Health Risk Assessment for Heavy Metals in Natural Cold-Bicarbonated Mineral Water, Wudalianchi

Z. H. Xie, J. H. Wang, Y. Liu, and C. Yang

Abstract—Natural cold-bicarbonate mineral water is rich in varies of trace elements in Wudalianchi, northern China. In this paper, heavy metals' (HMs) concentrations were measured. Furthermore, the health risk assessment of risk index (RI) and hazard quotient (HQ) was calculated. According to the dates, the average risk order were $\text{Ni} > \text{Fe} > \text{Mn} > \text{Ba} > \text{Cu} > \text{Hg} > \text{Zn}$ for South Spring and $\text{Ni} > \text{Fe} > \text{Mn} > \text{Hg} > \text{Ba} > \text{Cu} > \text{Zn}$ for North Spring. The risk level was lower than the maximum acceptable value recommended by International Commission on Radiological Protection (ICRP) $5.0 \times 10^{-5} \text{a}^{-1}$. The HQ values of Ba, Cu, Hg and Zn were < 1 , but the HQ values of Ni, Mn and Fe were > 1 . The results indicated that cold-carbonated mineral water wasn't potable water for daily drinking.

Index Terms—Health risk assessment, heavy metals, mineral water, Wudalianchi

I. INTRODUCTION

People pay more attention to drinking water quality nowadays [1]. Natural spring is pure, unpolluted and rich in varies of microelement [2]. Some springs contain special mineral ions [3], and they are regarded as medical water [4]. So it becomes more and more popular in the field of drinking water. There are many kinds of HMs derived from natural dissolved in mineral water, and lots of researches indicated that excessive HMs enter in the water would cause risk for human health [5].

Health risk assessment (HRA) has been recognized as a useful tool for identifying health risks of human activities [6]. It involves identifying the potential of a risk source to introduce risk agents into the environment, estimating the amount of risk agents that come into contact with the human-environment boundaries [7], and quantifying the health consequence of exposure [8]. Carcinogenic or non-carcinogenic methods can be used to assess potential health risk caused by HMs [9]. Non-cancer risk assessment methods based on Hazard Quotient (HQ) and Hazard Index (HI) are set by United States Environmental Protection Agency. With the rapid development of industry, researchers pay more attentions to HMs contaminations in water and their effects on human health [10]. For human being, appropriate amount of HMs like copper (Cu), zinc (Zn), iron (Fe), manganese (Mn) contribute to normal body growth and functions of living organisms [11], while the high

concentrations of other metals like cadmium (Cd), chromium (Cr), nickel (Ni) and lead (Pb) are considered highly toxic for human and aquatic life [12].

However, so far few research works have been, to our knowledge, conducted on HMs contaminations in mineral water and their effects on human health [13]. The natural cold-carbonated mineral water is one famous resource in Wudalianchi, which is considered of medical action to human. The objectives of this research were determined the HMs concentrations in mineral water and its potential health risk assessment.

II. MATERIALS AND METHODS

A. Study Area Description

Wudalianchi World Geopark is located in the north central Heilongjiang Province, China, at the intersection between Lesser Khingan Mountains and Songnen Plain. Its geographic coordinates is longitude $126^{\circ}00' - 126^{\circ}26'$ east and latitude $48^{\circ}34' - 48^{\circ}$ north. Fourteen young and old volcanoes stand in the 1060 square kilometers geopark, with their eruption ages ranging from 2.07 million years prehistory to 280 years before now. The area is characterized by cold temperature continental climate and the annual average rainfall is about 500 mm. There are hundreds of natural mineral springs pouring from underground; it can be seen from the Fig 1.

Fig. 1. The distribution of mineral spring sources in Wudalianchi

The South Spring and North Spring which are the typical mineral spring resources are located 1.3km south east of the Medical Spring Mountain, near the Bailong River west to Shilong; the South Spring is located to the east of the river and the North Spring to the west, about 0.5 kilometer away.

B. Sample Collection and Analysis

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On the basis of spring distribution and utilization degree, two spring resources i.e. South Spring and North Spring were selected for water sampling. According to the rainfall varied with seasons, twelve representative water samples (1L each) were collected during 2010 and 2011 in April, September and December. The mineral water samples were collected in cleaned plastic bottles pre-washed with 20% nitric acid (HNO₃) and double distilled water. Bottled water samples were directly taken from containers and filtered. Five drops of 1:3 diluted nitric acid was added to acidify the sample (pH<2). All samples were transported to the laboratory in cooled containers and stored in the fridge at 4 °C until analyses.

All filtered and acidified mineral water samples were analyzed for 7 HMs (Hg, Ni, Fe, Mn, Ba, Cu, Zn) by using atomic absorption spectrometer (Purkinje General, TAS-900 Super AFG) under standard operating conditions. In view of data quality assurance, each sample was analyzed in triplicate and after every 7 samples two standard. The reproducibility was found to be at 99% confidence level.

C. Health Risk Assessment

The hazards caused by HMs can be divided into two groups for calculating numerical estimates of risk: carcinogenic and non-carcinogenic. The hazard quotient (HQ) for non-carcinogenic risk can be calculated by the following equation, as in (1)

$$HQ = CDI / Rfd \quad (1)$$

where, according to USEPA database the oral toxicity reference dose values (Rfd) are 2.0E-02, 8E-01, 1.4E-01, 2.0E-01, 5.0E-03, 3E-04, 3.0E-01 mg/kg·day for Ni, Fe, Mn, Ba, Cu, Hg and Zn.

The risk index (RI) of non-carcinogenic can be calculated by the equation, as in (2)

$$RI = (1 \times 10^{-6} CDI) / Rfd \quad (2)$$

The chronic daily intake (CDI) through water ingestion was calculated according to the modified equation, as in (3)

$$CDI = (C \times DI \times EF \times EP) / (BW \times AT) \quad (3)$$

where, C, DI, EF, EP, BW and AT represent the concentration of HMs in water (mg/L), average daily intake rate (2 L/Day), exposure frequency (365 d/a), exposure period (70 a), body weight (60 kg) and average life span (25550 d), respectively.

III. RESULTS AND DISCUSSION

A. Water Characteristics

Wudalianchi mineral water is oxygen-and-carbon-based bicarbonates low-temperature iron spring; it is a composite mineral water. The content of free carbon dioxide in natural mineral water is about 1000-2000mg/l; therefore it tastes cool and delicious like soft drinks and it can dissolve many kinds of ions.

Table I and Table II summarize the HMs concentrations in

mineral water which collected from South Spring and North Spring sites.

Nickel concentrations in South Spring ranged from 0.248 to 0.283 mg/L, while in North Spring it ranged from 0.085 to 0.272 mg/L. The highest Ni concentration was observed in April and the lowest concentration was observed in September. Iron concentrations are very higher than other HMs' concentrations in both two springs, obviously. The concentrations ranged from 33.4 to 43.03 mg/L and 36.8 to 45.8 mg/L in South Spring and North Spring, respectively. Manganese concentrations in South Spring mineral water samples ranged from 3.69 to 6.77 mg/L, and 4.49 to 9.77 mg/L in North Spring. The highest concentrations and the lowest concentrations are observed in September and December of Fe and Mn. It can be seen that these two HMs' concentrations affected by the rainfall.

TABLE I: MINERAL WATER QUALITY MONITORING DATA, SOUTH SPRING (MG/L)

		2010			2011		
		APR.	SEP.	DEC.	APR.	SEP.	DEC.
Ni	data	0.265	0.283	0.265	0.248	0.260	0.248
	mean	0.262					
Fe	data	36.9	38.5	43.0	36.0	33.4	35.6
	mean	37.23					
Mn	data	5.38	4.89	6.77	4.91	3.69	5.95
	mean	4.37					
Ba	data	0.278	0.215	0.294	0.245	0.195	0.380
	mean	0.268					
Cu	data	0.003	0.003	0.005	0.003	0.002	0.005
	mean	0.003					
Hg	data	0.000 152	0.000 122	0.000 152	0.000 152	0.000 167	0.000 152
	mean	0.000150					
Zn	data	0.069	0.067	0.079	0.052	0.059	0.064
	mean	0.065					

Hg concentrations ranged from 0.000122 to 0.000167 mg/L in South Spring, and 0.000109 to 0.000170 mg/L in North Spring. Ba concentrations ranged from 0.195 to 0.380 mg/L in South Spring, and 0.455 to 0.848 mg/L in North Spring. Cu concentrations ranged from 0.0018 to 0.0052 mg/L in South Spring, and 0.00050 to 0.00092 mg/L in North Spring. Zn concentrations ranged from 0.052 to 0.079 mg/L in South Spring, and 0.021 to 0.055 mg/L in North Spring.

TABLE II: MINERAL WATER QUALITY MONITORING DATA, NORTH SPRING (MG/L)

		2010			2011		
		APR.	SEP.	DEC.	APR.	SEP.	DEC.
N i	data	0.103	0.235	0.221	0.085	0.272	0.133
	mean	0.175					
F e	data	41.2	41.2	45.8	39.4	36.8	40.0
	mean	40.7					
M n	data	8.29	6.70	9.77	7.45	4.49	7.87
	mean	7.43					
B a	data	0.701	0.615	0.848	0.455	0.491	0.698
	mean	0.635					
C u	data	0.000 79	0.000 80	0.000 92	0.000 50	0.000 72	0.000 78
	mean	0.00063					
H g	data	0.000 152	0.000 109	0.000 170	0.000 156	0.000 156	0.000 152
	Mean	0.000149					
Z n	data	0.025	0.037	0.055	0.021	0.035	0.044
	mean	0.0362					

In the study area, the HMs concentrations of Hg, Ba, Cu, Zn were very low and they were within the permissible limits of *Drinking Natural Mineral Water* standard GB 8537-2008 and *Standards for Drinking Water Quality* GB 5749-2006, it is listed in Table III. However, the HMs concentrations of Ni, Fe and Mn are higher than the limited values of standards.

TABLE III: LIMITED VALUE INDEX OF WATER QUALITY (MG/L)

	GB 8537-2008	GB 5749-2006
Ni	0.02	0.02
Fe		0.3
Mn	0.4	0.1
Ba	0.7	0.7
Cu	1.0	1.0
Hg	0.001	0.001
Zn		1.0

B. Human Health Risk Assessment

Local residents enjoy drinking the natural cold bicarbonate mineral water which pouring from the South Spring and North Spring. The basic information about amount of drinking water, age, body weight, drinking habits were collected by interviewing or reported. Therefore, the streams that were used for drinking purpose were also selected for HMs risk assessment.

TABLE IV: RISK INDEX (RI) AND HAZARD QUOTIENT (HQ) INDICES OF HMS OF SOUTH SPRING AND NORTH SPRING

	South Spring		North Spring	
	RI (a ⁻¹)	HQ	RI (a ⁻¹)	HQ
Ni	4.36E-06	4.37	4.28E-06	4.28
Fe	1.55E-06	1.55	1.69E-06	1.69
Mn	1.25E-06	1.25	1.77E-06	1.77
Ba	4.47E-06	0.04	1.1E-07	0.11
Cu	2.26E-08	0.02	4.84E-10	0.005
Hg	1.65E-08	0.016	1.65E-08	0.016
Zn	7.2E-09	0.007	3.99E-09	0.004

Table IV summarizes the calculated RI values and HQ values for consumption of drinking mineral water. The calculated results show that in Wudalianchi area, where people have drunk the South Spring and North Spring mineral water contaminated with HMs, the RI values were 7.2 E-09, 1.65 E-08, 2.26 E-08, 4.47 E-06, 1.25 E-06, 1.55 E-06, 4.36 E-06 a⁻¹ for Zn, Hg, Cu, Ba, Mn, Fe, Ni, and 3.99E-09, 1.65E-08, 4.84E-10, 1.1E-07, 1.77E-06, 1.69E-06, 4.28E-06 a⁻¹ for Zn, Hg, Cu, Ba, Mn, Fe, Ni, respectively. The risk level was lower than the maximum acceptable value recommended by International Commission on Radiological Protection (ICRP) 5.0×10⁻⁵a⁻¹.

HQ indices of HMs through consumption of mineral water in the South Spring and North Spring for Zn, Hg, Cu, Ba, Mn, Fe, Ni were 0.007, 0.016, 0.02, 0.04, 1.25, 1.55, 4.37 and 0.004, 0.016, 0.005, 0.11, 1.77, 1.69, 4.28, respectively. Therefore, the HQ indices of HMs in the study area were found in the order of Ni>Fe>Mn>Ba>Cu>Hg>Zn for South Spring and Ni>Fe>Mn>Hg>Ba>Cu>Zn for North Spring. The HQ values of Ba, Cu, Hg, and Zn were < 1, it was safe to drink. However, the HQ values of Ni, Fe, Mn were > 1, it

indicated that it was risk to drink the mineral water as daily drinking.

IV. CONCLUSION

Two natural cold bicarbonate mineral water sites, South Spring and North Spring, were studied in this paper. The concentrations of HMs like Ni, Fe, Mn, Ba, Cu, Hg, Zn had been detected. The RI and HQ values had been calculated and the human risk had been assessed. The results indicated that the HQ indices of HMs in the study area were found in the order of Ni>Fe>Mn>Ba>Cu>Hg>Zn for South Spring and Ni>Fe>Mn>Hg>Ba>Cu>Zn for North Spring. HQ values of Ni, Fe, Mn were > 1, it indicated that it was risk to drink the mineral water as daily drinking. And the local residents should pay more attention about it.

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