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GROUNDWATER FLUORIDE HAZARD ZONATION IN THE VOLCANOGENIC POLLUTED AREA, EAST JAVA, INDONESIA

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ABSTRACT: Volcanic activity can release numerous hazardous pollutants, including toxic elements such as fluoride. Despite the relevance of fluorine to human nutrition, the ingestion of excessive doses can have adverse health effects such as fluorosis disease. Asembagus, Banyuputih, and Jangkar (ABJ) subdistricts in East Java, Indonesia, have been polluted by fluoride from the effluent of Kawah Ijen volcano crater-lake water. To prevent and mitigate the severe chronic effects of prolonged exposure to fluoride, a hazard zonation of the polluted area was developed. A spatial multi-criteria evaluation (SMCE) approach was applied to visualize the fluoride hazard zones based on the intrinsic properties of acid-neutral drainage distance factors. The spatial hazard model with 5x5 m^2 grid resolution showed that 15% of the area was in the very low zone, 22% in the low zone, 49% in the moderate zone, 7% in the high zone, and 7% in the very high zone, respectively. The moderate zone was associated with acid irrigation networks that watered paddy fields only during the dry season, and its contribution and mechanism of transport to groundwater fluoride pollution were still unclear. The cross-operation technique also revealed that six villages were in the high hazard zone with potential for dental fluorosis, and five villages were in the very high hazard zone with the potential for skeletal fluorosis chronic effect. Based on the condition of the drinking water source, the optimization of clean water networks and groundwater quality improvement following drinking water standards is needed. Risk communication about fluoride hazard zones should also be addressed in Asembagus, Banyuputih, and Jangkar subdistricts to reduce and mitigate long-term health effects.

Keywords: Asembagus, Groundwater Pollution, Fluoride Hazard, Kawah Ijen

1. INTRODUCTION

Kawah Ijen in East Java, Indonesia, is the largest hyper-acidic volcanic crater lake on Earth. The effluent of hyper-acid water from the crater lake via the Banyupahit-Banyuputih river channel has been identified as a source of natural pollution in the northern part of the Kawah Ijen volcano [1]. The most polluted areas are Asembagus, Banyuputih, and Jangkar (ABJ) subdistrict. This acidic water enters the polluted area through the Banyuputih watershed system and agricultural irrigation channels, containing harmful pollutants such as fluoride (F^-).

In the Banyuputih river, the fluoride concentration is between 5.5 and 14.2 mg/L, and in the surrounding areas, the fluoride concentration in groundwater reaches 4.2 mg/L [2]. The high fluoride concentration was reported from the Kawah Ijen crater lake water, where the pH was lower than 0.4 and the fluoride concentration was up to 1,500 mg/L [3].

During the dry season, water from the Banyuputih river is also used for irrigating agriculture fields in the Asembagus and Jangkar areas. Approximately 2,800 kg of fluoride is discharged per day into the soil during irrigation [3]. The long-term application of this highly acidic and fluoride-polluted water for the irrigation process has changed the agricultural soil quality [4] and groundwater quality [2].

Fluoride is an essential micronutrient needed by the human body, especially for teeth and bones. A certain amount of fluoride is found in drinking water within the permissible concentration limit of between 0.5 and 1.5 mg/L as prescribed by the World Health Organization (WHO) [5]. Even so, fluoride contamination in water has become a significant problem globally. Some articles state that there will be a negative impact on the human body when exposed to higher fluoride intake.

Most of them reported dental and skeletal fluorosis as the impact of the higher fluoride intake [6]-[7]. Although the health status of fluoride is still well controlled in some countries, many cases of dental fluorosis have been reported [6]. Also, fluoride accumulation in the environment could affect health risks for plants, animals, and humans [8].

Asembagus subdistrict is an endemic area for fluorosis in Indonesia [9]. In the study area, the total daily intake of fluoride exceeds the possible limitations that can be the causal factor for dental and skeletal fluorosis [2]. Unfortunately, the groundwater is used as the drinking water source by the residents. This practice has caused many health problems for the residents, especially dental fluorosis and potentially skeletal fluorosis.

Due to the potential health risk caused by the high fluoride concentration in groundwater, this study presented a hazard map of groundwater fluoride in the ABJ subdistrict. Spatially, hazard quotient analysis in Asembagus was calculated by [2] and shown based on dug well samples and the village community. However, we used a different approach and technique on hazard zonation to complement and confirm the previous study.

The spatial pattern of the groundwater fluoride hazard was explained using the intrinsic factors approach of drainage networks. It was suspected as the possible source of groundwater fluoride pollution in the study area. Spatial analysis with multi-criteria evaluation has been used to develop the fluoride hazard index and zonation. The qualitative validation of the model was used to make sure that the hazard zones were correct based on the analysis of the research samples and previous findings.

2. MATERIALS AND METHODS

The research was organized according to the flowchart in Fig. 1. The general procedures included data collection (primary and secondary), spatial data preparation, parameter comparison, parameter index computation, hazard index calculation, and modeling, hazard index categorization, and model validation.

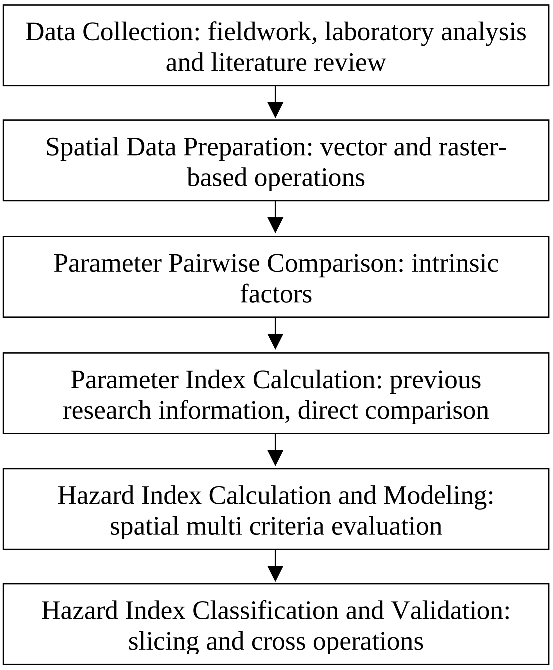

Fig. 1 Research flowchart and organization

2.1 Study Area and Samples Location

The study area is situated in the Situbondo regency, in the northern part of the Kawah Ijen volcano, East Java province, Indonesia, as shown in Fig.2. It consists of three administrative subdistricts, namely Asembagus, Banyuputih, and Jangkar, abbreviated as ABJ subdistrict for convenience. The ABJ subdistrict is a coastal plain with sandy-clayed volcanic deposition soils as the dominant surface material.

In total, five watershed systems are bordered in the study area, i.e., Sokmaelang, Jangkar, Banyuputih, Leket, and Klompret. The Banyuputih and Jangkar watersheds, as the main pathways for polluted water, are buffered by neutral river streams in the western (Sokmaelang) and eastern parts (Leket and Klompret).

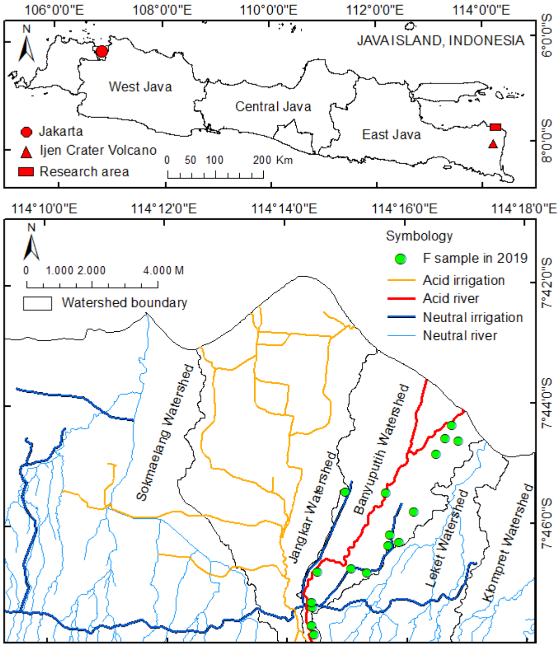

Fig. 2 Map and samples location of the study area.

Groundwater fluoride samples were taken from 18 dug wells during the dry season in July 2019. All samples were collected within the Banyuputih watershed boundary area. The consideration of sample location is based on the information that the acid river is the possible primary source of fluoride pollution in the study area [2]. During fieldwork, acid rivers and acid irrigation networks were identified using the basic map from Rupabumi Digital Indonesia on a 1:25,000 scale [10] and field tracking activities. Acid drainage networks are critical in this research to develop the intrinsic factor of fluoride hazard indexes.

2.2 Samples Analysis

The SPADNS spectrophotometric method was used to analyze groundwater fluoride concentrations from the collected samples. This approach works by combining soluted fluoride with zirconium. Certain zirconium dyes will react with fluoride to produce a colorless complex that will lighten with increasing fluoride concentration. Fluoride concentrations from samples were measured using a spectrophotometer at a 570 nm wavelength.

The fluoride concentration from the dug well was used to identify the correlation between acid drainage distance and groundwater fluoride concentration within the Banyuputih watershed. The Pearson coefficient correlation was used to determine the correlation. If there is a strong correlation, the possibility of acid drainage networks as the source of fluoride pollution is high. However, if there is no strong correlation, the possible source of fluoride in the groundwater will be from other sources.

2.3 Spatial Analysis and Modeling

2.3.1 Vector and raster data preparation

A geographic information system (GIS) was used to develop a fluoride hazard index. Both ArcGIS 10.8.1 and ILWIS 3.31 academic software packages were combined to analyze both types of vector and raster data sets. Vector-based analysis was applied mainly for index parameter preparation steps. A georeferenced corner was made to figure out the relationship between row and column numbers in a raster map. The coordinates, as well as the 5x5 m^2 grid resolution, were also made.

2.3.2 Drainage networks analysis

Drainage networks were analyzed using the distance calculation technique in ILWIS to generate buffer networks. This process is crucial to identifying the correlation of groundwater fluoride concentration with acid and neutral channel drainage networks. Distance to drainage networks was then grouped using slicing classification for 1000 m intervals.

Drainage density (Dd) is defined as the sum of the total length of stream channels within a drainage basin divided by the total area of the drainage basin [11]. It is the total length (Dl) of all channel segments inside a basin multiplied by the basin area, represented in unit length per unit area. Drainage density was calculated to identify the contribution of the dilution process from neutral and acid water.

2.3.3 Spatial multi-criteria evaluation

Spatial multi-criteria evaluation (SMCE) is a technique for supporting stakeholders in making a decision. The systematic hierarchy simplifies the complexity of parameters in the decision processes. Parameter maps as input for SMCE were grouped, standardized, and weighted in a criteria tree. The direct comparison was applied to calculate the weight of each parameter and sub-criteria for generating the hazard index using the principle in Table 1.

The primary evaluation used a problem analysis as the target. It analyzed a problem situation using one set of maps as evaluation criteria, namely the fluoride hazard index. The criteria tree editor will start with an empty tree and a placeholder for one data set. Finally, the fluoride hazard index was classified using the slicing technique based on the histogram model into five hazard zone categories, i.e., very low, low, moderate, high, and very high.

Table 1 Pairwise comparison in SMCE

Comparison	Normalized weights
Extremely more important than	0.900/0.100
Very strongly more important than	0.875/0.125
Strongly more important than	0.833/0.167
Moderately more important than	0.750/0.250
Equally important as	0.500/0.500
Moderately less important than	0.250/0.750
Strongly less important than	0.167/0.833
Very strongly less important than	0.125/0.875
Extremely less important than	0.100/0.900

3. RESULTS AND DISCUSSION

3.1 Groundwater Fluoride Concentrations

The fluoride concentration from samples varied from 1.4 to 3.3 mg/L (with a mean of 2.41 mg/L). Compared with previous research, the values were still within the range. Based on surveyed data in 1979, the range is from 0.20 to 2.70 mg/L [12]. As reported by [9], the groundwater fluoride concentration increased in 1999, reaching 0.41 to 3.25 mg/L. In 2001, the range was from 0.10 to 4.20 mg/L, analyzed by [2]. The relatively steady concentrations of fluoride in groundwater indicated that after 20 years of interval time, there was no significant fluctuation of fluoride concentration in the groundwater within the downstream area of the Banyuputih watershed.

Based on the chronic health effects, [13] classified the concentration of fluoride into four pollution category ranges: 0 to 0.5 mg/L (dental caries), 0.5-1.5 mg/L (promotes dental health and prevents tooth decay), category 1.5-4.0 mg/L (dental fluorosis-mottled teeth), and category 4.0-10 mg/L (dental and skeletal fluorosis). Thus, the fluoride concentration values in the study area were still relatively high for causing dental fluorosis-mottled teeth. Sample concentration analysis revealed that only 6% of the concentration of the samples was low and within the range of the dental caries issue. The remaining 94% are in the high category for causing chronic dental fluorosis-mottled teeth effects.

3.2 Drainage Networks and Intrinsic Factors

As shown in Fig. 3, there is a weak negative correlation (r = -0.4) between groundwater fluoride and acid river distance. The correlation indicated that the contribution of the acid river to the groundwater fluoride concentration is still unclear. However, [3] reported that the acid river has been flowing for more than a hundred years. This long exposure times make it possible to transport fluoride from acid river water to shallow aquifer systems. Moreover, [2] also analyzed that the spatial pattern of groundwater fluoride concentration was strongly controlled by the distance from acid drainage, where all the highest concentrations were in the areas surrounding the acid river (*r* = -0.7) and acid irrigation (*r* = -0.4).

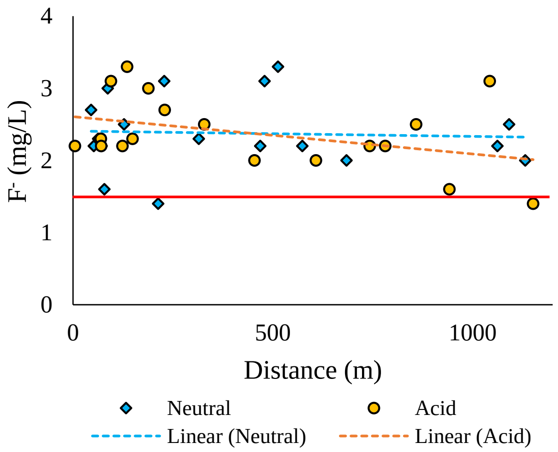

Fig. 3 Graphic plot between F^- concentration and distance to drainage networks

The acid riverbed of Banyuputih is naturally occurring in surface lithological conditions (Fig. 4), primarily by alternations of pumice breccia, tuffaceous sandstone, and sandstone [14]. Most lithological outcrops have been weathered or have had their mineral structures disrupted due to exposure to acidic water. This material characteristic drives the acid water to more efficiently infiltrate into the groundwater, and fluoride exposure will intensify with the duration of exposure to the acid river. Therefore, considering the proximity to the acid drainage, it is still proper to use acid drainage as the intrinsic factor for generating the hazard index.

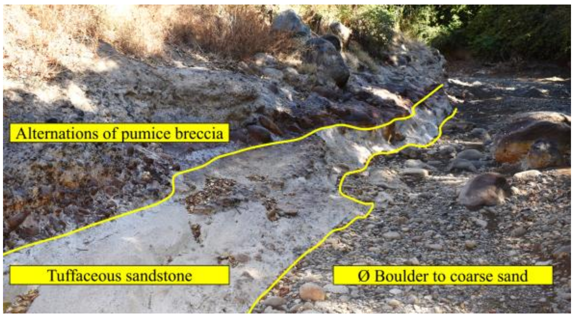

Fig. 4 Surface lithological of Banyuputih riverbed

Unlike the previous acid drainage, the neutral graphic shows no correlation between neutral drainage and groundwater concentrations (*r* = -0.1). All concentrations are relatively high in all distance ranges, indicating that the effect of dilution from neutral water seems to be very small. On the other hand, the Banyuputih watershed area is polluted by fluoride in all downstream areas, exceeding the limit of 1.5 mg/L (above the red line).

The drainage length (Dl) and density (Dd) characteristics can also explain the groundwater fluoride pattern. The drainage length calculation in Table 2 compared acid drainage length and neutral drainage length within every watershed system. The calculation results show that the Jangkar watershed has the longest acid drainage length, followed by the Banyuputih and Sokmaelang watersheds. The longest acid drainage length will influence the range of fluoride dispersion in the soil surface and groundwater. Since acid drainage does not flow in the Klompret and Leket watersheds, they show zero drainage length and density values.

Table 2 Drainage characteristics in the research area

Watershed	Acid		Neutral	
	Dl	Dd	Dl	Dd
Banyuputih	14.2	.65	9.9	.46
Jangkar	55.3	1.42	3.5	.09
Klompret	0	0	10.1	.94
Leket	0	0	42.6	2.61
Sokmaelang	12.2	.19	116.2	1.83

Noted: red color is the highest value, Dd (km) and Dl (m/km^2)

The drainage density calculation in Table 2 also compares acid drainage density and neutral drainage density. The calculation results show that the Jangkar watershed has the highest acid drainage density, followed by the Banyuputih and Sokmaelang watersheds. The highest acid drainage density will affect the concentration of fluoride dispersed into groundwater from the soil surface. Otherwise, the highest neutral drainage density will contribute to the dilution process of fluoride, decreasing its concentration before it reaches the groundwater aquifer system.

3.3 Parameter and Sub-parameter Maps

Parameter and sub-parameter maps were used to generate fluoride hazard indexes. In this study, four-parameter maps were prepared. A buffer map is a parameter in Fig. 5a-d that provides information about classified distances from drainage, both acid and neutral, with six class sub-parameters, namely, <1000 m, 1000-2000 m, 2000-3000 m, 3000-4000 m, 4000-5000 m, and > 5000 m.

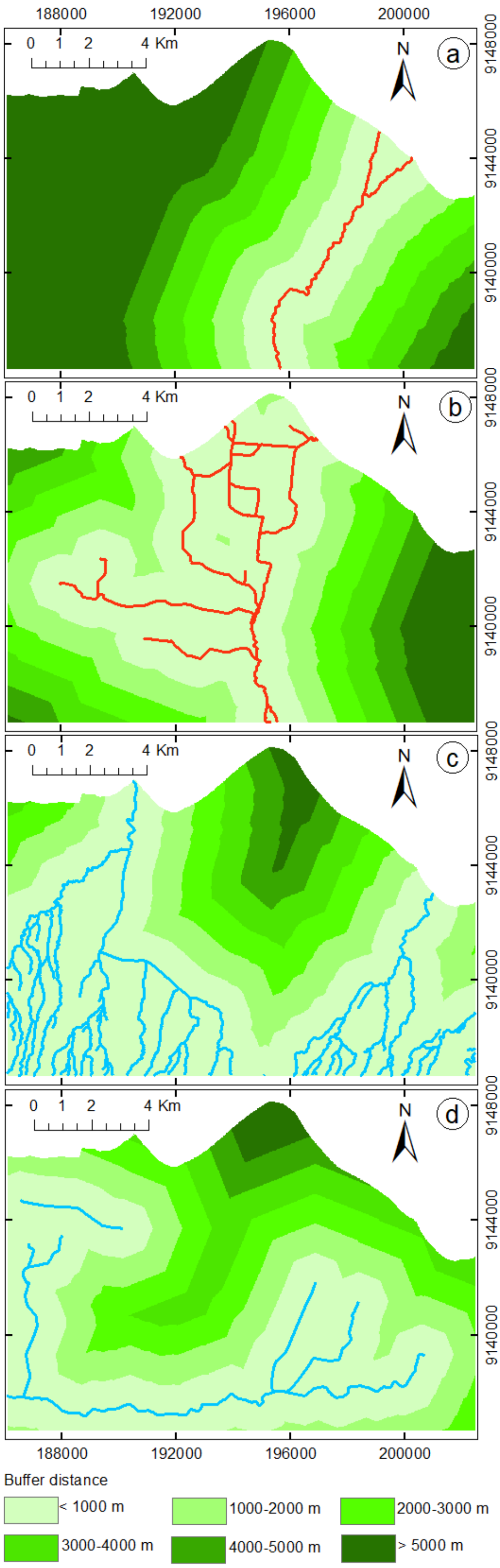

Fig. 5 Parameter map (a) acid river buffer, (b) acid irrigation buffer, (c) neutral river buffer, and (d) neutral irrigation buffer.

The buffer maps included acid river buffer, acid irrigation buffer, neutral river buffer, and neutral irrigation buffer. The 1000 m interval distance was considered from the correlation between drainage distance and groundwater fluoride concentration from 2019 samples, which all showed high concentrations within the 1000 m range, besides groundwater fluoride showed significant concentrations below 1000 m from the acid drainage [2].

The Banyuputih (5a) and Jangkar (5b) watersheds, which serve as the primary pathways for highly toxic water from the Kawah Ijen volcano's crater lake, are buffered by neutral river streams. Acid drainage is buffered in the western part by the Sokmaelang watershed, while it is buffered in the eastern part by the Leket and Klompret watersheds (5c).

Neutral irrigation (5d), mainly in the southern part of the ABJ subdistrict, comes from the Sampean Baru Canal. However, this neutral canal is not optimized to irrigate the paddy fields in the research area (observed during the field survey in 2019). During the dry season, the availability of water at the dam intake of Sampean Baru decreases, but the water demand in the paddy fields increases, not only in the study area but also in the other surrounding regencies. It is one of the reasons why the Banyuputih River's water is still used for irrigation purposes today, despite its poor quality for agricultural purposes based on the Indonesian regulation [15].

3.4 Fluoride Hazard Index and Zonation

The fluoride hazard index result shows that the range index is from 0.0 to 1.0 in Fig. 6a. The small value index indicates the low hazard potential, and the highest value indicates the high hazard potential. The hazard zonation was classified based on the histogram into five pollution zones: very low category (0-0.42), low category (0.42-0.57), moderate category (0.57-0.72), high category (0.72-0.86), and very high category (> 0.86).

The hazard map was crossed with the settlement area to analyze the number of villages in the ABJ subdistrict that were potentially polluted by groundwater fluoride. Village numbers 1-10 are in the Asembagus subdistrict; 11-13 are in the Banyuputih subdistrict; and 14-20 are in the Jangkar subdistrict. Fig. 6b shows the fluoride hazard class zonation in the study area. High (7%) and very high (7%) zones are the priority locations for mitigation and monitoring activity. Spatially, these locations include the villages of Bantal (1), Kedunglo (5), and Banyuputih (13).

The moderate hazard category has the most dominant area, with 49% covering the study area. It is associated with acid drainage irrigation that inundates paddy field areas in Asembagus and Jangkar subdistricts only during the dry season. Unlike the acid river, this acid irrigation channel did not continuously transport fluoride-containing water. The loading concentrations of fluoride can be high or low depending on the frequency and volume of acid water distributed into paddy fields during the dry season.

The irrigation networks were also constructed using concrete to protect the water from infiltration into the soil and groundwater. So, the contribution of fluoride transport from the irrigation channel into groundwater is still unclear, and the only possible way is through the infiltration of inundated paddy fields. On the other hand, the moderate category still needs to be analyzed in detail to reveal the contribution and mechanism of the acid irrigation network to groundwater fluoride pollution.

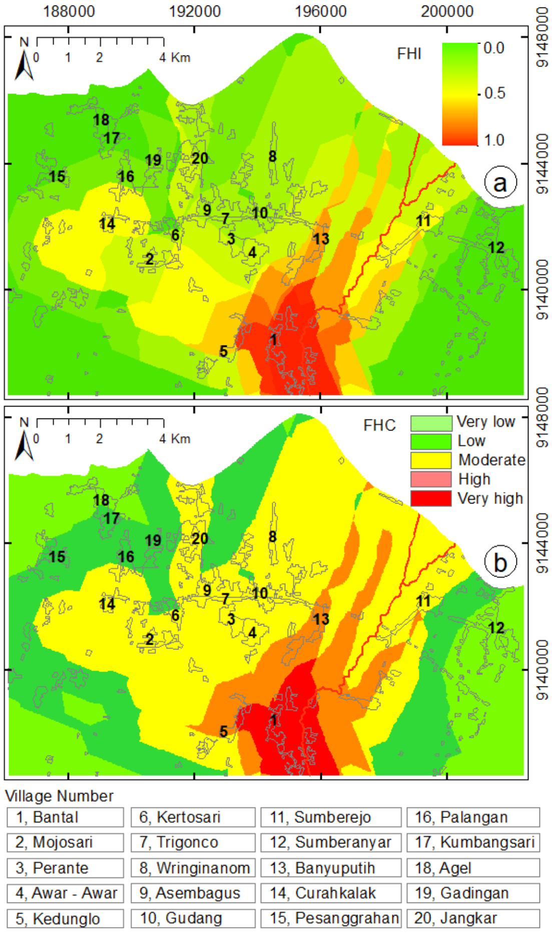

Fig. 6 Map of (a) FHI-fluoride hazard index and (b) FHC-fluoride hazard class zonation.

Low and very low hazard zones cover 37% of the study area. This category is located in the neutral drainage network, which is separate from the acid drainage networks. However, previous research reported that the fluoride concentration below 1.0 mg/L already causes chronic fluorosis based on the diet study of the ABJ community society [2]. It was also revealed that 26% of groundwater samples potentially cause dental caries, which was not correlated with fluoride concentration in drinking water but strongly related to dental fluorosis. It is also proven that 56% of samples are in the dental fluorosis-mottled teeth potential health chronic effect, while only 12% were in the recommended healthy range. Skeletal fluorosis also potentially occurs in the ABJ subdistrict due to 6% of samples having skeletal fluorosis potential chronic health effects.

3.5 Model Validation

Model validation is essential to confirm the accuracy of the spatial zonation. In this study, model accuracy was confirmed qualitatively using a comparison with previous research. A total of 20 communities (villages in this study) were sampled by [2], revealing that 14 villages received acidic water from the Banyuputih river. In this research, about eight villages, or 36%, confirm the 14 villages that received polluted water from the Banyuputih river in the high and very high category zones. These villages are Bantal (1), Awar-awar (4), Kedunglo (5), Trigonco (7), Sumberejo (11), and Banyuputih (13).

In this case, Sumberejo is the only village included in the high and very high zones based on the intrinsic factors, even though it did not receive acidic water from the Banyuputih river. The other villages that received polluted water are categorized in the moderate category and mainly in the Asembagus subdistrict consisting of Mojosari, Perante, Kertosari, Wringinanom Asembagus, Gudang, and Jangkar subdistricts, i.e., Curahkalak, Gadingan, and Palangan villages.

Model validation was also carried out by comparing the potential chronic effects [13] of groundwater fluoride samples from 2019 and the information samples from [2]. The model confirmed that a high percentage of dental caries is covered in very low zones. In the very low category, the chronic effects of dental caries cover 84% of the total hazard zone area, and the dental health range covers only 16%. Dental caries occur when the fluoride concentration in drinking water is below 0.5 mg/L.

In the low category, the chronic effects of dental caries cover 55% of the total area, the dental health range covers 27%, and the dental fluorosis-mottled teeth cover 18%. In this category, the model confirmed that all groundwater fluoride concentrations are below 1.5 mg/L. However, dental fluorosis-mottled teeth occur when the fluoride concentration in drinking water is between 1.5 and 4.0 mg/L, confirming that a small percentage of dental fluorosis-mottled teeth start to appear in the low category.

In the moderate category, it verified that the chronic effects of dental caries cover only 16% of the total area, while the dental health range covers 29%, and dental fluorosis-mottled teeth cover 54%. The model has confirmed that a high percentage of dental fluorosis-mottled teeth significantly increased in the moderate zones.

The model validation also showed that a large percentage of the dental fluorosis-mottled teeth chronic effects have been confirmed to occur in the high and very high zones. In the high category, dental health covers only 11% of the total area, and dental fluorosis-mottled teeth remarkably cover 89%. The very high category also verified that the dental health range covers only 1%, and the dental fluorosis-mottled teeth significantly cover 99% of the total area.

3.6 Fluoride Hazard Problem and Mitigation

The percentage of fluoride concentrations in drinking water and its chronic health effects supported dental caries and dental fluorosis-mottled teeth due to groundwater fluoride pollution in the ABJ Subdistrict [9]. Based on the percentage of hazard zones, Fig. 7 shows that the high and very high zones are in Bantal (1), Awar-awar (4), Kedunglo (5), and Trigonco (7-high zones only), Sumberejo (11), and Banyuputih (13) villages.

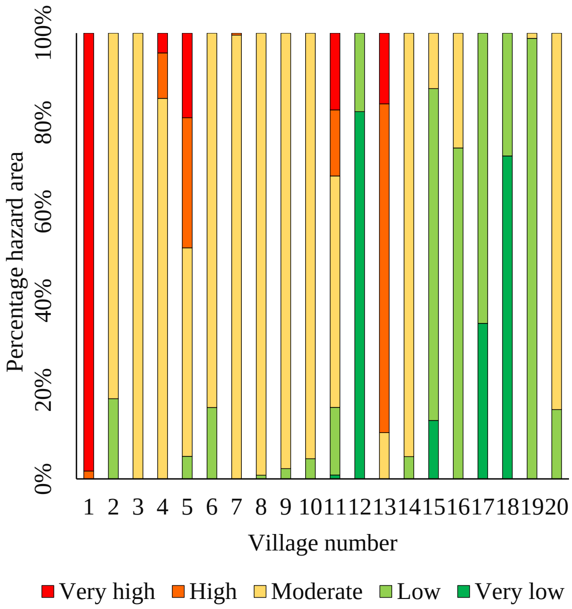

Fig. 7 Distribution of hazard zonation percentage area

The lack of fluorosis data in the ABJ Subdistrict is another issue, especially in the high and very high hazard zones. The shame and reluctance of the local community to consult on their health conditions in the health clinics, especially for dental-mottled teeth as an indication of fluorosis disease, makes the problem even more complicated. Age also plays an important role in the fluoride-health problem, as children have a higher risk of the fluoride-health problem than adults. For children, the high amount of fluoride in the body will impact their neuro-development more than in adults. For adults, a higher amount of fluoride will cause dental and skeletal problems [16].

Moreover, most of the inhabitants in the Asembagus and Banyuputih subdistricts preferred to drink water from their polluted wells for taste and economic reasons, as shown in Fig. 8. Also, the condition became severe when the municipality 1990 failed to solve this drinking water problem in the ABJ subdistrict [9]. Confirmed during the fieldwork observation in 2019, the condition is not so much different after a long time as stated by previous research. Thus, the problem is still occurring now and needs to be solved and mitigated immediately.

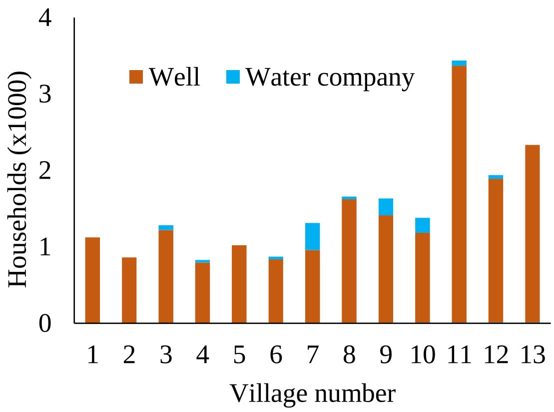

Fig. 8 The daily water source of household (1-10 in 2018 and 11-13 in 2017)

A preliminary assessment of fluoride transport mechanisms is needed to mitigate groundwater fluoride pollution. The hydro-geochemical approach can be the first basic information to explain the characteristics of groundwater fluoride contamination [17]. Not to mention that the climate conditions, particularly the dry season, also increase the likelihood of fluoride contamination in the water environment [18]. These climate factors should be considered and modeled for a complementary approach. All of these factors can be important pieces of information as they are fundamental to choosing the best mitigation techniques in the study area.

4. CONCLUSIONS

Groundwater fluoride hazard zones in the study area were classified into five categories, namely very low (15%), low (22%), moderate (49%), high (7%), and very high (7%). The large percentage of the moderate zone is attributed to acid irrigation networks, and their contribution and mechanism of transport to groundwater fluoride pollution need to be analyzed in detail. The spatial analysis also revealed that six villages were in the high category and five villages were in the very high category. To meet drinking water standards, it is necessary to optimize clean water networks and increase the quality of groundwater resources. Furthermore, risk communication about fluoride hazard zonation should be addressed to prevent and mitigate chronic health effects in the Asembagus, Banyuputih, and Jangkar subdistricts.

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6. REFERENCES

[1] Löhr, A.J., Bogaard, T.A., Heikens, A., Hendriks, M.R., Sumarti, S., Van Bergen, M.J., Van Gestel, C.A.M., Van Straalen, N.M., Vroon, P.Z., Widianarko, B., Natural pollution caused by the extremely acidic crater Lake Kawah Ijen, East Java, Indonesia. Environmental Science and Pollution Research, Vol. 12, Issue 2, 2005, pp. 89–95.

[2] Heikens, A., Sumarti, S., van Bergen, M., Widianarko, B., Fokkert, L., van Leeuwen, K., Seinen, W., The impact of the hyperacid Ijen Crater Lake: risks of excess fluoride to human health. Science of the Total Environment, Vol. 346, Issue 1-3, 2005, pp. 56-69.

[3] Delmelle, P., Bernard, A., Downstream composition changes of acidic volcanic waters discharged into the Banyupahit stream, Ijen caldera, Indonesia. Journal of Volcanology and Geothermal Research, Vol. 97, Issue 1-4, 2000, pp. 55–75.

[4] Van Rotterdam-Los, A.M.D., Heikens, A., Vriend, S.P., van Bergen, M.J., van Gaans, P.F.M., The effect of naturally acidified irrigation water on agricultural volcanic soils. The case of Asembagus, Java, Indonesia. Journal of Geochemical Exploration, Vol. 96, 2008, pp. 53 –68.

[5] WHO, Guidelines for drinking-water quality: The fourth edition incorporating the first addendum, Geneva, 2017, pp. 370-373.

[6] Ali, S., Thakur, S.K., Sarkar, A., and Shekhar, S., Worldwide Contamination of Water by Fluoride. Environmental Chemistry Letters, Vol. 14, 2016, pp. 291-315.

[7] Dasaiah S., Kurakalva R.M., and Pindi P.K., Data on fluoride concentration profile in groundwater of rural habitats in Mahabubnagar district, Telangana, India. Data in Brief, Vol. 32, 2020, pp.1-6.

[8] Zuo H., Chen L., Kong M., Qiu L., Lu P., Wu P., Yang Y., and Chen K., Toxic Effects of Fluoride on Organisms. Life Sciences, Vol. 198, 2018, pp.18-24.

[9] Budiparmana E.S., Hapsoro A., Irmawati E.S., and Kuntari S., Dental Fluorosis and Caries Prevalence in the Fluorosis Endemic Area of Asembagus, Indonesia. International Journal of Paediatric Dentistry, Vol. 12, 2002, pp.415-422.

[10] Geospatial Information Agency (BIG), 2019, Rupabumi Digital Map of Situbondo sheets, Scale 1:25000, Accessed online from https://tanahair.indonesia.go.id.

[11] Horton R.E., Drainage Basin Characteristics. Transactions of American Geophysical Union, Vol. 13, Issue 1, 1932, pp. 350-361.

[12] Rai I.G.N. The relation between prevalence of endemic hypoplasia teeth in children with fluoride content in the drinking water, urine, and carious teeth. Ph.D. Thesis. Surabaya, Indonesia: Airlangga University, 1980, pp. 62–84.

[13] Edmunds W.M., Smedley P.L. Fluoride in Natural Waters. in Essentials of Medical Geology, 2013, pp. 311-336.

[14] Agustiyanto D.A., Santosa S., Geological Map of The Situbondo Quadrangle, Jawa, Scale 1:100000, Geological Research and Development Centre, Sheet 1708-1, 1993.

[15] Government of Republik Indonesia, Regulation for Water Quality Management and Water Pollution Control, No. 82, 2001.

[16] Liu J., Peng Y., Li C., Gao Z., and Chen S., A Characterization of Groundwater Fluoride, Influencing Factors and Risk to Human Health in the Southwest Plain of Shandong Province, North China. Ecotoxicology and Environmental Safety, Vol. 207, 2021, pp. 1-10

[17] Gogoi, R.R., Khanikar, L., Gogoi, J., Neog, N., Deka, D.J., Sarma, K.P., Geochemical sources, hydrogeochemical behavior of fluoride release and its health risk assessment in some fluorosis endemic areas of the Brahmaputra valley of Assam, India. Applied Geochemistry, Vol. 127, 2021, pp. 1-18.

[18] Zhang Q., Xu P., Qian H., and Yang F., Hydro-geochemistry and Fluoride Contamination in Jiaokou Irrigation Subdistrict, Central China: Assessment based on multivariate statistical approach and human health risk. Science of the Total Environment, Vol. 741, 2020, pp. 1-15.