ± 49 μg L⁻¹) and the average world river concentrations (50 μg L⁻¹) (Casiot et al. 2009). The dissolved concentration of Al in WWTP effluent (3.41 μg L⁻¹) was also much lower than those observed in other treated effluents (38–58 μg L⁻¹) from semiconductor manufacturing (Hsu et al. 2011).

In natural water, the concentrations of Ti in filtered surface water were expected to be low at the ppb to sub-ppb level (Neal et al. 2011). This seems to be confirmed by the obtained results, where Ti occurred in 0.2 μm filtered (permeate 1) river waters with low concentrations of 0.088–0.122 μg L⁻¹. It is not surprising to find a high concentration of Ti in WWTP effluent, since Ti is the ninth most abundant element in the earth’s crust, as well as being used in numerous industrial applications, such as semiconductors photocatalysts in wastewater treatments (Kiser et al. 2009). The observed Ti concentration (1.229 μg L⁻¹) in outlet can be compared to the predicted concentration (0.7–16 μg L⁻¹) in an area where Ti is mainly associated with the use of Ti nanoparticles in consumer products or in construction (Mueller & Nowack 2008). But Ti concentration observed in this study was generally lower than the practical values reported in other WWTP effluents (<5–25 μg L⁻¹) (Kiser et al. 2009; Westerhoff et al. 2011).

Overall, the total concentrations of Si, Al and Ti in the downstream decreased compared to WWTP effluent (outlet), which could possibly be attributed to the dilution impact, or settling and sedimentation. Furthermore, the decrease in concentrations of Ti could also be attributed to adsorption onto metal-bearing (e.g. Al, Fe) oxide and hydroxide minerals at near-neutral pH (Cidu & Biddau 2007), considering that large quantities of Al and Fe were released into the river via WWTP effluent. When compared
to upstream, the total concentration of Si, Al and Ti increased in the downstream, which indicated a discharge of these elements from anthropological sources into natural water. It is supposed that WWTP effluent contributed to the variation of Si, Al and Ti concentrations in surface water, since much higher concentrations of these elements were also observed in outlet than river samples. However, it cannot be concluded that WWTP effluent was the only contributor corresponding to this variation. Other unknown sources (e.g. confluences, as shown in Figure 1) between sites upstream and outlet also possibly caused the increase in element concentrations at downstream.

Concentrations of elements (V and Se)

With regard to V and Se, samples from downstream (0.831 μg L⁻¹ for V, 5.996 μg L⁻¹ for Se) contained higher concentrations (from 1.5 to 1.6-fold) than those observed in both upstream and outlet. Compared to upstream, outlet exhibited a higher concentration for V, but a lower concentration for Se. The dissolved concentrations of V and Se in river water were comparable to those reported in other surface waters (Cortecci et al. 2009; Hu et al. 2009).

For V and Se, although samples from downstream contained higher concentrations of these elements than those observed in upstream, it seemed that this elemental increase was more largely attributable to other factors (e.g. geochemical behavior of elements, or other unknown sources) rather than the inputs of WWTP effluent, since the elemental concentrations in outlet were lower than those in the downstream. For example, the increase of Se concentrations in aquatic systems can arise from disturbance of Se-enriched sedimentary rocks and soils, and usage of fossil fuels (Hu et al. 2009).

Concentrations of elements (U, As, Sr, Sc and Fe)

For U and As, their total concentrations in the downstream decreased (21% for U, 45% for As) compared to upstream; their concentrations in outlet (0.550 μg L⁻¹ for U, 0.330 μg L⁻¹ for As) were lower than river samples (1.923–2.444 μg L⁻¹ for U, 0.474–0.862 μg L⁻¹ for As). The total concentrations of Sr (336.2 μg L⁻¹) and Sc (62.38 μg L⁻¹) in outlet were lower than those in river samples (523.7–542.4 μg L⁻¹ for Sr, 79.37–89.50 μg L⁻¹ for Sc). Whereas the variation in concentrations between upstream and downstream for Sr and Sc were negligible, similar concentrations were found in these two sites. For U, As, Sr and Sc, their dissolved concentrations in river water were comparable to those reported in other surface waters (Cortecci et al. 2009; Masson et al. 2009; Pokrovsky et al. 2010; Geboy et al. 2011).

For U, As, Sr and Sc, their respective total concentrations in outlet were lower than those in river samples, which indicated that there was no release of these elements into receiving water via WWTP effluent. Moreover compared to upstream, there was no increase in total concentrations for these elements in the downstream. Thus it is unlikely that there are other unknown sources between the sites of upstream and outlet which are related to this elemental discharge. The behaviors of elements in river water, e.g. Sr and U, are more likely influenced by water–rock interaction processes (Cidu & Biddau 2007).

In the case of Fe, the total concentration in outlet (972.77 μg L⁻¹) was 4.7 times higher than in upstream (208.49 μg L⁻¹) and over one order of magnitude higher than in downstream (61.67 μg L⁻¹); while its total concentration in the downstream decreased by 70% compared to upstream. The dissolved concentrations of Fe (20.54–24.39 μg L⁻¹) in river samples were much higher than those reported in the Amous river (1 ± 4 μg L⁻¹), but lower than the world river average levels (40 μg L⁻¹) (Casiot et al. 2009). In WWTP effluent, the dissolved concentration (90.17 μg L⁻¹) of Fe was much lower than those observed in other effluents (269–379 μg L⁻¹) (Hsu et al. 2011). The total concentration of Fe in downstream was lower than that in upstream. It seemed that WWTP effluent did not cause an increase of concentration for Fe in the river, despite Fe at higher concentration being released from the outlet into the river. This phenomenon could possibly be attributed to the dilution impact or settling and sedimentation.

Partitioning of elements

The percentages of elements in large particulate (>18 μm), particulate (0.2–18 μm), colloidal/nanoparticle (10 kDa–0.2 μm) and truly dissolved (<10 kDa) fractions are presented in Figure 5. First, a general analysis on partitioning results is given. In the second part, partitioning results as a function of different elements are discussed:

In the upstream, most elements were mainly found in truly dissolved fractions (64–81%); only Al and Fe mainly occurred in large particulate and particulate fractions. It can be noted that for Al, Fe and Ti, there was a considerable part associated with particulate and colloidal/nanoparticle fractions (27–39%), while for other elements, the particulate and colloidal/nanoparticle fractions only occupied a very small part (<10%), which was the same as in outlet. This is most probably in relation
with the solubility constant of Al, Fe and Ti oxides/oxyhydroxides.

In WWTP effluent (outlet), elements V, Se, U, As, Sr and Sc were mainly in truly dissolved fractions (61–91%); elements Al, Ti and Fe were mainly found in large particulate fractions (81–94%); only Si was almost equally bound to large particulate (49%) and truly dissolved (47%) fractions. For all elements, the sum of particulate and colloidal/nanoparticle fractions was generally below 10%.

In the downstream, Si, As and Sc, which were mainly within the truly dissolved fraction (68–86%), exhibited similar profiles to those in the upstream; Al, Ti and Se mainly occurred in large particulate fraction (63–74%), and a large proportion of Se was also associated with the truly dissolved fraction (33%). For other elements (V, U, Sr and Fe), significant proportions were found in both large particulate and truly dissolved fractions in the downstream. It can be noted that for most elements in the downstream, the sum of particulate and colloidal/nanoparticle fractions was generally below 10%.

Figure 5 | Elemental partitioning for different sampling sites.

From upstream to downstream, most elements were, more or less, increasingly accumulated in large particulate fractions. Only for Si and Fe was there a decrease in ratio of large particulate fractions, and they were increasingly accumulated in the truly dissolved fraction (from 76 to 86% for Si and from 13 to 41% for Fe). Compared to upstream, the total percentages of particulate and colloidal/nanoparticle fractions for most elements decreased or remained relatively constant in the downstream, with the exception of Si (increased slightly from 6 to 9%).

Partitioning of elements (Si, Al and Ti)

For the partitioning of Si (Figure 5), the proportion of each size fraction (except for large particulate fraction) increased in the downstream compared to upstream, which was also accompanied by the increase of concentration associated with each size fraction (Figure 4). These results clearly indicated the influence of the IZ, and the origin of such elemental increase could be associated with the use of Si nanoparticles in CMP processes. Due to the high abundance of Si in earth along with its wide applications, the concentrations of Si in small-sized forms (e.g. colloidal/nanoparticle forms) could be expected to be much higher than other elements within the comparable size range. As the major component observed in both river water and outlet, Si could possibly control the transport of many other elements. For example, nano-sized Si was reported to be present at far higher concentrations than nano-sized
Ti in WWTP effluents (Westerhoff et al. 2011), and there was a co-occurrence of small-sized Si, Ti, Fe and other metal atoms in WWTP effluents (Kiser et al. 2009). Similarly in this study (Figure 4), the concentrations of Ti and Al in raw water were increased by a factor 3.5 and 2.5 between the upstream and downstream respectively, which showed a similar profile to that of Si.

The majority (81%) of Ti was associated with large particulates in outlet, which is different from investigations of Kiser et al. (2009), where Ti in WWTP effluents was nearly all present in the <0.7 μm size fraction. The difference may be caused by different treatment processes of WWTPs and re-aggregation of colloidal-sized and nano-sized Ti particles in final effluents. As pointed out by Neal et al. (2011), Ti will be largely transported with the suspended sediment through the river system, which was consistent with the results that large quantities of Ti (63%) were found in large particulate forms in the downstream.

With regard to Al, it tended to accumulate in large particulate and particulate fractions at all sites. This observation was in good agreement with Pokrovsky et al. (2010), who found that over 80% of Al in river was accumulated in the >0.2 μm size fraction. Compared to upstream, there was a drastic increase in the proportion of large particulate fraction for Al in the downstream. This phenomenon could be attributed to several reasons: the aggregation of large quantities of colloidal- or nano-sized Al associated with the microelectronics industry which were released by WWTP effluent, or a secondary precipitation of Al which was widely used as coagulant in WWTPs.

Partitioning of elements (Fe, V, Se, U, As, Sr and Sc)

With regard to Fe, it was present predominantly in large particulate and particulate forms at all sites, which was consistent with the previous research on WWTP effluents or river samples (Sigg et al. 2000; Worms et al. 2010), although a significant proportion of Fe was also found within the truly dissolved fraction in the downstream. Given that Fe exhibited much higher concentrations than other elements over sampling sites, it could possibly control the transport of some other elements. For example, Al, Ti, Co, Cu and rare earth elements were reported to be strongly associated with Fe colloids or oxides/hydroxides (Cidu & Biddau 2007; Vasyukova et al. 2010). Correspondingly, the behaviors of some elements were expected to be consistent with that observed for Fe in samples. For example in this study (Figure 5), a similar profile of element partitioning was found for Al, Ti, and Fe in outlet, and for Al and Fe in upstream.

Compared to upstream, elements V, Se, U, As, Sr and Sc in the downstream were increasingly accumulated in large particulate fractions. This could possibly be due to the aggregation of small-sized particles or the co-precipitation/adsorption of dissolved elements onto large Fe/Al particles.

Flux decline analysis during filtrations

The declines of normalized flux (J/J0) during 0.2 μm and 10 kDa filtrations of water are presented in Figure 6. After

![Flux decline analysis during filtrations](https://iwaponline.com/wst/article-pdf/72/12/2277/465449/wst072122277.pdf)
filtration of about 3,000 mL water, the flux decline caused by feed water (<18 μm) in 0.2 μm filtration was between 5 and 17% (Figure 6(a)), which was much lower than the flux decline of 46–74% caused by permeate 1 (<0.2 μm) in 10 kDa filtration (Figure 6(b)). In one study on membrane fouling by natural waters (Howe & Clark 2002), the authors found that the majority of flux decline for MF and UF was due to dissolved matters (<0.45 μm), and small colloids ranging from about 3 to 20 nm appeared to be important membrane foulants. Thus the dramatic flux decline during 10 kDa filtration may be attributed to small colloids and/or dissolved matters existing in permeate 1 (<0.2 μm). With regard to 0.2 μm filtration, it has been reported that 0.2 μm polyethersulfone membrane had interwoven sponge-like microstructures and large pore openings of up to 18–20 μm, according to the morphology results of the same membrane used in another study (Fang & Shi 2005). It is highly possible that a fraction of dissolved matters in feed water with sizes much smaller than pores passed through the membrane. Thus the flux decline caused by dissolved matters was relatively lower in 0.2 μm filtration, compared to 10 kDa filtration.

However, it should be noted that small particles or materials with sizes in the same order of magnitude as the membrane pore size can also settle in the internal pore structures and trigger a pore blocking of 0.2 μm membranes. The reversibility of this fouling was low (the fouling was difficult to remove even after the acid rinse), which can possibly explain the low mass balance recoveries of some elements (e.g. Fe) during 0.2 μm filtration, as depicted in Figure 3. This further reveals the colloidal nature of Fe.

The permeate 1 (<0.2 μm) from all three sampling sites fouled the 10 kDa RC membranes rapidly, but the extent of fouling was slightly worse for the upstream and downstream than the outlet. A similar situation was found during 0.2 μm filtration. After filtration of 5,000 mL feed water, samples from upstream caused a 32% flux decline, which was higher than 13% flux decline caused by outlet. For both 0.2 μm and 10 kDa filtration, the difference in fouling extent between WWTP effluent (outlet) and river water (upstream and downstream) may be due to the differences in the amount and characteristics of fouling components from these two water sources.

**Fouling resistance**

Total fouling resistance ($R_f$) values versus filtrate volumes are plotted in Figure 7. During filtration of WWTP effluent from outlet, 0.2 μm and 10 kDa membranes generally had lower resistance and smaller increasing rates, as compared to water from upstream and downstream. The same volume of feed water from downstream led to a higher resistance than upstream during 0.2 μm filtration, but in 10 kDa filtration, permeate 1 from downstream caused a lower resistance than upstream.

Whatever the pore size/MWCO of membranes, fouling resistance increased with filtrate volume for all three samples. In the case of 0.2 μm filtration, the slope of the curve slightly increased with the permeate volume (Figure 7(a)), while for 10 kDa membranes (Figure 7(b)), a gradual decrease in slope was observed during the filtration process. According to Tracey & Davis (1994), an external fouling (cake formation or pore blocking) is represented by a curve with a decreasing slope and quasi-steady state of
fouling resistance. Thus, the external fouling might be the dominant fouling mechanism for the 10 kDa filtration (Figure 7(b)), which is also confirmed by a further fouling mechanism analysis (see ‘Fouling mechanisms’ section). In outlet, the trend of fouling resistance to reach a quasi-steady state was more evident, compared to upstream and downstream. This might indicate that the colloidal fraction (10 kDa–0.2 µm) is not composed of very small particles, i.e. with the sizes similar to 10 kDa membrane pore diameters.

Fouling mechanisms

Due to the lack of experimental flux decline data caused by the rapid filtration process, the fouling mechanisms for 0.2 µm filtration were not further analyzed. For 10 kDa filtration, the fouling mechanisms were analyzed by Hermia laws (Hermia 1982). For all three samples, the initial pore blocking was nearly absent due to the lack of positive slopes, whereas an earlier transition to cake filtration occurred, as indicated by the curve maxima and negative slopes. These curves were not clearly understood, but a similar observation was reported by Lee et al. (2013) during the study of ceramic membrane filtration of humic acid. Typically, the negative slope and cake filtration are observed after the flux curve passes the initial fast decline; however, as depicted in Figure 6(b), the flux curves were still far from reaching a plateau. Overall, the 10 kDa filtration of water seems to be less governed by blocking mechanisms with very fast development of cake filtration (Lee et al. 2013).

Data calculated by Equation (5) confirm that the 10 kDa membrane fouling during filtration of water in all three sampling sites can be mainly described by cake formation. The linear correlation became more evident ($R^2 > 0.99$) as the cumulative volume increased. The $t/V$ versus $V$ curve is approaching a linear relationship after a similar cumulative volume for three samples ($V = 0.98$ L, 1.09 L, and 0.96 L for upstream, outlet, and downstream, respectively). The investigation of cake filtration as the dominant fouling mechanism also coincides with the total fouling resistance analysis (Figure 7(b)), which suggests the occurrence of external fouling. These results are in good agreement with other studies (Lohwacharin & Takizawa 2009; Lee et al. 2013), which reported that cake filtration became the dominant fouling mode in the filtration of river water, as filtration proceeded.

To investigate the fouling models that correspond to the initial membrane fouling, the flux declines were then further analyzed using another three non-steady-state filtration laws, by plotting the experimental data to Equations (6)–(8). The correlation coefficients ($R^2$) of various blocking models are compared (Table 2). To confirm the model fitting, it is desirable that $R^2$ values are greater than 0.99 (El Rayess et al. 2012). For upstream, the intermediate blocking model provided a higher value of $R^2 (>0.99)$, while for outlet and downstream, the standard blocking model gave the highest $R^2$ values.

The flux decline analysis for 10 kDa filtration, based on non-steady-state theory, is presented in Figure 8. For upstream (Figure 8(a)), the best fitting intermediate blocking model reveals that particles in permeate 1 (<0.2 µm) accumulated on the 10 kDa membrane pore entrances during the initial stage of filtration. For outlet and downstream (Figure 8(b) and 8(c)), the good fit to the standard blocking model suggests that the initial fouling was dominantly caused by the accumulation of some small particles in the internal pore structures. The adsorption of organic matters with low molecular weight on internal pore walls can also lead to the pore constriction. Similarly, standard blocking was found to govern the initial membrane fouling during ultrafiltration of organic nanocolloids (Kwon et al. 2006) and surface water (Lohwacharin & Takizawa 2009). For all three samples, the initial fouling phases were followed by some forms of transition, and eventually cake formation governed the fouling.

It should be pointed out that more precise conclusions cannot be drawn based on the present results. The classical Hermia models combining two or more blocking mechanisms have been shown to be useful for membranes fouled by more than one mechanism, either sequentially or simultaneously (Giglia & Straeffer 2012). According to our results, it is not easy to conclude the initial fouling mechanism: (1) the Hermia law is ideal for application to unstirred filtrations, but the filtrations in this study were performed under 250 rpm stirring conditions; (2) it has been shown that these classical fouling models are inadequate when the rate of fouling depends on flow rate, and in that case, the combined blocking–adsorption models might be better to predict behaviors of membrane filters (Bolton et al. 2006; Giglia & Straeffer 2012).

<table>
<thead>
<tr>
<th>Intermediate blocking</th>
<th>Upstream</th>
<th>Outlet</th>
<th>Downstream</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard blocking</td>
<td>0.9913</td>
<td>0.9830</td>
<td>0.9606</td>
</tr>
<tr>
<td>Complete blocking</td>
<td>0.9890</td>
<td>0.9975</td>
<td>0.9968</td>
</tr>
</tbody>
</table>
CONCLUSIONS

In this study, surface water samples WWTP effluent (outlet) of the industrial zone (IZ), and upstream and downstream of the outlet release to the Arc river were analyzed to investigate the influence of anthropological sources (IZ site) on river water, by distinguishing ‘background’ geogenic sources from anthropological sources. This study was based on the fractionation of a large number of elements in raw water. Filter cartridge (18 \(\mu\)m) and stepwise membrane (0.2 \(\mu\)m and 10 kDa) filtrations were used to distinguish large particulate (>18 \(\mu\)m), particulate (2–18 \(\mu\)m), colloidal/nanoparticle (10 kDa–0.2 \(\mu\)m) and truly dissolved fractions (<10 kDa) for water samples. Element concentrations associated with each fraction, mass balance recoveries and partitioning of elements, and filtration data were analyzed.

The results clearly demonstrate that certain elements from the treated effluents originating from the microelectronics and nanotechnology industrial zone are released into receiving waters. In the downstream of WWTP effluent (outlet), elements Si, Al and Ti increased in total concentrations (in raw water) compared to upstream, indicating a discharge of these elements from anthropological sources into natural water. It is supposed that WWTP effluent contributed to the variation of concentrations for these elements in surface water. But it cannot be concluded that WWTP effluent was the only contributor corresponding to this variation. Additionally, the total concentrations (in raw water) of major elements in river water (upstream and downstream) were below accepted concentrations for drinking water. For other elements, WWTP effluent did not cause a noticeable increase of concentrations in surface water, despite some elements, e.g. Fe, with significantly higher concentrations being released from outlet into river. This phenomenon could possibly be attributed to the dilution impact or settling and sedimentation.

The anthropogenic inputs have an important influence on the distribution of elemental partitioning among large particulate, particulate, colloidal/nanoparticle and truly dissolved fractions. To better understand the variation of elemental partitioning over sampling sites, further studies are needed to investigate the exact speciation of elements in different size fractions.

During filtration of surface water, the flux decline in 10 kDa filtration was higher than in 0.2 \(\mu\)m filtration, which may be caused by small colloids/nanoparticles and/or dissolved matters existing in permeate 1 (<0.2 \(\mu\)m). Fouling mechanism analysis showed that the fouling of the 10 kDa membrane during filtration of surface water can be mainly described by the cake formation model, whereas during the initial phase of 10 kDa filtrations, intermediate or standard blockings possibly occurred. It should be pointed out that more data need to be obtained for studying membrane fouling in more detail.

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In addition, mass balance results showed that membrane filtration processes could realize a good fractionation for many elements (good recoveries) in water samples, but undesirable recoveries were also observed for some other elements. Incomplete recoveries could be attributed to the membrane fouling. To reach good recoveries of different types of elements and to improve the reliability of the investigation, further studies need to be carried out to take into account the effects of membrane fouling.

Figure 8 | Flux decline analysis for 10 kDa filtration based on non-steady-state theory: (a) intermediate pore blocking for upstream, (b) standard blocking for outlet, (c) standard blocking for downstream.
account the variability of the water and to optimize the recovery method and operational parameters of membrane fractionation processes. Other samples of feed water were collected in January 2011 with similar results but in winter. It will be also interesting to determine the element compounds retained inside the porous media of membranes, not just the elements on the membrane skins, which were obtained by acid wash after filtration runs in this study.

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