ASSESSMENT OF INTERACTION BETWEEN pH AND DIFFERENT FORMS OF CO_2 FROM NATURALLY UNDERGROUND WATER USED FOR DRINKING IN GORGOTA

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Abstract
In this work were evaluated the correlations between the different forms of carbon dioxide naturally existing in fountain waters and the pH. Water samples were taken from five wells equally placed on the surface of Gorgota area in Dambovita county and were taken in each of the four seasons (spring, summer, autumn and winter). It was evaluated two forms of carbon dioxide (one was the aggressive CO_2 and the other was that sequestered in bicarbonates molecules). It was used titration method based on the principle of calcium carbonate conversion in to bicarbonate form. The results showed that both forms of carbon dioxide naturally existing in underground waters are related to the pH, and also are fluctuating from a season to the other. For example, both forms of carbon dioxide significantly were influenced by pH in summer and autumn, the proof being the values of regression index which was 0.518 and respectively 0.794. That is showing a moderate to strong influence of pH in certain periods of the year. In spring, the influence of pH on carbon forms analyzed was insignificant one, the regression index value being only 0.173, and in the winter season was missing (R^2 = 0.07). Also, the influence of carbon dioxide forms on the water pH level varied also from a season to another. Thus, carbon dioxide bicarbonates strongly influenced the pH of waters in winter and spring season, so the regression index value was 0.540 and 0.795. But in winter and summer the influence was insignificant. The aggressive carbon dioxide significantly influenced water pH in the summer season, the fact is indicated by the value of regression index which was 0.952. In the others seasons the influence of aggressive carbon dioxide was insignificant.

Keywords: *carbon dioxide forms, pH, underground waters*

Received: 31.07.2017 Received in revised form: 24.08.2017 Accepted: 31.08.2017

Introduction

The carbonates there are in a permanently balance with the bicarbonates, their presence in water being conditionally linked with the presence of free carbon dioxide (Busuioc, G., David, I., 2017).

So, if aggressive CO_2 is in excess in winter time, it means that is decreasing the quantity of carbonates. In summer time, when CO_2 is deficient, it is producing an increasing of carbonates quantity (Surugiu, V., 2015; Nicoară, M., 2002 ;).

On the other hand, the bicarbonates have a reverse dynamics comparatively to carbonates, but also according to the presence of free CO_2 (Pricope, F., 2007). Therefore, in winter when free CO_2 is in excess, the bicarbonates are increasing, but in summer when the free CO_2 is deficient, it is a reverse phenomenon of decreasing the quantity of bicarbonates in the natural aquatic ecosystems. But it is a very normal cycle of carbon. The carbonates and bicarbonates make up the natural buffering system of the water, which keeps the pH at a value close to neutral (Mustață, Ghe., 1992).

Interrelation of buffering system carbonates-bicarbonates and pH of waters is due to the biological valences of water (Gavrilescu, E., 2012). So, in the night pH is easy increasing grace to aquatic organisms and acidifies the waters, but during the day time pH is decreasing because of sequestration the free CO_2 in photosynthesis process (Muntean, C., 2009; Grebenişan, I., 2014). This cycle of aquatic carbon is important for health of rural residents who drink all their life this type of water.

Materials and methods

The water samples analyzed were collected from five fountains situated on the area of locality Gorgota belonging to Dâmboviţa County. The fresh waters were sampled at the same time (9^{th} – 10^{th} o'clock) in the morning of every Wednesday in all four weeks of a month and for each season of year (spring, summer, autumn and winter). The daily period chooses for sampling fresh fountains waters after one night's break and because it comes before the people intervenes and disturbs it cycle.
The five fountains analyzed are located in the street, one for each direction of every cardinal points and one in the center of the locality.
For determination the forms of CO_2 were used the titration method based on the principle of conversion calcium carbonate into bicarbonate (David, I., 2016; Elekes, CC., David, I., Iliescu, N., 2011). The pH was determined by pH-metric method, being used the pH-Meter type WTW 3110 Set 2.
On determined the aggressive carbon dioxide form and CO_2 sequestered in bicarbonates.
Each result represents the average of four determinations on the successive sample collected as was explicated above and were expressed in mg/l. The statistic method applied for interpretation the results was mathematical regression (Somnea, D., et al., 1993).

Result and Discussion

It can be observed in Figure 1 that the concentration of CO_2 sequestered in bicarbonates has fluctuated a lot from a fountain to the other. The minimum quantity (79,3 mg/l) was found in the waters of west fountain and the maximum (140,3mg/l) was determinated in the waters of central fountain followed by that in the south of village. On the third place from this point of view were the fountains from north and east. The variability of this CO_2 form were quite large between 79,3 and 140 mg/l.

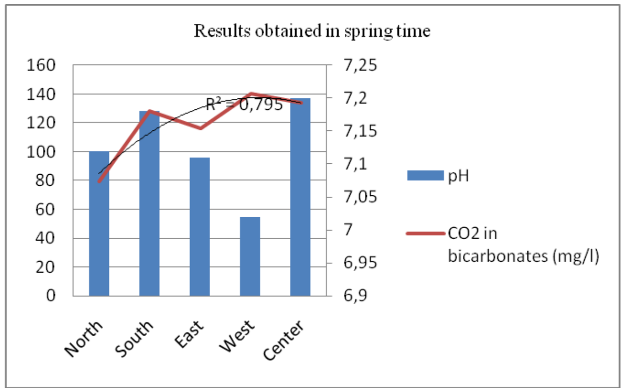

Fig. 1 The influence of CO_2 from bicarbonates on pH of waters in spring

The influence of pH on variability of water content inCO_2 sequestered in bicarbonates was very weak, the value of regression index being only 0,173 (Figure 2). The limit of variability of pH were very closed between 7,02 and 7,2 in spring time.
The greatest value of pH was measured in fountain waters from the center and the lowest one was in waters of fountains from west.

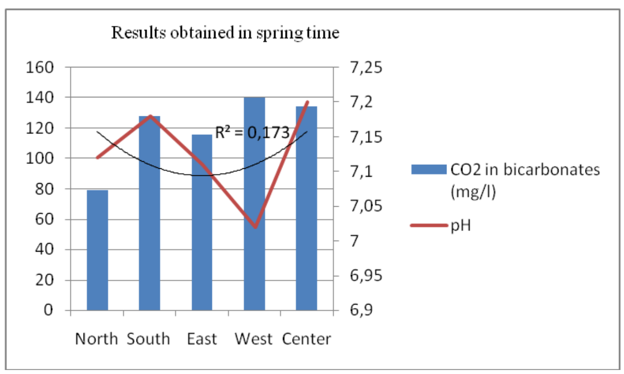

Fig. 2 The influence of pH on CO_2 from bicarbonates of waters in spring

In summer time the content of waters in CO_2 sequestered in bicarbonates was between 48,8 and 189,1mg/l (Figure 3).

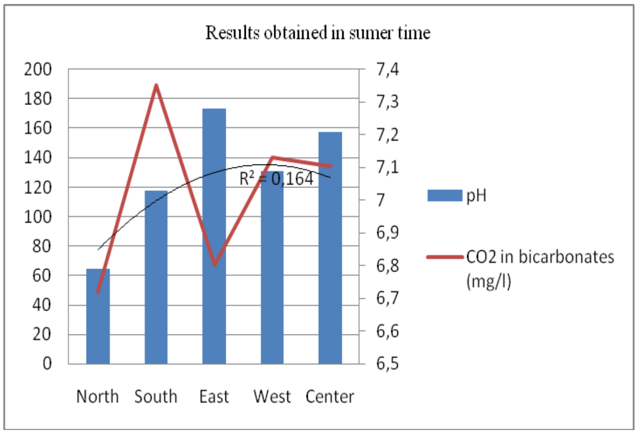

Fig.3 The influence of CO_2 from bicarbonates on pH of waters in summer

The maximum content (189,1mg/l) was registered in the waters of south fountain followed by that from, west, center and east in descending order. The lowest quantities (48,8mg/l) were determined in fountain from north. The content of CO_2 sequestered in bicarbonates did not influenced the pH of waters about the value regression index (0,164).

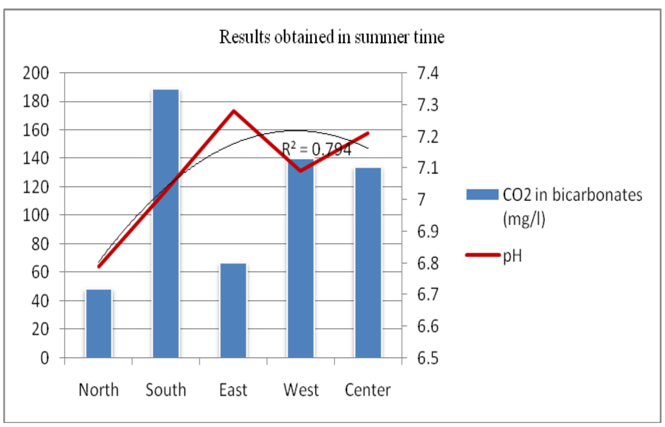

Fig. 4 The influence of pH on CO_2 from bicarbonates of waters in summer

Instead the influence of pH on the accumulation of CO_2 in bicarbonates form was strongly by the values of regression index (0,794) in summer time (figure 4). The values intervals of pH was a large one between 6,79 and 7,28, namely from easy acid to easy alkaline. The greatest value of pH was in the waters of east fountain followed by that from center and west in descending order. The lowest pH value was measured in the waters of fountain from north.

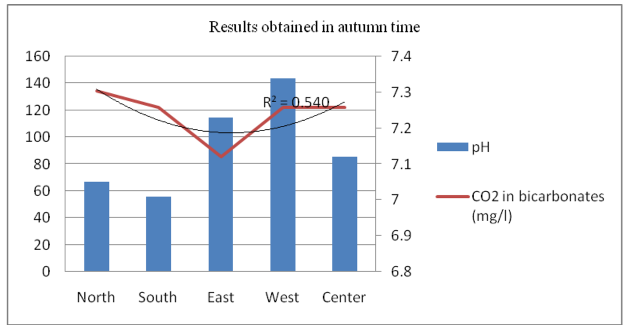

Fig. 5 The influence of CO_2 from bicarbonates on pH of waters in the autumn

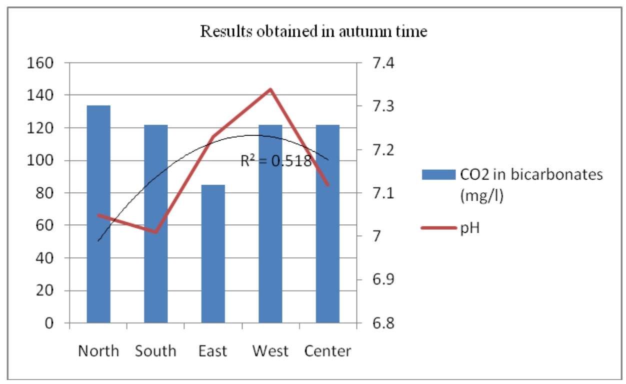

Fig. 6 The influence of pH on CO_2 from bicarbonates of waters in the autumn

Figures 5 and 6 show the interrelation between CO_2 sequestered in bicarbonates and the pH of fountains waters in autumn season. So the level of influence is a peer one, both regression index values are a little over 0,5.

The variability of CO_2 sequestered in bicarbonates was large, between 85,4 and 134,2 mg/l. Maximum values were in the fountain water from north followed by that from south, west and center with 122 mg/l each. The lowest content being determined in the waters of fountains from east (85,4mg/l).

The pH values interval was between 7,01 and 7,34, on the weak alkaline scale. The maximum value of pH was registered in fountains waters from west followed in descending order by that from east to equality with those from south, west and center. The minimum pH values were determined in the waters of fountain from south.

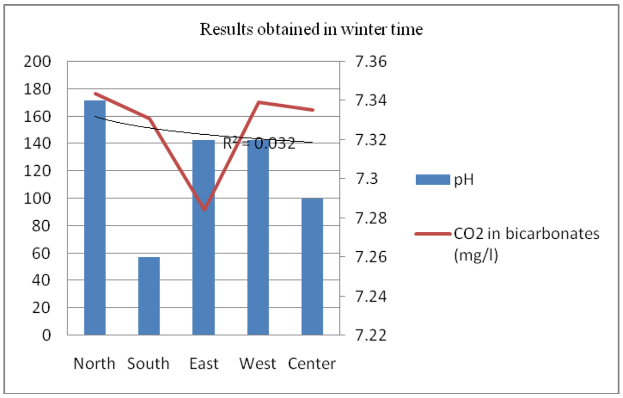

Fig. 7 The influence of CO_2 from bicarbonates on pH of waters in winter time

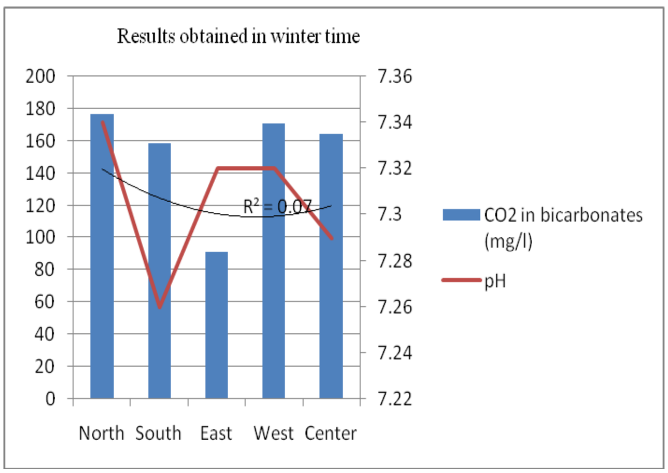

Fig. 8 The influence of pH on CO_2 from bicarbonates of waters in winter time

In winter time both these two parameters had no influence one another, in according with the values of regression indexes (Figure 7 and 8).

CO_2 sequestered in bicarbonates have varied on a large scale between 91,5mg/l and 176,9 mg/l. Maximum of content was determined in the waters of fountain from north of locality followed by those from west and center with values 170,8mg/l and 164,7 mg/l. The lowest values were obtained at the fountain waters from east, a little over 90mg/l.

The pH values of waters during winter fluctuated very closed in the slightly alkaline band, between 7,29 and 7, 34. The maximum value of pH was in waters of fountain from north followed in a very easy decreasing by that from west and east. The minimum value was obtained in the waters of fountain from south of village.

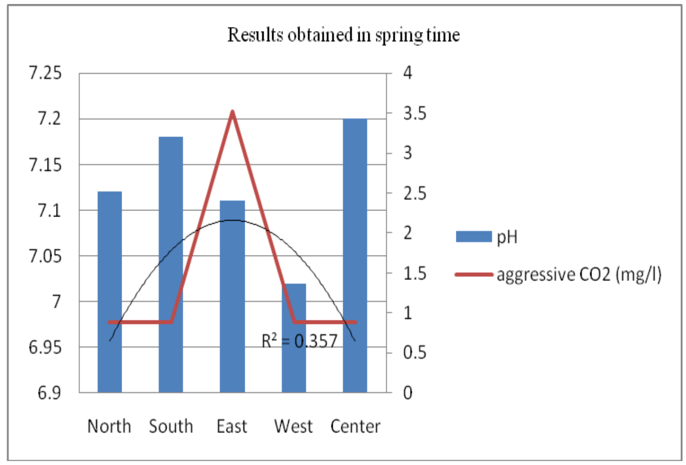

Fig. 9 The influence of aggressive CO_2 on pH from waters in spring time

The content of aggressive CO_2 was generally very low comparatively to the content of CO_2 sequestered in bicarbonates form. It will be not necessary to discuss again the values of pH because they are the same as in all the cases discussed above.

Regression index values from figure 9 (R^2= 0,357) shows a moderate influence of aggressive form of CO_2 on the pH in the spring time.

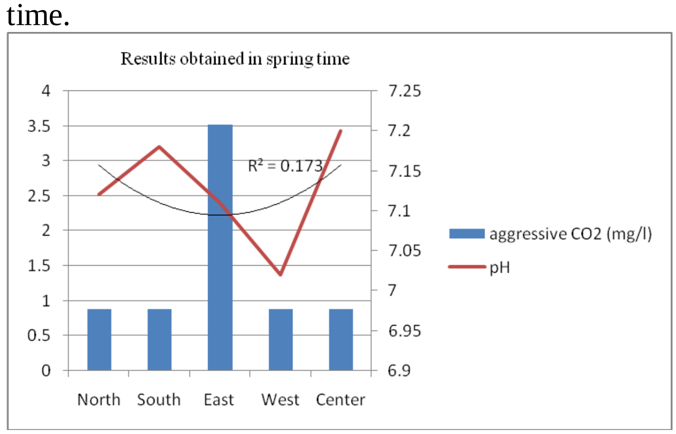

Fig. 10 The influence of pH on aggressive CO_2 from waters in spring time

The values of aggressive CO_2 were a little under 1mg/l for the waters of fountains from north, south, west and center (Figure 10). But in case of fountain from east of locality the concentration of aggressive CO_2 was 3,52mg/l. The regression index (0,173) shows none influence of pH on the concentration of aggressive CO_2 in spring time.

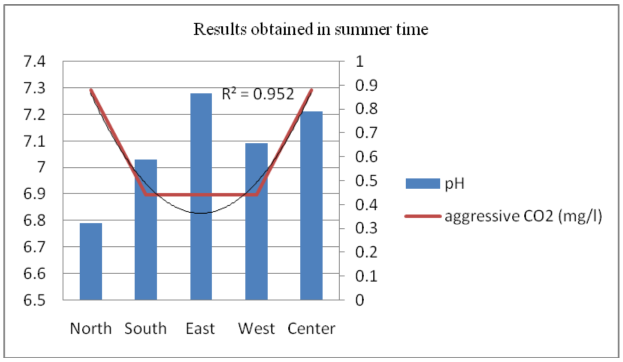

Fig. *11 The influence of aggressive CO_2 on pH from waters in summer time*

In summer time aggressive CO_2 had a very powerful impact on the fluctuation of pH of waters according to the value of regression index (0,952)(Figure 11).

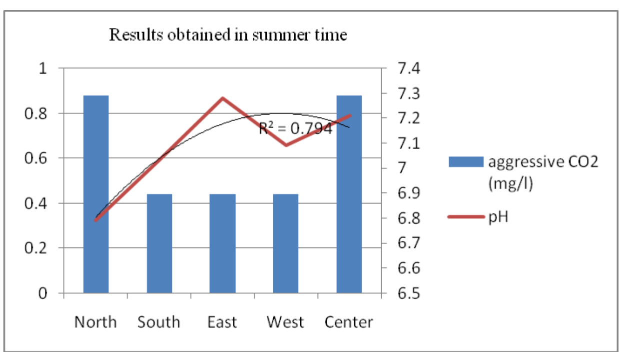

Fig. 12 The influence of pH on aggressive CO_2 from waters in summer time

The content of waters in aggressive CO_2 to equality as values (0,44 mg/l) in fountains waters from south, east and west (figure 12).The fountains from north and center had much more aggressive CO_2 (over 0,8mg/l). The pH influenced strong the accumulation of aggressive CO_2 in fountains waters in the summer time in according to the value of regression index (0,794).

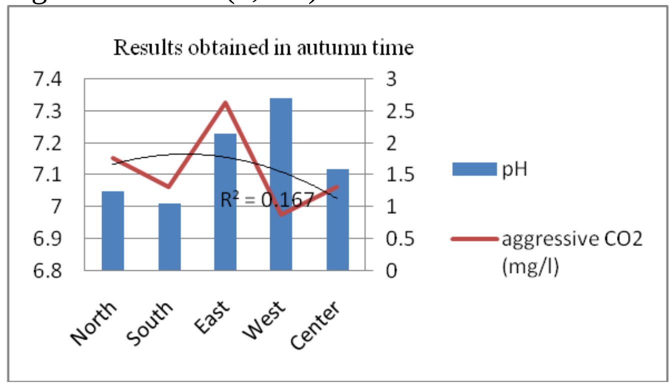

Fig. 13 The influence of aggressive CO_2 on pH from waters in autumn time

Concerning the influence of aggressive CO_2 on waters pH it was not remarkable comparatively to regression index value of 0,167 (figure 13) during autumn.

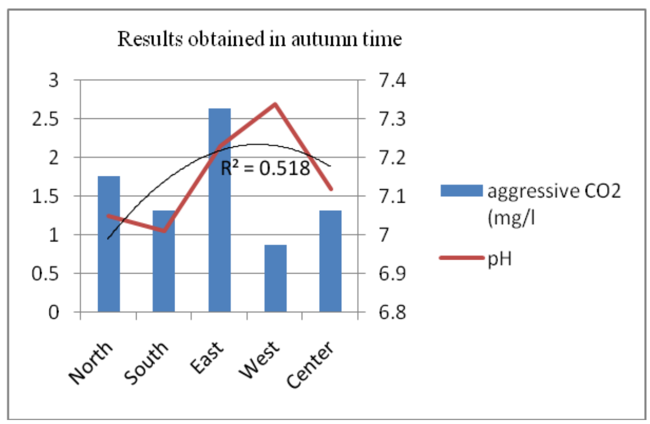

Fig. 14 The influence of aggressive CO_2 on pH from waters in autumn time

Maximum of aggressive CO_2 was registered in the waters of fountains from east (figure 14) and the minimum in fountains waters from west of village, in autumn time. The scale of aggressive CO_2 was between 0,88 mg/l and 2,64 mg/l. The pH had a significant influence on the accumulation of aggressive CO_2 in fountains waters, regression index being 0,518. The content of fountains waters in aggressive CO_2 had no influence on the modification of pH values in according to regression index (0,187) in winter time (Figure 15).

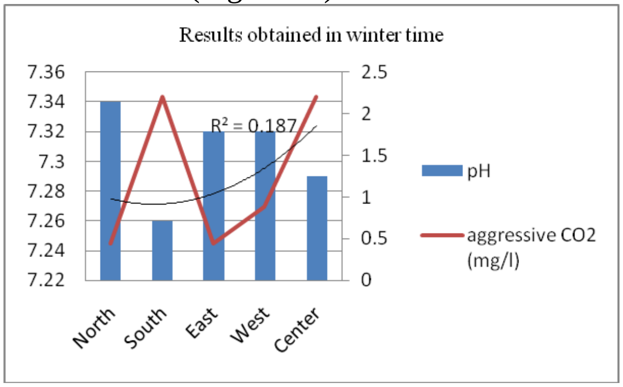

Fig. 15 The influence of aggressive CO_2 on pH from waters in winter time

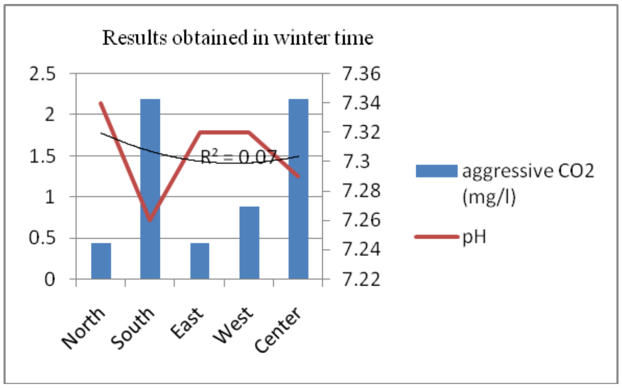

Fig. 16 The influence of pH on aggressive CO_2 from waters in winter time

The accumulation of aggressive CO_2in fountains waters fluctuated from 0,44 to 2,2 mg/l from a sampling point to the other in winter (figure 16). The greatest quantity was determined in fountains water from south to equality with that in center of village. In the others fountains, from west, east and north, the level of aggressive CO_2 was under 1mg/l. During the winter the pH had none influence on the accumulation of aggressive CO_2in the waters underground from Gorgota village.

In Table 1 on can see the level of temperature average of water at the moment of sampling the water for analyzing. In spring time the temperatures were between minimum 11°Cand maximum 14°C quite close to those registered in autumn (13-14°C). In summer time fountains waters had a greater values interval: minimum 14 and maximum 18°C. The lowest level of water temperature was in winter time, between 8,5 and 10 degree.

Table 1. The average of temperature at the time of sampling

No.	Season	Fountain location	Average of water t, °C
1	***Spring***	North	12,5
2		South	14,0
3		East	13,5
4		West	11,0
5		Center	13,0
6	***Summer***	North	16,0
7		South	18,5
8		East	14,0
9		West	17,5
10		Center	18,0
11	***Autumn***	North	14,0
12		South	13,5
13		East	13,5
14		West	13,5
15		Center	14,0
16	***Winter***	North	8,5
17		South	9,0
18		East	9,5
19		West	10,0
20		Center	9,0

Conclusions

Carbon dioxide from bicarbonates influenced pH of fountains waters in spring and autumn when the waters temperature was under 14°C generally.

The pH influenced the sequestration of CO_2 in bicarbonates molecules and the accumulation of aggressive CO_2in waters in summer time and autumn in the same measure. In these two seasons water's temperature was over 13 degree.

Aggressive CO_2 influenced pH of waters only in summer when water's temperature was over 15°C.
It seems that both processes of sequestration the CO_2 in bicarbonates molecules and the accumulation of aggressive CO_2in waters need a temperature level over 14°C.
But no matter of seasons, the fluctuations of waters pH are very close to neutral level, so it is not dangerous for human health.

Acknowledgement
This experiment was made with the contribution of some student from specialization Engineering and Environmental Protection in Agriculture field, promotion 2015: Ana Maria Pletescu, Georgiana Vlad.

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