

Geochemistry of chemical species in river water of Shibukuro-Tama-Omono River System containing acidic thermal water and mine drainage water in Akita Prefecture, Japan

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Abstract

Concentrations of dissolved ($0.004 \mu\text{m} >$), colloidal ($0.2\text{-}0.003 \mu\text{m}$) and particulate ($>0.2 \mu\text{m}$) forms of major elements and zinc in river water were examined at 14 locations of Shibukuro-Tama-Omono River System, from Tamagawa Dam Lake to the mouth of Omono River, to understand the variation of chemical compositions among the different forms of these elements. Chemical compositions of these chemical forms in river water were measured using PIXE, ion chromatography, and ICP-MS analyses. The anions and cations are present as the dissolved form. Zinc is present as three types of chemical forms. The dominant chemical form of zinc is dissolved form. Most of Zn as particulate form is thought to be clay minerals and diatom.

1 Introduction

The thermal water of Obuki Hot Spring in the Tamagawa Hot Spring area, Akita Prefecture is characterized by high acidity and high concentration of heavy metals. The acidic thermal water is neutralized by limestone at a neutralization plant near Tamagawa Hot Spring area and then is discharged into the Shibukuro River. The river water of the Shibukuro River merges with the river water of the Tama River and flow into Tamagawa Dam Lake (16 km downstream from Tamagawa Hot Spring area). The pH value of the river water at the Tamagawa Dam Lake is around 5. Toward downstream of Tamagawa Dam Lake, the Shibukuro-Tama River System unites with Omono River at the lower downstream in Daisen City and the pH value of river water of the system changes around 7. The geology also changes from Quaternary volcanic rocks at the upstream area through Miocene volcanic rocks at around Lake Tazawa to sedimentary rocks in Daisen City (Fig. 1).

In river water, the chemical forms of elements have wide variety such as particulate, colloidal and dissolved forms. The changes of pH and geology control the chemical forms of elements in river water and geochemical characteristics of river water. Information on the

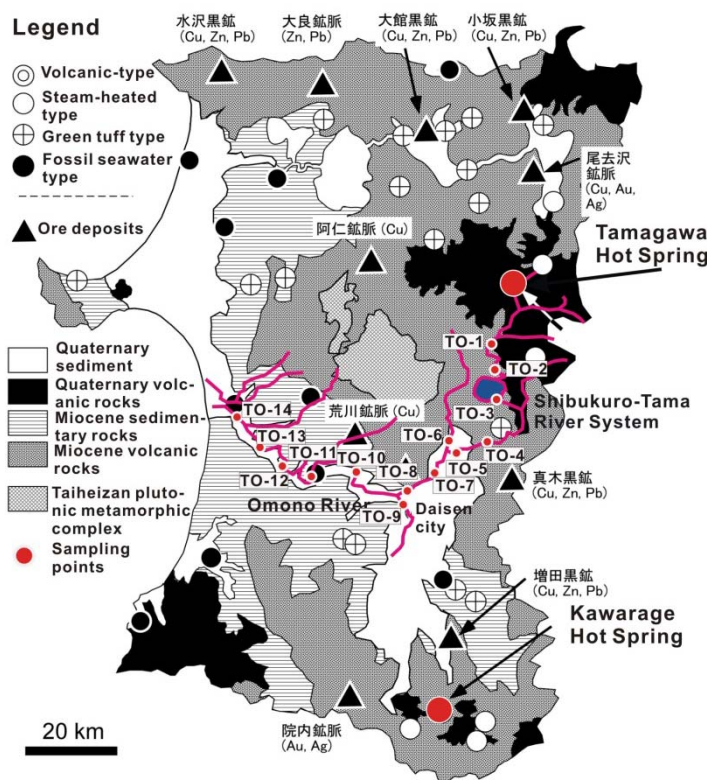


Fig. 1 Location of the study area and sampling points.

2 Materials and Method

2.1 Sampling of river water

All samples in this research were collected from the Shibukuro-Tama-Omono River System, which is located in Akita Prefecture (Fig. 1). The field surveys were carried out in December 2015, from the Tamagawa Dam Lake to the mouth of Omono River. The samples were collected at 14 locations (Fig. 1). At each site, samples for major and trace elements analyses were collected using successive filtration technique: unfiltered samples, filtrate samples using 0.2 μm filter and ultra-filtrate samples using 0.004 μm filter.

The unfiltered samples were collected and defined as “total mobile species”. The 0.2 μm filter were used to separate the suspended particles and materials that are present as colloidal and dissolved forms. The 0.004 μm filter were used to separate colloidal particle and then dissolved species remaining in the sample water. Water samples for trace elements analysis were collected in 50ml polyethylene bottles that are washed by HNO_3 , followed by addition of 3% HNO_3 to prevent precipitation. Samples for major ions analysis were not acidified (Ogawa *et al.*, 2012).

2.2 Methods for analysis of water samples

Measurements of pH, Eh and water temperature were done in the field. All samples were analyzed for major and trace elements according to chemical forms. The concentrations of major cations (Mg^{2+} , Ca^{2+} , Na^+ , K^+) and major anions (Cl^- , SO_4^{2-} , F^-) were determined using ion chromatography at Akita Industrial Technology Center. The concentration of Zn was

chemical forms is essential to understand processes such as weathering and geochemical fractionation of elements in natural environments. However, the studies that classify the chemical forms of elements in river water are not many. The purpose of this study is to examine the compositional variations according to the chemical forms (particulate ($>0.2 \mu\text{m}$), colloidal ($0.2-0.004 \mu\text{m}$), dissolved ($0.004 \mu\text{m}>$) forms) in terms of major elements and zinc to understand processes of transportation of these elements in river water.

determined by inductively coupled plasma mass spectrometry (ICP-MS) at Akita University. The particulate materials on the 0.2 μm membrane filter were observed by scanning electron microscopy and measured by X-Ray Diffraction at Akita University. The chemical compositions of the particulate materials were also measured by proton-induced X-ray emission (PIXE) at Nishina Memorial Cyclotron Center. Analytical procedures for PIXE are described by Sera and Yanagisawa (1992).

2.3 Comparison of Zn concentrations of particulate form determined by PIXE and ICP-MS

The concentration of Zn as particulate form determined by ICP-MS was calculated by subtraction of Zn concentration of the filtrated sample using 0.2 μm filter from Zn concentration of the un-filtrated sample measured by ICP-MS. On the other hand, the Zn concentration of particulate materials on the 0.2 μm membrane filter was determined by PIXE. The calculated Zn concentration of particulate form by ICP-MS was similar to the Zn concentration of particulate form measured by PIXE. Although the concentration determined by ICP-MS shows slightly higher concentration compared with the concentration determined by PIXE. After confluence point between Tama River and Omono River, the calculated and measured concentrations of particulate Zn show good agreement (Fig. 2).

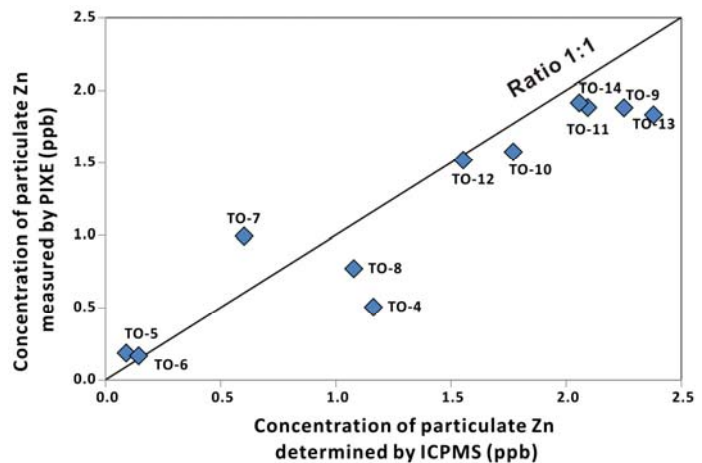


Fig. 2 Diagram showing relation between concentrations of Zn as particulate form determined by PIXE and estimated by data determined by ICP-MS.

3 Results and discussion

3.1 Variation in pH

Tama River that runs through the east region of Akita Prefecture has many tributaries. The Shibukuro River is one of the tributaries of the Tama River. In the river system, Obuki Cl-SO₄ type acidic thermal water (pH=1.2) of Tamagawa Hot Spring flows into river water of Shibukuro River, and then the river water of Shibukuro River merges into river water of Tama River. The river water reaches Tamagawa Dam Lake. The pH value of Tama River at Tamagawa Dam Lake is 4.9 (TO-1). Toward downstream, the Tama River

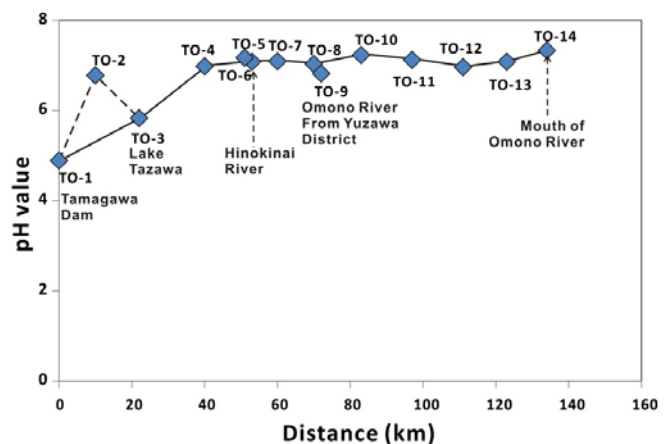


Fig. 3 Variation in pH from Tamagawa Dam Lake to the mouth of Omono River.

passes through Yoroihata Dam Lake. During the survey time, Yoroihata Dam Lake did not release river water of Tama River. Therefore, the pH value of river water was near neutral (TO-2, pH = 6.8) before flowing into Lake Tazawa. The pH value of river water decreased to 5.8 at Lake Tazawa (TO-3). In downstream of Lake Tazawa, the pH value of river water of Tama River increases to 7.0 (TO-8) because of joining of Hinokinai River that is one of tributaries having neutral pH value (TO-6, pH = 7.2). The river water of Omono River from Yuzawa area at Omagari has pH value 6.8 (TO-9). River water of Tama River flows into the Omono River from Yuzawa area. The river water of Omono River, after mixing with the river water of Tama River, reaches the mouth of Omono River in Akita City. The pH value of Omono River at the mouth of Omono River is 7.3 (TO-14) (Fig. 3).

3.2. Variation of chemical forms of major elements in river water

The concentrations of cation and anion of river water of Shibukuro-Tama-Omono River system are shown in Table 1. Because of high F^- , Cl^- and SO_4^{2-} concentration of thermal water from Tamagawa Hot Spring, and high Ca^{2+} concentration of thermal water after neutralization, the concentrations of these elements in river water at Tamagawa Dam Lake of the Shibukuro-Tama River show the highest values (0.53, 29.6, 23.2 and 16.6 ppm, respectively). Then these concentrations gradually decreased toward downstream (TO-8, 0.12, 12.3, 12.3 and 8.0 ppm, respectively). After mixing river water of Tama River with river water of Omono River from Yuzawa area at Omagari (TO-9, 0.07, 17.2, 11.7 and 7.4 ppm, respectively), the concentrations of F^- , SO_4^{2-} and Ca^{2+} in Omono River gradually decrease and/or keep constant to the mouth of Omono River (TO-14, 0.07, 12.3 and 7.6 ppm, respectively) while concentration of Cl^- increases to the mouth of Omono River (TO-14, 18.4 ppm). The concentrations of Na^+ , K^+ and Mg^{2+} have a different tendency. These concentrations increase from Tamagawa Dam Lake to the mouth of Omono River (from 4.7 to 11.6, 1.5 to 2.4 and 0.9 to 1.8 ppm, respectively) (Table 1).

Table 1 Water parameters and total concentration of major elements and Zn in Shibukuro-Tama-Omono River Systems.

Samples	Distance km	pH	T °C	F^-	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	Zn ppb
				ppm	ppm	ppm	ppm	ppm	ppm	ppm	
TO-1	0	4.9	9	0.53	29.6	23.2	4.7	0.9	16.6	1.5	8.9
TO-2	10	6.8	5	0.16	11.7	8.4	5.6	0.8	7.7	1.5	1.7
TO-3	22	5.8	10	0.46	17.2	18.4	4.9	0.7	10.5	1.5	7.2
TO-4	40	7.0	7	0.16	11.5	15.7	5.7	0.7	9.4	2.0	4.5
TO-5	53	7.1	8	0.15	11.9	15.7	6.0	0.8	9.5	2.1	3.3
TO-6	51	7.2	6	0.03	10.0	5.8	6.2	0.8	5.0	1.5	3.1
TO-7	60	7.1	7	0.11	12.1	11.3	6.7	0.9	7.6	1.9	4.6
TO-8	70	7.0	7	0.12	12.3	12.3	6.9	0.9	8.0	2.1	5.3
TO-9	72	6.8	5	0.07	17.2	11.7	11.2	1.9	7.4	2.2	10.4
TO-10	83	7.2	5	0.08	17.1	12.0	11.1	1.8	7.5	2.3	8.3
TO-11	97	7.1	5	0.09	17.2	12.0	11.1	1.8	7.5	2.3	8.0
TO-12	111	7.0	6	0.08	17.4	12.1	11.2	1.8	7.5	2.3	8.0
TO-13	123	7.1	6	0.07	17.9	12.2	11.3	1.8	7.6	2.4	8.8
TO-14	134	7.3	6	0.07	18.4	12.3	11.6	1.8	7.6	2.4	6.8

The variations of concentrations of Cl and Na that are present as dissolved, colloidal and particulate forms are shown in Table 2 and Fig. 4. Concentration of dissolved Cl⁻ and Na⁺ are almost 100% among the chemical forms. This fact suggests that no Cl⁻ and Na⁺ as colloidal and/or particulate forms are present. Other anions and cations (K⁺, Ca²⁺, Mg²⁺, F⁻ and SO₄²⁻) are also present approximately 100% as dissolved form in Shibukuro-Tama-Omono River system (Table 2). The change of pH value of river water of Shibukuro-Tama-Omono River System would not give effect to the state of chemical forms of major elements.

Table 2. Fraction of dissolved (D), colloidal (C) and particulate (P) forms of major elements (%) in river water of Shibukuro-Tama-Omono River Systems

Samples	F ⁻			Cl ⁻			SO ₄ ²⁻			Na ⁺			K ⁺			Ca ²⁺			Mg ²⁺		
	D	C	P	D	C	P	D	C	P	D	C	P	D	C	P	D	C	P	D	C	P
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
TO-1	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	99	0	1
TO-2	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	99	0	1
TO-3	94	6	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0
TO-4	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0
TO-5	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0
TO-6	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0
TO-7	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0
TO-8	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0
TO-9	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0
TO-10	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0
TO-11	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0
TO-12	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0
TO-13	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0
TO-14	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0

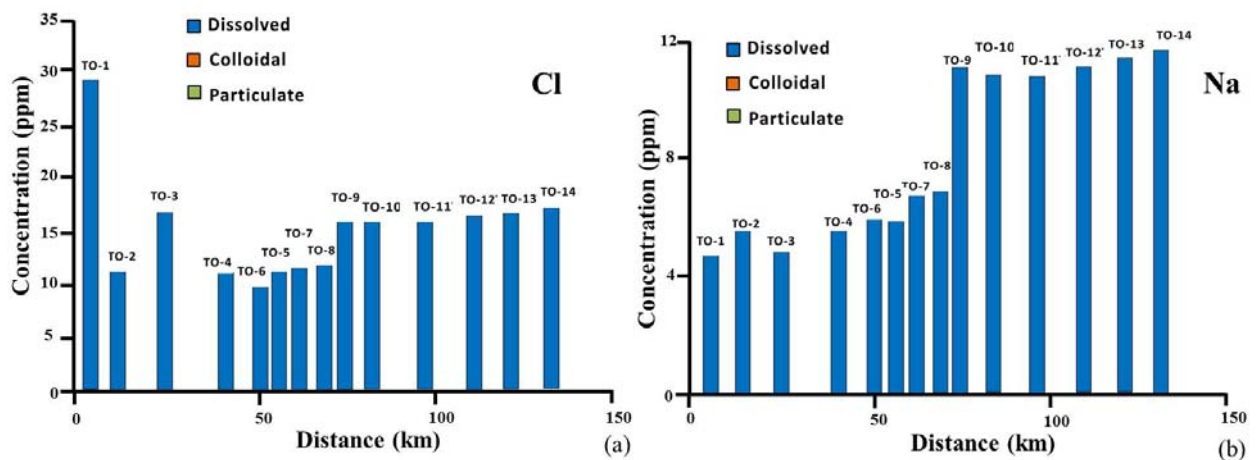


Fig. 4 Variation of concentration of (a) Cl and (b) Na according to chemical forms.

3.3. Variation of chemical forms of Zn in river water

The total concentrations of Zn decrease from Tamagawa Dam Lake (8.9 ppb) to downstream of Tama River (TO-8, 5.3 ppb) and then increase from TO-10 (8.3 ppb) at Omagari, in downstream of confluence point between Tama River and Omono River from Yuzawa area, to the mouth of Omono River. The sampling point TO-9 of Omono River from Yuzawa district shows highest concentration (10.4 ppb) (Table 1). The increase of Zn concentration at Omagari (TO-10) is caused by the mixing river water of Tama River and river water of Omono River from Yuzawa area (TO-9).

The chemical forms of Zn in river water vary according to pH values of river water. At Tamagawa Dam Lake (TO-1), the pH value is 4.9 and most of Zn at this site is present as the dissolved form (Table 3). Two percent (2%) of the total quantity of Zn is present as particulate form. At Lake Tazawa (TO-3), 100% of Zn occurs as dissolved form. Along mainstream of Tama River, the pH value of river water changes to neutral. All three fractions of Zn occur in significant amounts, although the dissolved form of Zn is dominant (TO-8, 80%, Table 3). After the mixing of river water of Tama River and river water of Omono River from Yuzawa area, the abundance of the particulate form of Zn increases in river water of Omono River. The particulate form of Zn is present from 19% to 30% (Table 3).

Table 3 Fraction of Dissolved, Colloidal and Particulate forms of Zn (%) in river water of Shibukuro-Tama-Omono River Systems

Samples	Dissolved %	Colloidal %	Particulate %
TO-1	98	0	2
TO-2	84	9	7
TO-3	100	0	0
TO-4	74	0	26
TO-5	89	9	3
TO-6	89	6	5
TO-7	87	0	13
TO-8	80	0	20
TO-9	76	2	22
TO-10	72	7	21
TO-11	73	1	26
TO-12	78	3	19
TO-13	71	2	27
TO-14	70	0	30

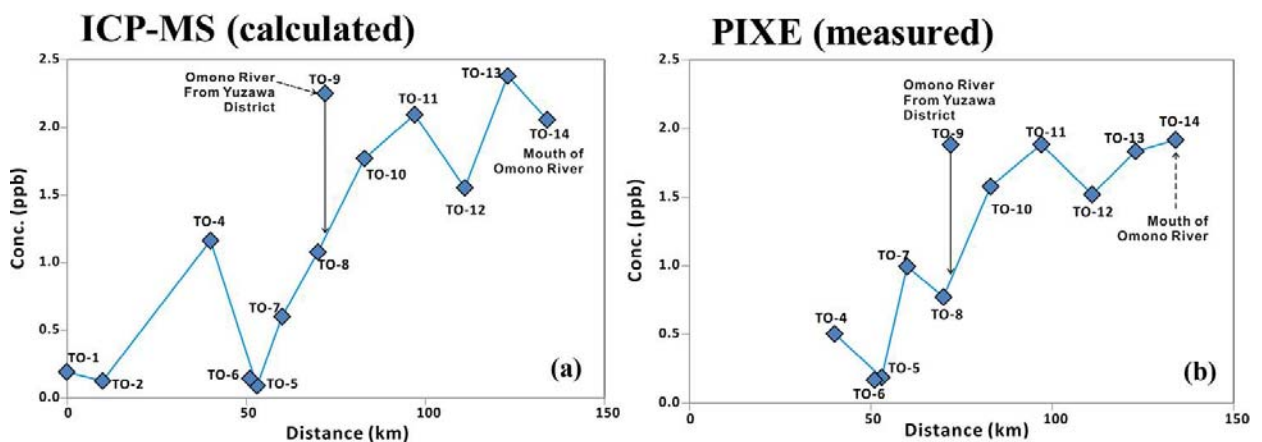


Fig. 5 (a) Zn concentration in particulate form determined by ICP-MS, (b) Measured concentration of particulate materials on the 0.2 μm membrane filter by PIXE.

The variation of Zn concentration in particulate form is shown in Fig. 5. Both variations of Zn concentrations as particulate form determined by PIXE and ICP-MS show similar tendency. Zn concentrations of particulate form increase at downstream of the confluence of Tama River and Omono River.

3.4. Host of zinc in river water

The observation and chemical analysis of particulate materials on the 0.2 µm filter of samples of TO-8 and TO-12 by SEM-EDX are shown in Fig. 6. Based on the qualitative analyses by SEM-EDX, the particulate materials are thought to be clay minerals (Fig. 6a) and diatom (Fig. 6b). The particulate material at TO-8 mainly consists of Si and Al with substantial of Cu and Zn. Based on the chemical composition, the particulate material is thought to be clay minerals.

In addition, based on the morphological features and chemical compositions of other particulate forms, diatom is present in river water at sampling TO-12 (Fig. 6b). A small amount of Zn is present in the diatom. It is also host of Zn as particulate form in river water. The clay minerals and diatom in the river could be a host of heavy metal(s) in the river water.

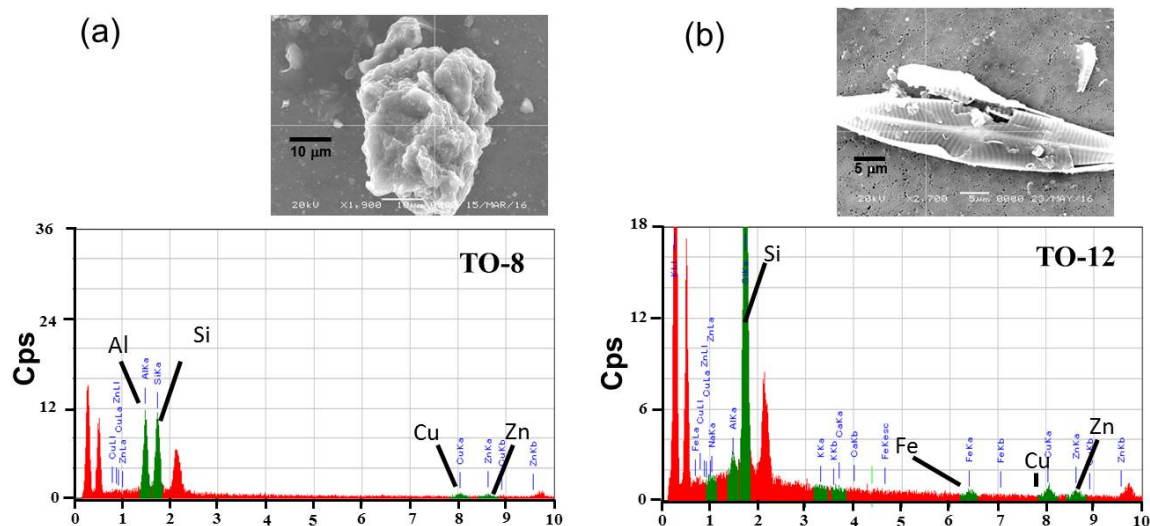


Fig. 6 Morphological features and chemical composition of particulate materials on a 0.2 µm membranes filter.

4 Summary

According to behavior of elements during filtration, two groups of elements can be distinguished: (i) species that are present in form of true dissolved inorganic species (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , F^- , Cl^- and SO_4^{2-}) and (ii) Zn which is present mainly as dissolved form with substantial amount of colloidal and/or particulate materials such as clay minerals and diatoms.

References

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