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Physicochemical properties and heavy metal concentrations in the drinking water of San Francisco, Agusan Del Sur, Philippines

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Abstract

Concerned about the safety of public drinking water supply, this study delved into the drinking water system in San Francisco, Agusan del Sur, Philippines. There were two areas of concern in this study: the physicochemical properties which include alkalinity, conductivity, pH, salinity, total dissolved solids (TDS), total hardness, total suspended solids (TSS), and turbidity; and the heavy metal contaminants which include cadmium, chromium, cobalt, copper, lead, manganese, and nickel. The physicochemical properties and chemical contaminants present in both untreated and treated water were described based on their measured levels and were evaluated using the PNSDW 2017 and WHO-GDWQ. The findings showed that there is a decrease of levels in conductivity, TSS, turbidity, and manganese after the water treatment. The levels of total hardness at 303.02 mg/L fail to conform to the PNSDW 2017 and WHO-GDWQ standards while the rest of the physicochemical properties (alkalinity, conductivity, pH, salinity, TDS, total hardness, TSS, and turbidity) are under the maximum allowable level (MAL). The levels of Cadmium, Chromium, Copper, Lead, Manganese, and Nickel are lower than the MAL value of the PNSDW 2017 and WHO-GDWQ. Manganese, which has no health-associated risk but might affect water acceptability, is measured at 0.008 mg/L and is lower than the MAL at 0.4000 mg/L in both standards. Generally, the water is not acceptable for drinking due to high levels of total hardness. Other mandatory parameters for microbiological quality are recommended to determine the suitability of the drinking water for human consumption.

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Introduction

Drinking water quality is one of the greatest factors affecting human health. However, the quality of the drinking water in many nations, particularly those that are developing, is not ideal, and this has led to an increase in the number of waterborne illnesses (Li and Wu, 2019).

Water pollution (surface and ground) may be considered as a naturally induced change in water quality or conditions induced directly by man's numerous activities which render it unsuitable for food, human health, industry, agriculture, or leisure per suit (Dix, 1981). Toxic chemicals in water pose the greatest threat to the safety of drinking water and their effects are enormous and can cause damage to human health, crops, and aquatic organisms.

Synthetic chemicals such as herbicides and insecticides as well as fertilizer runoffs from agricultural farmlands and industrial discharge have the potential to impact negatively on human health since they block vital metabolic processes in the body. Runoffs from domestic houses, solid waste dumps, and commercial establishments may contain detergents and nutrients, which causes algae blooms in water bodies leading to eutrophication. Human waste excreta may contain a concentrated population of bacteria, pathogenic bacteria in untreated sewage, and may cause acute gastrointestinal illness. This phenomenon has rendered most surface water bodies polluted (Anim *et al.*, 2010; Osei and Duker, 2008; Asante *et al.*, 2008).

In the Philippines, water contamination of the surface water is due to exposure of chemicals which has been rampant, especially in areas exposed to industrial processes, such as but not limited to mining, agricultural processing, manufacturing, farming, and aquaculture according to Philippine Environment Monitor (Jalilov, 2017). Caraga, the mining capital of the Philippines, has more than 15 mining companies distributed in the region. Two of the mining companies are specifically located in Agusan del Sur which might have been affecting the Magdiwata Watershed which supplies water to the Municipality of San Francisco, Agusan del Sur (PSA, 2020).

The river network of Magdiwata Watershed extends from various municipalities of the province and is vulnerable to chemical contaminations. Periodic assessment of Magdiwata river networks has been conducted by the San Francisco Water District to ensure that the public water is free from waterborne microbes and chemical contaminants. However, external assessment, surveillance and/or monitoring must be done also to validate the test findings of the local supplier. Additional and external assessments for public drinking water support the integrity of water quality management.

As such, this research assessed the physicochemical properties and heavy metal contaminants in the public water system of San Francisco, Agusan del Sur before and after water treatment. Additionally, the assessment findings were evaluated against the existing and recent local and international drinking water standards which provided a picture of its general usability for drinking and utility purposes.

Materials and methods

Study area

The water assessed in this research is the public drinking water of San Francisco, Agusan del Sur. Aside from proximity advantage, the researcher identified the said research locale due to the immediate social contribution that the study can provide through information dissemination as this research served as an external assessment to the quality of water consumed by more than 8,093 consumers (active connections as of May 2019) of the 19 out of 27 Barangays in Agusan del Sur (SFWD, 2020).

San Francisco is one of the 14 municipalities in Agusan del Sur with a land area of 392.53 km^2. It has 27 barangays and a population of 74,542 constituting to 10.63% of the province's total population (Census of Population, 2015). The municipal center of San Francisco is situated at approximately 8° 30' North, 125° 59' East, on the island of Mindanao. Elevation at these coordinates is estimated at 33.7 meters or 110.5 feet above mean sea level (PhilAtlas, 2016). The municipality's lush forest is situated in Mt. Diwata. The Mt. Diwata was declared as a permanent watershed and forest reserve by virtue of President Proclamation No. 282 dated October 25, 1993, signed by then President Fidel V. Ramos. This issuance from the Office of the President has increased the forest cover from 42% in 1997 to 92% in 2015. Household occupants within the protected area also decreased from 176 in 1997 to 43 in 2019 (SFWD, 2020). The watershed in Mt. Diwata is the life source of all water resources in the locality that sustain the supply of water in San Francisco, Agusan del Sur.

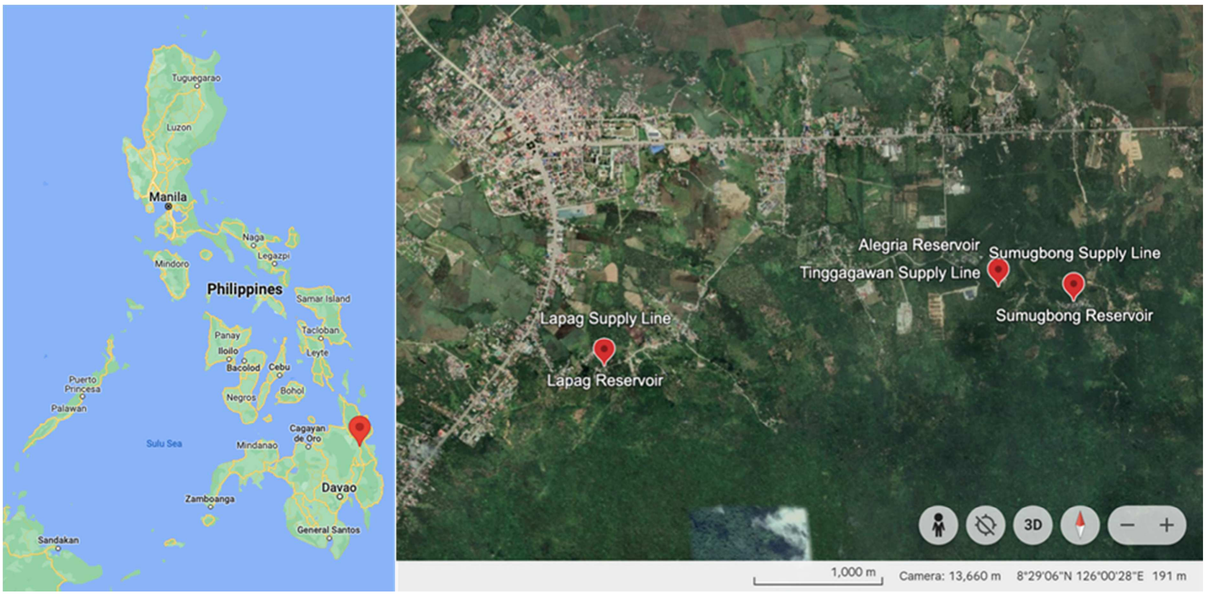

Fig. 1. Map of San Francisco, Agusan del Sur, Philippines

Table 1. Sampling scheme for untreated and treated water

Sample code	Sample type (Water)	Latitude	Longitude	Collection place	Sampling period
1A	Untreated	8°28'54.74"	126°00'059.33"	Sumugbong Supply Line	Once a month for three (3) consecutive months
2A	Untreated	8°29'08"	126°00'03"	Tinggangawan Supply Line	
3A	Untreated	8°29'19"	125°59'35.1"	Lapag Supply Line	
1C	Treated	08°29'46.81"	126°0'55.08"	Sumugbong Reservoir	
2C	Treated	8°29'35.37"	126°0'2.05"	Alegria Reservoir	
3C	Treated	08°29'10.52"	125°59'35.30"	Lapag Reservoir	

Fig. 1 below shows the map of the Municipality of San Francisco, Agusan del Sur located in Region 13 (Caraga Region), Philippines.

Sampling scheme

San Francisco, Agusan del Sur has one (1) public drinking water distribution system (DWDS) that sources its water from eleven surface waters located in three Barangays—Brgy. Alegria, Brgy. Karaos, and Brgy. Bayugan II. Among these eleven raw water sources, nine of them dominantly supply drinking water in San Francisco's industrial and suburban areas. The water from these nine sources undergoes pre-filtration, sedimentation, and chlorination stages until they are stored in three reservoirs—Sumugbong Reservoir in Brgy. Alegria, Alegria Reservoir, in Brgy. Alegria, and Lapag Reservoir in Brgy. Karaos. Because they are the main sources of public drinking water in San Francisco which provides potable water to the majority of the population, the researcher selected them as the focus of the study. Table 1 shows the sampling scheme used in this study.

The sampling period was conducted for a period of three (3) months with a once-a-month sampling frequency from three major supply lines (for untreated water) and their corresponding reservoirs (for treated water). Untreated water were collected at the supply lines of Sumugbong, Tinggangawan (both found in Brgy. Alegria) and Lapag (found in Brgy. Karaos). These supply lines are connected to the collection box (Fig. 2), and sample collection is done through a faucet. The same sample collection is implemented for treated water through a faucet from the reservoir (Fig. 3).

Fig. 2. Collection box

Fig. 3. Reservoir

Untreated water samples collected through faucet cover changes in physicochemical properties that happened during water transit from surface water down to the collapsible dam before the raw water reached the collection box. These changes might have affected the quality of water being treated. In the same sense, the researcher collected samples of treated water at the reservoirs' outlet faucet to limit the changes in physicochemical properties that might happen during water distribution.

Sampling requirements (container material, minimum volume sample, mode of preservation, and holding time) set in Annex D of the Philippine National Standards for Drinking Water (PNSDW) 2017 were adopted by the researcher. 250 mL sealed polyethylene bottles were used in the collection of treated and untreated water. These bottles which are free from bacterial and chemical contaminants were carried to the sampling sites using sealed thermoresistant polystyrene boxes. At the sampling site, the faucet was flushed in three minutes thereby stabilizing the water temperature and flushing the stocked sediments. The sample bottle was then unsealed carefully and rinsed with water samples. The bottle was positioned carefully not to touch the faucet orifice. After filling the bottle, the lid was carefully covered the bottle. Sample bottles were stored back in the polystyrene boxes containing ice for sample preservation until they were analyzed in the laboratory of the University of Science and Technology of Southern Philippines.

The DWDS of San Francisco, Agusan del Sur distributes its treated water through a multi-valve system. This means that all treated water coming from the reservoirs passes through the main pipe. They are controlled by individual valves so that when one reservoir fails to supply water, the other reservoirs can still provide treated water to households. The said DWDS does not implement localization during water distribution. No reservoir is intended to directly supply water to a specific locality. With this composite water collection technique, the researcher mimicked the sample preparation. At the laboratory, equal parts of untreated water from the three supply lines were mixed before analyses. The same sample preparation was also implemented for treated water samples.

Data collection methods

Physicochemical parameters

Alkalinity, conductivity, pH, salinity, total dissolved solids, total hardness, total suspended solids, and turbidity are the physicochemical parameters analyzed in the study. The pH was determined using a pH meter (Hach sensION+ portable pH meter). The conductivity, total dissolved solids, and salinity were analyzed using a multi-meter (Hach sensION 5 meter). For the turbidity of the treated and untreated water samples, a turbidimeter (Hach 2100Q portable turbidimeter) was used. On the other hand, the standard EDTA titration method (PCARRD, 1991) was used in analyzing the samples' total hardness.

Heavy metal contaminants

In the determination of the heavy metal contaminants in the sample water, the researcher obtained 200 to 300 mL of water sample and placed the sample into a digestion flask. The sample was concentrated by heating and allowing the sample to evaporate until the sample size lowered to approximately 5 to 10 mL. The sample was then cooled down, and a 20-mL of concentrated sulfuric acid was added. The sample was digested in a hot plate under a fume hood for 1 to 2 hours. As the digestion was completed, a 2-mL H_2O_2 was added and continued heating for 30 minutes. The sample solution was then cooled down to room temperature. The flask's inside was rinsed with 50 mL of distilled water. The solution was filtered using ordinary filter paper and received filtrate to 100 mL volumetric flask. The solution was diluted to the mark. The solution was then tested in the atomic absorption spectrophotometer (Perkin Elmer Analyst 200), and determined the metal concentration. The concentration of metals in the samples was based on the standard calibration curve obtained by running three standard solutions of known metal concentration in the flame atomic absorption spectroscopy.

Data analysis

Arithmetic mean was used to determine the average level of every parameter measured in every sample. Independent-sample t-test was used in determining any significant differences between the levels of the physicochemical characteristics and heavy metal contaminants before and after the water treatment. The levels of physicochemical characteristics and heavy metal contaminants determined in the treated water were compared against the maximum allowable levels (MAL) of the PNSDW and World Health Organization (WHO) Guidelines for Drinking Water Quality (GDWQ) standards. Measured levels above the MAL are considered unacceptable based on their associated health risks.

Results and discussion

Physicochemical properties

The results of the physicochemical properties of the drinking water system before and after the water treatments are shown in Table 2. Mean comparison of the levels of the physicochemical properties before and after water treatment is shown in Table 3. Generally, these physicochemical properties have no associated health-risks but are important operational water quality parameters.

Table 2. Physicochemical properties of the drinking water system before and after the water treatment

Physicochemical properties	Untreated water		Treated water		Maximum allowable level (MAL)	
	$\bar{x}$	sd	$\bar{x}$	sd	PNSDW 2017	WHO GDWQ
Alkalinity (mg/L)	89.58	49.80	84.78	46.21	no guideline	[b]300.0**
Conductivity (µS/cm)	224.33	20.00	208.20	12.34	no guideline	[b]750.0**
pH	7.21	0.49	6.99	0.29	6.50–8.50	[a]6.50-8.50**
Salinity (ppt)	0.10	0.00	0.10	0.00	no guideline	[b]100.0*
TDS (mg/L)	120.14	11.80	112.47	8.11	600.00	[a]600.0*
Total Hardness (mg/L)	315.56	55.93	303.03	40.93	300.00	[a]300.0*
TSS (mg/L)	3.1×10^{-4}	$1.3\text{x}10^{-4}$	1.8×10^{-4}	8.3×10^{-4}	no guideline	[c]20.0*
Turbidity (NTU)	0.50	0.15	0.36	0.09	5.00	[a]5.0*

[a]WHO (2017), [b]WHO (2011), [c]WHO (2004)

*Not of health concern at levels found in drinking water. May affect the acceptability of drinking water.

**Not of health concern at levels found in drinking water. Important operational water quality parameter.

Table 3. Independent sample t-test of the physicochemical properties

Physicochemical properties	t	df	p
Alkalinity	0.212	16	0.417
Conductivity	2.059	16	0.028
pH	1.133	16	0.137
Salinity	NaN[a]		
TDS	1.611	16	0.063
Total Hardness	0.529	16	0.302
TSS	2.634	16	0.009
Turbidity	2.327	16	0.017

For all tests, the alternative hypothesis specifies that the levels of physicochemical properties in the untreated water are greater than treated water.

[a]The variance in Salinity is equal to 0 after grouping.

Table 4. Concentrations of selected heavy metals in drinking water before and after water treatment

Heavy metal contaminants (ppm)	Untreated water		Treated water		maximum allowable level (MAL)	
	$\bar{x}$	sd	$\bar{x}$	sd	PNSDW 2017	WHO GDWQ
Cadmium (Cd)	0.004	0.002	0.004	0.002	0.003	0.003
Chromium (Cr)	0.013	0.007	0.009	0.005	0.050	0.050
Cobalt (Co)	0.009	0.004	0.006	0.001	no guideline	no guideline
Copper (Cu)	0.020	0.013	0.014	0.007	1.000	2.000
Lead (Pb)	0.025	0.028	0.011	0.011	0.010	0.010
Manganese (Mn)	0.015	0.006	0.008	0.005	0.400	0.400
Nickel (Ni)	0.016	0.009	0.011	0.002	0.070	0.070

Table 5. Independent sample t-test of the heavy metal contaminants

Heavy metals	t	df	p
Cadmium (Cd)	0.364	16	0.360
Chromium (Cr)	1.485	16	0.078
Cobalt (Co)	1.781	9.179	0.054[a]
Copper (Cu)	1.138	16	0.136
Lead (Pb)	1.383	16	0.093
Manganese (Mn)	2.802	16	0.006
Nickel (Ni)	1.370	16	0.095

For all tests, the alternative hypothesis specifies that the levels of physicochemical properties in the untreated water are greater than treated water.

[a]Welch t-test is used due to cobalt's unequal variances.

The levels of conductivity, TSS and turbidity of the treated water have significantly reduced when compared to its untreated form. However, there is no significant decrease in the levels of alkalinity, pH, TDS, and total hardness despite water treatment.

The results are similar to the findings of Sastry *et al.* (2013) where there is a decrease in the values of physicochemical properties of water after the treatment of municipal water. The aforementioned values include the pH, conductivity, turbidity, TSS, and TDS. Banana *et al.* (2016), in their study on the Quality of Drinking Water from Wells and Water Treatment Plants at West Libya also showed similar results to the findings where the physicochemical properties measured before and after the water treatment at five (5) water treatment plants revealed a decrease of values denoting an improvement of water quality.

Heavy metal contaminants

Five (5) of the selected heavy metals reflected in Table 4 have associated health risks. These are cadmium, chromium, copper, lead, and nickel. Cobalt has no guideline value from both PNSDW 2017 and WHO-GDWQ standards, while manganese may only affect the acceptability of the drinking water. Their mean comparison using independent-sample t-test is shown in Table 5.

Table 6. Levels of physicochemical properties in the drinking water system and their conformity to PNSDW and WHO-GDWQ

Physicochemical properties	Levels (Treated water)	Conformity based on maximum allowable level (MAL)			
		PNSDW (2017)	Conformity	WHO GDWQ	Conformity
Alkalinity (mg/L)	84.78	-	-	300.00[b]	Passed
Conductivity (µS/cm)	208.20	-	-	750.00[b]	Passed
pH	6.99	6.5–8.5	Passed	6.5–8.5[a]	Passed
Salinity (ppt)	0.10	-	-	100.00[b]	Passed
TDS (mg/L)	112.47	600.00	Passed	600.00[a]	Passed
Total Hardness (mg/L)	303.03	300.00	Failed	300.00[a]	Failed
TSS (mg/L)	$1.8x10^{-4}$	-	-	20.000[c]	Passed
Turbidity (NTU)	0.36	5.0000	Passed	5.0000[a]	Passed

[a]WHO (2017), [b]WHO (20011), [c]WHO (2004)

Table 7. Levels of heavy metal contaminants in the drinking water system and their conformity to PNSDW and WHO-GDWQ

Heavy metal contaminants	Levels (Treated water)	Conformity based on maximum allowable level (MAL)			
		PNSDW (2017)	Conformity	WHO GDWQ	Conformity
Cadmium (Cd)	0.0017 mg/L	0.0030 mg/L	Passed	0.0030 mg/L	Passed
Chromium (Cr)	0.0000 mg/L	0.0500 mg/L	Passed	0.0500 mg/L	Passed
Cobalt (Co)	0.0047 mg/L	-	-	-	-
Copper (Cu)	0.0140 mg/L	1.0000 mg/L	Passed	2.0000 mg/L	Passed
Lead (Pb)	0.0000 mg/L	0.0100 mg/L	Passed	0.0100 mg/L	Passed
Manganese (Mn)	0.0077 mg/L	0.4000 mg/L	Passed	0.4000 mg/L	Passed
Nickel (Ni)	0.0000 mg/L	0.0700 mg/L	Passed	0.0700 mg/L	Passed

Only the level of Manganese has significantly decreased after the water was treated. There is no significant decrease in the levels of cadmium, chromium, cobalt, copper, lead and nickel despite water treatment.

The results are similar to the findings of Kotoky and Sarma (2017), in their comparison of treatment efficiencies of the water treatment plants in Guwahati City of Assam, India, where the treated water from the six (6) water treatment plants has lower levels of Pb and Mn as compared to the untreated water.

The levels of physicochemical properties of the treated drinking water of San Francisco, Agusan del Sur, and their conformity to PNSDW 2017 and WHO-GDWQ are reflected in Table 6. Generally, the physicochemical properties, except the total hardness, passed both PNSDW 2017, and WHO-GDWQ standards. Similarly, the levels of all heavy metals reflected in Table 7 are below the maximum allowable levels of the PNSDW 2017, and WHO-GDWQ standards.

PNSDW 1993, 2007, and 2017 issuances contain guideline values for pH, TDS, total hardness, and turbidity only. Based on the maximum allowable level (MAL) indicated in the PNSDW 2017, the recent local guidelines in the Philippines, levels of measured pH, TDS, and turbidity conform with the aforementioned standards, except for total hardness at 303.03 mg/L slightly beyond the acceptable MAL at 300.00 mg/L.

WHO water quality standards have a wider reference for the conformity of the physicochemical properties of drinking water with reference to WHO's issuances in 2004, 2011, and 2017. Based on WHO-GDWQ, 4th Edition (2017), among the measured pH, TDS, total hardness, and turbidity, only the total hardness, measured at 303.03 mg/L, fail to conform with the MAL of 300.00 mg/L. Based on WHO-GDWQ in 2011, the measured alkalinity, conductivity, and salinity passed the MAL. Lastly, per WHO-GDWQ in 2004, the measured TSS at $1.8x10^{-4}$ mg/L passed the MAL at 20.00 mg/L.

The indicators above, though they do not have associated health risks, are important parameters that may affect the consumers' acceptability for drinking water, and the operational processes of the water treatment plants. The measured salinity at 0.10 ppt is described as "fresh" and thus can be used in both drinking and in all types of irrigation use per Classification of Water Adopted from the Department of Water, Government of Western Australia (2013). The measured TDS at 112.47 mg/L is described as "excellent" per Acceptability Scale of Total Dissolved Solids, while the measured hardness at 303.03 mg/L may increase scaling problems per Degrees of Hardness in ADWG 2011.

The levels of cadmium, chromium, copper, lead, manganese, and nickel are lower than the maximum allowable value of the aforementioned metals based on the guideline values found in the PNSDW 2017 and WHO-GDWQ 2017. Copper's MAL per PNSDW 2017 and WHO-GDWQ 2011 varies at 1.0000 mg/L and 2.0000 mg/L. Either way, the measured level of copper at 0.0140 mg/L passed the two different guideline values. Manganese, which has no health-associated risk but might affect water acceptability, is measured at 0.0077 mg/L and is lower than the MAL at 0.4000 mg/L in both standards. Cobalt measured at 0.0047 mg/L has no guideline value for both PNSDW and WHO Guidelines for Drinking Water Quality due to the unverified health risk of the said element.

In small quantities, certain heavy metals are nutritionally essential for a healthy life but they become toxic when they are not metabolized by the body and accumulate in the soft tissues.

Conformation with the set standards for drinking water by both the international, and national is of paramount importance because of the capacity of water to spread a myriad of contaminants that are harmful to health especially when consumed in excess amounts. The data in Table 7 above are similar to the findings of Lasheen *et al.* in 2008. The levels of cadmium, chromium, copper, lead, manganese, and nickel in the final effluent were less than that of the intake water in some water treatment plants in Greater Cairo, Egypt. The levels of the heavy metals laddered down when the intake of water passed several treatment steps after coagulation and sedimentation. In their assessment, the aforementioned heavy metals were less than the MAL of the WHO, and their national drinking water quality standards (Egyptian drinking water standards).

Conclusion

Based on the research findings, the multistage filtration processes effectively reduced heavy metal concentrations and physicochemical parameters in the untreated water, which is crucial for mitigating associated health risks. Regular monitoring of water quality against established standards enables the public water system to identify and improve specific filtration stages, ensuring safe drinking water delivery. While most physicochemical parameters in the treated water met both PNSDW and WHO-GDWQ standards, total hardness exceeded the maximum allowable value, suggesting a need for improvement to enhance consumer acceptability. Notably, the treated water's heavy metal levels fell below maximum allowable values, making it suitable for human industrial and agricultural applications. Its suitability to human consumption can be determined if other mandatory parameters for drinking water quality are included. The assessment of drinking water quality emphasizes the importance of monitoring causal factors like agricultural fertilizer use, concentration trends, and climatic influences to maintain effective hazard control and ensure consistent water quality.

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