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A Study on the Environmental Chemistry of Toxic Trace Elements in the Large Area Water Body

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This paper adopts the research approach of trace element environmental chemistry, conducts a tracer study on the cyclic process of toxic trace elements in the chemical substances in the watershed from the perspective of time and space, and studies the content, the distribution, the distribution characteristics mechanism in different phases as well as the influencing factors of toxic trace elements and other trace elements. Test results have demonstrated that the water chemistry characteristics of the small watershed in the southern Jiangxi Province affect the content and the distribution pattern of the dissolved trace elements. The pH value of the river water is the most significant factor that controls the behaviors of the dissolved trace elements in the river water. The content of the dissolved trace drops with the increase of pH value. Trace content and its value have showed an inverse relationship.

1. Introduction

The crystal chemical properties of toxic trace elements are extremely similar, which is the main reason for their close geochemical properties, similar geochemical behaviors and close symbiosis in the process of geology. Toxic trace elements in the natural terrestrial water mainly originate from the chemical weathering of soil and rock, the industrial wastewater discharge, the leakage and discharge of mine waste water and the application of agricultural micro-element fertilizers and other human activities, as well as atmospheric sedimentation and suspended particles. Generally, they have a very low content, and are mainly concentrated in the suspended portion. Toxic trace elements in the dissolved state have a extremely low content. Besides, the differences in the physical and chemical properties of the water body itself lead to the changes in the content of toxic trace elements in the water body in terms of time and space. This paper makes a preliminary study on the content and the distribution characteristics of toxic trace elements in the water body of the southern Jiangxi Province, clarifies the origin and the behavior of toxic trace elements in the river basin (concerning land scale, it is the supplementary study on toxic trace elements in large rivers), and comprehends the factors that control the abundance and the distribution model of toxic trace elements in the river, such as the stability of the organic matter as well as the adsorption and deposition process.

2. Experiments

2.1 Collection of River Water Samples

In mid-July 2016, 16 water samples in the southern area of Jiangxi Province were collected from the tributaries of the upper reaches of the Ganjiang River, and their distribution and the specific locations are illustrated in Table 2-1. Specifically, there involve three groundwater samples, one rainwater sample, and river samples from two main waterways of Ganjiang River and 33 tributaries.

The collected water samples are partially placed into a pre-prepared pure water bottle and stored as raw water and kept in darkness. The other portion is subjected to low pressure filtration. 0.45 μm and 0.2 μm cellulose acetate filters are adopted for filtration under a reduced pressure. The first three times of filtration are to clean the filters, and filter liquor is treated as waste. Since the fourth filtration, filtered water begins to be collected in a prepared polyethylene container. Avoided by all means, the membrane should not be taken away after the water on it dries (Shi et al., 2010). Ultra-pure hydrochloric acid is added to the collected filtered water, and the sample is acidified to a PH value of less than 2. During sampling, on-site sampling records should be made and the labels of the stored samples should be verified.

Table 1: Specific locations of sampling sites in the Southern Jiangxi

Number	Location	River system	N	E	H (m)
1	Xingguo 1	Ping river	26°23′11.4″	115°18′55.3″	189
2	Xingguo 2	Ping river	26°17′35.3″	115°23′40.9″	146
3	Ningdu 1	Mei river	26°30′16.3″	116°1′55.4″	246
4	Ningdu 2	Qin river	26°16′16.2″	116°1′5.5″	243
5	Ruijin 1	Mianshui river	25°49′11.9″	116°0′6.9″	227
6	Ruijin 2	Mianshui river	25°38′35.2″	115°48′28.3″	221
7	Huichang 1	Xiangshui river	25°33′43.5″	115°47′29.2″	198
8	Huichang 2	Gongshui river	25°36′35″	115°45′47.5″	166
9	Luokou 1	Gongshui river	25°41′28″	115°39′20.4″	157
10	Luokou 2	Lianshui river	25°44′10.8″	115°38′20.1″	159
11	Yudu 1	Gongshui river	25°55′9.4″9.4	115°37′43.6″	166
12	Gan county 1	Gan river	25°56′26.4″	114°57′33″	117
13	Gan county 2	Gan river	25°3′26.3″	114°58′10.3″	115
14	Gan county 3	Ping river	25°59′26″	115°9′18″	113
15	Gan county 4	Tao river	25°53′26.3″	115°5′32″	115
16	Gan county 2	Mei river	26°1′1.1″	115°25′52.9″	126

2.2 Test Analysis on River Water Samples

Laboratory test analysis. Determination of positive ion: Acidified filter samples are measured by ICP-OES (Model VISTA-MPX) manufactured by Varian Corporation in USA (Toro et al., 2011). Determination of negative ion: Raw water-filtered samples are assessed using ICP-90 ion chromatograpHs manufactured by Dionex Corporation in USA. Determination of DOC: The filtered samples are measured by High Temperature TOC/TNb Analyzer high TOC II + N in Germany. All samples are tested by means of ICP-MS analysis meter. The blank samples and the standard samples are treated at the same time, and the instrument analysis results and the error of the standard given value lie within the allowable range. Table 2 illustrates the relative standard deviation values of some elements measured by the instrument. The values are the calculated value of ten repeated measurements of the sample. The measurement time is 10 mins, and the relative standard deviation of all the elements is below 3%.

Table 2: Relative standard deviations measured by a high-resolution multi-receiving plasma mass spectrometry

Element	Co	Zn	As	In	Pb	U
RSD (%)	1.031	1.946	2.062	1.362	1.435	2.430
Element	Ce	Eu	Hg	F	Cr	Mn
RSD (%)	1.040	2.368	1.495	0.959	1.379	1.648

3. Geochemistry of Toxic Trace Elements in the Water Body

3.1 Characteristics of Dissolved Toxic Trace Elements in the River Water

Comparisons are made concerning the content of the dissolved toxic trace elements in 0.45 μm filtered water and 0.2 μm filtered water in the small watershed of the southern Jiangxi Province, except that some individual samples appear to be abnormal due to contamination or errors in the measurement process. Generally speaking, the content of 0.45 μm filtered water is significantly higher than that of 0.2 μm filter water. The content of light toxic trace elements obviously drops, and the content of heavy toxic trace elements is less obvious, as demonstrated in Table 3.

The change in the pore size of the filter causes a change in the content of trace elements in the dissolved state, which indicates that the filtered fine particles contain a portion of trace elements, especially light trace elements. This conclusion remains consistent with the previous study. In other words, most trace elements are contained in fine particles. As the filter pore is downsized, more particles are filtered out, so more trace elements are filtered with the particles and the content of trace elements in the filtrate will be significantly reduced. Besides, the difference in the trace element variation indicates that, relative to the heavier trace elements, the light trace elements are preferentially adsorbed and shifted, and the heavy trace elements are preferentially complexed with the inorganic ligand to form a water-soluble substance.

Table 3: Content of the dissolved light and heavy trace elements and the total trace elements in the water body of Southern Jiangxi Pronvince

Number	0.2μm			0.45μm		
	∑Ce	∑Y	∑REE	∑Ce	∑Y	∑REE
1	0.03	-	0.03	0.93	0.12	1.05
2	0.06	-	0.06	0.59	0.12	0.7
3	0.13	0.03	0.16	0.98	0.14	1.12
4	0.18	0.04	0.22	1.32	0.16	1.48
5	0.17	0.02	0.2	1.31	0.16	1.48
6	0.18	0.02	0.19	2.57	0.19	2.76
7	0.07	-	0.07	0.46	0.09	0.54
8	0.25	0.09	0.34	0.25	0.09	0.34
9	0.12	0.04	0.16	0.97	0.11	1.09
10	0.14	0.04	0.18	0.38	0.1	0.47
11	0.1	0.02	0.12	0.71	0.11	0.82
12	0.06	-	0.06	1.33	0.17	1.49
13	0.16	0.04	0.2	2.24	0.21	2.34
14	0.85	0.49	1.34	0.86	0.19	1.06
15	0.24	0.14	0.38	1.67	0.37	2.04
16	0.19	0.07	0.26	0.91	0.18	1.09

3.2 Distribution and Differentiation Mechanism of Dissolved Trace Element in the Water Body

This paper builds on the general geochemical method and normalizes the content of the dissolved toxic trace elements in the water body of the south Jiangxi Province (<0.45 μm). Figure 1 illustrates the distribution pattern diagram of toxic trace elements in each sampling point.

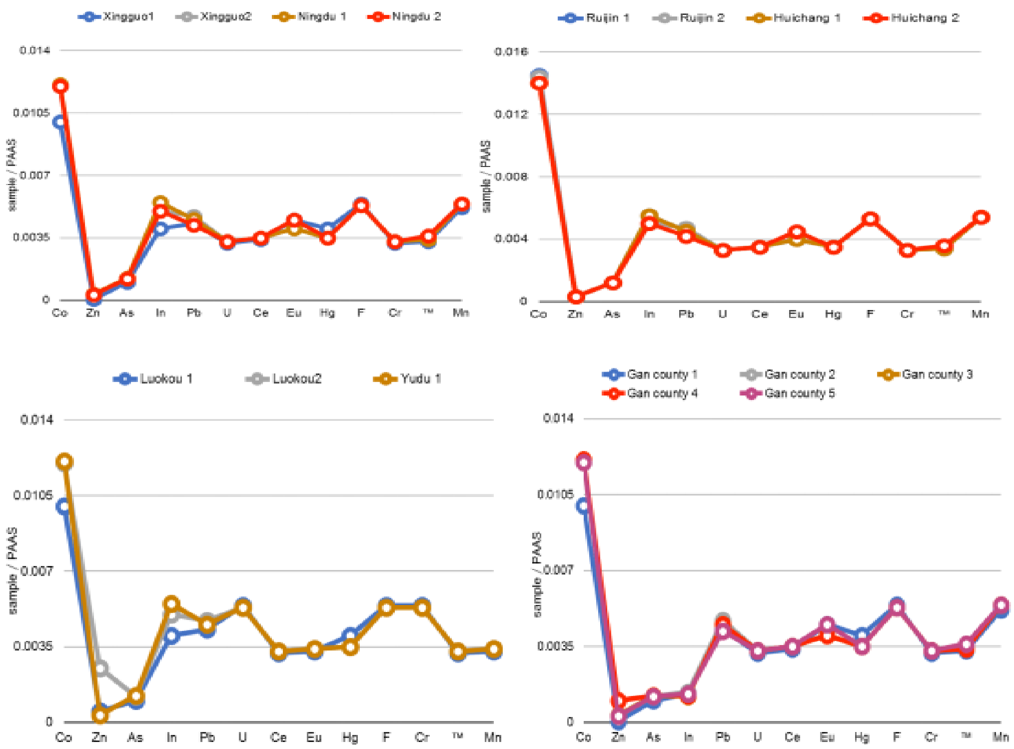

Figure 1: Normalized model of the dissolved trace elements in the small watershed of the south Jiangxi Province

The distribution of heavy metal elements in the environment and its changing characteristics are co-controlled by some special geological environment, natural process and human actions. The enrichment of heavy metal elements in the environment endangers human health. In the hypergene water body, heavy metal elements are both important environmental trace elements and a significant group of tracer materials in the geochemical research. Due to the differences in water chemistry, the behavior and the distribution of different heavy metal elements are also different in the mixing process of river waters. Only four samples—Sample Xinfeng 1, Xinfeng 2, Gan 1 and Gan 2 are less than the unit of 1. Eu/Eu* ratio lies in the range of 0.61 to 3.031, with a mean value of 1.63. It is suggested that the study area shows unapparent positive anomalies, as indicated in Table 4.

Table 4: The main parameters of the dissolved toxic trace element differentiation in the water body of the southern Jiangxi Province

Number	Ce/Ce*	Eu/Eu*	Cr/Pb	Hg/As	Co/Mn
1	0.0468	2.2228	1.7766	0.1643	0.2919
2	0.0045	1.7763	1.2690	0.3172	0.4025
3	0.2636	1.5121	1.1373	0.5598	0.6367
4	0.0489	1.5714	1.6872	0.2123	0.3582
5	0.0574	1.3496	1.9823	0.1634	0.3240
6	0.0326	1.7302	2.1256	0.898	0.1908
7	0.0106	1.5776	2.5123	0.0624	0.1564
8	0.0520	1.9687	2.1559	0.1056	0.2277
9	0.0614	1.4619	2.0903	0.1646	0.3440
10	0.0520	1.9687	2.1559	0.1056	0.2277
11	0.0828	1.92-1	1.3395	0.3242	0.4342
12	0.1045	1.2523	0.6552	0.7806	0.5114
13	0.0212	1.7147	1.2238	0.0330	0.0404
14	0.1291	1.2160	2.4321	0.2178	0.5297
15	0.0679	1.6534	0.9801	0.4783	0.4688
16	0.0995	2.0949	0.6892	0.7455	0.5138

In addition to Ce negative anomalies and Eu anomalies, the shale normalization pattern indicates a medium-heavy trace enrichment model apart from the unusually high La content of light toxic trace elements.

3.3 Controlling Factors of the Distribution Pattern of Toxic Trace Elements

3.3.1 Distribution and Basin Geological Environment of Toxic Trace Elements

When the pH value of the water body is reduced, the electronegativity of the colloid in the normal water environment usually declines, and the adsorption generated by the positive ions in the water body also falls. At this time, REE adsorbed on the particulate matter and the colloids are partially released to the water body. By adjusting the adsorption and desorption properties of the suspended particulates and the colloids, the pH value controls the content of toxic trace elements in the water body. With the increase of pH, the trace elements are adsorbed on the lake particles in the order of light, medium and heavy trace.

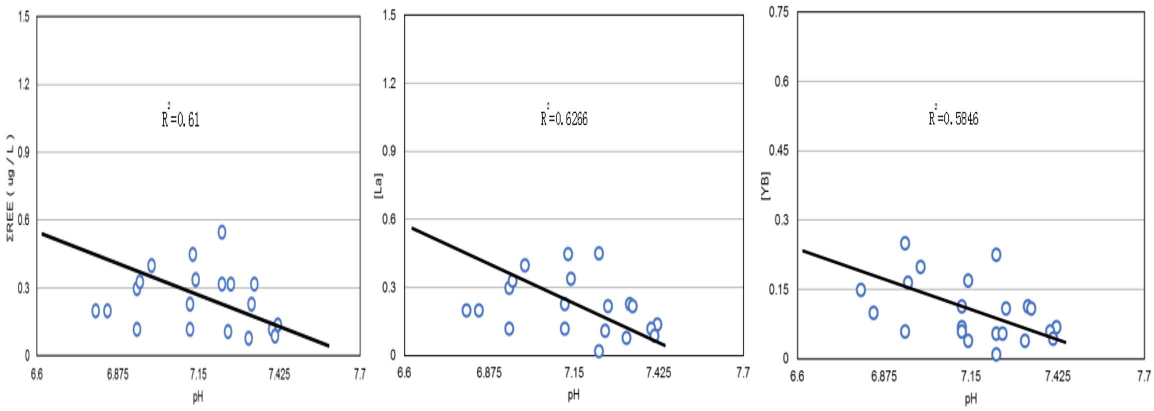

Figure 2: Relationship between the content and the distribution pattern of the dissolved trace elements in small watershed in the southern Jiangxi Province and their values

As shown from Figure 2, the content of dissolved trace elements in the southern Jiangxi Province basin decreases with the rise of pH value, and the trace content and the pH value show a favorable inverse correlation. Compared with the global waters, the concentration of the dissolved trace elements of the small watershed in the southern Jiangxi Province is lower than that of some developed countries. The main reasons may involve a higher pH value and a higher constant value of positive ion, so a large amount of colloidal substances in the water body are difficult to exist, thereby reducing the concentration of the dissolved trace elements in the river.

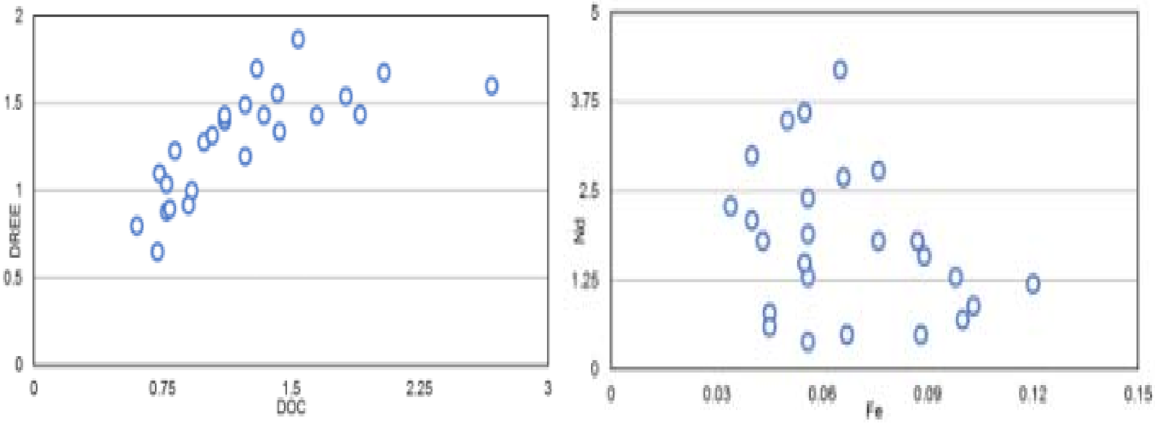

Figure 3: Relationship among dissolved REE, DOC and Fe in the water body of the southern Jiangxi Province

Dissolved organic carbon (DOC) in the water body is also a key factor that controls the content of DREE. As indicated by Figure 3, the dissolved trace elements in the small watershed of the south Jiangxi Province are positively correlated with the content of DOC, and the content of light toxic trace elements is in a negative correlation with the content of the dissolved Fe. With the growth of the content of dissolved Fe, the content of the dissolved light toxic trace elements in the water body gradually drops. This is because DOC and Fe are the most significant components of colloidal substances, and the colloidal particles in the water body affect the dissolved toxic trace elements through the adsorption. Meanwhile, it is proved that the adsorption of heavy toxic trace elements is preferred in the adsorption process.

3.3.2 Ce/Ce* and Eu/Eu*

Negative anomalies of Ce are independent of the lithology of the source rocks (carbonate rocks) and are mainly controlled by pH. Based on the changing relationship between (Ce/Ce*) SN and the value of river water (Figure 4), the negative anomalies of Ce element in the water are obviously correlated with the pH value of river water. As the pH value of river water rises and the alkalinity enhances, Ce anomalies in the water are more transparent.

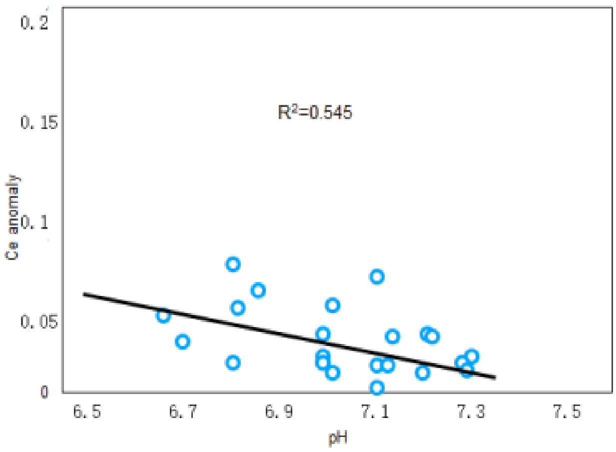

Figure 4: The relationship between the anomalies of Ce and pH

In the water body, Ce has two chemical valence states—Ce3+ and Ce4+, thus showing different chemical properties from the adjacent toxic trace elements. Under alkaline conditions, when Eh=0.3V, soluble trivalent Ce in the water is oxidized to the insoluble tetravalent Ce in most cases. Ce4+ preferentially combines the Fe-Mn oxide on the particulate matter and enters the particulate phase, or precipitates from the water in the form of CeO2, resulting in that the distribution pattern of the dissolved trace elements in the river indicate negative anomalies.

4. Conclusion

In summary, differentiation occurs to the toxic trace elements in the weathering process and the migration process. Ultimately, the dissolved toxic trace elements in the river water body demonstrate a relative enrichment characteristics of heavy trace. In addition, the water chemistry (such as PH, Eh, inorganic and organic complex anion content, etc.) of water bodies, the material exchange process of the water/ particle interface and the microbial action will affect the behaviors of toxic trace elements in the river water. The distribution pattern of the dissolved trace elements in the small watershed of the southern Jiangxi Province demonstrates negative anomalies of Ce and positive anomalies of Eu, which corresponds to the positive anomalies of Ce and the negative anomalies of Eu shown in the surface soil under the same background conditions.

Reference

Akai J., Anawar H.M., 2013, Mineralogical approach in elucidation of contamination mechanism for toxic trace elements in the environment: Special reference to arsenic contamination in groundwater, Physics & Chemistry of the Earth Parts A/b/c, s 58–60(4), 2-12, DOI: 10.1016/j.pce.2013.04.011

Gałuszka A., Migaszewski Z.M., 2015, Geochemical background of potentially toxic trace elements in soils of the historic copper mining area: a case study from Miedzianka Mt., Holy Cross Mountains, south-central Poland, Environmental Earth Sciences, 74(6), 4589-4605, DOI: 10.1007/s12665-015-4395-6

Guagliardi I., Buttafuoco G., 2013, A multivariate approach for anomaly separation of potentially toxic trace elements in urban and peri-urban soils: an application in a southern Italy area, Journal of Soils & Sediments, 13(1), 117-128, DOI: 10.1007/s11368-012-0583-0

Hussain M., Rao T.P., 2014, Toxic Trace Element Contamination in Ground Water of Bollaram and Patancheru, Andhra Pradesh, India, American Journal of Chemistry, 4(1), 1-9, DOI: 10.5923/j.chemistry.20140401.01

Lin M., Lee C., 2011, Potentially toxic trace elements accumulating in marine sediment and bivalves in the outfall area of a desalination plant. Desalination & Water Treatment, 25(1-3), 106-112, DOI: 10.5004/dwt.2011.1753

Outridge P.M., Noller B.N., 1991, Accumulation of Toxic Trace Elements by Freshwater Vascular Plants, Reviews of Environmental Contamination & Toxicology, 121(3), 1-63, DOI: 10.1007/978-1-4612-3196-7_1

Shi H., Iii E.C.W., 2010, Toxic trace element assessment for soils/sediments deposited during Hurricanes Katrina and Rita from southern Louisiana, USA: A sequential extraction analysis, Environmental Toxicology & Chemistry, 29(7), 1419–1428, DOI: 10.1002/etc.218

Toro E.C., Ogris R., 2011, Rapid radiochemical separation and determination of toxic trace elements in biological and environmental materials following neutron activation, International Journal of Radiation Applications & Instrumentation.part C.radiation Physics & Chemistry, 38(3), 931-932, DOI: 10.1016/1359-0197(91)90268-7

Waheed S., Rahman S., 2009, INAA and AAS of different products from sugar cane industry in Pakistan: Toxic trace elements for nutritional safety, Journal of Radioanalytical & Nuclear Chemistry, 279(3), 725-731, DOI: 10.1007/s10967-008-7332-2