CO_2 AND O_2 CONTENT IN MOUNTAIN RIVERS OF AZERBAIJAN AND ITS DEPENDENCE FROM WATER TEMPERATURE

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The gases dissolved in river waters have been identified according to data for 1980-2014 years. The long-term average quantity of dissolved gases in river waters has been calculated. It was determined that there is more detailed information about 3 gas (oxygen (O_2), carbon 4-oxide (CO_2) and hydrogen (H_2)) dissolved in river waters of Azerbaijan. According to the relation established between dissolved gases and values of long-term average of water temperature has been determined the quantity of dissolved gases in river waters of Azerbaijan.

Introduction

Natural gas plays an important role in the formation of the chemical composition of the water. Biochemical decomposition, the oxidation of organic substances and other processes are directly taking place under the influence of the dissolved gases. The study of dissolved gases, despite their small quantity, is very important because of the ability of their concentration to determine development conditions of biological and chemical processes, water quality and aggression against the concrete. According to their distribution, gases conditionally are divided into 3 groups: a) more spread – N_2, O_2, CO_2 and CH_4; b), less spread – H_2, H_2S, He, Ar; c), limited spread – NH_3, SO_2, HCl etc. Gases which are more and less spread in reciprocal exchange with water play an important role. But the gases of limited spread due to a high aggressiveness react with rocks of environment and lose its importance as a gaseous component.

The object of the study and used materials

As an object of research, 20 areas on 19 rivers flowing from mountainous regions were selected for hydro-chemical observations. In order to determine gases dissolved in river waters were used long-term data of the Department of National Monitoring on the Environment of the Ministry of Ecology and Natural resources (formerly the State Hydrometeorology Committee) chemical analysis of water samples regularly taken from rivers during 1980-2014 (Annual data, 1980-1994; Hydrochemical Newsletter, 1995-2014).

Research results

It is known that all the gases are dissolved in liquids with which they are in contact. The solution of the gas in water is determined by the quantity of coefficient and, shows at a given temperature the volume of gas dissolved in the unit of liquid. They use a quantity of saturation and elasticity to quantify the characteristics of the gas in mineral water. The total gas saturation is expressed as the sum of the gas dissolved in 1 liter of water ($1cm^3$). Any gas saturation signifies a gas quantity in a single volume of water. Total gas elasticity is found as the sum of elasticity of each component in a gas mixture. If the elasticity of gas, dissolved in water is more than the elasticity in the atmosphere, the gas is separated from water in form of bubbles on the earth's surface. The solubility of gas depends on its nature, water temperature and mineralization.

In natural waters, poorly soluble gases being in molecular state don't enter in chemical contact with water. Oxygen (O_2), carbon (CO_2) and hydrogen (H_2) are considered more important water-soluble gases. Despite the bad solution of oxygen in the water, because of high chemical activity it is in pure state only in the atmosphere. In the Earth's crust, the oxygen is formed in biochemical way and comes from the atmosphere; it is involved in the biological circulation of atoms connected to alive substances. In the form of molecule dissolved in natural waters oxygen is more important. Its participation paves the way for the existence of life in the water. Since the surface waters are rich of oxygen, sometimes its concentration reaches 40-50 mg/l. The quantity of oxygen in water is affected by 2 opposite groups of process. One of them enriches water with oxygen, and the other reduces the amount of oxygen in water. The enrichment of water by oxygen is mainly due to oxygen allocated from the atmosphere and water plants in results of photosynthesis. The separation of oxygen in result

of photosynthesis occurs by getting carbon 4 dioxides by aquatic plants. That is while the collection of O_2 occurs during the day; the consumption takes place at night. In this regard, the maximum amount of O_2 in water is observed in the afternoon (decreasing oxygen quantity is equal to the consumed quantity) while the minimum amount (increasing quantity of oxygen being equal to consumed amount) is observed early in the morning. The breathing of organisms, which reduces the amount of oxygen dissolved in water, is the process of fermentation and decay of organic residues. This process occurs continuously, accelerated with increasing temperature. Also, the reduction of oxygen in water is due to the allocation of part of it to the atmosphere. Changes of the amount of oxygen dissolved in natural waters are shown between 0-15 mg/l, minimum limit for the normal development of aquatic organisms is 5mg O_2 (Алекин, 1970).

According to the analysis of the available material, the amount of oxygen dissolved in the mountain rivers is changing between 8,20 mg/l (Gudialchay-Khachmaz) and 10, 96 mg/l (Nakhchivanchay-Nakhchivan); oxygen deficiency was not observed. However, as a rule, in all rivers, only 1-2 km below the point, away from stations, is observed the decrease of the oxygen dissolved in water by 11,5 % or in 1,2 times (Abduyev, 2009). The reason for this consists in increased number of organic residues thrown into rivers in settlements and the utilization of more oxygen for the fermentation and decay of remains. The study indicates the increase of the temperature of the oxygen dissolution with the rise of its quantity and having the concentration of 100% during a normal enrichment of water on oxygen. Let's mention, that none of studied rivers reach 100% oxygen concentration, and maximum concentration is observed in Goychay region (92,6%). Depending on the quantity of organic substances entering into rivers and time of decomposition, the oxidation temperature of water corresponds to annual regime of CO_2 and is characterized by minimum quantity in summer months and maximum quantity in winter months (Fig.1).

The relation between dissolved O_2 and water temperature shows its annual change trend- the growth at low temperatures in winter and decrease in summer at high temperatures.

In addition, in rivers occur events which change in opposite oxygen amount. It refers to photosynthesis process accompanied by increase in oxygen during the warm period of the year; in winter, a dominance of groundwater poor in oxygen nutrition and finally, to the formation of ice cover, which isolate the river water from the atmosphere. In rivers with poorly developed biological processes O_2 quantity is changing from 6-8 mg/l in summer to 8-12 mg in winter. However, as a result of biological processes, but also powered by groundwater, the saturation in oxygen of water is reduced in winter of 30-50% and increases again in summer to 90-100%.

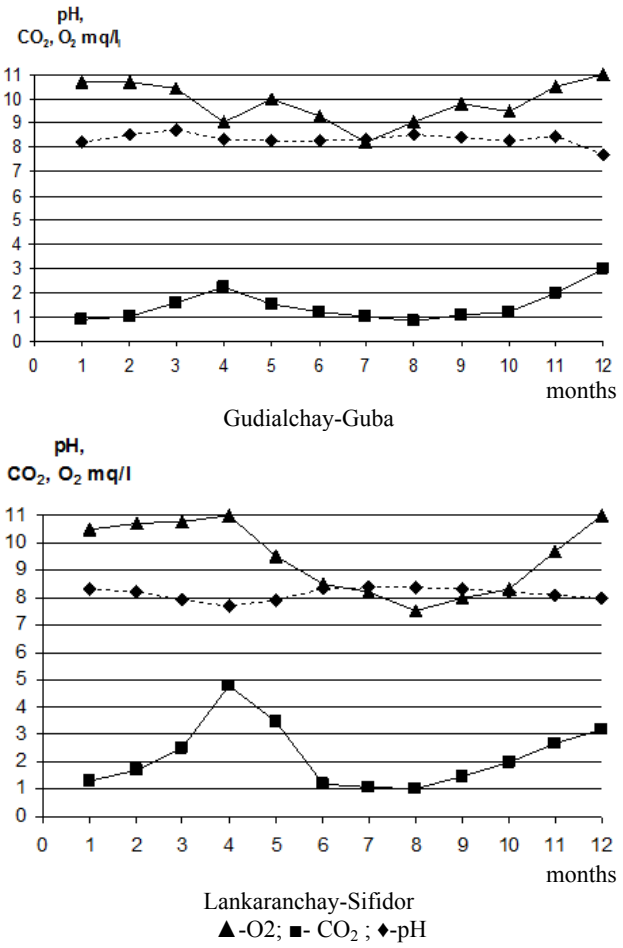

Fig. 1. Hydrogen (pH), carbon dioxide (CO_2) and oxygen (O_2) ions annual mode

The amount of oxygen sharply goes down in cases of intensive development of biological processes (water plants, live nature, rich organic substances) as well as during the nutrition of soil by groundwater poor in oxygen, especially in winter, when ice cover impedes the oxygen to pass through the atmosphere. In the meantime its quantity varies between 20-30%. Sometimes it is even observed lower than the indicated level (to 10%) and kills all living creatures. One of the important water-soluble gases is carbon dioxide 4. Carbon dioxide form a gas stack in the Earth's crust, so capable to dissolve at

high temperature it is located especially in water (or petroleum). CO_2 dissolved in water creates a weak carbonic acid. The presence of compounds with carbon dioxide in water is determined by hydrogen ion concentration that is by the quantity of pH. Thus, it plays an important role in the acidic environment (pH<7) in water in free-form of CO_2, in the form of CO_3 in alkaline environment (pH>10), when being 7<pH>10 in form of HCO_3 (Алекин, 1970). Carbon 4-oxide, in this or any other quantity is available in all natural waters. In the surface of open water reservoirs, under the strong influence in the process of photosynthesis spent by water plants, in some cases (in summer, on well-lighted and warmed surface waters) almost the disappearance of CO_2 is observed and as a result pH increases and gets price more than 8,5. The main sources of carbon 4 dioxide are the remains of organic biochemical process of decomposition, their oxidation, and breathing of water organisms. The allocation of the gas dioxide to the atmosphere, its passage to the carbonate rocks, the uptake by water plants in the process of photosynthesis refer to processes that reduce the quantity of carbon 4 dioxide in natural waters. Due to the easy transition of the carbon 4 dioxides dissolved in water into the atmosphere, ions, to living organisms, it is involved as a key factor in migration of carbon in nature. The amount of carbon dioxide in natural waters is usually 3-4 mg/l, reaching in occasional cases 10-12 mg/l. The rate of the amount of CO_2 in the atmosphere is about 0,6 mg/l. In accordance with the changes of carbon dioxide the hydrogen carbon changes too. In the solution, the ion of hydrogen (H) carries the acidity properties, and ion of hydroxide (OH) possesses the main property. As they are in equal amount in chemically pure water, this water is considered neutral water. The hydrogen ion concentration is denoted by the symbol pH. The quantity of this ion determines the reaction of the solution. Depending on the number of pH the reaction of the solution changes as follows (Алекин, 1970):

pH=1-3 when sour; pH=4-6 when weak sour; pH=7 when neutral;

pH=8-10 when weak alkaline; pH=11-14 has a reaction when alkaline.

In natural waters, the indices of hydrogen ion concentration mainly depend on water-soluble carboxylic acid and the amount of a variety of organic acids. The pH indices of natural waters are mainly equal to 5,5-8,5. Despite the small quantity of pH, its study is very important, as this ion concentration determines the development conditions of biological and chemical processes, water quality and the aggressiveness toward concrete. Thus, the pH indicator is used to control chemical analysis of the water, determine some components in water, study migration forms of microelements, search of mineral deposits (in particular, sulfide deposits) and so on.

The information on the amount of dissolved gases in the mountain rivers of Azerbaijan is listed in some studies (Гаджиев, 1984; Рустамов, Кашкай, 1989). According to G.A.Hajiyev who studied chemical flow of the Major Caucasus rivers (1984), O_2 was changing between 4,15-9,10 mg/l there. According to researches of S.H.Rustamov, R.M.Gashgay (1989), in the majority of rivers O_2 is wavering from 2 to 6 mg/l. In some rivers (Kurekchay, Gudialchay, Jeyrankechmez) at the time of floods it rises to 8-9 mg/l. In these rivers, the maximum quantity of O_2 is changing respectively between 15,4; 10,4 and 10,7 mg/l. However, these studies provide information only on the amount of O_2. There is no information on amount and regime of the both CO_2 and H_2. In order to study the amount of dissolved gases in river waters of Azerbaijan, and regime they have used stationary data in the hydrological yearbooks and bulletins on the quality of surface water. Analyses of the data show that the amount of gases dissolved in rivers is identified only in samples of 1-2 months of most years. In samples of water from rivers taken during a long-term, the amount of dissolved gases (oxygen, carbon dioxide and hydrogen) was regularly identified, and 20 river localities have been selected. 8 of these river localities are situated in the Major Caucasus, 7 in the Lesser Caucasus, 2 in the Middle Araz, 3 in Lankaran region. Perennial average numbers of dissolved gases on noted river localities were calculated and are given in the table.

Analysis of the data in the table shows that, the perennial average of oxygen dissolved in the studies rivers is of 8, 45-10,9 mg /l, the perennial average of carbon dioxide is 1,8-3,9 mg/l, the mentioned amount of hydrogen (pH) ions varies between7,78-8,43. Studies reveal the increase of oxygen with the elevation of temperature of its dilution and the concentration of 100% during the normal enrichment of the water by oxygen. We have to note that in none of the studied rivers the concentration of oxygen reaches 100% and maximum concentration is observed in Goychay (92,6%). In other rivers the O_2 concentration varies between 77, 5-91,8 %. Depending on the amount of organic substances coming into rivers and the period of their decomposition, according to the annual regime of carbon

dioxide, the temperature of water oxidation is specified by minimum quantity during summer months and the maximum in winter months (Fig.1). In the regime of the hydrogen ion and carbon dioxide, their amount increases in winter under the ice as a result of the oxidation process in the river waters and nourishment by underground water. With the disappearance of the ice cover and the part of its surplus allocated to the atmosphere, the amount of CO_2 and pH goes down. In summer a strong development of water plants causes a decrease in the amount (Fig.1).

Perennial average and calculated numbers of gases dissolved in river waters and the pH indicators

№	River-locality	Water t°, C°	Oxygen, O_2, mg/l			pH			Carbon 4 oxid, CO_2, mg/l		
			Actual	Calculated	Tolerance	Actual	Calculated	Tolerance	Actual	Calculated	Tolerance
1	Gudialchay-Guba	10,4	9,95	10,2	+3	8,35	8,36	0	1,7	1,8	+6
2	Gudialchay - Khachmaz	14,4	9,19	9,31	+1	8,25	8,22	-1	2,8	2,4	-14
3	Valvalachay-Tangaalti	10,9	9,98	10,0	0	8,43	8,36	-1	1,8	1,8	0
4	Balakanchay-Balakan	11,5	10,2	9,92	-2	8,38	7,44	-11	1,8	1,9	+6
5	Talachay-Zagatala	11,9	9,60	9,82	+2	8,28	8,29	0	2,1	2,0	-5
6	Kurmukchay-Gakh	11,5	9,57	9,92	+4	8,23	8,29	+1	2,7	2,0	-26
7	Turyanchay-Aghdash	12,4	9,64	9,72	0	8,31	8,29	-1	1,8	2,1	+17
8	Geychay-Geychay	13,2	9,72	9,54	-2	8,35	8,22	-2	2,0	2,2	+10
9	Aghstafachay-Gazakh	14,3	9,34	9,31	-1	8,31	8,22	-1	2,1	2,4	+14
10	Tovuzchay-Tovuz	14,9	9,29	9,18	-1	8,17	8,18	0	2,8	2,5	-11
11	Shamkirchay-Shamkir	11,8	9,54	9,81	+3	8,28	8,29	0	2,0	2,0	0
12	Goshgarchay-Dashkasan	11,4	8,45	9,96	+9	8,30	8,32	0	2,1	1,9	-10
13	Gargarchay-Khankandi	11,4	9,69	9,96	+3	8,15	8,32	+2	3,2	3,2	0
14	Kendalanchay-Girmizi-Bazar	10,3	9,60	10,2	+6	8,26	8,38	+1	2,7	3,0	+11
15	Khakarichay-Lachin	10,2	9,80	10,3	+5	8,22	8,38	+2	2,8	3,0	+7
16	Nakhchivanchay-Nakhcivan	10,6	10,9	10,2	-7	8,20	8,36	+2	3,3	3,1	-6
17	Gilanchay-Nurgut	10,4	10,4	10,2	-2	7,90	7,94	0	3,9	3,0	-23
18	Vilashchay-Shikhlar	13,4	9,38	9,49	+1	8,16	8,22	0	2,6	2,3	-12
19	Lankaranchay-Sifidor	13,5	9,47	9,45	0	8,21	8,22	0	2,4	2,4	0
20	Istisu-Alasha	15,0	9,19	9,18	0	7,78	7,79	0	2,6	2,6	0

The temperature is a physical property of river water more easily and quickly to determine. In this regard, hydrological yearbooks and hydrochemical bulletins give more comprehensive and systematic data on water temperature. Therefore, the determination of the amount of dissolved gases being complex and not always possible, it is more appropriate to use the temperature data to identify it easily and quickly. Studies (Алекин, 1970; Самарина, 1977) show that the amount of gases dissolved in water varies depending on temperature. Our investigation (Abduyev, 2009) determined that the amounts of pH, CO_2 and oxygen, dissolved in water decrease with the increasing temperature. In other words, there is an inversely proportionality of the amounts of the dissolved oxygen, pH, CO_2 to water temperature.

In the table the amount of gases dissolved in Azerbaijani rivers water have been identified according to the relationship of perennial average values of water temperature and calculated dissolved gases (Fig. 2).

Correlation coefficients of established connections are as follows: 0,92 for pH=f(t), 0,89 for O_2=f(t), and 0,81 for CO_2=f(t). The mathematical expression of the relation obtained between water temperature and carbon dioxide is as follows:

$$CO_2=-0,035t+2,894, \quad (1)$$

where CO_2 is the perennial average value of carbon dioxide, t is the perennial average temperature of water.

The relation established between perennial average values of dissolved oxygen and water temperature has the following mathematical expression:

$$O_2=-0,167t+11, 68. \quad (2)$$

The mathematical approximation of the relation established between perennial average temperature and the pH amount is as follows:

$$pH=-0,024t+8,519. \quad (3)$$

The error of the value of oxygen dissolved in water, calculated with mathematical expression, in 19 cases (95%) is less than ±7 from true value. Only in one case (5%) the error is ±18%. The error of the value of pH, calculated with mathematical expression, in 19 cases (95%) is less than ±2% from the true value. In one case (5%), it is up to ±11%. In the proposed mathematical expressions, in comparison with the other 2 gases (oxygen and hydrogen), the error of estimated values of carbon dioxide from the true values is relatively large. So, in 12 cases (60%) the error of carbon dioxide from the true value is to ± 10%, in 8 cases (40%) it is ±11-26%. It can be explained by the hesitation of the amount of carbon dioxide in larger range.

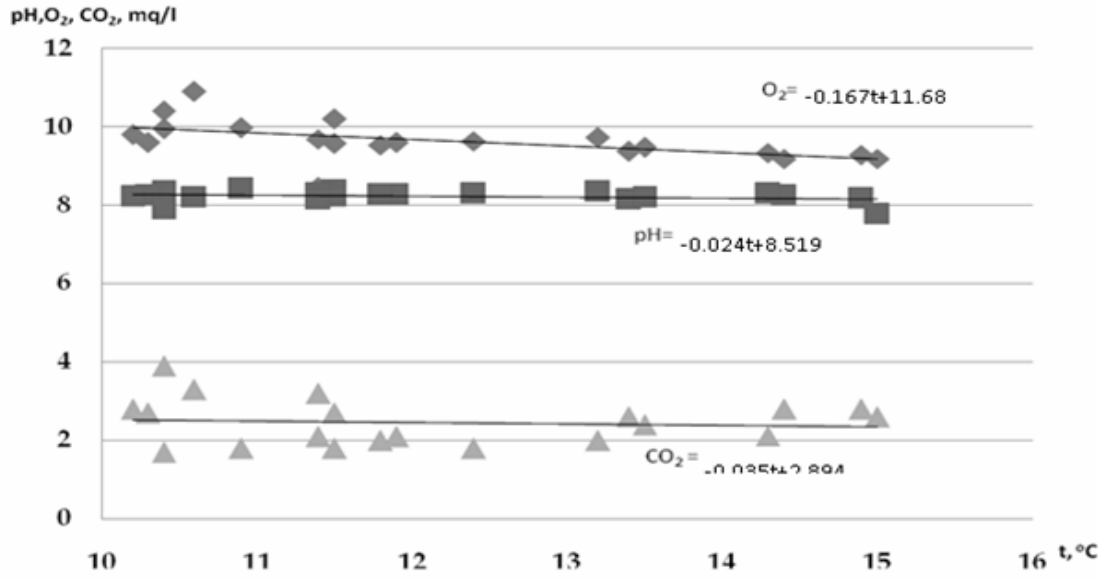

Fig. 2. Connection of perennial average values of water temperature with hydrogen (pH), oxygen (O_2), carbon dioxide (CO_2)

Thus, it is possible to determine the amount of dissolved gases in the rivers of Azerbaijan by the proposed mathematical expressions, when water temperature is known.

REFERENCES

ABDUYEV, M.A. 2009. Çay sularının qaz rejimi (Azərbaycan Respublikası daxilində). Bakı Dövlət Universitetinin 90 illik yubileyinə həsr olunmuş Coğrafiya cəmiyyətinin BDU filialının əsərlərində: *II cild. Azərbaycanın müasir ekocoğrafi şəraitinin dəyişməsində antropogen amilin rolu.* Bakı, 476-483.

АЛЕКИН, О.А. 1970. Основы гидрохимии. Гидрометеоиздат. Ленинград. 444 с.

ГАДЖИЕВ, Г.А. 1984. Химический сток и загрязнение рек Большого Кавказа в пределах Азербайджанской ССР. Автореф. дисс. на соиск. учен.степ.к.г.н. Баку. 24 с.

ГИДРОХИМИЧЕСКИЙ БЮЛЛЕТЕНЬ ГГМ ПО ОКРУЖАЮЩЕЙ СРЕДЕ. 1995-2014 гг.

ЕЖЕГОДНЫЕ ДАННЫЕ О КАЧЕСТВЕ ПОВЕРХНОСТНЫХ ВОД СУШИ. Часть 1. Реки. 1980-1994 гг.

РУСТАМОВ, С.Г., КАШКАЙ, Р.М. 1989. Водные ресурсы Азербайджанской ССР. Элм. Баку. 180 с.

САМАРИНА, В.С. 1977. Гидрогеохимия. Ленинград. 360 с.

Reviewer: corresponding member of ANAS A.A.Feyzullayev