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Article

Heavy metal contamination of hand-pressed well water in HuNan, China

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SUMMARY

Unprocessed water from hand-pressed wells is still commonly used as a source of drinking water in Chenzhou, the "Nonferrous Metal Village" of China. Because of the industry of mining and smelting, groundwater is vulnerable to having undue amounts of heavy metals and causing serious health problems. To study the heavy metal contamination levels and potential health effects in this area, 160 household water pump samples were collected in this research. The samples were analyzed through Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and the concentrations of 20 metal elements, which are either monitored in drinking water or the main metal elements in local mineral resources, including aluminum (Al), boron (B), beryllium (Be), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), potassium (K), lithium (Li), magnesium (Mg), manganese (Mn), sodium (Na), nickel (Ni), lead (Pb), silicon (Si), zinc (Zn), zirconium (Zr) and silver (Ag), were measured. Results showed that although none of the samples had dangerous levels of heavy metals, the concentrations of Al, Fe, and Mn in many locations substantially exceeded those suggested in the Chinese Drinking Water Standard and the maximum contaminant levels of Environmental Protection Agency (EPA). The percentage of samples with the concentration of Al, Fe, and Mn higher than Chinese standards are 20.6%, 12.5%, and 14.4%, respectively. The samples with the highest concentrations exceeded the standard by 54 times, 11 times, and 13 times, respectively. Although these elements do not cause immediate poisoning, long-term ingestion might lead to damages to the brain and other health issues. Therefore, we suggest that water treatment systems should be built for these households to ensure the quality of their water.

INTRODUCTION

According to the research report from Chinese Center for Disease Control and Prevention, 74.87% of rural population use underground water such as hand-pressed wells water, and 25.13% use surface water such as open wells water and spring water (1). Despite blazing developments of China and the increasing prevalence of tap water in recent years, it is still common for remote villages to use a hand-pressed well as drinking water resource in each household. A hand-pressed pump is a tool for drawing groundwater (2). There is a piston on top and a valve at the bottom, both of which are one-way valves, preventing air from going downward. Upward movement of the piston draws water upward, and downward movement creates a vacuum under the valve. After the water is released, air replenishes the chamber, resetting the pump. Thus, with vertical movements of the hand, water is drawn up (**Figure 1**). This mechanism is versatile and widely used, but it does not provide an easy way to protect its users from drinking polluted water, such as by purifying groundwater through a filter.

Due to the dissolution of underground materials and mining, groundwater is vulnerable to being polluted (1, 3). Pumped water without purification may contain high levels of metals, including toxic heavy metals, which is defined as metals and metalloids with densities of more than 5 g/cm^3, such as lead (Pb), arsenic (As), cadmium (Cd), mercury (Hg), and hexavalent chromium (Cr(VI)), which would do profound damage to the human body (1). Lead is not an essential element for the human body, and excessive intake can damage the nervous, skeletal, circulatory, enzymatic, endocrine, and immune systems (4). Children, pregnant women, and elderly people are particularly sensitive to lead exposure,

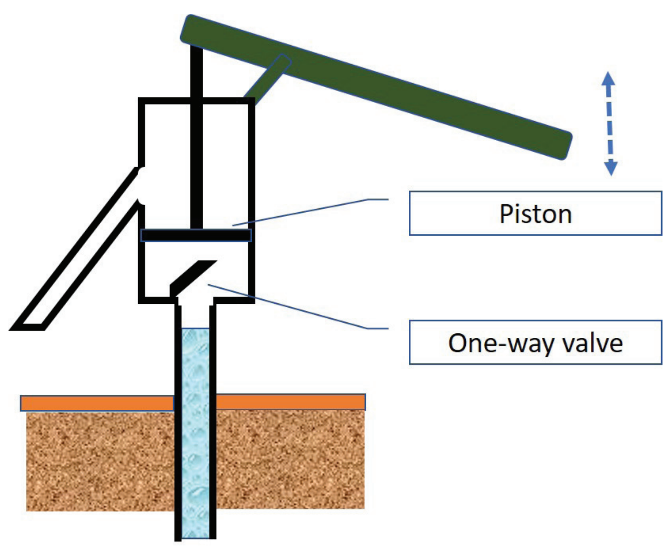

Figure 1: Schematic drawing of a hand-pressed pump. It is a popularly used tool for drawing underground water in Southern China. The piston and the one-way valve prevent air from going downward. Upward movement of the piston draws water upward, and downward movement creates a vacuum under the valve. With vertical movements of the hand, water is drawn up.

and lead also has significant negative effects on intelligence quotients and physical development in children (4). A study from Shen et al. (5) and governmental information (6) show that irreversible damage to their intelligence development occurs when children's blood lead levels are above 10 μg/dL. Minerals, such as iron (Fe), aluminum (Al), silicon (Si), calcium (Ca), magnesium (Mg), and zinc (Zn), are essential elements of the human body, but excess intake can be harmful (7-11). For example, a study by Abeywickarama *et al.* showed that drinking water from natural springs with high mineral content, particularly calcium, carried the risk of kidney stone formation (7). Another mineral, Zn is an important element for the human body, but it can also have harmful effects if in excess. It is an essential component of various enzymes and enzyme activators and supports growth, tissue regeneration, and the immune system (4). Nevertheless, excessive Zn intake can cause stomach cramps, nausea, and vomiting; high-dose, long-term Zn exposure can affect cholesterol balance, diminish immune system function, and even cause infertility (4). The level of Zn in a healthy adult is approximately 1 μg/mL in serum. Harmful effects generally begin at Zn levels 10-15 times higher than the amount needed for good health (8). Al is toxic to some extent, prolonged intake damages the brain, leading to dementia (9) and it could also cause anemia, or osteoporosis, and damage the development of infants and children (10). Besides, a high amount of Fe intake could result in immediate vomiting and worsening conditions in 20 hours with fever, pneumonia, shock, coma and convulsion, and death (11).

There have been quite a few reports and news stories on heavy metal pollution around Chenzhou, China and areas around it. You Town has been exposed, producing rice containing high levels of cadmium (12). With huge reserves and a wide variety of mineral resources, Chenzhou City in South Hunan, China, is called the "Nonferrous Metal Village," and it is the most important area of the multi-mineral belt in Hunan Province (**Figure 2**) (1). As the major non-ferrous metals industry base in China, 112 different types of mineral deposits had been found in Chenzhou as of 2017. The reserve amounts of 46 of the deposits have been determined. Chenzhou holds the highest amount of tungsten deposit and the second highest amount of bismuth deposit in mass globally. Additionally, it has the highest amount of molybdenum deposit, the third highest amount of tin deposit, and the fourth highest amount of zinc deposit in China. YongXing Town of Chenzhou is named "China's Capital of Silver." In total, there are 1112 mining enterprises in Chenzhou (13). However, no survey has yet been conducted in the whole Chenzhou area with so many mineral activities, and a large population is potentially exposed to relatively high contaminant levels.

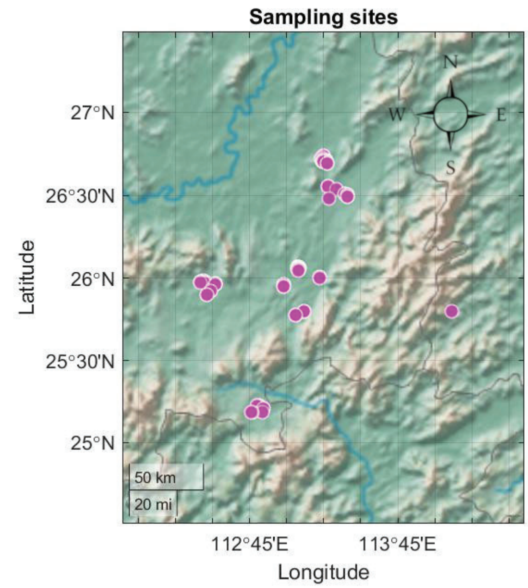

Figure 2: Map of the sampling area, Chenzhou. Chenzhou lies in the south of Hunan Province, Southern China, and has a total area of 19,387 km2. The dots represent the sampling sites of hand-pressed well water covering the counties of Chenzhou such as Anren, Guiyang, Yizhang and Zixing.

We hypothesized heavy metal levels in the hand-pressed well water of this area would exceed the related drinking water safety limits. In this study, we collected water samples from hand-pressed wells in the countryside of Hunan Province, then measured the contaminant levels using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (14). Results for each metal were evaluated using EPA standards and the Chinese Drinking Water Standard (15, 16), and we determined that Al, Fe, and Mn in the water were at unsafe levels in some places and recommended that measures such as installation of water purification system and implementation of education program to be takes for this region.

RESULTS

In total, 160 hand-pressed well water samples were collected and determined by ICP-OES. ICP-OES is a powerful instrument. It can perform up to 60 elements of simultaneous

	Al	B	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Pb	Si	Zn	Zr	Ag	Total hardness
Wavelength(nm)	396.152	182.591	313	396.8	214.438	228.616	267.716	324.754	259.941	766.491	670.78	279.553	257.611	258.592	231.604	220.353	251.612	213.856	339	328	
DL(mg/L)	0.009	0.002	0.0006	0.002	0.0005	0.0008	0.002	0.002	0.002	0.07	0.002	0.002	0.0006	0.03	0.002	0.006	0.02	0.0005	0.001	0.002	
Concentration(mg/L)	BDL-10.8	BDL-0.986	BDL	121.9	BDL-0.003	BDL-0.036	BDL-0.001	BDL-0.06	BDL-3.30	BDL-42.7	BDL-0.852	BDL-56.4	BDL-1.3	BDL-15.5	BDL-0.007	BDL	BDL-6.77	BDL-1.02	BDL	BDL	BLD-540
Sample no.(> Chinese drinking water standard)	33	3	0	0	0		0	0	20				23		0	0		1		0	6
% (> Chinese drinking water standard)	20.6%	1.9%	0.0%		0.0%		0.0%	0.0%	12.5%				14.4%		0.0%	0.0%		0.6%	0.0%	0.0%	3.8%
Chinese drinking water standards(mg/L)	0.2	0.5	0.002		0.005		0.05(CrVI)	1	0.3				0.1		0.02	0.01		1		0.05	450
EPA MCL(mg/L)	0.05-0.2		0.004		0.005		0.1TCr	1	0.3				0.05			0.015		5		0.1	

BDL: Below detection limit.
MCL: Maximum contaminant level. The level of a contaminant in drinking water below which there is no known or expected risk to health.

Table 1: Summary of heavy metals concentration in hand-pressed well water from South Hunan of China, and the DL and wavelength of ICP-OES.

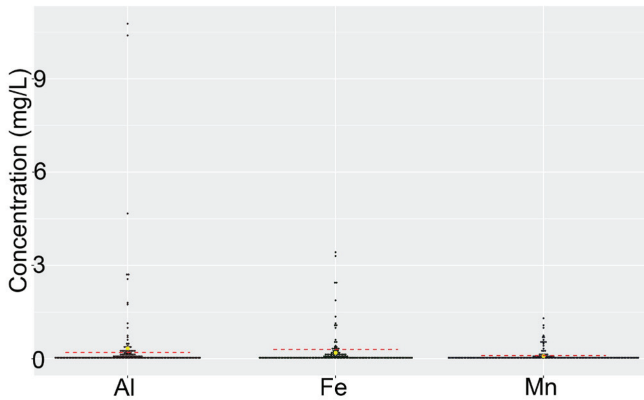

Figure 3: Distribution of Al, Fe, and Mn concentration (mg/L) in all hand-pressed well water samples in Chenzhou. For each element, the red dotted line represents the Chinese drinking water limit and the yellow dot represents the mean values of all 160 samples. The percentage of sample numbers above the Chinese drinking water limits for Al, Fe, and Mn were 20.6%, 12.5%, and 14.4%, respectively.

elemental analysis, with wider linear working range, typically 0.1 to 1000 μg/mL (17). In ICP-OES, the sample, usually in form of a solution, is changed into an aerosol by a nebulizer and is further carried into the hot plasma for atomization. Characteristic emission spectra for each element are produced and dispersed by diffraction grating and detected by CCD. Quantitative analysis is conducted by analyzing the spectra intensity, as it depends on the amount of each element within the sample.

The ICP-OES the results have been summarized (**Table 1**). The total hardness is one important item in water monitoring. It is defined as the sum of Ca, Mg, Fe, and Mn contents and related to industry application and taste of the water. It can be measured directly in the form of carbonate or be calculated by the sum of the metal ions and expressed by the concentration of $CaCO_3$ in water. Based on the atomic weight of Ca, Mg, Fe, and Mn, as well as molecular weight of $CaCO_3$, the following hardness equation can be inferred (18):

$$\text{Total hardness value} = \left({}^{Ca}\!/_{12} + {}^{Mg}\!/_{12} + {}^{Fe}\!/_{18.6} + {}^{Mn}\!/_{27.5}\right) \times 50$$

The determined heavy metal concentrations in hand-pressed well water have been compared with the drinking water standards in China and the USA (15, 16). The common toxic heavy metal elements such as Pb, Cd, Ni, Cr, and Be were not found or were below Chinese and EPA drinking water standards. On the other hand, some other metals were found to be substantially above the drinking water standards, especially Al, Fe, and Mn (**Figure 3**). We found that the Al concentration in 20.6% of samples were above the drinking water limit. The highest concentration was 53 times above the standard, which was from Liufengzhen, Guiyang County, Chenzhou (**Figure 4**). 12.5% of samples had Fe content higher than the standards, and the highest concentrations were 11 times above the standard value. The highest concentration of Fe was found in both Liufengzhen of Guiyang County and Yongle of Anren County (**Figure 5**). Furthermore, the results showed that 14.4% of samples contained Mn contents higher than the standards, and the highest concentration was 13 times of the standard values. The Mn concentration from the drinking water of Santongchong of Anren County, Zhushangcun of Anren County, Liufengzhen of Guiyang County, and Dongjiangdong of Yizhang County were very high (**Figure 6**). In summary, the common toxic heavy metals such as Pb, Cd, Ni, Cr and Be were not found or were below Chinese and EPA drinking water standards, while other less toxic ones such as Al, Fe, and Mn were at unsafe levels in some sites.

DISCUSSION

Health effect of Al, Fe, and Mn, and their source

The metal levels in the hand-pressed well water in

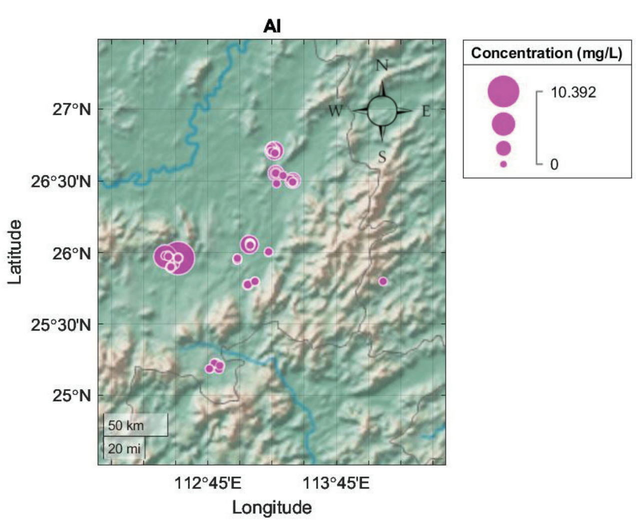

Figure 4: Al concentration (mg/L) in hand-pressed well water in Chenzhou. Dot sizes represent Al concentration. The highest concentration was found in Liufengzhen, Guiyang County and was 54 times greater than the standard.

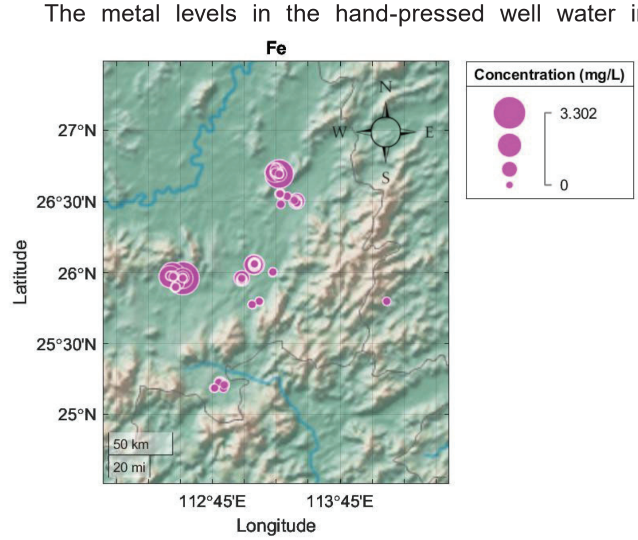

Figure 5: Fe concentration (mg/L) in hand-pressed well water in Chenzhou. Dot sizes represent Fe concentration. The highest concentrations were 11 times above the standard value, which were found in both Liufengzhen of Guiyang County and Yongle of Anren County.

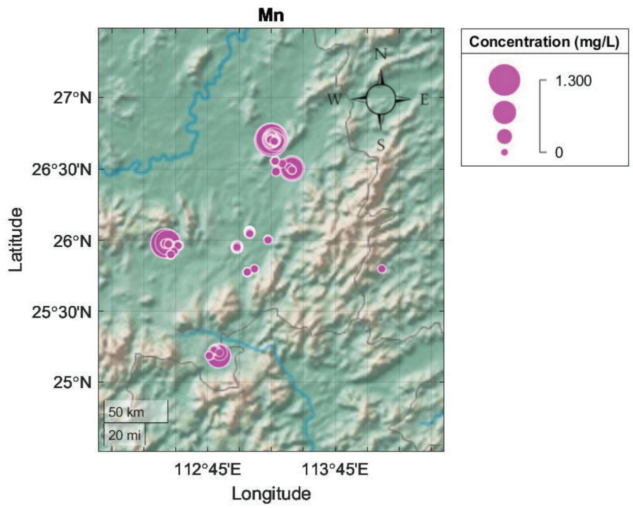

Figure 6: Mn concentration (mg/L) in hand-pressed well water in Chenzhou. Dot sizes represent Mn concentration. The highest concentrations were 13 times greater than the standard values, which were from Santongchong of Anren County, Zhushangcun of Anren County, Liufengzhen of Guiyang County, and Dongjiangdong of Yizhang County.

Chenzhou can potentially be influenced by local industrial activities of mining and smelting. In the study the status on the heavy metal levels in those households who still use hand-pressed well water as a drinking water resource was investigated. Results showed no increase in toxic heavy metals, while high levels of Fe, Mn, and Al in several areas across Chenzhou were discovered. Al, Fe, and Mn are listed as contaminants in National Secondary Drinking Water Regulations of EPA which are non-enforced guidelines. Nevertheless, they are somewhat toxic: aluminum is toxic to some extent, although it does not cause immediate poisoning. Only 10-15% of aluminum ingested gets excreted, while the rest piles up within the body, binding with various proteins and enzymes and affects many biological processes, and prolonged intake damages the brain, leading to dementia (9). It could also cause anemia, or osteoporosis, and damage the development of infants and children (10). Households which use hand-pressed well water in Liufengzhen of Guiyang County are at very high risk of Al exposure, which could cause the above health effects. Oral exposure to high amounts of manganese, on the other hand, can result in adverse neurological effects, and neurodevelopmental effects. Changes in behavior, memory, and learning ability have been observed in children exposed to extremely high levels of manganese (19). High levels of Mn in the drinking water of Santongchong of Anren County, Zhushangcun of Anren County, Liufengzhen of Guiyang County, and Dongjiangdong of Yizhang County could potentially cause such health problems to the people. Additionally, research has shown that intake of a high amount of iron could result in immediate vomiting and worsening conditions within 20 hours with fever, pneumonia, shock, coma, and convulsion followed by death (11). Our finding that both Liufengzhen of Guiyang County and Yongle of Anren County contain high amounts of Fe in hand-pressed well water shows there could be such a health risk for local residents. Among all the findings, Liufengzhen of Guiyang County has the highest levels of Al, Fe, and Mn in the hand-pressed well water. In this region we would suggest the installation of a filter system to the hand-pressed pump.

How these high levels of Fe and Al could emerge could have different reasons. Groundwater chemistry involves interaction of groundwater with aquifer minerals. Geochemical composition of groundwater is affected by several natural factors, including weathering, dissolution, and precipitation of minerals, mixing of different types of water, evaporation, decay of organic materials, selective uptake of ions by vegetation, and resident time of water. The above processes govern the content of major, minor, and trace elements in groundwater (7, 20). Among all the major elements in the earth, Al and Fe have the highest concentrations in the Earth's crust, at 8% and 5%, respectively; they could enter the groundwater through various processes (9). Furthermore, acid rains, due to industrialization and smelting activities, could potentially have pH of 5.0 or lower, greatly increasing the solubility of Al and Fe (9).

Take home message for the reader

Considering how great some of the samples exceeded the standard and how sparsely the household hand-pressed wells spread, we strongly suggest that household water treatment systems should be used to process pump water. There are many devices employing the principles of filtration, absorption, reverse osmosis, and ionic exchange on the market that could purify groundwater (21).

However, education levels of many villages are quite low, and their residents lack the necessary knowledge about water process and water processing, and the effects of metal pollution will only show in the long term. Therefore, it is necessary to inform and remind people to regularly check the quality of processed water and replace the filters to ensure proper functioning of the devices following related guidelines from the water purification system suppliers or local authorities. To implement that, an educational program is proposed for those areas with high amounts of Al, Fe, and Mn in the hand-pressed well water. Brochures containing information on the levels of heavy metals in hand-pressed well water, health risks, and safety measures such as water treatment devices and their maintenance could be delivered to the residents through local village committees. Moreover, lectures on the safety of drinking water could be taught to the students in local elementary or secondary schools. With the increased awareness of this issue and necessary measures taken, the potentially harmful health effects associated with high levels of Al, Fe, and Mn in the hand-pressed well water of this area could be eliminated.

For Liufengzhen of Guiyang County where the highest levels of Al, Fe, and Mn in hand-pressed well water were found, future actions including further investigations on the root cause and implementation of an educational program are necessary. Besides, considering the high amount of non-ferrous ores in Chenzhou and the high amount of mining activities in this area, it is necessary to further investigate the local water quality, focusing on the areas close to the ores or mining activities to check if there any direct influences.

METHODS

Sampling

Chenzhou City lies between 24°53′ and 26°50′ N latitude and between 112°13′ and 114°14′ E longitude, Hunan Province, Southern China. The total area of the city is 19,387 km^2. The climate is subtropical, and the average rainfall is about 1500 mm yearly. The water quality survey points were randomly selected. The sampling sites cover the counties of Chenzhou City including Anren, Guiyang, Yizhang, and Zixing. (**Figure 2**).

Before sampling, a preliminary investigation was conducted to find out the areas in which hand-pressed well water was still used, and sampling was planned accordingly. Water samples were collected with the assistance of a local person working as a driver and guide from May 27th to May 31st, 2018, after summer holiday started in McCallie School. PET sampling bottles were rinsed with sample water three times before sampling. 100 mL of water samples were collected, and samples were acidified in situ with concentrated nitric acid to pH < 2. Finally, a total of 160 hand-pressed well water samples were collected.

Analysis and quality control

Sample analysis was conducted at the lab of the Shanghai Institute of Organic Chemistry (SIOC), Chinese Academy of Sciences after the collection of samples. Heavy metal concentrations in water were measured at an ICP-OES (SPECTRO ARCOS FHS12, Germany), with operation parameters: RF power: 1430 W, plasma gas (Ar) flow rate: 12 L/min, auxiliary gas (Ar) flow rate: 0.9 L/min, nebulizer gas (Ar) flow rate: 0.78 L/min.

The 20 elements of multi-element standard solution, including Al, B, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Si, Zn, Zr, and Ag, was prepared from 100 or 1000 mg/L certified stock solutions (Agilent Technologies) and diluted gravimetrically with 2% HNO_3 to 5 different concentrations with 0 ppm (blank), 0.1 ppm, 0.2 ppm, 0.5 ppm, 1.0 ppm. Pure water with a resistivity of 18.2 MΩ/cm, produced by a Milli-Q water purification system (Millipore, USA) was used for standards preparation.

Water samples were measured, and quality control measures were taken according to the standard (9). Duplicate blanks using 2% nitric acid in each batch of measurement were employed. Duplicate measurements of samples were conducted in every 10 samples. Quality control samples were measured at the end of each batch measurement. The detection limit (DL) of each element was the concentration corresponding to a signal of three times of the standard deviation of 11 times the measurement of the blank solution. The DL and wavelength of each element are listed in **Table 1**.

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