

Size fractionation of trace elements in the surface water and groundwater of the Ganjiang River and Xiushui River basins, China

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Abstract. The research of trace element behaviour and size fractionation is significant to understand the processes in the water–rock system. Moreover, the aqueous speciation of trace elements is strongly related to their distribution and toxicity. In this research, trace elements behaviour and their size fractionation are investigated in the natural water (the surface water and shallow groundwater) of the Ganjiang River and Xiushui River basins. Trace element concentrations were measured by ICP-MS. The authors estimated the size fractionation of the trace elements between suspended forms ($>0.45\mu\text{m}$) and dissolved fractions, which included truly dissolved (1 kDa) and colloidal particles ($0.45\mu\text{m}$ –1 kDa), after filtration through a $0.45\mu\text{m}$ acetate cellulose membrane filter. The distinct features of the trace element size fractionation were identified. The size fractionation of the trace elements under different conditions (in the surface water and shallow groundwater) was studied.

1. Introduction

The Ganjiang River and the Xiushui River are the main rivers of the Poyang Lake basin which disemboved into Poyang Lake from the west. This territory is the part of a unique wetland system, which is the habitat of rare animal species. Moreover, it is an important part of economy of Jiangxi Province (China). Wide alluvial plains make this area one of the main agricultural regions in China; these territories are often irrigated for rice and other crops cultivation. In such rural regions as the Ganjiang River and Xiushui River basins, where population density is quite high, intensive agricultural activity is developed, and often, there are no sewer systems, the vexed problem is shallow groundwater and surface water pollution by fertilizers, domestic sewage, manure and other livestock waste. Therefore, the investigation of the shallow groundwater and surface water chemical composition of agricultural regions is important to support the ecosystem sustainability.

Trace elements are the essential part of natural water chemical composition. They are usually contained in natural water at low concentrations but have a great significance to human health [1]. Some of them have a healthy influence. The others, on the contrary, are not required for human body function, and, as numerous works have showed, they may provoke various pathological processes [2, 3]. However, there is a lack of information about the concentrations and behaviour of the trace elements in the natural water of the Ganjiang River and Xiushui River basins.



The distribution and toxicity of trace elements are strongly related to their aqueous speciation. Thus, both the total concentrations of trace elements and their chemical forms determine their bioavailability and potential environmental pollution [4]. Trace elements in natural water may migrate in different forms: particles ($>0.45\mu\text{m}$), colloids ($0.45\mu\text{m} - 1\text{ kDa}$), and dissolved forms ($<1\text{ kDa}$) [5]. Saito et al. [6] and McNaught and Wilkinson [7] reported that colloids in natural water have at least one of their dimensions from 1 nm to $1\mu\text{m}$. Nystrand and Österholm [4] have demonstrated that the dissolved forms of trace elements are the most mobile and available to biota; hence, the dissolved fraction of trace elements may be identified as the most toxic fraction. However, there is the increasing number of evidences that natural colloids are carriers for toxic substances [6, 8]. It is also important that the concentrations of trace elements should be considered in the investigation of a redistribution process in the water-rock system. In most cases, the precise evaluation of processes in the water-rock system is impossible without data on trace element content in natural water. The size fractionation of trace element species influences the element capability to transport and react with other water compounds.

The present work is focused on the investigation of trace element behaviour and size fractionation in the natural water (the surface water and shallow groundwater) of the Ganjiang River and Xiushui River basins, along with the study of the main ion composition and geochemical conditions of this area. The authors of the article have compared the concentrations of the trace elements after filtration through a $0.45\mu\text{m}$ acetate cellulose membrane filter. This procedure was used to separate a suspended fraction ($>0.45\mu\text{m}$) from a dissolved fraction ($<0.45\mu\text{m}$). The dissolved fraction includes colloidal ($0.45\mu\text{m} - 1\text{ kDa}$) and truly dissolved particles ($<1\text{ kDa}$) and is called “semi-dissolved” according to Nystrand and Österholm [4]. It allows identifying the distinct features of behavior and the size fractionation of the trace elements under different conditions in the natural water of the Ganjiang River and Xiushui River basin.

2. Materials and Methods

2.1. Study area

The study area is situated in Jiangxi Province (southeast China). It is the part of the Poyang Lake catchment, in particular, the Ganjiang River basin and the Xiushui River basin, which are two of the five major rivers feeding Poyang Lake.

The territory belongs to the subtropical humid climate zone with the average annual temperature 17.5°C [9]. The annual precipitation is 1400–2400 mm [10]. Irregular rainfall distribution during the year is controlled by the East Asian monsoon. The wet season lasts from March – April to June, then rainfall decreases from July to September, with evapotranspiration reaching its maximum point [11]. After September the dry season begins and lasts till December–February. The study area has a relatively flat relief, with alluvial plains being predominant [9].

Shallow aquifers within the study area are porous water-bearing rocks composed of Quaternary fluviolacustrine and deltaic sand-clay sediments, including red earth.

2.2. Sampling and analytical procedures

Field work in the study site was conducted in October, 2013, during the dry season. Sampling points were located to the west of Poyang Lake in the lower course of the Ganjiang River basin and the Xiushui River basin (figure 1). In the course of research, the following waters were studied: the shallow groundwater, which was sampled from public and private household wells (18 samples), and the surface water from the main rivers, the Ganjiang and the Xiushui, and from Poyang Lake (5 samples). The surface water samples were collected near the riverbank (the Xiushui River) or using a boat in the middle of the stream (the Xiushui River, the Ganjiang River, Poyang Lake).

Two sterile 50 mL polyethylene vials were used to collect water at each sampling point. The water sample for the first vial was collected without any preparation; another water sample was immediately filtered through a $0.45\mu\text{m}$ acetate cellulose membrane filter of 30 mm in diameter using a pre-cleaned syringe. About 5 mL of the filtered water was eliminated at the beginning of filtration.

The unfiltered and filtered water samples were analysed for 42 elements using ICP-MS (PerkinElmer NexION 300D) in the Fundamental Research Laboratory of Hydrogeochemistry of Education and Research Centre “Water” (Tomsk Polytechnic University, Russia).

At each sampling point 600 mL of water was collected using polyethylene bottles and analysed for main ions (HCO_3^- by titration with 0.1M HCl; SO_4^{2-} , Cl^- , Ca^{2+} , Mg^{2+} , Na^+ , K^+ by ion chromatography (ICS 1000, ICS 2000)), nitrogen compounds (NO_3^- , NO_2^- , NH_4^+) by photolorimetry (KFK-2). Electrical conductivity, temperature and pH were measured *in situ*.

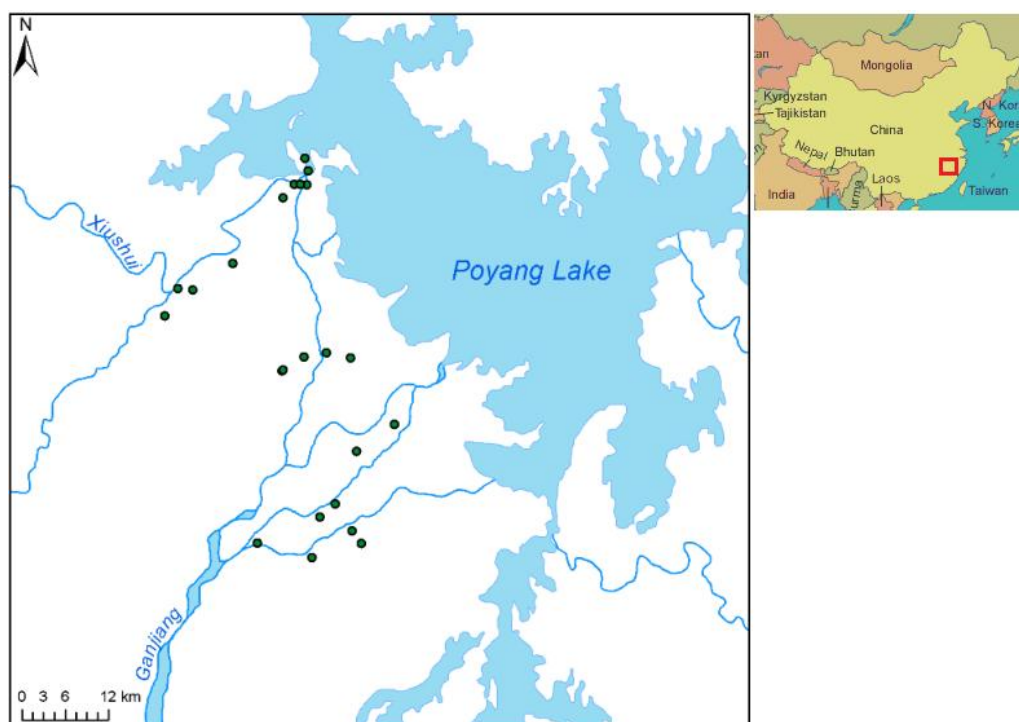


Figure 1. The scheme of the sampling points location.

3. Results and Discussions

The shallow groundwater of the study area is basically fresh with TDS up to 500 mg/L. The average value of TDS is about 196.9 mg/L (table 1). The acid-alkaline properties of the shallow groundwater vary significantly from 5.90 to 7.05. Geochemical conditions change from acid to neutral. An average pH value is 6.36.

As mentioned above, the study area is characterized by subtropical humid climate, where water exchange is active and there are no significant salt deposits in the upper part of the earth crust. According to the theory of the water–rock system evolution [12, 13] the shallow groundwater of such area should be $\text{HCO}_3\text{--Ca}$ and $\text{HCO}_3\text{--Ca--Mg}$. In fact, the main ions in the shallow groundwater are HCO_3^- and Ca^{2+} . However, we observed the increased role of chloride and nitrate and, less often, of sodium, potassium and sulphate in the shallow groundwater of the Poyang Lake basin, which changes the chemical type of the groundwater [14, 15].

The surface water of the study area is ultrafresh ($\text{TDS} < 200$ mg/L) with the average TDS value 92.3 mg/L (table 1). Geochemical conditions are usually neutral with the average pH value 7.05. The main ions of the chemical composition are HCO_3^- and Ca^{2+} . However, the average concentrations of the main ions are lower than that in the shallow groundwater. In particular, it concerns NO_3^- , which is no longer significant in the chemical composition of the surface water, whereas Cl^- , SO_4^{2-} and Na^+ remain the important components in the chemical composition and make a significant contribution to

the TDS value. Especially, it concerns Cl^- and Na^+ , which reach 30% of the anion and cation concentrations, respectively.

Table 1. The chemical composition of the natural water of the Ganjiang River and Xiushui River basins, mg/L, Eh – mV.

Values	pH	Eh	HCO_3^-	SO_4^{2-}	Cl^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	NO_2^-	NO_3^-	TDS
Shallow groundwater													
Min.	5.90	-91	18.3	0.67	1.38	2.18	1.18	8.30	0.74	<0.05	<0.02	0.15	49.5
Max.	7.05	176	170.8	111.4	58.9	47.5	9.70	43.4	76.0	6.40	0.3	93.9	523.7
Average	6.36	26.2	86.2	20.9	20.4	20.6	5.72	16.5	8.14	1.32	NA	17.2	196.9
Surface water													
Min.	6.70	51	32.3	8.50	6.10	10.0	1.59	4.80	1.32	0.15	<0.02	0.93	67.3
Max.	7.30	140	43.9	16.5	17.2	16.7	2.70	10.9	2.61	0.58	3.15	5.4	115.9
Average	7.05	85	38.9	12.9	12.0	13.6	2.28	8.27	2.00	0.30	NA	2.36	92.3

Note: NA – not available.

The investigated waters are characterized by the low Eh-value, which varies from -91 to 176 mV. The average Eh-value is no higher than 85 mV even for the surface water. Usually the Eh values are much higher in shallow groundwater and surface water.

We identified two groups of the trace elements characterized by the peculiar features of size fractionation between a suspended phase and dissolved phase (table 2). On the one hand, Li, Be, B, Si, Sc, V, Mn, Fe, Co, Ni, Zn, As, Se, Rb, Sr, Mo, Cd, Cs, Ba, W, Re, Tl, U were found basically in the dissolved form in accordance with the fact that their average concentrations in the filtered and unfiltered samples are distinguished slightly. On the other hand, the concentrations of some elements (Al, Ti, Cu, Sn, Ga, Y, Pb, rare earth elements) significantly decreased after filtration through a 0.45 μm membrane filter. This demonstrates that this group of the trace elements tends to migrate in the suspended phase.

Table 2. The average concentrations of the trace elements in the unfiltered and filtered water samples, mg/L.

Element	Water sample		Element	Water sample		Element	Water sample	
	Unfiltered	Filtered		Unfiltered	Filtered		Unfiltered	Filtered
Li	0.00268	0.00265	Ga	0.00009	0.00004	Nd	0.000329	0.000089
Be	0.00007	0.00006	As	0.01430	0.01308	Sm	0.000071	0.000018
B	0.0075	0.0077	Se	0.0008	0.0007	Eu	0.000022	0.000013
Al	0.100	0.008	Rb	0.00728	0.00751	Gd	0.000078	0.000021
Si	10.06	9.64	Sr	0.0973	0.0978	Tb	0.000012	0.000004
Sc	0.0003	0.0003	Y	0.000354	0.000148	Dy	0.000056	0.000017
Ti	0.009	0.002	Mo	0.0013	0.0014	Ho	0.000012	0.000005
V	0.0021	0.0019	Cd	0.000085	0.000091	Er	0.000032	0.000012
Mn	0.915	0.925	Sn	0.00006	0.00002	Yb	0.000031	0.000011
Fe	9.32	8.88	Cs	0.000122	0.000083	W	0.000181	0.000162
Co	0.00113	0.00097	Ba	0.0837	0.0839	Re	0.000006	0.000006
Ni	0.0015	0.0013	La	0.000371	0.000111	Tl	0.000027	0.000025
Cu	0.00075	0.00035	Ce	0.000690	0.000125	Pb	0.00187	0.00029
Zn	0.012	0.006	Pr	0.000084	0.000023	U	0.000092	0.000057

However, average concentrations do not always reflect all peculiarities of trace element behaviour. The case in point is Fe behavior. In several sampling points where the Eh-value is below 0 mV, the Fe concentrations are high in both filtered and unfiltered samples. The oxidation degree Fe^{2+} results in the absence of significant differences between the concentrations of Fe in the filtered and unfiltered

samples. The Fe ion with this oxidation degree is formed under specific reduction conditions. It leads to the accumulation of Fe in the dissolved phase. At the sampling points with the positive Eh-values the concentrations of Fe are much lower and tend to decrease significantly after filtration procedure. The authors suppose that this decrease occurs due to Fe hydroxide precipitation under oxidizing conditions.

It is typical that in the surface water, unlike the shallow groundwater, the transport of most trace elements occurs in the suspended form (figures 2a, b). Obviously, the high content of suspended matter in the surface water contributes to the trace element transport with large sized particles. In the research described, Be, V, Co, Cd, Cs and U, which usually migrate in the dissolved form, tended to be transported in the suspended phase (figure 2b).

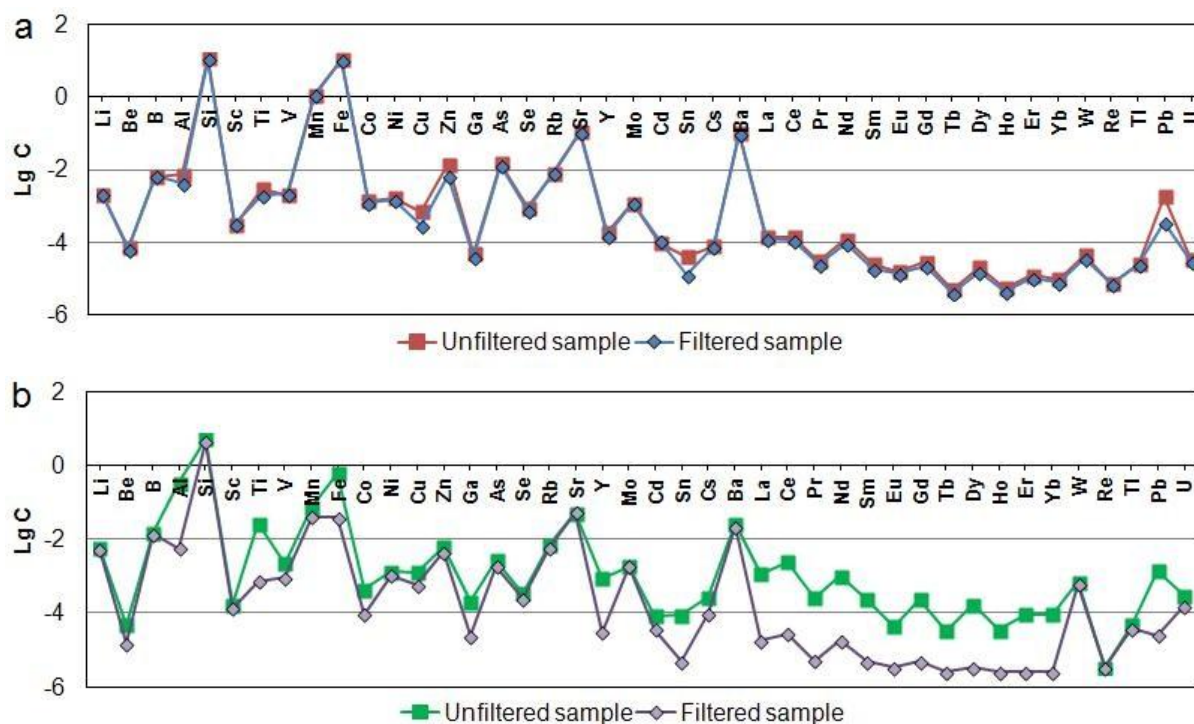


Figure 2. The concentrations of the trace elements in the most typical unfiltered and filtered samples: (a) the shallow groundwater; (b) the surface water.

4. Summary and Conclusions

In the investigated waters the authors have identified two groups of the trace elements characterized by peculiar features of the size fractionation between the suspended phase and the dissolved fraction. The first group includes Li, Be, B, Si, Sc, V, Mn, Fe, Co, Ni, Zn, As, Se, Rb, Sr, Mo, Cd, Cs, Ba, W, Re, Tl, U, which were found in the dissolved form. In the second group, Al, Ti, Cu, Sn, Ga, Y, Sn, Pb and rare earth elements migrate in the suspended fraction.

It has been found that the trace elements in the surface water tend to migrate in the suspended phase, whereas the trace elements in the shallow groundwater usually migrate in the dissolved form.

The size fractionation of Fe basically depends on geochemical conditions rather than the presence of the suspended matter in the natural water. Reduction conditions lead to accumulation of Fe in the dissolved phase. Under oxidizing conditions, Fe tends to migrate in the suspended phase, which might be caused by the hydroxide precipitation process.

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