MANGANESE AND OTHER GEOTHERMAL MINERALS EXPOSURE TO RESIDENTS IN KETENGER VILLAGE, BANYUMAS, INDONESIA

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Abstract— Manganese (Mn) is one of the potential contaminants minerals geothermal water. Preliminary studies conducted in Ketenger village, the nearest village with Baturaden hot spring, showed that the concentration of Mn in water supply has exceeded the reference value. Mineral contamination problem in Ketenger village is not only Mn, but also other potential geothermal minerals, such as chromium (Cr), iron (Fe), sulfide (S^{2-}), nickel (Ni), cobalt (Co), and zinc (Zn). It becomes a concern because generally the residents still use ground water as the water source for their daily needs, including drinking and cooking. Therefore, this study aimed to determine the distribution of mineral contamination in drinking water and food and to estimate the health risks possibility from the exposure. Four minerals (Mn, Fe, S^{2-}, and Cr^{6+}) were analyzed in drinking water, carbohydrate sources, vegetables, fishes, and fruits. The test results indicate that Mn concentration in drinking water is 0.35 mg/L, has exceeded the maximum contaminant level (MCL) according to the US EPA (MCL = 0.005 mg/L), whereas other minerals still comply with the standards. In addition, we found that the average of Mn concentration in the carbohydrate sources is quite high (1.87 mg/Kg). Measurement results in Chronic Daily Intake (CDI) and the Risk Quotient (RQ) found that exposure to manganese and other geothermal minerals in drinking water and food are safe from the non-carcinogenic effects in each age group (RQ<1). So, geothermal mineral concentrations in drinking water and food has no effect on non-carcinogenic risk in Ketenger's residents because of CDI is also influenced by other parameters such as the duration of exposure and the rate of consumption. However, it was found that intake of essential minerals (Mn and Fe) are deficient in every age group. So that, the addition of Mn and Fe intake is recommended.

Keywords— CDI, contaminant, geothermal minerals, manganese, RQ.

I. INTRODUCTION

Indonesia has actively mountains scattered throughout the region. The active volcano is a geothermal source that often utilized both for geothermal power plants as well as hot spring tourism. However, geothermal water contains minerals that in high concentrations can cause toxic effects to humans. Geothermal water and its consequences on health have been reported in several scientific publications [1]-[3].

Manganese (Mn) is one of the potential contaminants in geothermal water besides hydrogen sulfide (H_2S), arsenic (As), boron (B), mercury (Hg), and other trace metals such as lead (Pb), cadmium (Cd), iron (Fe), and zinc (Zn) [4]-[7]. Mn and Zn are included in transitions metal group of elements. These elements are essential, but at high concentrations can be transformed into toxic substances [8]. Residents living around the geothermal resource is at risk of geothermal minerals exposure through drinking water and the food they consume. Drinking water is primary medium for chronic intake of metals and metalloids with relative contribution to all environmental media up to 80% [9]. Baturaden is one of the areas located in Mount Slamet, Central Java, where there are geothermal resources in it. Baturaden geothermal exploration started in 2008 and the results showed that the potential for unexpected geothermal Baturaden Mount Slamet reached 235 Megawatt [10]. Baturaden hot spring has long been used as a tourist attraction. Known as 'Pancuran tujuh', this hot water flowing to some villages. This situation raises concerns that the mineral geothermal water may be distributed in a variety of media exposure to environmental contact with humans such as ground water, grown foods (such as vegetables, grains, fruit), and aquatic biota (such as fish, catfish, eel) [11].

Preliminary studies conducted in Ketenger village, the nearest village with Baturaden hot spring, showed that concentration of Mn in ground water in Ketenger village has exceeded the reference value. Mineral contamination problem in Baturaden is not only Mn but also other potential minerals such as Cr, Fe, S^{2-}, Ni, Co, and Zn. It becomes a concern because generally the residents still use ground water as a water source for their daily needs, including drinking and cooking. Therefore, this study aimed to determine the distribution of mineral contamination in drinking water and food and to estimate the health risks possibility from the exposure.

II. METHODS

The present study employed environmental health risks assessment (EHRA) design based on EHRA *Guideline* [12] and *Human Health Risk Assessment Toolkit Chemical Hazards* [13]. It consists of four stages: (i) hazard identification, (ii) exposure assessment, (iii) dose-response assessment, and (iv) risk characterization. The study was conducted in Ketenger village, District Baturaden, Banyumas regency, Central Java province in December 2015. A total of 40 households including 80 respondents were drawn randomly based on inclusion criteria which is

having resided no less than 5 consecutive years in Ketenger village. Respondents were grouped into three based on their ages, namely adult (≥18 years), adolescent (13-17 years), and children (6-12 years).

Hazard identification performed by literature study about the characteristic of Mn. After that, exposure assessment perfomed by identifying anthropometric exposure factor and activity pattern of respondents. This stage also conducted analyzing concentration of Mn (C) in drinking water and food selected samples.

Anthropometric exposure factor consist of body weight (Wb) and consumption rate (R). Meanwhile, activity pattern consist of exposure frequency (fE), exposure duration (Dt) and average time of exposure (tavg). Questionnaire used to obtain data: fE, Dt, R, and tavg. Data of Wb was obtained by measuring respondents' body weight.

Drinking-water samples were taken randomly from households subject as many as 12 samples. Food samples was determined based on the results of food frequency questionnaire (FFQ) that was indicated as often and commonly consumed food by local people. Food samples were divided into four groups: source of carbohydrates, vegetables, fruit, and fish. The food samples were taken from household, farm or from local food seller. Subsequently, the samples were analyzed in laboratory of Environmental Health Department, Faculty of Public Health, Universitas Indonesia. Drinking-water samples were analyzed using periodate oxidation while food samples using a wet oxidation method. Mn content was measured using Spectrophotometer HACH DR / 2010.

Data from exposure assessment used for the calculation of Chronic Daily Intake (CDI) as the analysis of dose response with the following formula:

$$CDI = \frac{C \times R \times fE \times Dt}{Wb \times tavg}$$

After the CDI value is obtained, the step of risk characterization can be done by determining risk quotient (RQ) value. RQ value is determined by comparing the CDI with a reference dose of manganese (RfD). RQ>1 means that the drinking water and food consumed is not safe from non-carcinogenic risk while RQ≤1 means the contrary.

III. RESULT

Data distribution on anthropometry characteristics, activity patterns, and consumption patterns of population in each age group (children, adolescents, and adults) are presented in Table 1, whereas distribution of mineral concentrations in drinking water and foods consumed by Ketenger Village residents is presented in Table 2.

Table 1. Characteristics of Anthropometric Exposure Factors, Activity Patterns, and Consumption Patterns on Ketenger Village Residents, Banyumas

Characteristic	Mean ± SD	Median	Range	Distribution[(c)]
General Anthropometric				
Adult				
Age (year)	42,85±1,84	42	27-86	NN
Weight (kg)	60,15±1,48	59,6	43-90	NN
Height (cm)	154,4±1,98	155	105-176	NN
Adolescent				
Age (year)	14,77±1,64	14	13-17	N
Weight (kg)	53,44± 12,70	52	36,5-90,4	NN
Height (cm)	163,12±8,75	162	150-181	N
Children				
Age (year)	9,44±1,78	10	5-12	N
Weight (kg)	30,57±10,36	29	19,8-64,2	NN
Height (cm)	128,04±15,22	126	100-165	N
Activity Pattern				
Adult				
D_E (year)[(a)]	30			
Life span (year)[(b)]	24,85±1,84	24	9-68	NN
f_E (day/year)[(a)]	350			
t_E (hour/day)	24±0			
Adolescent				
D_E (year)[(a)]	6			
Life span (year)[(b)]	1,77±1,64	1	0-4	N
f_E (day/year)[(a)]	350			
t_E (hour/day)	24±0			
Children				
D_E (year)[(a)]	6			
Life span (year)[(b)]	3,4±1,78	4	0-7	N
f_E (day/year)[(a)]	350			

Characteristic	Mean ± SD	Median	Range	Distribution[c]
t_E (hour/day)	24±0			
Consumption rate				
Adult				
Drinking water (L/day)	1,119±0,11	1	0,2-2,5	N
Source of carbohydrate (kg/day)	0,553±0,045	0,5	0,05-1,6	NN
Fruits (kg/day)	0,061±0,013	0,025	0-0,3	NN
Vegetables (kg/day)	0,024±0,006	0,011	0-0,2	NN
Fish (kg/day)	0,024±0,008	0	0-0,29	NN
Adolescent				
Drinking water (L/day)	1,565±0,70	1,5	0,25-2,5	N
Source of carbohydrate (kg/day)	0,488±0,20	0,6	0,1-0,75	N
Fruits (kg/day)	0,042±0,05	0,014	0-0,14	N
Vegetables (kg/day)	0,019±0,02	0,009	0-0,071	NN
Fish (kg/day)	0,011±0,03	0	0-0,12	NN
Children				
Drinking water (L/day)	0,681±0,612	0,3	0,2-2,5	NN
Source of carbohydrate (kg/day)	0,289±0,221	0,2	0,05-0,921	NN
Fruits (kg/day)	0,017±0,031	0,005	0-0,114	NN
Vegetables (kg/day)	0,039±0,051	0,02	0-0,2	NN
Fish (kg/day)	0,004±0,007	0	0-0,017	NN

a) using default [14]
b) Life span is lifetime exposure duration in year, calculated as follows: current age-18 (adult), current age-13 (adolescent), and current age-6 (children).
c) Distribution: N= normal, NN= not normal; Normality: (Skewness÷Standard Error of Skewness= ±2)

Table 2. Mineral Concentration in Drinking water and Foods Consumed by Ketenger Village residents, Banyumas

Parameter	Mean ± SD[c]	Median[c]	Range[c]	Distribution	Contamination Level[a]
Source of Carbohydrate					
Mn	1,867±2,214	0,900	0,3-4,4	N	13,28
Fruits					
Mn	0,633±0,306	0,700	0,30-0,90	N	4,5
Vegetables					
Mn	0,833±0,208	0,900	0,60-1,00	N	5,95
Fish					
Mn	1,4±0,361	1,3	1,1-1,8	N	10
Drinking water					
Mn	0,358±0,287	0,350	0,000-1,100	NN	2,5
Total Fe	0,150±0,345	0,005	0-1,2	NN	0,007
Cr^{6+}	0,790±0,111	0,015	0-0,34	NN	5
S^{2-}	0,004±0,005	0,003	0-0,02	NN	Ttd[b]

a) Contamination level is calculated by: mineral concentration÷RfD; RfD (*reference dose*) Mn= 0,14 mg/kg/day; RfD Fe= 0,7 mg/kg/day, RfD Cr^{6+}= 0,003 mg/kg/day [15].
b) NA: cannot be applicable because the value of RFD and MRL are unknown, and decreasing RFD is different in each age groups
c) mg/kg in foods and mg/L in drinking water. 1 L water ≈ 1 kg.

Table 3. CDI (Chronic Daily Intake) and RQ (Risk Quotient) from Manganese Exposure and Other Geothermal Mineral on Ketenger Village Residents, Banyumas

Mineral	CDI[a] (mg/kg/day)			RQ[b]			RfD
	Children	Adolescent	Adult	Children	Adolescent	Adult	(mg/kg/day)
Mn							
Carbohydrate	0,0217	0,0567	0,0187	0,155	0,405	0,134	0,14
Fruits	0,0002	0,0016	0,0003	0,001	0,011	0,002	
Vegetables	0,0009	0,0005	0,0002	0,007	0,003	0,001	
Fish	0	0	0	0	0	0	
Drinking water	0,006	0,0342	0,0079	0,044	0,245	0,056	
Fe Total (drinking water)	8,75E-05	0,0005	0,0001	0,0001	0,001	0,0001	0,7
Cr^{6+} (drinking water)	0,0003	0,0015	0,0003	0,0875	0,049	0,113	0,003
S^{2-} (drinking water)	5,25E-05	0,0003	6,76E-05	0,292	NA[e]	0,822	0,0001797[c] 0,0000822[d]

a) CDI is calculated using formula: CDI = $\frac{C \times R \times tE \times fE \times Dt}{Wb \times tavg}$; C= mineral concentration (mg/ L for drinking water and mg/ kg for food), R = consumption rate (L/ day in drinking water and kg/ day on food), tE = daily exposure time (hour/ day) apply on inhalation exposure, fE = exposure frequency (day/ year), Wb = body weight (kg), tavg = average time of exposure, life span x 365 day per year (for non-carcinogenic). For normal distribution, the value used is the average value while for not normal distribution, the value used is the median value
b) RQ is calculated using formula: CDI÷RfD
c) RFD value of children: derived using default values of children anthropometric. The default value are: R = 1 L, fE = 350 years, Dt = 6 years, Wb = 16 kg, tavg = 6 years x 365 day / year. tE does not apply due to oral exposure.
d) RFD adult values: derived using default values of adult anthropometric, used to set the standard by rearranging the equation LADD = RFD. LADD = $\frac{C \times R \times tE \times fE \times Dt}{Wb \times tavg}$. The default value are: R = 2 L, fE = 350 day, Dt = 70 years, Wb = 70 kg, tavg = 70 x 365 day / year. tE does not apply due to oral exposure.
e) NA: cannot be applicable because default value for adolescent not available

Table 4. Daily Intake of Various Mineral Consumed by Ketenger Village Residents, Banyumas

Mineral	Children		Adolescent		Adult	
	Intake total[c] (mg/day)	DRI[d] (mg/day)	Intake total[c] (mg/day)	DRI[d] (mg/day)	Intake total[c] (mg/day)	DRI[d] (mg/day)
Male						
Mn[a]	0,769	1,5	3,01056	1,9 – 2,2	1,648222	2,3
Fe[b]	2,34E-03	10	0,0256	8 – 11	6,08E-03	8
Female						
Mn[a]	0,864	1,5	3,06936	1,6	1,59619	2,3
Fe[b]	2,63E-03	10	0,0261	8 – 15	5,89E-03	8

a) Mn intake derived from source of carbohydrate, vegetables, fruits, fish, and drinking water
b) Fe intake were calculated from sources of drinking water only
c) intake total is calculated from CDI x Wb
d) Dietary Reference Intake according to Institute of Medicine, National Academy of Sciences [8]

IV. DISCUSSION

Test result of mineral content (Mn, Fe, Cr^{6+}, and S^{2-}) in drinking water and Mn in various types of foods can be seen in Table 2. The type of foods analyzed that obtained based on the Food Frequency Questionnaire (FFQ) consist of rice, cassava, and sweet potato as the source of carbohydrate; spinach, cassava leaves, and water spinach as vegetables group; bananas, papaya, and orange as fruits group; and freshwater fish (tilapia species). Some minerals classified as essential mineral (Fe and Mn), whereas Cr^{6+} and S^{2-} are not an essential mineral. Cr that needed by our body is Cr^{3+} but Cr^{6+} is toxic to the body [16].

Based on table 2, the average concentration of minerals tested still meets drinking water standards according to Regulation of Indonesia's Minister of Health [17]. Based on this regulation, the concentration standard of Mn is below 0.4 mg/L and Fe is below 0.3 mg/L. S^{2-} parameters also still meet the standards of the World Health Organization [18] that is between 0.05-0.1 mg/L, and Cr^{6+} levels are still within safe limits according to the US EPA (<0.1 mg /L) [16]. These results showed the same as preliminary study of drinking water carried in the same area. Meanwhile, the mineral contain in food samples that can be measured in this study was only Mn and showed quite high concentration. But there are no specific regulation that regulate the maximum concentration of Mn in variety food measured in this study.

From the overall minerals measured, there are two essential minerals (Mn and Fe). The requirement intake of these minerals set in the Regulation of the Indonesia's Minister of Health Number 75 in 2013 about The Nutrition Adequacy Rate (Angka Kecukupan Gizi/AKG) advisable for the Indonesian nation [19]. The recommended intake is listed in Table 4 and showed the difference in certain age groups between women and men.

Values of Chronic Daily Intake (CDI) and the Risk Quotient (RQ) of exposure to manganese and other geothermal minerals in drinking water and food are presented in table 3. The calculation is based on each source of food. Based on table 3, all minerals in drinking water and food is safe from non-carcinogenic effects in each age group (RQ<1). It can happen because of CDI depends on other parameters such as exposure duration and rate of consumption. Because of RQ values is <1, so further analysis for Mn and Fe as essential minerals are needed to determine whether the intake categorized as deficiency or not. The calculation results can be seen in Table 4.

Table 4 illustrates the value of mineral daily intake from drinking water and food consumed by the residents. The intake was measured to determine nutritional adequacy status of each age group based on

the Dietary Reference Intakes from Institute of Medicine [8]. After the accumulation of Mn intake from food sources, it showed that intake of Mn in all age groups are in the category of deficiency. Similarly, Fe intake from drinking water also categorized as deficiency.

According to the Illinois Department of Public Health [20], in general, Fe intake from drinking water is 5% of total body's intake requirement. Therefore, based on AKG recommendation, minimum intake of Fe from drinking water in children should be 0.45 mg/L, in adolescent males should be 0.75 mg/L, in adult males should be 0.65 mg/L and in both adolescent and adult females should be 1.3 mg/L. Therefore, Fe intake of drinking water consumed by children, adolescents and adult in Ketenger village, still categorized as deficient. Thus, intake of Fe and Mn from other food sources or supplements are needed. That is because iron deficiency can cause various health problems such as anemia [21].

Additional intake of Mn is also required. It is because of Mn deficiency can cause various health problems such as skeletal abnormalities, ataxia, problems of the reproductive system, wound healing, lipid, and carbohydrate metabolism, osteoporosis, epilepsy, and disturbance growth [22]. Sources of Mn additional intake can be obtained from varied menu of food or supplements.

CONCLUSION

Based on the results from calculation of CDI and RQ value of manganese and other geothermal minerals exposure from drinking water and food, showed that drinking water and food consumption is safe from non-carcinogenic effect in each age group (RQ <1). In this study, mineral concentration of geothermal water has no effect on non-carcinogenic risk because of chronic daily intake depends on other parameters such as exposure duration and rate of consumption. Moreover, it was found that the intake of essential minerals (Mn and Fe) categorized as deficient at each age group. Thus, the addition of Mn and Fe intake through variation of diet or from supplements are required.

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