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The influence of the acid water of the Banyupait River on the community health in Bantal village, Asembagus, Indonesia

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ABSTRACT

The pH of Mount Ijen crater water is 0-2, resulting in water that is acidic and sulfurous. A fault near the Mount Ijen Crater causes seepage so that acidic water flows into the Banyupait River. Chemical elements and heavy metals originating from the river pollute groundwater and plants. As a result, people around the river consume heavy metals. This research aims to determine the quality of river water and groundwater, as well as determine community factors that are susceptible to dental fluorosis. The methodology used is field mapping and laboratory analysis. For water samples, the Atomic Absorption Spectrophotometer (AAS) method is used. The pH of river water at the research location exceeds the quality standard, namely pH 4-5.5. Meanwhile, groundwater fluorine and sulfate elements exceed quality standards, namely fluorine of 0.6171 mg/L and 0.6870 mg/L, and sulfate ranging from 325-683 mg/L. These two elements cause symptoms of dental fluorosis. Meanwhile, the community factors most susceptible to dental fluorosis are people in the adult age category, and the last level of education is elementary school. This is because the Banyupait River water and groundwater are exposed to fluorine and sulfate water originating from seepage from the Mount Ijen Crater.

Key words: acid water, Banyupait, crater, fluorine, health

HIGHLIGHTS

- Mount Ijen crater water exhibits extreme acidity, containing sulfurous compounds, leading to the acidification of the Banyupait River.
- Pollution of groundwater and plants occurs at the Banyupait River, posing health risks to nearby communities.
- Groundwater quality parameters, notably fluorine and sulfate levels are identified as contributors to dental fluorosis symptoms.

1. INTRODUCTION

Water is a source of life for humans and other living things. Humans use natural water to meet their daily needs: drinking, cooking, bathing, washing latrines, and irrigation. However, based on the results of interviews with residents of Bantal Village who live near the Banyuputih River, the river water has a white color in the dry season with a bitter taste, so livestock such as cows do not want to consume the water (Sumarti & Zaennudin 2017).

Excessive fluorine (F^-) consumption can cause discoloration and the appearance of spots on tooth enamel, namely dental fluorosis. In addition to impacting teeth, excessive fluorine consumption also affects bones, which is called dental fluorosis (Sumiok *et al.* 2015). Meanwhile, high sulfate (SO_4^{2-}) levels can cause the risk of diarrheal disease (Munfiah 2013). The impact is that of the 4,784 residents in Asembagus Subdistrict, Situbondo Regency, 98% have teeth with brown stains or yellow spots that spread on the tooth surface (Soerahman *et al.* 2012). This research aims to determine the water quality of the Banyupait River and groundwater, as well as determine the community factors that are susceptible to dental fluorosis in terms of age. Where geologically, the research area is an area exposed to metals and non-metals, due to the flow of the Banyupait River which originates from the Ijen Volcano Crater. So that people living around the Banyupait River will be exposed to metals and non-metals. Thus, these two things constitute the novelty of this research.

2. GEOLOGICAL SETTING

Ijen Crater is a lake formed in the Pleistocene period (Sitorus 1999), and according to Caudron *et al.* (2015), this lake is a natural acid lake. Meanwhile, according to Sitorus (1999), the stratigraphy of Ijen Volcano can be divided into three groups of volcanic deposits which can be explained as follows:

Pre-caldera volcanic deposits are the oldest of the Upper Pleistocene age (294.00 $\pm$ 0.03 Ma). These deposits consist of pyroclastic flow deposits and lava flows. The lava flow is composed of basalt, andesite, and dacite. The age of this lava flow is 297.00 $\pm$ 0.03 Ma. Toward younger deposits are caldera volcanic deposits consisting of overlying and pyroclastic fall deposits that cover the entire north side of the caldera. The caldera formation occurred between 300,000 and 50,000 years ago, between the youngest pre-caldera deposits and the oldest post-caldera deposits.

Post-caldera volcanic deposits begin with the appearance of Belawan Lake sediments. The lake deposits consist of alternating shale, sand, and travertine. In addition, there are river deposits and lava deposits. Then these deposits are covered by pyroclastic flows and falls, pyroclastic waves, lahars, debris avalanches, and lava flows.

Post-caldera volcanic deposits can be grouped into two parts, namely the side and the inside of the caldera. The volcanic cones located on the side of the caldera lined from the west are Mount Jampit (Pendil), Mount Ringgih, Mount Suket, Mount Rante, Mount Merapi, and Mount Ijen. The volcanic cones that grow in the caldera's interior include Mount Widodaren, Mount Cilik, Mount Gempol, Mount Kawahwurung, Mount Anyar, Mount Lingker, Mount Mlaten, Mount Cemara, and Mount Gendingwaluh. This volcanic cone is overgrown with several composite cones: (Mount Blau, Mount Pawenen, Mount Kukusan, and Mount Genteng), the dome of Mount Geleman, and the pyroclastic cone of Mount Papak. Pyroclastic flow and pyroclastic scoria deposits at Suket Volcano are 37,900 $\pm$ 1,850 years old. According to Sitorus (1999), these deposits' ages range from 37,000 to 45,000 years.

The geological structure that develops in Ijen Volcano is a normal fault which can be grouped into two periods of fault formation deformation. The graben structure marks the initial phase, while the final phase is characterized by the presence of the Blawan and Jampit faults (Figure 1). Ijen Crater Dam was built during the Dutch era, and the dam's current condition is

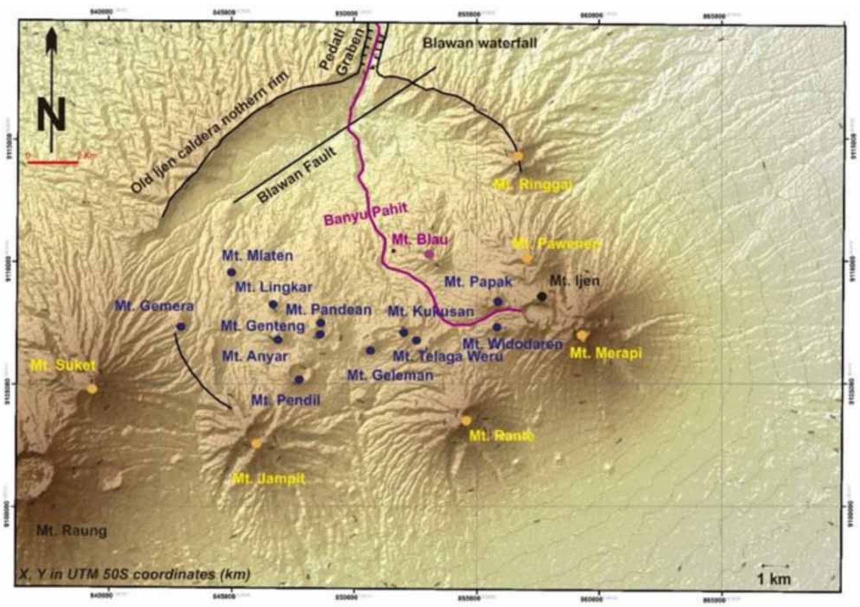

Figure 1 | Map showing the distribution of volcanic cones and faults at the summit of Ijen Volcano (modified from Caudron *et al.* 2015).

leaking on the sides and top so that the crater water flows directly following the Banyupait River (Hochstein & Sudarman 2015). River water from the Ijen Crater dam has a pH between 0.35 and 0.89 (Delmelle & Bernard 1994; Hochstein & Sudarman 2015). The lake's pH value has been consistently low (pH = 0–0.4) over the last 50 years and yields native sulfur (Delmelle *et al.* 2000).

Ijen Crater water which is very acidic has a concentration of 200,000 tons of aluminum and 1,000 tons of titanium (Zelenov 1969). In addition, according to Sriwana & Kadarsetia (2010), Ijen Crater water contains very high concentrations of Cl^- (25,000 ppm), S^{2-} (25,000 ppm), and F^- (1,300 ppm). Meanwhile, according to Wittiri & Sumarti (2010), the chemical composition of Ijen Crater solfatara condensate is very dangerous, because it contains $SO_4^{2-} = 24,259.86$ ppm and $Cl^- = 33,389.26$ ppm, $NH_3 = 2,789.19$ ppm, $Ca^{2+} = 44.30$ ppm, $Al^{3+} = 36.24$ ppm, $Fe^{3+} = 33.68$ ppm, $SiO_2 = 22.65$ ppm, $Mg^{2+} = 9.20$ ppm, $Na^+ = 4.08$ ppm and $Mn^{2+} = 0.56$ ppm. Although the water of Ijen Crater has experienced dilution from the acid spring, Kali Sat and Kali Sengon are neutral, and downstream river water is still acidic. It contains high levels of F^- (Sumarti & Zaennudin 2017).

The influence of other river water entering the Banyupait River causes the pH of the water to rise slightly, and the physical condition of the water changes. However, Aminuddin & Andiani (2015) explained that the pH of the water along the Banyupait River did not transform into residential areas, rice fields, and sugar cane plantations.

3. RESEARCH METHODS

We did mapping for one month. The research area was in the Banyupait River channel which originates at the Ijen Crater through Bantal Village. In the Bantal area, the flow of the Banyupait River is divided into two routes, namely the eastern route which flows directly to the sea (Madura Strait), while the western route is an irrigation canal used to irrigate agricultural land (Figure 2). Sugarcane plants are very dominant in this area. Even in the Asembagus area, there is also a sugarcane factory.

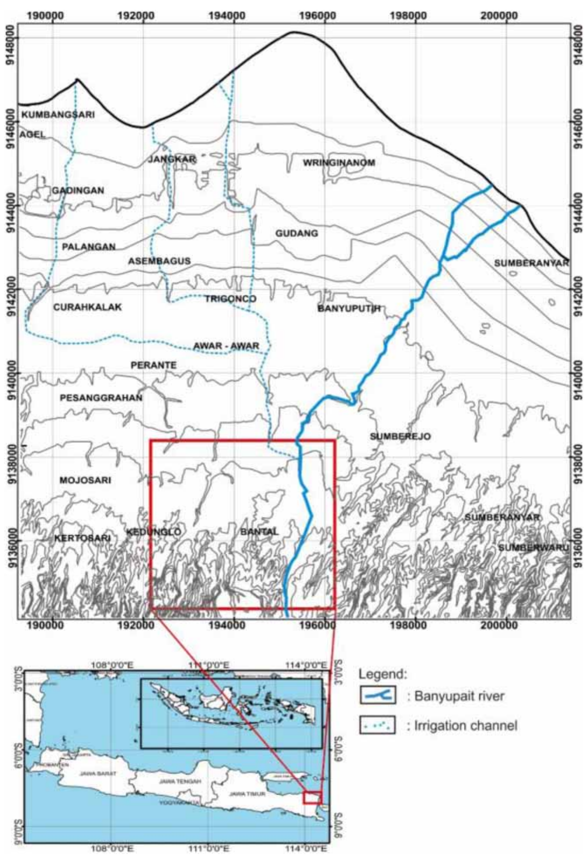

Figure 2 | Map showing the location of the Asembagus area, which is a research area.

We conducted research using survey methods or geological mapping and laboratory analysis, namely water quality analysis. Geological mapping is carried out to study the types of rocks, stratigraphy, and geological processes that occur in the research area. Apart from that, the results of geological mapping can explain the types of rocks that store groundwater containing heavy metals in the research area. Meanwhile, water quality analysis is used to study the chemical characteristics of water from the Banyupait River and its surroundings caused by water seepage from the Ijen Volcano Crater. So as a result of this seepage, residents living around the Banyupait River experience a decline in their level of health.

Water sampling was carried out in the eastern Banyupait River drainage area, while in the western Banyupait River drainage area it was artificially irrigated. Thus water samples are taken from rivers, irrigation, and wells. These samples are then carried out with pH measurements and chemical analysis of the water which will be followed by examination in the laboratory.

Water quality analysis is represented by samples obtained from river flows, irrigation, and water obtained from dug wells (shallow wells) with a depth of around 20–25 m. The samples were taken from upstream in Bantal Village to coastal areas or river estuaries. Water quality samples for river flows are represented by four water samples. Meanwhile, the other nine water samples were samples from shallow wells or groundwater. Each sample was taken with a volume of 2 L. Water analysis using the Atomic Absorption Spectrophotometer (AAS) method was carried out at the Center for Environmental Health Engineering and Disease Control (BBTKLPP) in Yogyakarta.

Water samples are taken to determine chemical elements and heavy metals such as pH, Fe^{3+}, SO_4^{2-}, F^-, Mn^{2+}, and Cu^{2+}. The results of the water quality test will also be compared with the intended quality standards. By knowing the water quality of the Banyupait River and groundwater, it is hoped that we can find out the causes of dental fluorosis suffered by the people in Bantal Village.

In general, in the research area, river water is used as a water source for agriculture and livestock. Apart from that, well water in the research area is also used as a source of primary needs, such as raw water for drinking, washing, bathing, and latrines. Thus, quality standards refer to class I water quality standards, namely Republic of Indonesia Government Regulation No. 82 of 2001 and Water Quality Standards Minister of Health Regulation No. 32 of 2017 concerning Environmental Health Quality Standards and Water Health Requirements for Sanitation and Hygiene Needs.

4. RESULTS AND DISCUSSION

4.1. Geology of the research area

The morphology of the research area from south to north is a morphological formation of wavy hills, volcanic foot plains, and beaches.

The rocks that make up the coastal area consist of alluvial deposits of beach sand. While the volcanic foot plains are composed of volcanic lava breccias from the Bogor Formation. The undulating hillside morphology is composed of the flow of old Ijen pyroclastic deposits.

Agustiyanto & Santoso (1993) compiled the stratigraphy of the Asembagus area composed of Old Ijen volcanic rock (Old Quaternary Volcanic Rock). The Old Ijen volcanic rock mated to be Pleistocene, Holocene, and Bogor Formation (Young Quaternary volcano), which includes Old Ijen volcanic rocks, consists of volcanic breccias, pumice breccias, tuff, and basalt lava, while the Bogor Formation rocks consist of alternating breccias between various breccia materials, pumice breccias, tuffaceous sandstones, and sandstones. The mapping results in the study area indicate that the study area is composed of rock units from the old to the young order: the Pyroclastic Breccia Old Ijen, the Lahar Bogor, and river and coastal alluvial sediments (Figure 3). Old Ijen pyroclastic flow rock units exposed in the study area include Mount Banter and Bantal to the east (Pandre).

The division of lithological units in the Bantal area is based on lithological characteristics such as structure, texture, and composition, whereas the naming of lithological units is based on lithological units. From the field mapping results in the study area (Figure 3), the following five lithological units were found: the Pyroclastic Falls Old Ijen Unit, the Pyroclastic Flow Old Ijen 1 Unit, the Pyroclastic Flow Old Ijen 2 Unit, and the Lahar Bagor Unit. The rocks description of each of these lithological units are as follows.

Pyroclastic Falls Old Ijen Unit

The units of Old Ijen Pyroclastics Falls in the study area are located in the volcanic valley of Mount Ijen with a north–south distribution. This pyroclastic deposit unit has a distribution area of about 15% of the research area. The lithology in the study area shows a massive sedimentary structure and graded bedding with a grain size of fine sand – gravel (0.125–4 mm). The fragments consist of blocky andesite, pumice in volcanic sand, or lapilli-sized bedrock. The blackish grey color is very striking

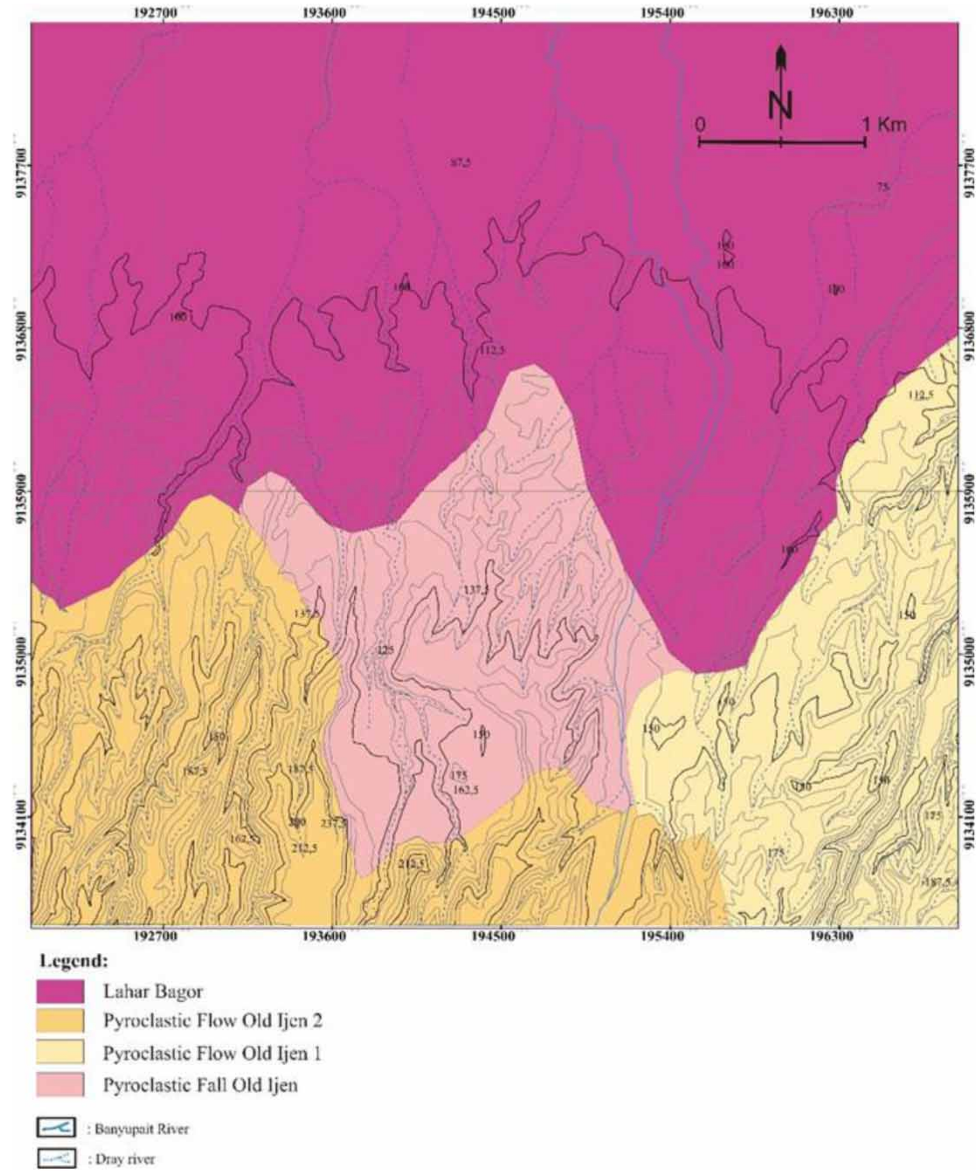

Figure 3 | Geological map of Bantal Asembagus.

for this deposit, and the fragments have a subrounded with a poorly sorted and open-packed. This rock unit has not shown good compaction, but the grain size of the fragments is relatively uniform.

Pyroclastic Flow Old Ijen 1 Unit

The Pyroclastic Flow Old Ijen 1 Unit is scattered in the eastern part of the study area with a north–south distribution with a distribution area of about 10%. This rock unit has a massive sedimentary structure, and the grain size is medium-gravel sand (0.25–64 mm). The fragments are pumice, scoria, and blocky in a volcanic ash matrix. The degree of rounding of the fragments is somewhat angular with poorly sorted sorting and open packaging. The pumice fragment was more dominant than the other fragments.

Pyroclastic Flow Old Ijen 2 Unit

The pyroclastic flows 2 unit in the study area is located in the volcanic ridge area with a north-south trending distribution in the western part of the study area. The Pyroclastic Flow 2 Unit has a distribution of about 15% in the study area. The distribution of this unit is in the western part of the lot. Massive layered sedimentary structures are often found in this rock unit and cover the underlying rock unit. The grain size of the fragments is about medium sand–gravel (0.25–64 mm) with pumice and andesite fragments that are not well sorted. The color of the lithology is blackish brown with the appearance of a normal gradation sediment structure and a slightly angular degree of rounding. The degree of sorting looks poorly sorted and shows open packaging. The fragments consist of basalt and pumice (0.25–64 mm) embedded in the volcanic ash-sand matrix. This unit shows a harder compaction level than the underlying pyroclastic deposits.

Lahar Bagor Unit

The Lahar Bagor Unit in the study area is located on the lower slopes of Ijen Volcano with an east–west distribution. This unit is the result of material breakdown from Old Ijen Volcano. The results of field observations of these pyroclastic deposits show fragments of grain size ranging from fine sand to gravel (0.125–46 mm). The fragments are composed of pumice and basalt floating above the volcanic ash matrix. The color of the lithology is blackish grey, with the degree of roundness of the fragments being angular with poor sorting, and the grain packing shows openness.

4.2. Water quality

Chemically, the Banyupait River water in the Asembagus area has a river water pH of around 3–7.3 and an SO_4^{2-} content of around 220–683 ppm. The results of the ^{18}O and D isotope analysis show that the water is meteoric water (Yudiantoro *et al.* 2022). Water quality is the nature of water and the content of living things, substances, energy, or other components in the water. Water quality is expressed in several parameters, namely physical parameters (temperature, turbidity, dissolved solids, etc.), chemical parameters (pH, dissolved oxygen, BOD, metal content, etc.), and biological parameters (presence of plankton, bacteria, etc.) (Government Regulation of the Republic of Indonesia No. 20 of 1990 concerning Water Pollution Control). Chemical elements and heavy metals observed in the study area were: pH, Fe^{3+}, SO_4^{2-}, F^-, Mn^{2+}, and Cu^{2+}. The pH value generally describes how much acidity or alkalinity water is. For example, waters with a value of $pH = 7$ are neutral, $pH < 7$ is said to be acidic, while $pH > 7$ is said to be alkaline (Effendi 2003).

Iron (Fe^{3+}) is mainly found in anaerobic and acidic waters. Therefore, deep and shallow groundwater contains a lot of high iron. The presence of iron levels can cause the color of the water to turn yellow-brown after some time in contact with the air, it can also cause unpleasant odors, and yellow spots on clothes and can cause problems or health problems for people who consume it regularly continuously (Nur 2011).

Sulfate is one of the important ions in water availability because of its essential effect on humans when its supply is in large quantities. The maximum limit of sulfate in water is around 250 mg/L for water consumed by humans (Erviana 2018).

Natural waters usually have fluorine levels of less than 0.2 mg/L. Deep groundwater has a fluorine content of up to 10 mg/L. Marine waters are around 1.3 mg/L (Effendi 2003). Fluorine can enter groundwater. The fluorine concentration in groundwater is generally higher than the fluorine concentration in surface water due to the interaction between water and rock (Pauwels 2007).

Manganese (Mn^{2+}) is a metal cation with chemical characteristics similar to iron. Manganese exists in manganese (Mn^{2+}) and manganic (Mn^{4+}) forms. In the soil, Mn^{4+} is in the form of manganese dioxide compounds. The manganese content in natural waters is about 0.2 mg/L. Higher levels can occur in deep groundwater and deep lakes. Acidic waters can contain manganese around 10–150 mg/L. Sea waters contain manganese of around 0.002 mg/L. Manganese levels in freshwater vary widely from 0.002 mg/L to more than 4.0 mg/L. On the other hand, water for agricultural irrigation in acidic soils has a manganese content of about 0.2 mg/L, while for neutral and alkaline soils, it is around 10 mg/L (Effendi 2003).

Copper (Cu^{2+}) is an essential heavy metal, so although it is toxic, it is needed by humans in small amounts. The toxicity of Cu^{2+} will only work if it has entered the organism's body in large quantities or exceeds the tolerance value of the related organism (Palar 1994). Connel & Miller (1995) stated that Cu^{2+} is an essential metal that if in low concentrations, can stimulate the growth of organisms, while in high concentrations, it can be inhibitory. Furthermore, Palar (1994) stated that aquatic biota is very sensitive to excess Cu^{2+} in the waters as a place of life. A dissolved Cu^{2+} concentration that reaches 0.01 ppm will cause the death of phytoplankton. Within 96 hours, biota belonging to Mollusca will die if the Cu^{2+} dissolved in water bodies is 0.16–0.5 ppm.

4.2.1. The river water quality

The Banyupait River, with a pH of 4–5.5 (acidic), comes from Mount Ijen Crater, flowing south to north along the study area. The quality standard used is the Class II Water Quality Standard in Government Regulation of the Republic of Indonesia No. 82 of 2001 sampling. There are four points of river water. The results of laboratory trials can be seen in Table 1.

Table 1 | Water quality of the Banyupait River

No.	Parameter	Unit	Quality standards[a]	Laboratory test results R-1	R-2	R-3	R-4
1	pH	–	6–9	4[b]	4.2[b]	4.8[b]	5.5[b]
2	Fe^{3+}	mg/L	–	2.7524	3.2344	1.5797	1.4
3	F^{-}	mg/L	1.50	0.6176	0.7233	0.5622	0.0308
4	SO_4^{2-}	mg/L	–	457	637	457	640
5	Mn^{2+}	mg/L	–	0.8376	0.006	0.8404	0.8404
6	Cu^{2+}	Mg/L	0.02	0.006	0.006	0.006	0.006

[a]Class II Water Quality Standards in Government Regulation of the Republic of Indonesia No. 82 of 2001.
[b]Not included in quality standards.

The results of river water quality tests at the research site (Figure 4) showed that the four samples of river water taken exceeded the pH quality standard, around 4–5.5. An increase in the pH value of river water samples indicates that dilution and self-purification or natural purification can be influenced by flow discharge. The fluorine and sulfate parameter values in river water samples show fluctuating values, namely up and down between river water samples R-1 to R-4. The lowest Fe concentration in the R-4 river is 1.4 mg/L, while the highest value of Fe^{3+} is in water samples R-2 river with a value of 3.2344 mg/L. The lower value of iron in river water in the downstream or north direction can be influenced by the higher Fe content in soil and rock in the upstream area. The rise and fall of water quality parameter values can be due to the influence of different flow rates on river water intake.

The river water in the research area is the Banyuputih River, with a pH of 4–5.5 (acidic) originating from the Mount Ijen Crater, flowing from south to north along the research area. Twenty years ago, Banyuputih River water was used for drinking water. However, now it is only used to drain agricultural land and drink livestock. So the quality standard used is class II

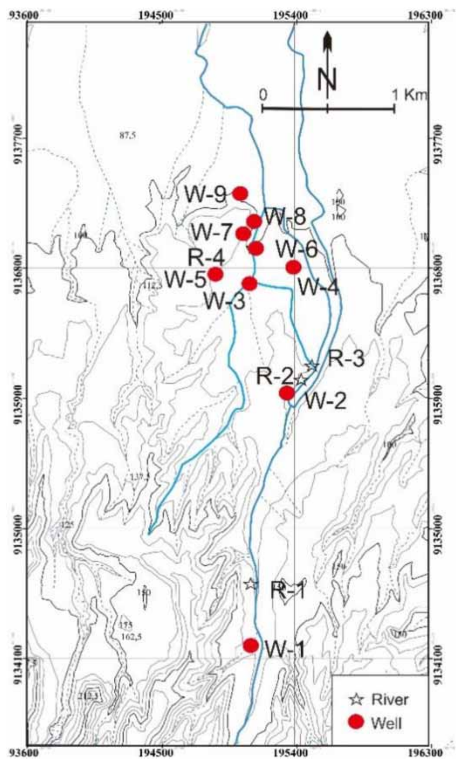

Figure 4 | Map of river water quality and groundwater in the study area.

water quality standard in Government Regulation of the Republic of Indonesia No. 82 of 2001 concerning Water Quality Management and Water Pollution Control. The sampling points of river water taken at the research location are four points which can be seen in Figure 4. The results of laboratory tests shown in Table 1 show that one parameter, namely the pH of the six parameters tested, exceeds the quality standard values set.

The results of the river water quality test at the research site showed that four samples of river water taken exceeded the pH quality standard. The low pH value in the Banyuputih River comes from the Ijen Crater water source with a pH < 1, which then flows into the Curah Macan River to the Banyupahit River with a pH of 1–2. River water sample 1 (R-1), taken from the main river (before the branch), has a pH value of 4. River water sample 3 (R-3), a river after the second western branch, has a pH value of 4.8. Meanwhile, river water sample 4 (R-4) taken in the river after the third western branch has a pH value of 5.5. River water sample 2 (R-2) is the first branch of the main river with a slight increase in pH value of 4.2. An increase in the pH value of the river water samples indicates that the occurrence of dilution and self-purification or natural purification can be influenced by flow discharge.

The fluorine and sulfate parameter values in river water samples show fluctuating values, namely ups, and downs between river water samples 1–4. Other discharges can also influence differences in water quality values in rivers, such as domestic waste (settlements). In addition, sulfate is one of the acid-forming components, so its value can affect the acidity of the water. According to Sudadi (2003), most of the element iron is found in soils containing sedimentary rocks containing iron oxides, carbonates, and sulfides. Therefore, the lower iron value in river water in the downstream or north direction can be influenced by the higher Fe content in soil and rock in the upstream area and changes in natural waterways to artificial ones. The parameter values of manganese and copper tend to be consistent in each river water sample and are below the quality standard. That indicates that dilution, flow rate, and self-purification can reduce the content of manganese and copper in the water river quite well.

The solubility of metals in water is affected by the pH value. Increasing the pH value will reduce the solubility of metals in water. That is due to a change in the form of carbonates into hydroxides, forming bonds with particles of water bodies so that they settle. The content of chemical elements and heavy metals will increase when there is a decrease in pH. Dilution and water flow can affect the concentration of heavy metals in water, and dilution can reduce metal concentrations in water (Effendi 2003). The acidic Banyuputih River water can dissolve chemical elements and heavy metals from Mount Ijen Crater water's seepage and contaminate the surrounding groundwater.

4.2.2. Groundwater quality

The people of Bantal Village use well water or groundwater for drinking, cooking, bathing, and toileting. So that the quality standard used is the standard Water Quality Class I Government Regulation of the Republic of Indonesia No. 82 of 2001 and Quality Standards for Sanitary Hygiene Requirements Regulation of the Minister of Health No. 32 of 2017. Groundwater quality testing was carried out by taking groundwater samples from nine different wells, generally, the depth of the wells was around 20–30 m (Figure 4). The results of laboratory examinations can be seen in Figure 5 and Table 2. The results of laboratory tests can be seen in Figure 5 and Table 2.

The results of water quality testing on groundwater samples at the research site show that two parameters exceed the quality standard. Fluorine and sulfate are parameters that exceed the quality standard. The fluorine content in groundwater sample W-2 is 0.6171 mg/L and water sample W-4 is 0.6870 mg/L, exceeding the Class I Water Quality Standard. Government Regulation of the Republic of Indonesia No. 82 of 2001 is 1.5 mg/L. The sulfate content of groundwater samples W-1 to W-9 ranged from 325 to 683 mg/L to exceed the Class I Water Quality Standard of Government Regulation of the Republic of Indonesia No. 82 of 2001 and the Environmental Health Quality Standard for Water Media for Sanitary Hygiene Needs Regulation of the Minister of Health No. 32 of 2017 is 400 mg/L.

The type of river in the research area is influent so that river water can infiltrate and then enter the aquifer and pollute groundwater. Based on geological mapping, groundwater aquifers are found in the pyroclastic falls Old Ijen unit. The parameters tested apart from fluorine and sulfate had levels that did not exceed quality standards. Fluorine values that exceed the quality standard in groundwater samples 2 (W-2) and groundwater 4 (W-4) can be influenced by the distance of the river to the well and the direction of groundwater flow to low areas.

The sulfate value in groundwater samples has a fluctuating value and exceeds the quality standard, this is because groundwater flow and aquifer types in the study area are composed of breccias and sandstones that easily pass water (Isnaini 2010). Therefore, parameters of fluorine and sulfate in groundwater that do not follow quality standards can affect public health if

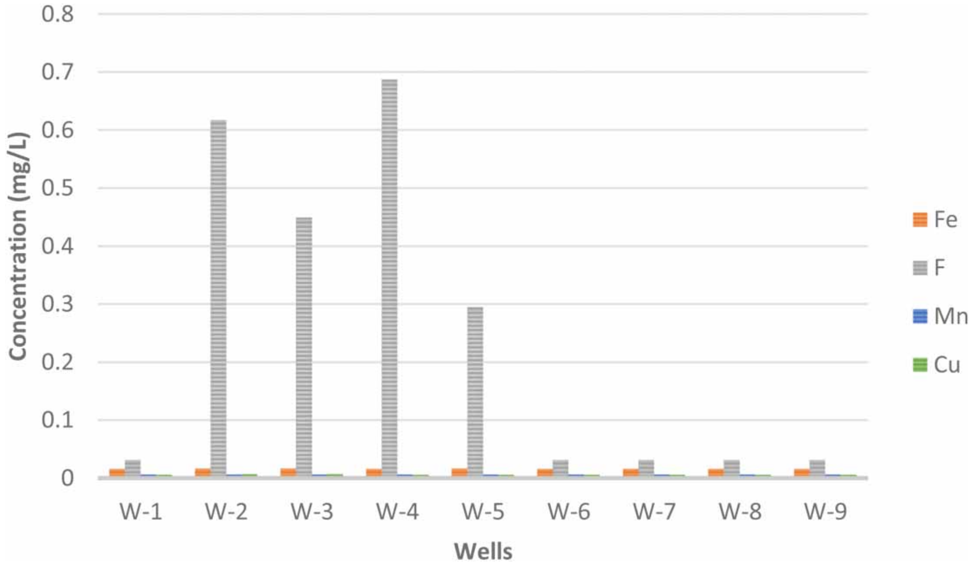

Figure 5 | Quality of well water around the Banyupait River from upstream in Bantal Village to the river mouth.

Table 2 | Groundwater quality from shallow wells in the study area

No.		**Parameter**					
Unit	**Sample**	**pH** –	**Fe^{3+}** mg/L	**F^{-}** mg/L	**SO_4^{2-}** mg/L	**Mn^{2+}** mg/L	**Cu^{2+}** mg/L
Quality standards 1		6.5–8.5	1.0	1.5	400	0.5	0.02
1	W-1	6.5	<0.0162	<0.0308	422	<0.0066	<0.0060
2	W-2	6.5	<0.0168	0.6171	177	<0.0066	0.0071
3	W-3	6.0	<0.0168	0.4491	454	<0.0066	0.0071
4	W-4	6.5	<0.0162	0.6870	630	<0.0066	<0.0060
5	W-5	6.5	<0.0168	0.2946	325	<0.0066	<0.0060
6	W-6	6.4	<0.0162	<0.0308	643	<0.0066	<0.0060
7	W-7	6.3	<0.0162	<0.0308	683	<0.0066	<0.0060
8	W-8	6.0	<0.0162	<0.0308	426	<0.0066	<0.0060
9	W-9	6.4	<0.0162	<0.0308	496	<0.0066	<0.0060

consumed for a long time. The pH value ranges from 6 to 6.5, indicating that the pH of groundwater in the specific study area can be influenced by the type of aquifer, rock type, permeability, geological structure, and the slope of the rock through which water passes below the surface.

The concentration of fluorine in groundwater is influenced by the concentration of fluorine in rocks, the residence time of water in rocks, pH, the presence of ions and colloids, temperature, the ion exchange capacity of the aquifer, and the content of Ca^{2+} and HCO^{3-} ions in the water. The pH value influences the solubility of fluorine in groundwater at pH 5–6.5; the solubility of fluorine in water tends to be low (Yidana *et al.* 2012). The degree of rock solubility interaction can increase the dissolution of fluorine-containing minerals in the rock. Groundwater flowing through granite rocks has a higher fluorine content than that drained by sedimentary and metamorphic rocks (Ramamohana *et al.* 1993).

The increase in fluorine concentration is influenced by the groundwater table's depth, which causes groundwater's residence time in the aquifer to be longer (Saxena & Ahmed 2001). The sulfate concentration in groundwater is in a depressed aquifer, so there are naturally many sulfur minerals or evaporite rocks (Gourcya 2013). The aquifer in the study area consists of breccia and sandstone, affecting the higher fluorine and sulfate content in the groundwater, and the higher depth of the groundwater table is 15–35 meters causing a longer residence time of groundwater.

The pH of groundwater in the study area is included in the Class I Water Quality Standard. Government Regulation of the Republic of Indonesia No. 82 of 2001 is pH 6–9 and shows a normal pH. When the pH is expected, the metal will tend to precipitate. Fe^{3+}, Cu^{2+}, and Mn^{2+} elements in groundwater are also influenced by the length of contact time between water and soil and aquifers, namely the time since the water enters the soil (recharge time) (Ayotte 2011).

4.3. Dental fluorosis

Dental fluorosis is an abnormality of the enamel structure with spots or defects (mottled enamel) as a result of excessive fluoride intake during the formation of teeth. The disorders occur in tooth deformity (hypoplasia) and tooth discoloration (hypo calcification). The appearance of shiny white spots characterizes them, as white lines crossing, blurry, yellow to brown colors on the surface of tooth enamel (Mariati 2015). Fluorine in drinking water has been shown to inhibit the occurrence of dental caries, but excessive consumption during the remineralization period will result in dental fluorosis (Agtini & Sintawati 2005).

The results of water quality testing on groundwater samples at the research location showed that two parameters exceeded the quality standard. Fluorine and sulfate are parameters that exceed quality standards. The fluorine content in groundwater sample W-2 was 0.6171 mg/L and in sample W-4 was 0.6870 mg/L, exceeding the Class I Water Quality Standard from Government Regulation of the Republic of Indonesia No. 82 of 2001 is 1.5 mg/L. Meanwhile, the content of sulfate in the groundwater samples also exceeded the Class I Water Quality Standards from Government Regulation of the Republic of Indonesia No. 82 of 2001, namely 325–683 mg/L as represented by samples 1–9. Apart from that, it also exceeds the value of the Environmental Health Quality Standard for Water Media for Sanitation Hygiene Needs, Minister of Health Regulation No. 32 of 2017 is 400 mg/L.

The type of river in the study area is influent so that river water can experience infiltration and then enter the aquifer and contaminate groundwater. The value of fluorine that exceeds the quality standard in groundwater samples 2 (W-2) and groundwater 4 (W-4) can be influenced by the distance from the river to the well and the direction of groundwater flowing to low areas. In addition, the increase in fluorine concentration is controlled by the depth of the groundwater table. The pH value ranged from 6 to 6.5, indicating that the pH of the groundwater in the study area was normal. This can be influenced by the type of aquifer, rock type, rock permeability, geological structure, and the slope of the rock through which water passes below the surface. While the concentration of sulfate is high in groundwater, it will increase the sulfur mineral content in groundwater. The pH of groundwater in the study area is included in the Class I Water Quality Standard. Government Regulation of the Republic of Indonesia No. 82 of 2001 is pH 6–9 and shows a normal pH. When the pH is expected, the metal will tend to precipitate (Ayotte 2011).

People in Bantal Village consume well water for their daily needs. Well water is used for cooking and drinking, but if the well is dry, the community uses other water sources from other village springs. In addition, the community also consumes local foodstuffs whose agricultural land is drained by the Banyupait River, such as rice and chili. Therefore, the pattern of water and local food consumption is significant and affects the incidence of dental fluorosis. In addition, exposure to drinking water in adults lasts longer, so they are more likely to experience dental fluorosis. So far, to overcome the incidence of dental fluorosis, the people of Bantal Village have had to let the water sit overnight before boiling the water. Then after boiling, the water can be consumed as drinking water and for food processing. Apart from that, this can be done using membrane technology, which is one of the most effective and promising technologies for effectively removing metal elements from drinking water and wastewater (Acarer 2023). Or use other filter media such as activated carbon, zeolite, anthracite, and coconut shell (Joko 2010).

Based on the results of interviews, people in Bantal Village have been consuming well water for 20–40 years. However, in children who have consumed well water since birth, symptoms of early dental fluorosis can also appear in the form of white incision lines on the teeth. In addition, a person's level of education can also affect the presence of symptoms of dental fluorosis. The last education level is Elementary School, which tends to be more susceptible to dental fluorosis due to lack of information and knowledge about health and water consumption and tends to stay in Bantal Village for the rest of their life (not wandering).

The accumulation of extended exposure to drinking water causes symptoms of dental fluorosis in the early stages of children to the late stages as adults, which is marked by a change in the color of the teeth to brown. Therefore, almost all the people of Bantal Village who are included in the adult age category experience dental fluorosis.

The results showed that there were 105 people with symptoms of dental fluorosis from 111 samples in the study area, so the prevalence rate of patients with dental fluorosis was 94.59%. Therefore, the prevalence value of patients with dental fluorosis in the study area is high, as indicated by the number of old and new cases of dental fluorosis. Prevalence is the number of people in a population who suffer from the disease at a specific time, which in this study is October 2020 (Sulistiani 2014).

Dental fluorosis can occur in both men and women. Based on the data from community interviews that have been conducted, the distribution of the number of female dental fluorosis sufferers is 60 people (57%), and men are 45 people (43%) data can be seen in Figure 6.

All age groups can be affected by dental fluorosis, but in this study, data were obtained that the age group 16–45 years (adults) had the highest distribution of dental fluorosis. As many as 44 people (42%) are compared to other age groups. On the other hand, the age group is 0–5 years (toddlers) and 12–15 years (adolescents). The age group with the lowest prevalence of dental fluorosis, namely seven people (7%), age group 6–11 years (children) 14 people (13%), and the elderly age group (>45 years) 33 people (31%) the data can be seen in Figure 7.

Based on the calculation results, the distribution of dental fluorosis in the study area is dominated by the community with female sex in the age group 16–45 years (adults). The adult age group has been consuming groundwater for a long (long exposure duration), so they are more susceptible to dental fluorosis. A red zone marks the distribution of the incidence of

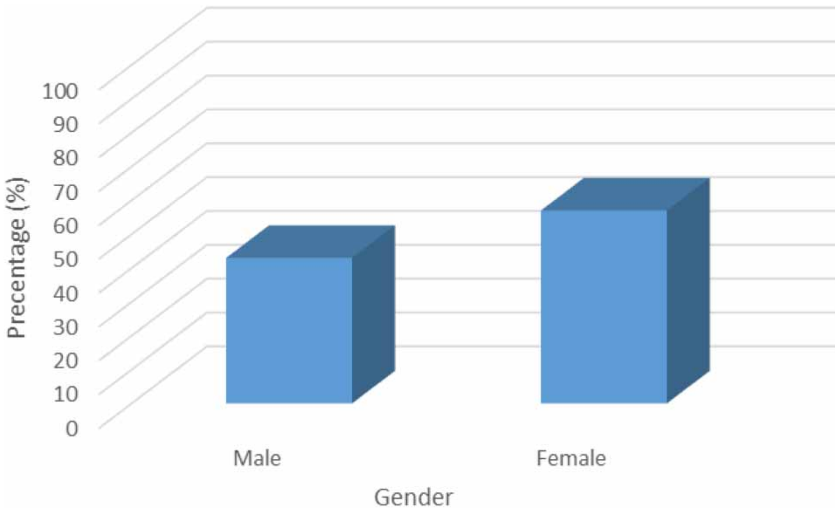

Figure 6 | Distribution of patients with dental fluorosis by gender in the study area.

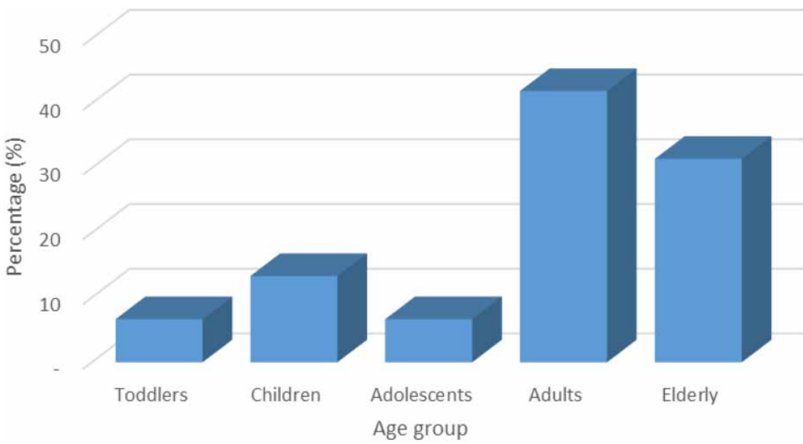

Figure 7 | Distribution of dental fluorosis patients by age group in the study area.

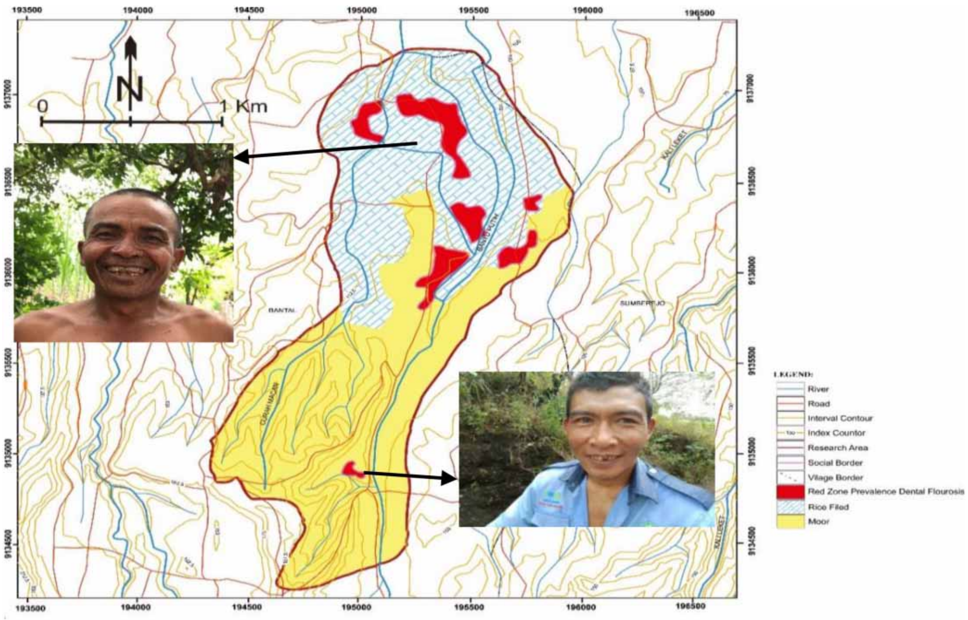

Figure 8 | Distribution of dental fluorosis incidence.

dental fluorosis in the study area. The zone is included in the very high prevalence of 94.59%. The distribution of dental fluorosis in the study area can be seen in Figure 8.

5. CONCLUSIONS

The Bantal area is composed of pyroclastic deposits from the eruption of Old Ijen Volcano and lahar deposits. Above this lithology flows the Banyupait River, whose water comes from the seepage of Ijen Crater, which has a very acidic pH and contains several heavy metal elements. From the upper reaches of the Banyupait River, this river branches into the west and east Banyupait Rivers. Finally, both rivers empty into the north coast of the Asembagus area.

The results of the chemical analysis of river water show that river water at the research site has one parameter that exceeds the quality standard, namely the pH parameter. The west branch of the Banyupait River experienced a dilution with a pH value of 4.2–5.5, and the east branch of the Banyupait River was the main river flow with a pH value of 4.

Meanwhile, the results of the chemical analysis of groundwater at the research location have two parameters that exceed the quality standards for fluorine and sulfate, namely fluorine of 0.6171–0.6870 mg/L. On the other hand, sulfate ranges between 325 and 683 mg/L. The chemical characteristics of this groundwater are stored in the pyroclastic falls Old Ijen unit.

Therefore, the groundwater quality in the study area affects the health of the people living around the study area. Symptoms of dental fluorosis indicate the declining level of public health around the river. The groundwater quality parameters affecting dental fluorosis symptoms are fluorine and sulfate. In contrast, the community factors most susceptible to dental fluorosis are people in the category of adult age, and the last level of education is elementary school. People who are exposed to fluorine and sulfate are generally people who live around the Banyupait River and these elements come from the water from the Ijen Volcano crater which seeps into the Banyupait River.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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