

Evaluation of Trihalomethanes and Residual Chlorine in the Drinking Water of the City of Huancayo – Peru

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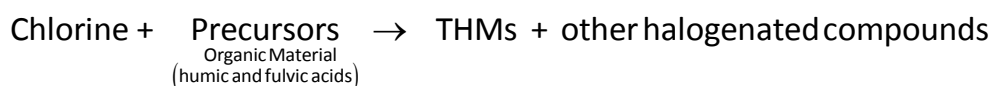
Summary:

The present study has the purpose to evaluate the residual chlorine and trihalomethanes in the drinking water supply of the city of Huancayo and to consider the influence of the concentration of chlorine in the formation of trihalomethanes. Thirteen representative samples were taken in the distribution networks between October 2015 and January 2016, including a control sample. In-situ parameters such as temperature and pH were evaluated using a multiparameter and free chlorine with a chlorine comparator, while total carbon organic (TOC) and trihalomethanes were analyzed in the laboratory. The relationship between residual chlorine and total trihalomethanes was analyzed using the Pearson correlation coefficient with a level of significance of 0.05, demonstrating that there is not significant correlation between residual chlorine and total trihalomethanes in the drinking water of the city of Huancayo. The results of the investigation indicate that the concentration of chlorine does not generate trihalomethane formation, since the reported values are below those established in the national and international regulations and the statistical analysis does not show relationship between both parameters. The study identifies additional variables such as temperature, pH, season, TOC and the source of raw water that should be investigated and for this reason it is recommended to study the formation of other disinfection by products as well as a deeper evaluation on the influence of the quality parameters in the formation of trihalomethanes in other environmental conditions of the area.

Keywords: Trihalomethanes, THM, drinking water, emerging pollutants, residual chlorine, disinfection by products, SPD

INTRODUCTION:

In recent years, research worldwide has reported the formation of disinfection by products DBP (Gómez, 2014, Núñez, 2005, Rosero, 2004, Bracho, 2009, Zafra, 2008, Rodríguez, 2007), despite the fact that chlorine has significant benefits for public health and water treatment because of its oxidation power, it sometimes participates in substitution or addition reactions forming DBP (Cervera, 2008), among them Trihalomethanes. These reactions do not only occur during the treatment of water, because it is usually necessary to add a certain amount of chlorine after disinfection in order to guarantee the presence of residual chlorine in the distribution network and prevent the reappearance of microorganisms, in this way the formation of BDP can also occur in the distribution network according to the World Health Organization (WHO, 2006). The risk associated with the consumption of trihalomethanes is long-term and its effects are only remarkable if it is consumed throughout life, similar to most carcinogenic products (Zafra, 2008). Trihalomethanes are compounds that are formed in the process of disinfection of water when chlorine is used as a disinfectant. The trihalomethanes found in drinking water are chloroform, bromoform, dichloromethane and bromoform. The general chemical reaction of this phenomenon is presented as:



Residual chlorine is considered to be one of the most influential factors in the formation of trihalomethanes. So the relationship between the concentration of residual chlorine and the formation of trihalomethanes depends on the dose of the disinfectant, which directly affects the formation of the BPD, because the chloroform concentration increases directly with the residual chlorine (La Opinión, 1998). In Peru, the most widely used disinfectant in distribution networks is chlorine (SUNASS, 2003) because it is the most studied, low cost and high efficacy compound (Craun, 1996).

In Peru there is currently a Regulation of Water Quality for Human Consumption D.S. 031-2010-SA (Ministry of Health, 2010), which establishes in article 66 that, before the distribution of drinking water, the supplier must leave residual chlorine in order to protect the water from possible microbiological contamination during distribution. Due to the global problem of the BPD, this regulation provides acceptable values for trihalomethanes and residual chlorine that ensure the necessary health conditions to make the water suitable for human consumption. Total trihalomethanes are considered an organic chemical parameter whose Maximum Permissible Limit is 1.0 mg/L while the residual chlorine is classified as an inorganic chemical parameter whose value should be between 0.5 to 5 mg/L. Residual chlorine is one of the parameters of quality that receives greater attention and is continuously monitored; but the same does not happen with Trihalomethanes, which do not receive adequate control due to limited capacity to perform monitoring and analysis of organic compounds (Chung, 2008), despite being a parameter also required by Peruvian legislation. This subject is

worrisome because the General Law of Water Resources No. 29338 (National Water Authority, 2008) in article 40 establishes that the Peruvian State must guarantee all people the right of access to drinking water services, in sufficient quantity and in conditions of safety and quality to satisfy personal and domestic needs.

Therefore, it is necessary to know the presence and quantity of trihalomethanes in drinking water, since a large part of the population does not know the theme due to the few studies that have been conducted in Peru. In many cities, such as Huancayo, there are not data on this parameter, causing the population to consume water without knowing if it meets the conditions suitable for their health.

For this reason, this study evaluates the influence of residual chlorine on the concentration of total trihalomethanes in drinking water in the city of Huancayo.

MATERIALS AND METHODS:

Twelve representative samples were taken in the distribution networks and one control sample in the Chamiseria area. Of these twelve samples, seven samples were taken in October 2015 and six samples in January 2016.

For the determination of THMs, 500 mL of water was collected in amber glass bottles after letting the water run for a few minutes and disinfecting the tap; 10 drops of hydrochloric acid were added to preserve the sample and 4 drops of 10% sodium thiosulfate. The bottles were stored in a cold and dark environment until their analysis and all samples were processed within 48 hours of sampling. The samples were taken following the literals 7.1 Sampling of Water for Human Use and Consumption and 7.3.2 Sampling in Rivers, Streams, and Channels (in the case of the control sample) from the methodology established in the water sampling instructions of the General Analytical Services laboratory (Servicios Analíticos Generales SAC, 2014). Chloroform, bromoform, bromodichloromethane and dibromochloromethane were determined for each of the samples. In addition, the parameters of free chlorine, pH, conductivity, turbidity and temperature were determined in-situ and were recorded in the chain of custody and field notebook.

The free chlorine was determined with a chlorine comparator; the pH, temperature and conductivity with a multiparameter, the turbidity with a turbidimeter, the trihalomethanes through the EPA method 8260, Rev 3. Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) 2006 and the organic carbon through the Determination of organic carbon method by sulfochromic oxidation - colorimeter.

RESULTS AND DISCUSSION:

From the results obtained in the laboratory, it was found that all the samples were below the detection limit of the equipment (<0.001 mg/L); even without obtaining exact values it is observed that all comply with the maximum permissible limits of total trihalomethanes, according to the D.S N ° 031-2010-MINSA which establishes

the value of 1 mg/L (Ministry of Health, 2010). Four types of trihalomethanes were evaluated: chloroform (CHCl_3), bromodichloromethane (CHBrCl_2), chlorodibromomethane (CHBr_2Cl) and bromoform (CHBr_3); since they are the most common trihalomethanes (Sánchez, 2011) and the national regulations consider them for the determination of total trihalomethanes according to the following formula:

$$C_{TOTAL\ THM} = \frac{C_{chloroform}}{LMP_{chloroform}} + \frac{C_{dibromochloromethane}}{LMP_{dibromochloromethane}} + \frac{C_{bromodichloromethane}}{LMP_{bromodichloromethane}} + \frac{C_{bromoform}}{LMP_{bromoform}} \leq 1$$

Where, C: concentration in mg/L, and LMP: maximum allowable limit in mg/L.

As mentioned, the laboratory results reported by Test Report N° 095240-2015 and 10308-016 (General Analytical Services S.A.C, 2015, 2016) show values lower than 0.001 mg/L for the four types of trihalomethanes. For calculation purposes and taking into account that all are below the maximum permissible limits, the maximum detectable concentration was taken for each of the trihalomethanes obtaining a value of 0.05115 mg/L of total trihalomethanes in all sampling points. Additionally, a comparison was made with international standards with values established by the World Health Organization (WHO, 2006) in which a value of 0.0396 was obtained (table N° 1 and table N° 2).

In addition, the values of free chlorine are also within the maximum permissible limits since they vary between 0.5 and 5 mg/L as established by national and international standards, the Ministry of Health and WHO respectively; except point 5 (P5) of table N° 1, which shows a value of 0.42 mg/L. This quality parameter is very related to the contact time of the chlorine with the water during the disinfection process in the drinking water treatment. The WHO considers it necessary to leave residual disinfectant so that the disinfection process continues in the pipes of the distribution networks (WHO, 2006). Table N° 1 shows the values of trihalomethanes according to the contact time of the chlorine with the water represented by the distance of the points with respect to the treatment plant, with P1 being the nearest point and P6 the furthest point, where it is evident that all trihalomethane values are below the limit.

The relationship between residual chlorine and total trihalomethanes with values established in the national regulations was analyzed using the Pearson correlation coefficient at a significance level of 0.05. This statistic postulates the null hypothesis that a correlation only exists if the value of absolute r is greater than the critical r value. The analysis shows an absolute r value of 2.22E-16 in the first sampling and 7.2026E-17 in the second (Table N° 3 and Table N° 4). Both values are lower than the value of critical r (0.811) therefore the null hypothesis is accepted, that is to say, there is not significant correlation between the residual chlorine and total trihalomethanes in the samples of drinking water of the city of Huancayo indicating that there is not influence of residual chlorine on the formation of trihalomethanes. Although chlorine is one of the most influential factors in the formation of trihalomethanes; its effect

generally depends on the dose of the disinfectant, which directly affects the formation of the BPD, since the chloroform concentration increases directly with the chlorine residual (La Opinión, 1998).

Table 1: Concentration of free chlorine and trihalomethane in the drinking water supply of the city of Huancayo – October 2015 (self made)

Sample Point	Description	Cl free (mg/L)			Dibromoclorometano (mg/L)			Bromodichlorometano (mg/L)			Bromoformo (mg/L)			TTHM's (mg/L)			
		In-Situ	Nacional	Internacional	Laboratory	Nacional	Internacional	Laboratory	Nacional	Internacional	Laboratory	Nacional	Internacional	Fórmula	Nacional	Fórmula	Internacional
P0	Chamiseria	0	0.5 - 5	0.5 - 5	<0.001	0.05	0.1	<0.001	0.06	0.06	<0.001	0.1	0.1	0.05115	1	0.0396	1
P1	Palian	0.78	0.5 - 5	0.5 - 5	<0.001	0.05	0.1	<0.001	0.06	0.06	<0.001	0.1	0.1	0.05115	1	0.0396	1
P2	OEFA	1.07	0.5 - 5	0.5 - 5	<0.001	0.05	0.1	<0.001	0.06	0.06	<0.001	0.1	0.1	0.05115	1	0.0396	1
P3	UC	0.56	0.5 - 5	0.5 - 5	<0.001	0.05	0.1	<0.001	0.06	0.06	<0.001	0.1	0.1	0.05115	1	0.0396	1
P4	Instituto Continental	0.55	0.5 - 5	0.5 - 5	<0.001	0.05	0.1	<0.001	0.06	0.06	<0.001	0.1	0.1	0.05115	1	0.0396	1
P5	Cementerio	0.42	0.5 - 5	0.5 - 5	<0.001	0.05	0.1	<0.001	0.06	0.06	<0.001	0.1	0.1	0.05115	1	0.0396	1
P6	Capilla	0.65	0.5 - 5	0.5 - 5	<0.001	0.05	0.1	<0.001	0.06	0.06	<0.001	0.1	0.1	0.05115	1	0.0396	1

Table 2: Concentration of free chlorine and trihalomethane in the drinking water supply of the city of Huancayo – January 2015 (self made)

Sample Point	Description	Cl libre (mg/L)			Dibromoclorometano (mg/L)			Bromodichlorometano (mg/L)			Bromoformo (mg/L)			TTHM's (mg/L)			
		In-Situ	Nacional	Internacional	Laboratory	Nacional	Internacional	Laboratory	Nacional	Internacional	Laboratory	Nacional	Internacional	Fórmula	Nacional	Fórmula	Internacional
P7	San Antonio	1.22	0.5 - 5	0.5 - 5	<0.001	0.05	0.1	<0.001	0.06	0.06	<0.001	0.1	0.1	0.05115	1	0.0396	1
P8	Palian	0.9	0.5 - 5	0.5 - 5	<0.001	0.05	0.1	<0.001	0.06	0.06	<0.001	0.1	0.1	0.05115	1	0.0396	1
P9	Instituto Continental	0.5	0.5 - 5	0.5 - 5	<0.001	0.05	0.1	<0.001	0.06	0.06	<0.001	0.1	0.1	0.05115	1	0.0396	1
P10	Chávez y Ferrocarril A	1.2	0.5 - 5	0.5 - 5	<0.001	0.05	0.1	<0.001	0.06	0.06	<0.001	0.1	0.1	0.05115	1	0.0396	1
P11	Colegio 17 de setiembre	1.1	0.5 - 5	0.5 - 5	<0.001	0.05	0.1	<0.001	0.06	0.06	<0.001	0.1	0.1	0.05115	1	0.0396	1
P12	Mariátegui	1.2	0.5 - 5	0.5 - 5	<0.001	0.05	0.1	<0.001	0.06	0.06	<0.001	0.1	0.1	0.05115	1	0.0396	1

Table 3: Coefficient of correlation between Total Trihalomethanes and Residual Chlorine - October 2015 (self made)

FIRST SAMPLE		
	Cl free 1	TTHM's (mg/L)
Cl free 1	1	
TTHM's (mg/L)	2.21591E-16	1

Table N° 4: Coefficient of correlation between Total Trihalomethanes and Residual Chlorine - January 2015 (self made)

SECOND SAMPLE		
	Cl free 1	TTHM's (mg/L)
Cl free 1	1	
TTHM's (mg/L)	7.20256E-17	1

The formation of trihalomethanes is not only influenced by the presence of chlorine; there are other factors that favor the formation of this type of pollutant compound such as the season of the year (Rodríguez, 2007). In the city of Huancayo, the highest rainfall occurs in the months of January, February and March so, considering that the samples were taken in October 2015 and January 2016, a higher organic load would be expected and therefore a higher demand for chlorine in the second sampling, but as shown in table N° 6, the TOC values are below 0.20 mg/L. In this case the national regulations do not consider this parameter within the D.S. N°031-2010-MINSA but the Colombian Regulation Resolution 2115 of 2007 (Ministry of Social Protection, 2007) establishes 5 mg/L of TOC as the maximum acceptable value. Studies carried out in Venezuela show that by reducing the content of organic matter present in water, the formation of trihalomethanes also is significantly reduced (Dudamel, 2015).

Finally, there are the temperature and pH parameters, which directly affect the reaction kinetics of trihalomethanes (R.C. Chawla, 1983). There is a direct relationship between both factors and the formation of trihalomethanes. In the case of pH, the values are shown in tables N° 5 and 6 which are within the permissible levels established by D.S. N° 031-2010-MINSA and the Drinking Water Quality Guide Levels of the WHO where the range of 6.5 to 8.5 is established as appropriate. This parameter is important because it affects the distribution of chlorinated by products; so the reduction of pH decreases the concentration of trihalomethanes but leads to an increase in the formation of other disinfection by products such as haloacetic acids, while increasing the pH reduces the production of haloacetic acids but increases the formation of trihalomethanes (WHO, 2006). The results of international investigations show that the concentration of trihalomethanes increases with increasing pH (Saidan, 2013); on the other hand, studies carried out in Colombia show that adding lime at chlorine application points promotes the formation of trihalomethanes (Rosero, 2004).

In the case of temperature, the values taken in the field are shown in tables N° 5 and 6 with average temperatures of 15°C in the first sampling and 17°C in the second sampling. The temperature is a parameter that favors the speed of reaction between the precursors causing a greater formation of trihalomethanes (Rodríguez, 2007); however, the temperature is related to the season. Trihalomethane concentrations are higher in summer and fall than in the rest of the year (Santa Marina, 2010). In the case of this study, the samples were taken in October 2015 and January 2016, times when temperatures are not the highest recorded in the city.

Table 5: pH, temperature and total trihalomethanes values – October 2015
(self made)

Sample Point	Description	Parameters In-Situ		TTHM's (mg/L)	
		pH	Temperature (°C)	LMP	VR_OMS
P0	Chamiseria	6.87	14	0.05115	0.0396
P1	Palian	6.39	13.9	0.05115	0.0396
P2	OEFA	6.48	15.4	0.05115	0.0396
P3	UC	6.79	17.1	0.05115	0.0396
P4	Instituto Continental	6.65	16	0.05115	0.0396
P5	Cementerio	6.78	16.9	0.05115	0.0396
P6	Capilla	6.88	17.9	0.05115	0.0396

Table 6: pH, temperature and total trihalomethanes values – January-2016
(self made)

Sample Point	Description	Parameters In-Situ		COT (mg/L)	TTHM's (mg/L)	
		pH	Temperature (°C)		LMP	VR_OMS
P7	Reservorio San Antonio	6.5	15.5	<0.20	0.05115	0.0396
P8	Palian	7.17	15.9	<0.20	0.05115	0.0396
P9	Instituto Continental	7.54	17.9	<0.20	0.05115	0.0396
P10	Chávez y Ferrocarril A	7.47	20	<0.20	0.05115	0.0396
P11	Colegio 17 de setiembre	7.32	17.7	<0.20	0.05115	0.0396
P12	Mariátegui	7.58	15.4	<0.20	0.05115	0.0396

CONCLUSIONS

The results of the investigation indicate that the chlorine concentration does not generate trihalomethane formation since the reported values are below those established in the national (D.S. N° 031-2010-MINSA) and international regulations (OMS, 2006). In addition, the correlation indexes between both parameters are not significant. Even though the formation of trihalomethanes is given by two main precursors such as residual chlorine and organic matter, these are not the only variables that participate in this process; since there is a significant influence of factors such as the season of the year (times of sampling), TOC (<0.20 mg/L),

temperature ($<17^{\circ}\text{C}$ on average), pH (between 6.5 and 8), and raw water source (surface water and water wells). After analyzing these factors, it can be predicted that there is not presence of total trihalomethanes ($<0.05115\text{ mg/L}$) in the city of Huancayo because the formation variables in addition to the residual chlorine are within the national maximum permissible limits, WHO reference values. and Colombian regulations for the case of the COT.

RECOMMENDATIONS

It is recommended to carry out studies on the formation of other possible disinfection by products given the environmental conditions. Considering that quality parameters such as temperature, pH, turbidity, presence of TOC as well as the chlorine dose and contact time of chlorine with water cause a direct effect on the formation of trihalomethanes, it is necessary to perform a deeper analysis of the impact of these. In addition, a parameter that was not evaluated in this study is the presence of bromine, which has a great influence on the formation of brominated trihalomethanes, since the presence of this type of compound in drinking water can be the cause of a higher concentration of trihalomethanes. This study was developed in the urban area of Huancayo, but it is known that the conditions of the rural areas can greatly affect the results obtained in this study, because in many of these areas there are not adequate infrastructures for water treatment and the use of chlorine in disinfection is poorly controlled. Considering the effect that temperature also has, studies in rural areas with temperatures higher than the scope of this study are also necessary.

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