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On-Site Chlorine: A Promising Technology in Drinking Water Treatment in Santa Cruz, Bolivia

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Abstract: Water availability and quality are still challenges around the world, but access to safe drinking water is essential for human development. This study analyzed the chemical parameters of drinking water quality in the Santa Cruz de la Sierra region of Bolivia. Residual chlorine, pH and concentration of dissolved solids were measured in water supplied by drinking water and basic sanitation service providers (EPSA). The water quality results indicated that the water supplied met the requirements established by the Bolivian Standard NB 512 in terms of residual chlorine, pH and concentration of dissolved solids. However, a decrease in residual chlorine concentration was observed as the water moved away from the disinfection point. Microbiological testing is recommended to ensure the absence of viable organisms in the distributed water. In conclusion, this study highlights the importance of chlorination, as the only treatment performed in the study area, the pH and the concentration of dissolved solids as indicators of drinking water quality. Automation of chlorination processes and continuous monitoring of these parameters is suggested to ensure a safe and high-quality water supply in the study area.

Keywords: drinking water; water quality; chlorination

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1. Introduction

Access to clean and safe drinking water is one of the most important challenges facing humanity in the 21st century. Water constitutes the vital resource for life; therefore, the supply of potable water is one of the essential services to ensure the health and well-being of the community [1–4]. Although significant progress has been made in this field in recent decades, there are still many parts of the world where safe drinking water is a critical unmet need [5]; particularly in low- and middle-income countries, access to safe drinking water and adequate water treatment is still scarce, leading to a number of public health and environmental problems [6]. In Santa Cruz de la Sierra, the water sources are underground and have stable physicochemical characteristics when analyzing the parameters over the years. That is why water treatment plants [7] only require a chlorination and/or disinfection system. Chlorination alone can ensure quality water in specific areas without an excess of minerals and/or suspended solids [8,9].

A widely used method for water purification in Bolivia is water disinfection through chlorination, along with other industrial methods such as ozone and ultraviolet light, among others applied to water. Chlorination can be carried out in different forms [10], using liquid chlorine, solid chlorine, or chlorine gas [11], all of which are efficient with their corresponding advantages and disadvantages, including the formation of by-products. The method of choice for the water utility provider (EPSA) in the study area is liquid chlorine, supplied in large quantities each month. However, liquid chlorine tends to degrade over

time, which leads us to propose in situ chlorination using the electrochemical method to produce hypochlorite, presenting a promising and safe alternative for this process. This method employs electrochemical devices that generate active chlorine from the salt dissolved in the water, eliminating the need to transport and store hazardous chemicals.

In this study, the research was carried out in the drinking water cooperative Pampa de la Isla COOPAPPI, in the sectors of well 7, corresponding to the Guápilo area, to evaluate the effectiveness and feasibility of in situ chlorination using the electrochemical method. Measurements were taken in the homes of users near the study well to determine the concentration of residual chlorine in the water after the disinfection process, confirming the efficiency of the method and compliance with Bolivian regulations [12].

Water is an essential element for human beings, but it is not available to everyone and is becoming increasingly scarce. The Bolivian standard NB512 establishes physical, chemical, pesticide [13,14], etc., parameters to determine whether drinking water is potable [15]. Due to the importance of this regulation and the desire to preserve the health of the citizens of Santa Cruz, the development of sodium hypochlorite by electrolysis is proposed. This would allow water service providers (EPSAs) to include it in their water supply network, ensuring that the substance received by members has low microbiological levels, as indicated by Bolivian standards. In addition, periodic monitoring of supply networks is proposed since the responsible use of this chemical compound is crucial to avoid health problems [16,17].

1.1. Chlorination as a Water Treatment for Disinfection

In the process of disinfecting drinking water, three stages can be differentiated, in which it is necessary to apply different procedures:

1.1.1. Pre-Chlorination

In this stage, the amount of chlorine necessary to overcome the breaking point is added. This ensures that the residual chlorine level is suitable for subsequent disinfection. In general, chlorine dosing is done in proportion to the flow rate of water to be treated.

1.1.2. Disinfection-Storage-Maintenance

This stage takes place inside the warehouse and is the moment when the disinfection itself takes place. If the residence time is long, it is necessary to maintain a residual level of chlorine to ensure that no new microbiological contamination has been possible. In order to carry out the corresponding chlorine supply, a monitoring and dosing system is necessary in the tank. The same working methodology would be applied to tanks that act as a lung and receive water that has already been previously treated or in a closed system such as a swimming pool.

1.1.3. Post-Chlorination

Once the water has left the reservoir and is distributed for use, additional chlorine may be required to ensure that residual chlorine levels are as required at the point of consumption. These are rechlorination stations in extensive distribution networks. In this case, the in-line control equipment is of great importance, as it will be ultimately responsible for maintaining the chlorine level.

2. Materials and Methods

2.1. Materials

2.1.1. Types of Chlorine

For the determination of the chlorine samples, the three types of disinfectant substance used in our country and authorized by the competent water authority were taken into account, such as liquid chlorine in the form of sodium hypochlorite, solid chlorine in the form of calcium hypochlorite and chlorine gas, as such.

2.1.2. Chlorination Prototype

The prototype developed, shown in Figure 1, has a capacity of 25 L, for which a voltage source and 6 electrodes were adapted that will act as cathodes and anodes to carry out the chemical reaction using the electrochemical method, in which the sodium hypochlorite will be obtained through the passage of the electric current in a saturated solution of sodium chloride. This will be done through the electrochemical method, which will guarantee obtaining chlorine in situ so that the cooperative is supplied in the well and can generate the necessary amount for disinfection and dosage according to the required water flow.

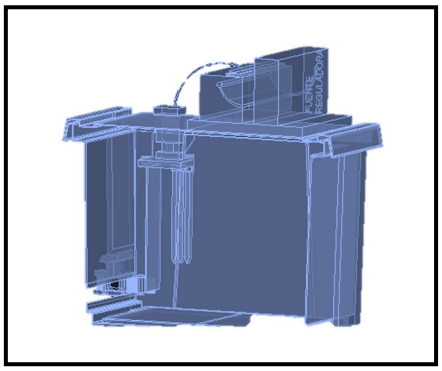


Figure 1. In situ chlorination prototype.

For the operation of the developed prototype, a concentrated solution of sodium chloride is prepared and subjected to electric current, where chemical reactions are carried out in each of the electrodes present to obtain it; these electrodes used have materials that are easy to obtain and clean. To this end, laboratory tests were carried out to verify the stability of the hypochlorite obtained; through oxide titration reduction with potassium iodide, where it was evident that, by subjecting the concentrated brine solution to 12 Volts and 10 Amps, stability was achieved in the % of active chlorine, in addition to the fact that the time that elapses to obtain it is shorter compared to other voltage and amperage values, it is for this reason that it is decided to increase the number of electrodes available to carry out the chemical reaction in a way that is faster and more efficient for the operator. The chemical reaction that takes place is as follows:

In sodium chloride, chloride (Cl^-) and sodium (Na^+) ions are taken into account by the semi-reaction:

$$NaCl \rightarrow Na^+ + Cl^- \quad (1)$$

In water, hydrogen ions (H^+) and hydroxyl ions (OH^-) are present, which are shown in the semi-reaction:

$$H_2O \rightarrow H^+ + OH^- \quad (2)$$

These ions, present through the passage of 12 V and 10 A direct current through the graphite and stainless-steel electrodes acting as cathode and anode, respectively, transform chlorine into chlorides and release sodium ions. This takes place at the anode.

In the cathode, hydrogen is converted into gaseous hydrogen when an electron is captured, leaving in the water the hydroxyl ions that bind to the sodium to form the sodium hydroxide NaOH that remains in solution with the rest of the brine that has not been consumed in electrolysis, which in the presence of chlorine Cl_2 binds to it to form sodium hypochlorite.

$$Cl_2 + 2NaOH \leftrightarrow NaClO + NaCl + H_2O \quad (3)$$

Obtaining the desired hypochlorite concentration allows us to have a residual free chlorine remnant in the drinking water network.

2.1.3. Portable Chlorine Meter

The pocket free chlorine meter or checker is of the brand HANNA HI701; it is a digital colorimeter to perform chlorine tests with a measurement range of 0 to 2.5 mg/L of residual chlorine that has two cuvettes with lids and HI701-25 reagents with DPD reagents (N,N Diethyl paraphenylenediamine) for precise and simple measurements whose values are shown on the screen of the equipment after 5 min of the reaction of the reagent with the sample. This equipment complies with the UNE-ISO17381 Standard for water quality. It has a 525 nm LED light source that, when activated, passes through the glass cell that contains the sample with the reagent, which changes the coloration of the water; finally, the intensity of light received by a silicon photocell is translated into a numerical value that indicates the concentration of residual free chlorine in the water in parts per million (ppm) (Oscar and Anna Nardo, Limena, Italy Hanna Instruments, 2018)

2.1.4. Sampling Points

The samples were collected at fixed sampling points near well 5 of the drinking water cooperative "Pampa de la Isla", located by what is indicated in NB-512 in point 24, which specifies that the location of the sampling points must follow the criteria of being in areas of high population density. Areas at risk of contamination are representative of the network and at points near and far from the well of influence. For this purpose, the following summary of the fixed sampling points in the service area of the well is available, as shown in Figure 2.



Figure 2. The map corresponds to the location of the sampling points of the wells where (**A**) It is the place of the country, and (**B**) it is the place of the province and (**C**), the place of water sampling.

2.2. Method

To perform the in situ chlorination tests, a prototype was developed, as shown in Figure 1. It consists of an electrolytic tank of 25 L in volume in which a voltage source and 6 electrodes that will act as cathodes and anodes to carry out the chemical reaction in which sodium hypochlorite will be obtained through the passage of the electric current in a saturated solution of sodium chloride. This will be done through the electrochemical method, which will guarantee obtaining chlorine in situ so that the cooperative is supplied

in the well and can generate the necessary amount for disinfection and dosage according to the required water flow, as shown in Figure 3.

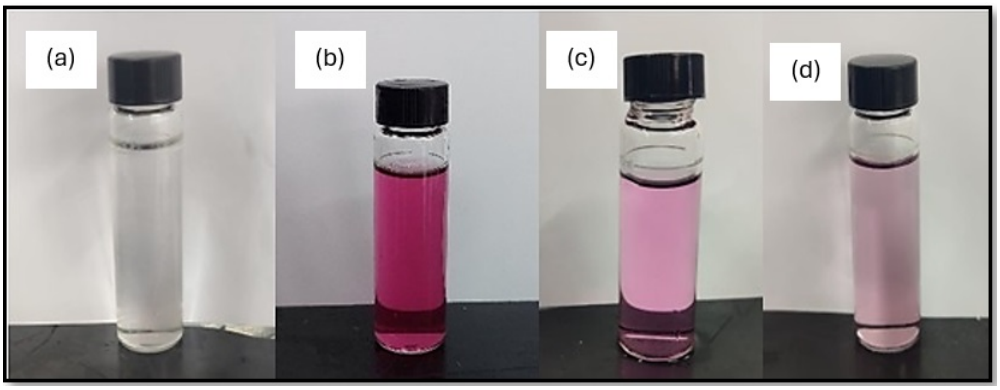


Figure 3. Water samples taken at different sampling points to measure the residual chlorine level. Measurement of residual chlorine with portable equipment at (**a**) sample target, (**b**) close sampling point, (**c**) midpoint, and (**d**) far point of the distribution network.

The method for the measurement of residual free chlorine, which is the amount of chlorine that remains unreacted in the water and that guarantees the purification of the water, is established by the Bolivian standard and indicates that the DPD Spectrophotometric, iodometry, or DPD Colorimetric method must be used for analysis. In our case, we use the colorimetric method DPD (N, N Diethyl paraphenylenediamine), which consists of taking the sample of water that has been chlorinated, that is, at a tap belonging to the distribution network to which the DPD is added and with the help of counters ample of deionized water that is the target and with which the color change is compared, whose value is obtained with the digital colorimeter, which measures the passage of light through the sample and gives us as a result the value of the concentration of residual free chlorine present in our water sample in units of concentration known as parts per million-ppm. Having the presence of residual free chlorine in a sample guarantees the absence of micro-organisms present in the water, as shown in Figure 4.

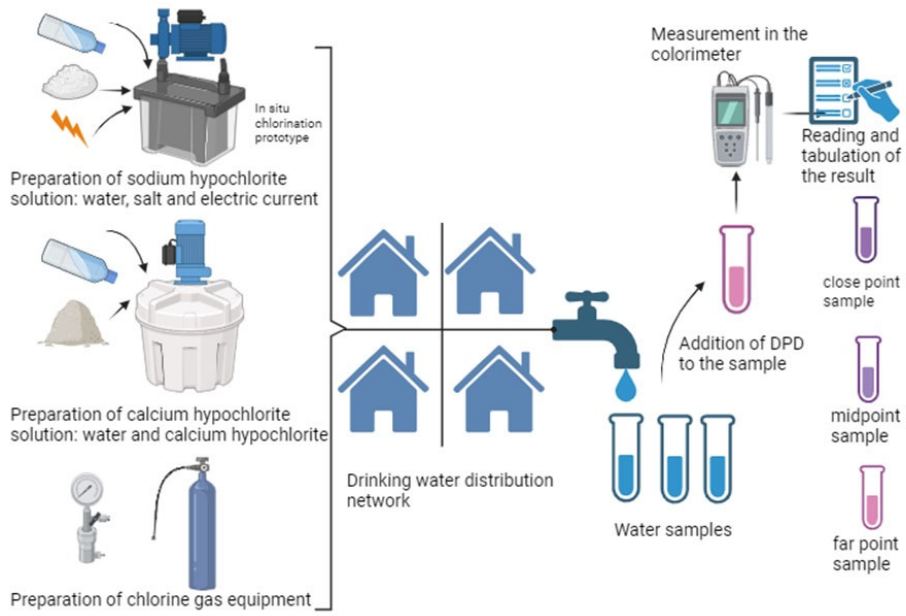


Figure 4. Experimental diagram of the on-site chlorination method from production to measurement with DPD in taps of drinking water distribution network partners.

2.2.1. Calculation of the Well Flow Rate to Determine the Volume of Chlorine

For the determination of chlorine that is needed for dosing in the distribution network, it is necessary to know the flow rate of the water supply well; for this, a portable ultrasonic flowmeter LANRY DF6100-EH was used that was added to the outlet of the well to determine the flow rate of the water it supplies and identify the hours of greatest demand for water of the population that is supplied in the test well. It is necessary to know the information of the well, since, in that way, it will be possible to calculate and define the amount of disinfectant that will be needed daily, which will help us to compare the 3 chlorination methods used and which of them is most efficient.

2.2.2. Determination of the Amount of Sodium Hypochlorite and Calcium Hypochlorite for Water Disinfection

Here, we determine the amount of chlorine needed in disinfection as a treatment for water purification.

To determine the amount of chlorine to be produced, it is necessary to know the flow rate of the well, the working hours of the well, and with this, the volume of water to be disinfected is determined. It is also important to know the concentration of hypochlorite given by the manufacturer and the dose in mg/L by which it is theoretically desired to exit at the wellhead. For this purpose, the following formula was used:

$$V_{clorine} = \frac{V_{water} \times D_{water}}{C_{clorine}} \quad (4)$$

where:

$V_{chlorine}$ is the volume of chlorine needed in liters for sodium hypochlorite and in grams for calcium hypochlorite; it must be divided by 10 to convert units.

V_{water} is the volume of water that is going to be disinfected; for this, you must know the flow rate of the well and the hours of service in liters.

D_{water} is the dose or concentration of the chlorine solution with which you want to leave the wellhead, in mg/L.

$C_{chlorine}$ is the concentration of chlorine indicated by the manufacturer in mg/L.

2.2.3. Determination of the Amount of Chlorine Gas for Water Disinfection

The amount of chlorine gas required in disinfection as a treatment for water purification is determined using Equation (5).

It is necessary to know the flow rate of the well, in addition to the dose of chlorine to be injected in mg/L; this value must be in the range of 0.2 to 1.5 mg/L, which is the value required by the Bolivian standard. For this purpose, the following formula was used:

$$D = C \times Q \quad (5)$$

where:

D is the chlorine required, to be regulated in volumetric indicator of the chlorometer (gr of chlorine/hour).

C is the dose of chlorine to be injected, the desired chlorine concentration in the water, (in mg/L).

Q is the flow rate of the water to be treated (in m^3/h).

To evaluate the quality of the water in the distribution network and check the efficiency of the disinfection method, as well as its scope compared to traditional methods using known disinfectants, depends on the concentration that is read in the portable device, in addition to the pH and TDS, at the sampling points strategically located in the supply network of the study well. The monitoring at the sampling points of the distribution network was carried out from 18 October to 21 October 2022, for a period of four days, for each of the 10 points located throughout the service area of the study well. The recorded values correspond to the main characteristics that describe the behavior of the water,

allowing us to conclude about its potability. These records facilitated the elaboration of graphs that allowed to describe the behavior in the concentration of residual free chlorine in the water distribution network compared to the 3 methods evaluated.

Once the data of the initial characteristics of the water have been collected and it has been mentioned by the operators of the service that they feel satisfied working with sodium hypochlorite—since it is in a liquid state, it is easier to handle—the prototype is developed that uses the electrochemical method to obtain it; the hypochlorite obtained will be prepared daily to prevent the concentration from being reduced and ensure that it does not generate too much waste that could have been used in the past nor clog the chlorinator.

3. Results

Results of the Electrochemical Method

The results of the determination of the well flow after the study carried out are 13.34 L/s, in which it was determined that the hours of greatest consumption of the population are in the morning shift from 5 to 6:30 and at night from 6:00 p.m. to 9:00 p.m

For the measurement of the amount of chlorine in each of the methods, the data shown in the tables below were obtained according to the calculations made in each one by the type of chlorine used; for example, for liquid chlorine, 15 L, 10 L and 20 L as shown in Table 1 and Figure 5.

Table 1. Residual chlorine results at network sampling points based on liquid chlorine used in disinfection.

Residual Chlorine in the Distribution Network	Liquid Chlorine		
	M1: 20 L	**M2: 15 L**	**M3: 10 L**
	$\bar{x}$+ SD	**$\bar{x}$+ SD**	**$\bar{x}$+ SD**
Nearby Point	0.65 ± 0.04	0.59 ± 0.05	0.53 ± 0.03
Midpoint	0.44 ± 0.04	0.36 ± 0.04	0.35 ± 0.04
Far Point	0.24 ± 0.04	0.24 ± 0.06	0.24 ± 0.04

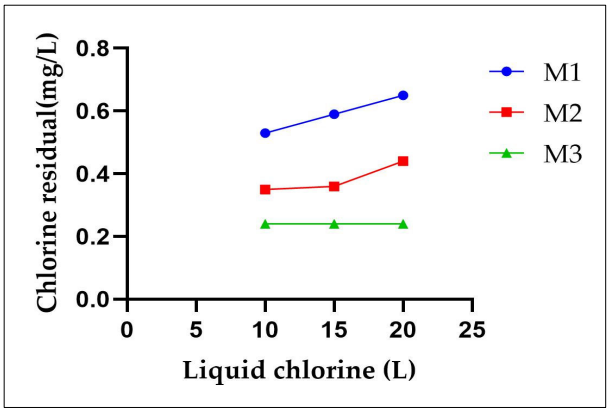


Figure 5. This image shows the measurement of liquid chlorine, specifically sodium hypochlorite, that was added to the supply network. It also presents the results obtained from the chlorine residue. It can be noticed that as the distance increases, the chlorine residue decreases. In this way, it is determined that the M2 sample is the best option according to the NB 512 standard.

In the Figure 6 and Table 2, shows the amount of sodium hypochlorite, in solid form, that was added to the water distribution network and shows the results of residual chlorine. It may be noted that the farther away the sample is, the lower the amount of residual chlorine. This depends on the amount of solid chlorine that was added to the drinking water distribution network. The M2 additive sample was determined to meet the requirements of NB 512.

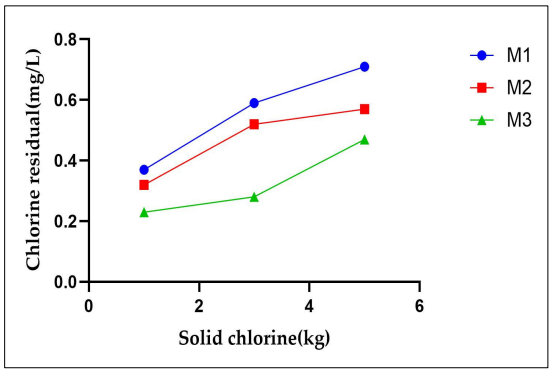


Figure 6. Solid Chlorine.

Table 2. Residual chlorine results at network sampling points based on solid chlorine used in disinfection.

Residual Chlorine in the Distribution Network	Solid Chlorine		
	M1: 5 Kg	M2: 3 Kg	M3: 1 Kg
	$\bar{x}$+ SD	$\bar{x}$+ SD	$\bar{x}$+ SD
Nearby Point	0.71 ± 0.06	0.57 ± 0.04	0.47 ± 0.02
Midpoint	0.59 ± 0.01	0.52 ± 0.05	0.28 ± 0.05
Far Point	0.37 ± 0.01	0.32 ± 0.03	0.23 ± 0.02

In Figure 7 and Table 3, shows the amount of chlorine gas that was added to the distribution network and shows the levels of residual chlorine obtained. It can be noticed that as the distance increases, the level of residual chlorine decreases, which depends on the amount of chlorine gas that was added to the drinking water distribution network. The results indicate that the M2 additive sample meets the requirements set by the NB 512 standard.

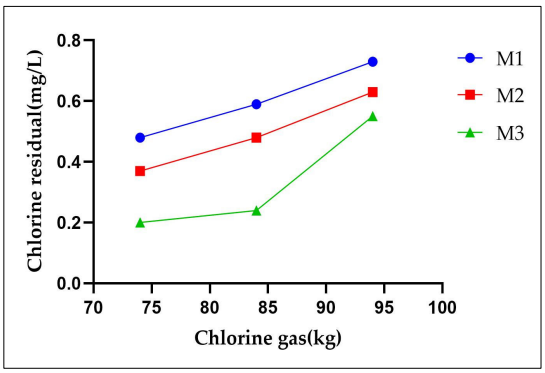


Figure 7. Chlorine Gas.

Table 3. Residual chlorine results at network sampling points based on chlorine gas used in disinfection.

Residual Chlorine in the Distribution Network	Chlorine Gas		
	M1: 74 Kg	M2: 84 Kg	M3: 94 Kg
	$\bar{x}$+ SD	$\bar{x}$+ SD	$\bar{x}$+ SD
Nearby Point	0.48 ± 0.03	0.59 ± 0.02	0.73 ± 0.02
Midpoint	0.37 ± 0.04	0.48 ± 0.02	0.63 ± 0.02
Far Point	0.20 ± 0.01	0.24 ± 0.03	0.55 ± 0.01

From the Table 4 of initial parameters, the following results are presented in Table 5:

Table 4. Appropriate values for Quality Water.

Variable	Values	Fountain
PH	6.5–8.5	European Community Environment Legislation. Regulation 98/83. Water Quality 2000
Chlorine Concentration	0.20–1.50 ppm	NB 512
TDS–Total Dissolved Solids	1.000 ppm	NB 512

Table 5. Chlorine concentration in water [ppm].

Distance Well 05–Home [in Meters]	Chlorine ppm		
	Average	Maximum	Minimum
[0–149]	0.28	0.7	0
[150–299]	0.3	0.66	0
[300–449]	0.09	0.32	0
[450–599]	0	0	0
Total Overall	0.20	0.70	0.00

In Figure 8 show that the residual chlorine value decreases as the distance increases.

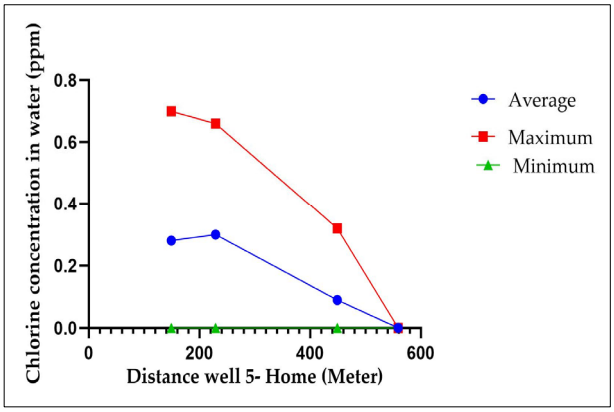


Figure 8. Chlorine Gas.

In Table 5, we refer to the fact that initially, taking samples from taps of partners close to the water distribution source, there is residual chlorine with a maximum of 0.7 ppm, although the Bolivian Standard allows us higher values. There may be user rejection due to the characteristic smell of chlorine, according to the EPSA that provides the service. It can also be seen that as it moves away from the distribution source, the value of residual chlorine decreases, which gives us indications that it has been consumed along the distribution network, perhaps reacting with some compounds or minerals found in the water or present in the network. To ensure that disinfection is being effective, microbiological tests should be carried out to guarantee the non-presence of living organisms in the drinking water distributed throughout the area.

The Figure 9 shows that the pH level remains constant throughout the distribution network, and we can say that the chlorine content does not modify the physicochemical characteristics of the water.

The Figure 10 shows that the level of total dissolved solids remains the same throughout the distribution network, which means that chlorine is not reacting to form chlorination by-products that can be harmful to health.

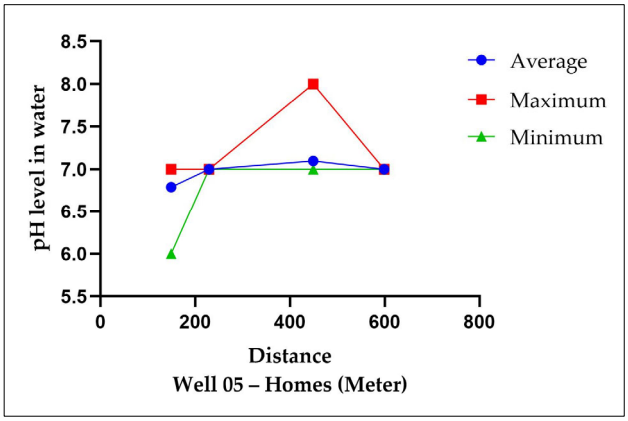


Figure 9. Ph level in water.

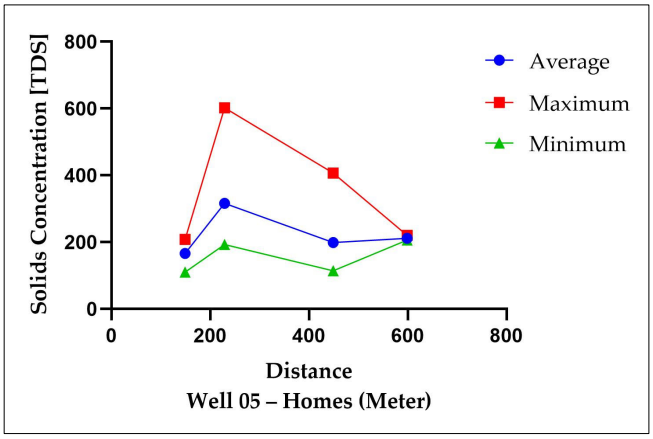


Figure 10. Solids Concentration.

4. Discussion

In Santa Cruz, the water supply comes from underground wells with depths greater than 200 m, which ensures the stability of the sources. In addition, the absence of living organisms is due to the lack of oxygen available at these depths for them to survive.

Water disinfection is the only treatment carried out by many of the city's water service providers (EPSAs). This ensures the provision of safe water for the population's consumption. While there are several methods of chlorination, each with its advantages and disadvantages [18,19]. The Bolivian Standard does not require a specific method, but rather requires the continuity of chlorination during the water supply service. Any of the mechanisms used undergoes the same process of disinfection and chemical reactions, forming hypochlorous acid and hypochlorite ions within the pH range set by NB512. These reactions result in the presence of residual free chlorine, as shown in Table 5 based on measurements obtained by the electrochemical method with DPD.

The study area around well 5, where the samples were taken, has pH levels within the values established by the Bolivian standard. This indicates that the water can be consumed without fear of direct contamination of aquifers. Any sudden or spontaneous variation in pH should serve as an alert for the service operator to make immediate decisions regarding water supply. A considerable increase in pH can raise alkalinity levels, possibly due to the increase in water hardness caused by the formation of minerals or salts in the treatment process. Conversely, a significant reduction in pH could indicate acid contamination. Table 6 shows the values within the ranges allowed by the Bolivian standard, ensuring an adequate water supply in the area, free of any contamination that alters the pH of the water [20,21].

Table 6. pH levels in water.

Distance Well 05–Homes [m]	Nivel de pH		
	Average	Maximum	Minimum
[0–149]	6.79	7.00	6.00
[150–299]	7.00	7.00	7.00
[300–449]	7.10	8.00	7.00
[450–599]	7.00	7.00	7.00
Total Overall	6.93	8.00	6.00

The level of total dissolved solids (TDS) in water serves as an important indicator for water quality monitoring. With the necessary equipment available, obtaining the results in Table 7 was easy. This table provides reliable information on suspended solids in EPSA-supplied water. While it does not specify the exact solids present, given the quality of the water monitored by EPSA, it can be inferred that they include calcium and magnesium ions, along with carbonates and bicarbonates characteristic of water hardness. These levels, however, do not pose a danger or risk to human health.

Table 7. Dissolved solids concentration [TDS].

Distance Well 05–Home [in Meters]	Solids Concentration [TDS]		
	Average	Maximum	Minimum
[0–149]	166.00	208.00	110.00
[150–299]	316.25	602.00	193.00
[300–449]	198.90	407.00	114.00
[450–599]	211.71	220.00	206.00
Total Overall	197.61	602.00	110.00

5. Conclusions

The level of residual free chlorine concentration obtained from the remnants of disinfection carried out through the direct pumping of sodium hypochlorite with a certain percentage concentration, into the water distribution network of the EPSA providing the drinking water service, shows acceptable levels according to Bolivian standards. The dosage is conditioned by the water flow supplied by the well to the population it serves, which varies based on hours and user consumption. These variables, along with the distance, affect residual chlorine readings as they move away from the disinfection point. The concentration of residual chlorine decreases along the distribution network route. To correct and/or improve this disinfection process, automation of chlorination can be implemented, taking into account not only the well flow and supply hours but also the chlorine level required to ensure that even the last user at the end of the distribution network receives water with residual chlorine of 0.2 ppm, as demanded by Bolivian regulations, to ensure potable water [22].

Another variable of interest in this study is pH, a crucial indicator for the supply of drinking water. This value is measured by two methods: one through the colorimetric method, where the color change of the paper is compared and associated with the characteristic colors of each pH range, and the other digitally through equipment with electrodes that provide a direct reading. pH should not exhibit variations, as it is one of the most stable quality indicators over time. It only varies in the presence of foreign and different substances in the water, which would indicate contamination. The pH is also one of the

most sensitive variables; if a variation occurs, it will be noticeable and immediate. This aids the service operator in making prompt decisions while supplying water to the population.

Finally, Total Dissolved Solids (TDS), as the name suggests, indicate the concentrations of parts per million in chemical units. They are measured digitally through equipment that instantly reveals the quantity of solids in the water. This value may increase with more suspended minerals or the generation of products or by-products of disinfection in the distribution network. Generally, TDS is due to the presence of carbonates, bicarbonates, calcium, and magnesium in the distribution water. To reduce these values, filtration can be performed, but this procedure is considered when values exceed acceptable norms or when the organoleptic characteristics of water change, as many minerals are essential for the body's needs.

The proposed technology meets the minimum requirement for residual chlorine levels mandated by current Bolivian regulations, and no chemicals are added to the water as it works with the salts present.

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