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RESIDUAL CHLORINE IN WATER SUPPLY SYSTEMS

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Abstract *Water disinfection is practiced in surface water, groundwater in fissured soils, karst or poorly filtered. This study determined the efficiency of chlorination of water plants treating surface water (river Suceava) and accumulations of water. Disinfection of water may have undesirable effects by persistence in drinking water of substances used to treat it or their byproducts, such as chlorophenols or trihalomethanes (case of chlorination) that aldehydes, phenols and carboxylic acids (treatment with ozone). The analysis results show that chlorine values depend greatly on temperature, contact time, pH and oxidisability. Like other studied parameters chlorine shows an increase in concentration for warm summer period, due to the requirement for chlorine in water. In the study in three years to monitor the chlorine was found that it tends toward a slight increase due to application of chlorine in water and rehabilitation works for the city water network. Physical-chemical quality parameters of water distributed by the two plants that treat surface water (Dragomirna and Mihoveni) were within the limits allowed under the law.*
Key words: *water disinfection, contact time, pH, organic matter content, temperature*

1. Introduction

Water disinfection with chlorine, played and still plays an important role in reducing diseases spread by water.

Chlorine is a strong oxidant which produces in water several substances including hypochlorous acid (HOCI) and hypochlorite ion (OCI).

Both substances kill microorganisms by attacking the cell wall lipids and changes cell membrane permeability[2], (at concentrations of 0.2 mg / l) [7], by destroying the enzymes and nucleic acids (at doses of 40.3 mg / 1) [7].

HOCl and OCl concentration values vary depending on the pH level.

If the pH is too high, the HOCl concentration is not enough, ideally, the pH level should be between 7 and 8, value of 7.4 is the ideal pH.

In slightly alkaline water (pH = 7.5), chlorine is found in equal proportions in the two forms.

The more alkaline becomes water (high pH) more increases the hypochlorite formed and vice versa, the more acide becomes water pH (pH<7) more increases the amount of hypochlorous acid formed.

In terms of power to destroy bacteria, hypochlorous acid is more effective.

Hypochlorous acid and hypochlorite ion are strong oxidizers for organic and inorganic substances contained in water [4].

Once it is introduced into water, chlorine (HOCl and ClO-) oxidizes some minerals (salts of iron, magnesium, nitrites, etc.) resulting chlorides and oxidised compounds.

Cantitatea de clor consumată în aceste reacţii constituie cererea de clor imediată.

The amount of chlorine consumed in these reactions are immediate chlorine demand.

After immediate chlorine demand, the remaining amount of chlorine acts on ammonia (when it is present in water), leading to the formation of chloramines [4] (bound active chlorine).

Between hypochlorous acid (HOCl) and ammonia following reactions are possible[11]:

$$NH_3 + HOCI \longrightarrow H_2O + NH_2CI$$

$$NH_3 + 2HOCI \longrightarrow 2H_2O + NHCI_2$$

$NH_3 + 3HOCl \longrightarrow 3H_2O + NCl_3$

Further introduction of chlorine is called in the literature the breaking point and will cause the oxidation of chloramines (which is desirable).

$4NH_2Cl + 3Cl_2 + H_2O \longrightarrow N_2 + N_2O + 10HCl$

Continuing the addition of chlorine over the breaking point it will produce a proportional increase in free active chlorine, used for the disinfection.

If water containing natural organic substances (humic acid) or artificial (pesticides, phenols), chlorine may cause certain organic compounds, with unpleasant taste and smell or even dangerous, suspected to be carcinogens [5] [6], as trihalomethanes, chlorophenols or influence premature births [2].

Residual chlorine can be present in two forms namely hypochlorous acid or hypochlorite, which is called free chlorine and chloramine which is called bound chlorine. The amount of free residual chlorine and bound chlorine is total chlorine.

2. Materials and Methods

The presence of residual chlorine in water disinfection is an important health subject indicating on the one hand that was introduced a sufficient quantity of chlorine to ensure disinfection, and on the other side shows the water distribution system integrity. Free residual chlorine is more valuable than bound chlorine because it is much more sensitive.

For the analysis was used the method with metiloranj [10], that molecular chlorine discolores metilorange solution proportional to its concentration.

2.1. Reagents: 0.46 ‰ metiloranj solution,); sulfuric acid solution (H_2SO_4) 1:3 , solution of potassium bromide (KBr) 1%. All reagents were acquired from Merck; (Darmstadt, Germany).

Standardization of metilorange solution is achieved so that 1 ml metiloranj to be by discolored by 0.1 mg of chlorine. Metiloranj, working solution is obtained from metiloranj solution prepared as above, diluted 10 times(1 ml of this solution is discolored 0.01 mg Cl). Parallel is a done a blank using doubly distilled water. The quantity of metiloranj used in the blank is subtracted from the amount of metiloranj used in the sample.

3. Results and Discussion

Using the method described, were monitored between 2008 - May 2011, water stations Dragomirna, Mihoveni, Radauti and Berchişeşti in which raw water is disinfected with chlorine.

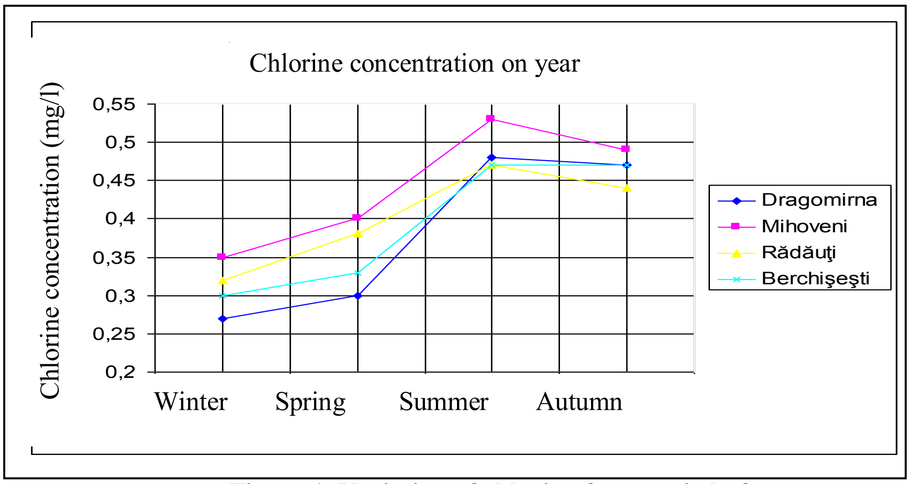

Figure 1. Variation of chlorine for a period of one year

Minimum chlorine is achieved in winter since the activity of microorganisms in the winter is very low, chlorine concentration is less, and the more temperatures rise, increases the solubility of chlorine in water, but also the chlorine demand to destroy pathogens.

Surface waters of Dragomirna and Mihoveni require higher chlorine demand to those of ground waters as Berchişeşti and Radauti.

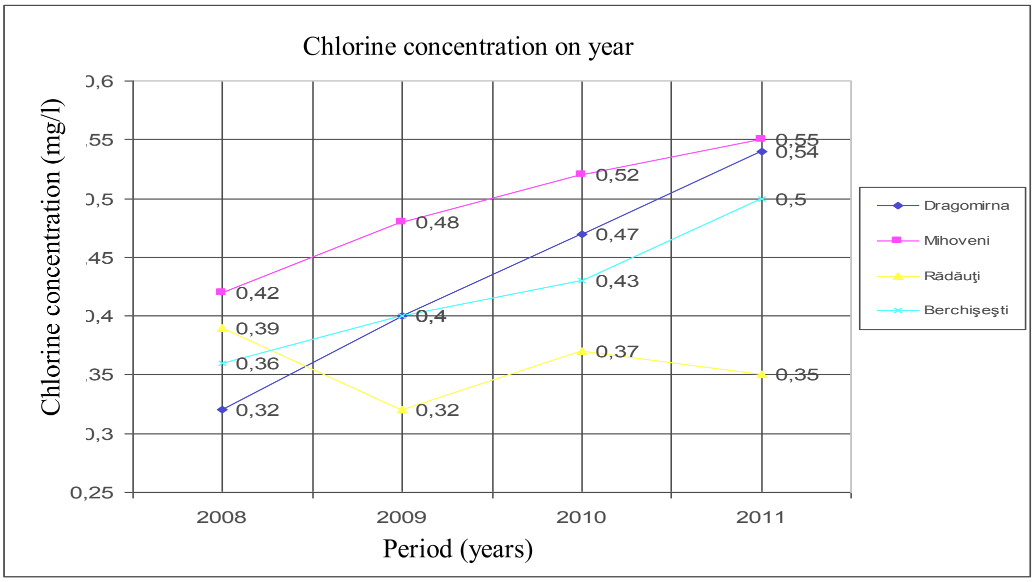

Figure 2. Variation in total chlorine for a period of three years
Waters of the three stations were monitored between 2008 - May 2011.

Figure no.2 shows a constant concentration in Radauti areas, unlike the other three stations that have an upward trend, growth due to the requirement of chlorine in water, due to water hyperchlorination to achieve rehabilitation programs Suceava, replacement of water pipelines.

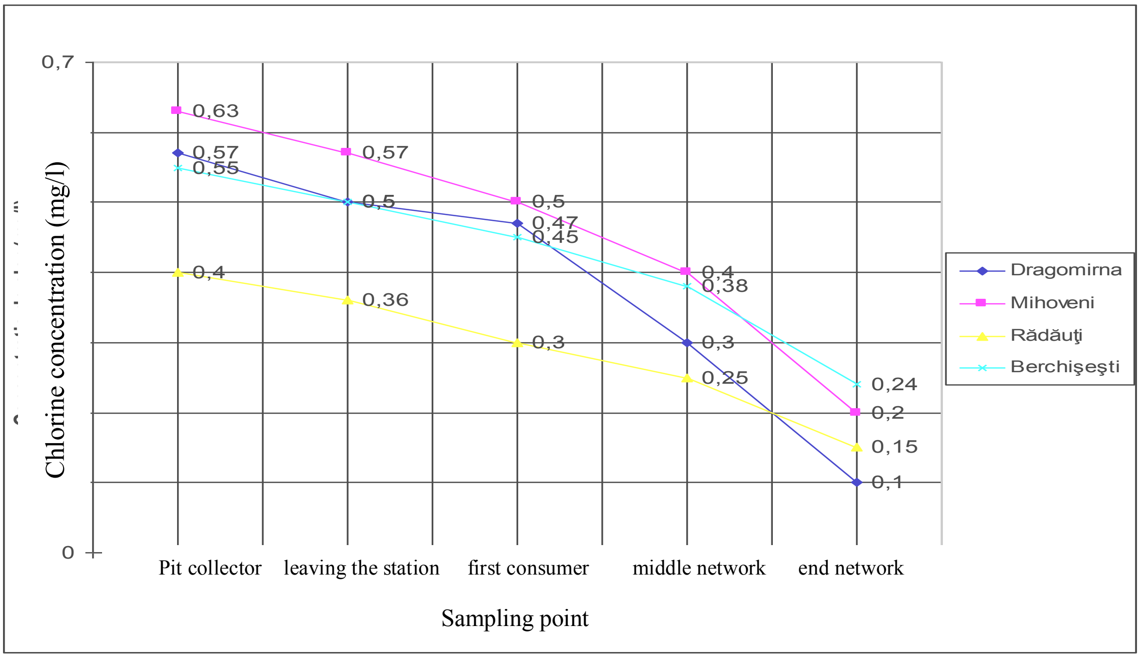

Figure 3 . Total chlorine variation depending on the sampling point

From Figure 3 it can be seen retention of chlorine in water, residual chlorine decreasing as the water is away from the shaft collector, where there is the dosage of chlorine in water.

Chlorine retention is dependent on the length of water network and the number of pathogenic microorganisms in water.

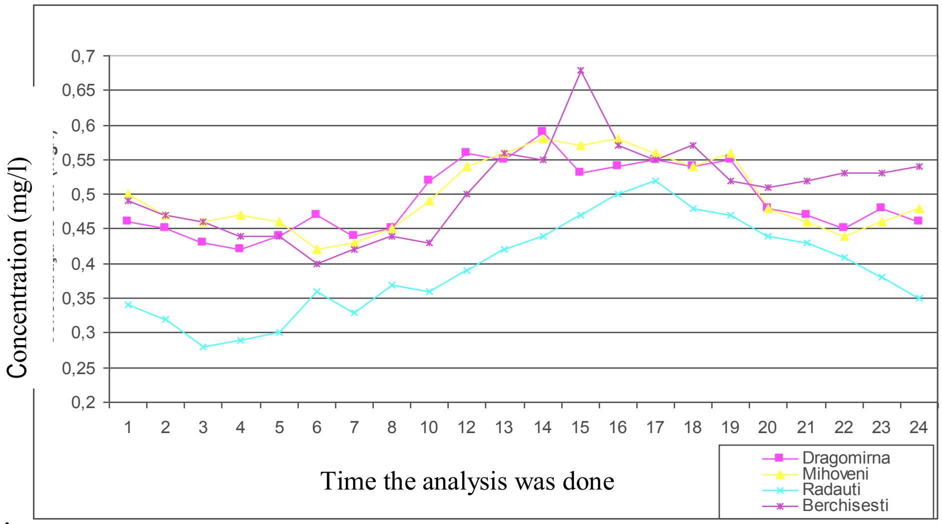

Figure 4. Variation of total chlorine in the course of the day

If the length of the network is too high and it does not keep the need of chlorine in water and the pressure in the pipeline, chlorination points and pressure boosting can be made. Chlorine concentration was monitored over 24 hours, chlorine demand changing in hour to hour, depending on time of day.

Temperature has an important role in the solubility of chlorine in water, since decreases water temperature, the chlorine is harder dissolved in water. Since in the same diagram we can not compare these parameters due to different units of measurement, we will analyze in turn. The content of organic substances in water influence the demand of chlorine, so there are concerns for its reduction by different methods, which results in decreased demand for chlorine.

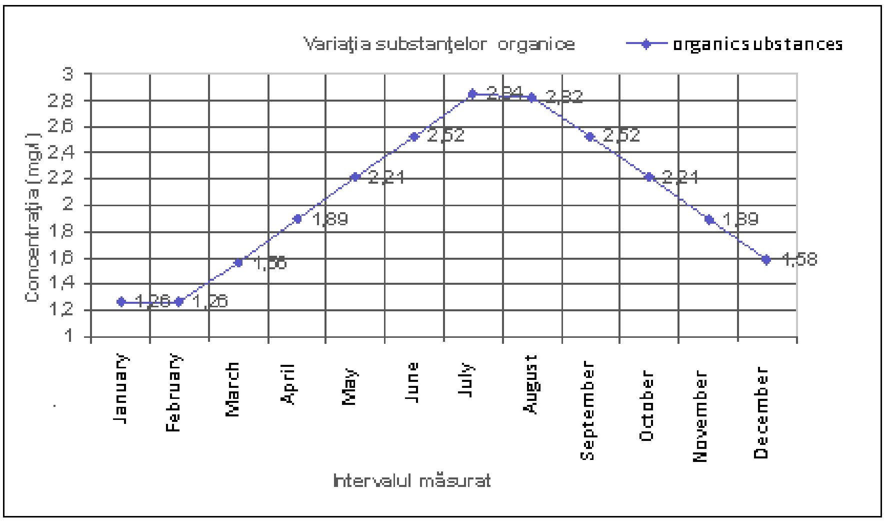

Figure 5.Variation of organic matter content in between January and December

The diagram oxidabilităţii shows an upward trend of analysed values in the range from February to July, a flat from July to August and a decrease in August-December, increasing of organic matter in water due to the growth of microorganisms during the summer.

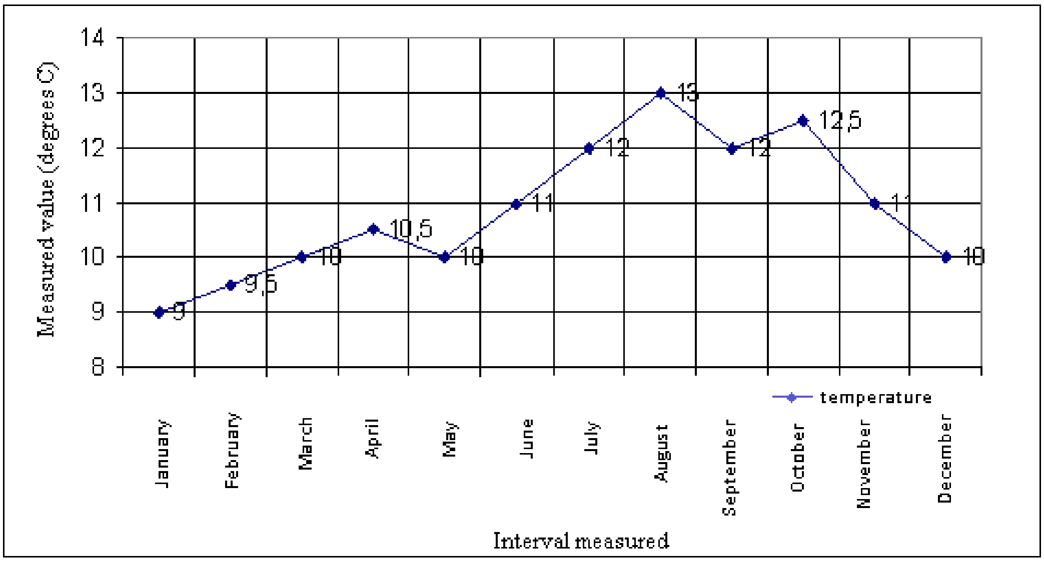

Figure 6. Temperature variation between January-December

Usually, deep water has a constant temperature throughout the year with little changes of values in summer.

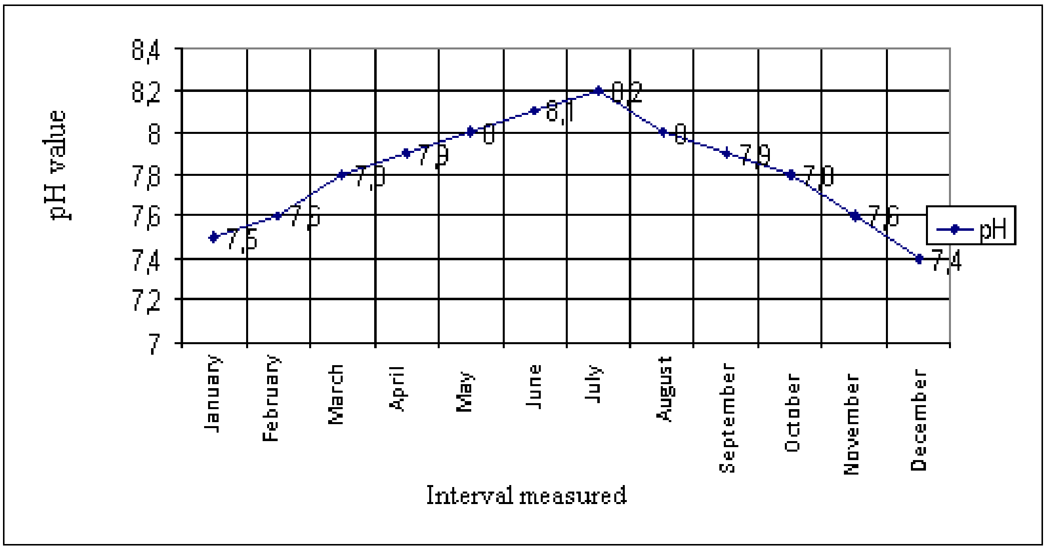

Figure 7. Variation of pH in between January and December

Water pH also belongs to the category of parameters that influence the chlorine in water and shows high values in summer and values approaching neutral value of 7.

Drinking water legislation (Law 458/2002) provides a pH in the range 6.5 to 7.5.

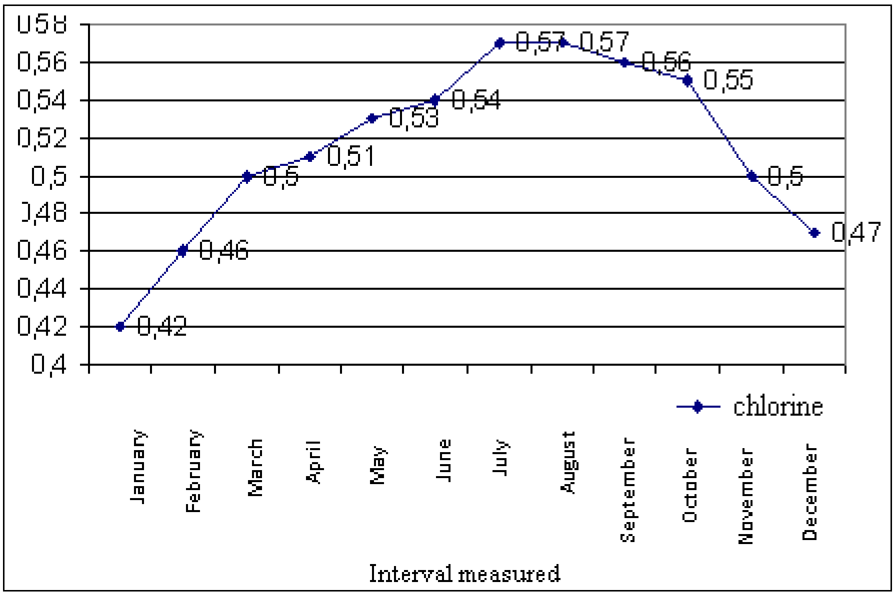

Figure 8. Variation of total chlorine between January and December

Figures 5, 6, 7, shows that chlorine values depend largely of temperature and pH oxidisability. Like other parameters studied chlorine shows an increase in concentration during the warm summer months, due to increased activity of microorganisms. From the same water samples taken at different time intervals 10, 20, 30 and 45 minutes, 1 hour, 12 hours and 24 hours were determined free and bound chlorine.

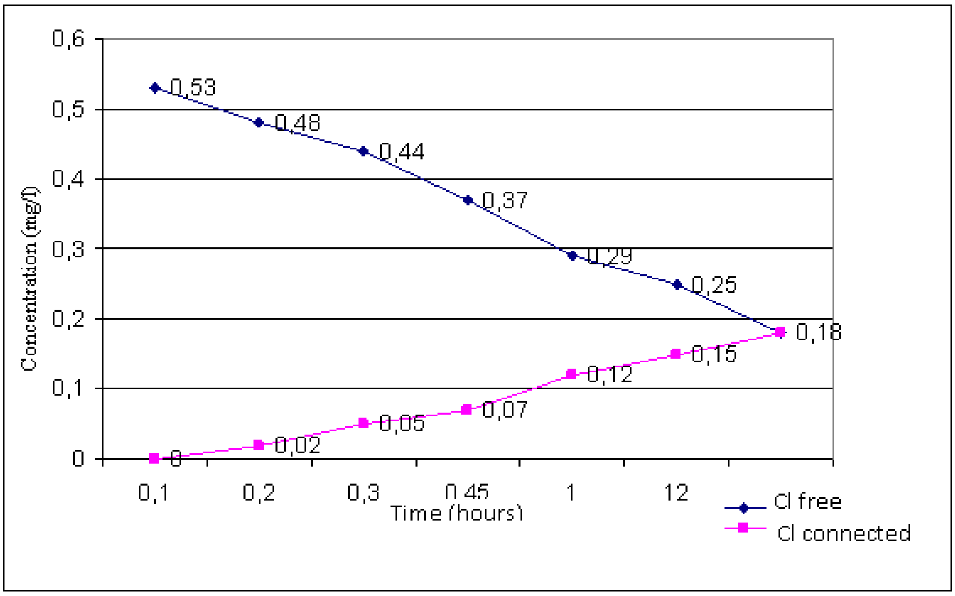

Figure 9. Variation of free and bound chlorine in 24 hours

As can be seen from Figure 9, free residual chlorine (HOCl, HCl), decreases over time, and free residual chlorine must be at least 80% of total chlorine. Bound chlorine as chloramines and other chlorine compounds is inversely proportional to the free chlorine and its concentration increases with the passage of hours which thus explains the taste and odor in drinking water. If the free residual chlorine must be 80% of total chlorine it can see the water after 12 hours water no longer meets the above condition.

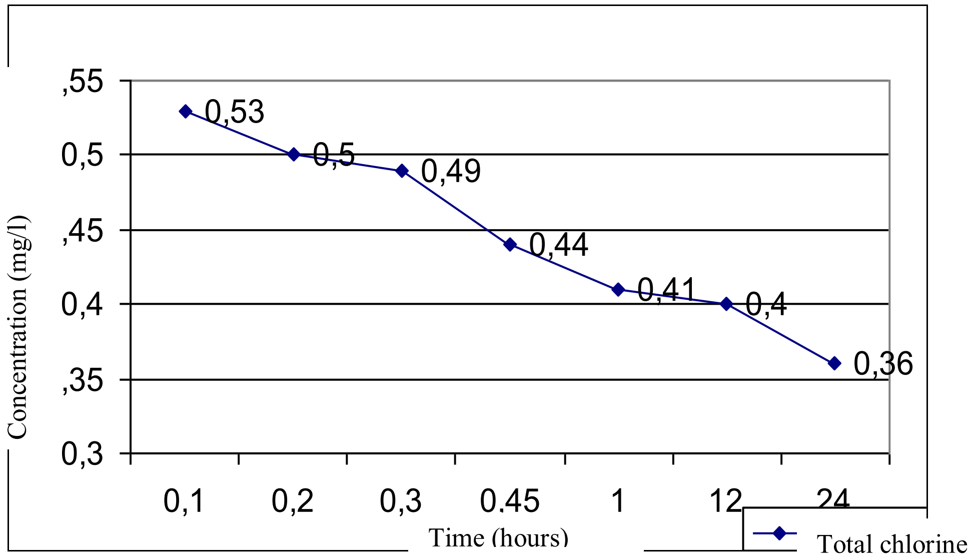

Figure 10. Variation of total chlorine in 24 hours in the same water sample

4. Conclusions

This study determined the effectiveness of chlorination stations dealing with surface water (river Suceava) and accumulation of water.

Disinfection of water may have undesirable effects by persistence in drinking water of substances used to treat it or their by-product [1], as chlorophenols, or trihalomethanes (if chlorination) that aldehydes, phenols and carboxylic acids (for ozone using). As disinfection methods, their effectiveness decreases in the following order:

Cl gaseous $>O_3 > UV > Cl_2O >$
$HClO > ClO^- >$ chloramines

Because O_3 and UV are very expensive and requires a smaller volume and flow of water and a very high price the method of disinfection with chlorine is the most used.

Chlorine is effective due to its retention in water, destroys pathogens throughout the network of water distribution of a large volumes of surface and groundwater, with flow rates and variable pressures from one station to another.

In the study for the three years to motorized chlorine was found that it tends toward a slight increase due to the demand of chlorine in water.

Relative to sampling, chlorine concentration decreases as it moves away from the treatment plant so at the end of the network the chlorine concentration is 0.1 mg/l. Within 24 hours the chlorine demand varies greatly depending on the population water demand which is lower during the night between 23-5 and higher between 6-22.

Annually, the requirement for chlorine is variable increasing in summer and decreasing during autumn and spring. Temperature and pH have an effective contribution to the chlorine in the water as could be determined from diagrams.

Physical-chemical parameters of water distributed by the two plants that treat surface water (Dragomirna and Mihoveni) were within the limits allowed under the law.

Concentration of organic substances, an important indicator for water chlorination, was within acceptable limits (5 mg O_2 / l).

Water disinfection with chlorine generates chlorine compounds presented in water supplied by the four stations.

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