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Full Length Research Paper

Climate Change Impact Assessment on Hydrochemical and Hydrological Regimes of Rivers

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Changes in water resources availability, stream flow and in river ecosystems are the major expected impacts of climate changes in river basins. The climate change is expected to influence the quantity as well as the quality of water resources by, for instance, increasing "natural' pollution. Consequently, it may lead to deterioration of water resources and destruction of ecosystems, along with extinction of endemic species of flora and fauna. In order to investigate the impact of climate changes on the river flow and on the content of salt concentration in river water The River Flow Substance Quantity Transfer Index (RFSQTI) was applied. The index relates the surface water quality and the hydrochemical and hydrological variables, and as a result provides flux of a given chemical substance by tone along the stream flow. The study was conducted in Marmarik River, thought to have no direct anthropogenic influence. The results indicated reduction in river flow and decrease and increase in the concentration of light and heavy ions, respectively, portrayed by the increase in the hardness of river water, suggesting a change in the water river source, with increase in the proportion of the ground water to surface water source. In the absence of major anthropogenic impacts, these changes are attributed to climate change. They attributed these changes to climate changes. The possible implications of the observed changes in the riverine ecosystems, water supply and water demand, as well as in the agriculture in the river basin are further discussed.

Keywords: *Climate change, River flow, Mineralization, Hardness, Hydrochemical regime.*

INTRODUCTION

One of the serious contemporary challenges in the World is the global climate change, impact which has already felt across the globe. Due to increase in air temperature and reduce of precipitation, the shortage of water supply and an increase in water demand are enhanced. According to the World Bank assessment, Armenia is among the most sensitive countries in the Europe and Central Asia region in regard to climate change, the impact of which has been already revealed on freshwater resources of the country. Based on long-term meteorological studies, there is a decrease in the maximum and minimum river flow by 3-5% for the most of the rivers in the country (UNDP, 2013; Sarkisyan, 1999). In the last 80 years, the average annual air temperature in the country has been increased by 0.85^{0}C and the average annual precipitation has been decreased by 6% (CCIC, 2009). However, changes in temperature in various regions of Armenia and during different seasons show different trends, as well as the spatial distribution of average annual precipitation (Hydrological Year Books, 1969-2013). Due to these meteorological changes, in recent decades (1980-2010), the intensity and frequency of hazardous hydrometeorological phenomena have increased by 1.2-1.8 cases per year (CCIC, 2009).

The water resources in the central part of Armenia are particularly scarce in the densely populated Hrazdan River watershed, including it the major tributary of Marmarik River (CCIC, MNP, 2009). Around 50% of the total volume of the Marmarik river flow is subject to significant annual variations: the river flow in dry years less than 65% of the one in an average year, as well as there are significant seasonal variations in the river flow.

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Around 55% of the total river flow of the Hrazdan and Marmarik Rivers in a normal year comes from spring snow melt and rainfall, and the ratio of maximum to minimum flow can reach to 10:1 (CCIC, MNP, 2009).

The hydrochemical regime for each river is determined by hydrological parameters (feeding source, river flow, air temperature, precipitations, etc.), changes of which will influence by the hydrochemical content of river water. Thus, the global climatic change, is expected to influence the quantity as well as the quality of water resources by, for instance, increasing “natural’ pollution. Consequently, it may lead to deterioration of water resources and destruction of ecosystems, along with extinction of endemic species of flora and fauna (Margaryan et al., 2010).

There are several hydrological studies related to quantitative assessment of river flow conditions due to changes on climate indicators that are listed in the USAID (2012) research report. Most of these studies used often, hypothetical scenarios of possible changes of air temperature and deposits, as a rule, due to climate change (USAID, 2012). However, there are seldom studies on the water resources quality changes caused by climate change. The hydrochemical qualitative and quantitative changes are likely to occur in the case of alteration of the hydrological regime. The existing methods of water quality assessment under climate change are based on several mathematical models (Smith, 1976). Sometime they are difficult to apply, and need long-term data series. The present study investigates the impact of the climate change on water resources, namely, the river runoff and concentration of the major ions, applying new and easy assessment approach method, which combines the water quantity and quality. The study was conducted in the Marmarik River Basin (the main stream of Hrazdan River) in Armenia, thoughtfully to have minor anthropogenic influence.

METHODOLOGY

Study area

The selection of the Marmarik River Basin (as a pilot river basin) is based on the following principles and criteria: availability of series (long period) of systematic observations and existence of all major hydrological and hydrochemical data (Hydrological Year Books, 1969-2013; Hydrochemical Year Books, 1982-2013), and the water basin has to be representative for the country in terms of hydrologic, hydrochemical and climatic characteristics (Chilingaryan et al., 2002).

Marmarik River Basin is locked between Tsaghkunyats and Pambak mountains (Figure 1), on average, at an altitude of 2300 m above sea level. The basin’s relief is typical mountainous with very fractioned valleys and gorges. This catchment basin is dominated with impervious rocks. About 12 per cent (50 sq.km) of the basin’s area is covered with forest where big-anther oak and Caucasian hornbeam dominate. The river’s length is 37 km and its catchment basin’s area is 427sq.km. The river head locates in Tsaghkunyats mountain chain at an altitude of 2520 m above sea level. The river’s tributaries are Gomur, Erkarget and Ulashik rivers. Marmarik River feeds on melting snow (55%), rain (18%) and groundwater (27%) (Chilingaryan et al., 2002).

Marmarik River is the biggest tributary to Hrazdan River. The River’s water is mainly used for irrigation, hydro energy, municipal and sanitary service and industrial purposes (Chilingaryan et al., 2002). As of 2007, about 3.4 million cubic m water intake was made in Marmarik River basin for irrigation, about 3.6 million cubic m – as drinking water and for municipal and sanitary services, about 4.7 million cubic m – for industrial needs and 38.4 million cubic m – for hydro energy purposes. In fact, annual amount of water intake in Marmarik River basin for general purposes makes about 32.3 per cents of the River’s annual flow, while the rest is in free flow, 111 million cubic m per annum, and ecological flow 6.3 million cubic m (Statistical Year Books, 1995-2013).

The long-term statistical data of meteorological observation (Hydrological Year Books, 1969-2013; Statistical Year Books, 1995-2013) indicated that the mean-annual air temperature and precipitation has increased at the region of Marmarik River Basin. There is lack of data about melting ice, which are in a little amount and located higher than 3800m sea level. However, the increasing air temperature was accompanied by increasing evaporation, which may have cause the reduction in the river flow. Also, annually increased precipitation has distributed unequal during the seasons. Most of the amount of rainfall occurs during the spring. Due to abundant precipitation in the spring the floods in the Marmarik River reach, very often, the environmental risk level. The precipitation reduces to less than 2 times in summer and autumn (for example, there were no any registered rainfall on November of 2010 (Hydrological Year Books, 1969-2013)), which leaded to low water in river (Hydrological Year Books, 1969-2013; Statistical Year Books, 1995-2013).

The River Flow Substance Quantity Transfer Index (RFSQTI)

Nowadays, hydrochemical assessment of rivers is based on integrated methods, which can uniquely determine the ecological status of water body, the level of water pollution and its change due to anthropogenic impact. Frequently, as the general tool for expressing integrated assessment result of water pollution of a waterbody is the Water Quality Index (WQI) (Margaryan, 2009). WQIs have different structure, the list of accounted

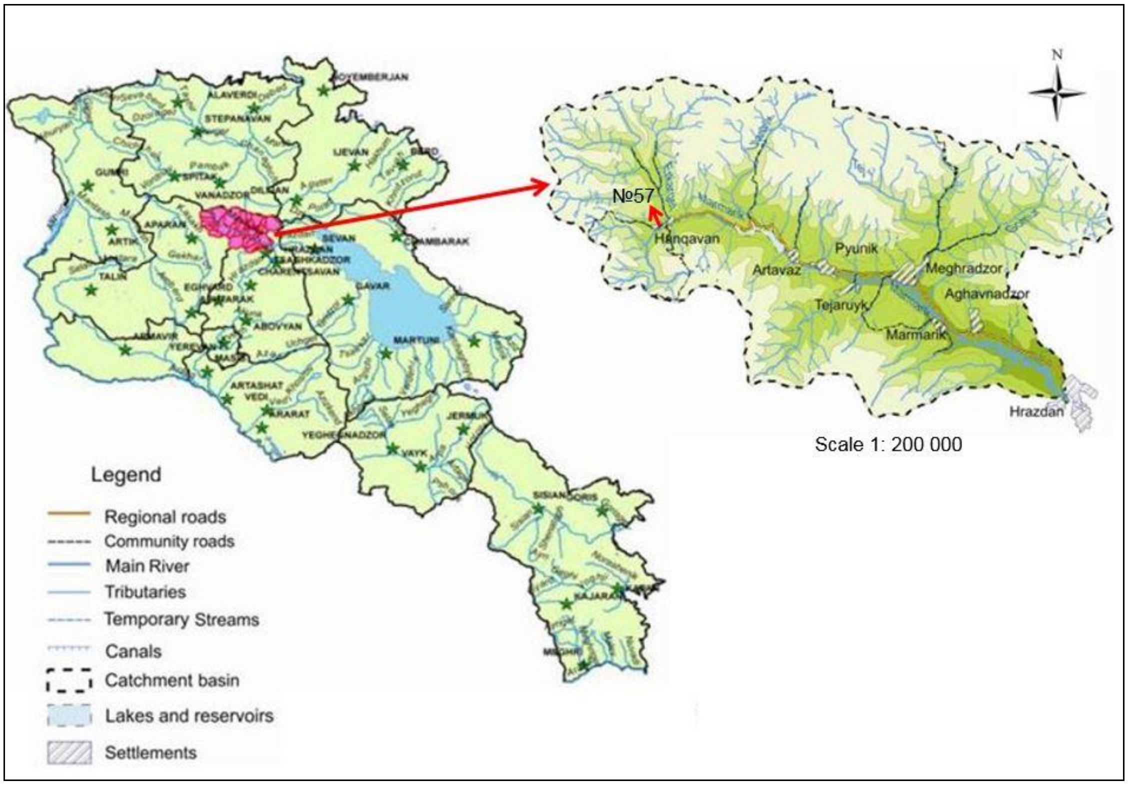


Figure 1. Location of Marmarik river basin in Armenia

hydro parameters and unique assessment mechanism of water pollution depending on the purpose of water consumption. All kinds of WQIs are directed to sum up the main hydrochemical, biological and/or hydrological data in a single integrated unit, through which it becomes possible to classify water body by pollution level. The calculation of WQI is based on logarithmic modifications of each hydrochemical or biological or hydrological parameter data through a set of mathematical equations, which also include maximum available concentration and background concentration for the parameter. Only a few amount of these WQIs can integrate both hydrochemical and hydrological data at the same time (USAID, 2012).

In order to combine the hydrological and hydrochemical parameters for integrated assessment of water resources changes as a result of climatic changes of the region, it was suggested new model – The River Flow Substance Quantity Transfer Index (RFSQTI) (Nikanorov, 2004; Margaryan et al., 2010). Through RFSQTI it is possible to calculate annual or monthly quantity of transferring substance by river flow. Also, it is allowed for long-term calculation dynamics, usually per five years.

The model has wide spectrum of hydrochemical parameters, such as mineralization, heavy metals, hardness, total nitrogen, phosphorus and etc, flux calculation.

If the absence of significant anthropogenic impacts on water body is considered, the annual flux of subject substance can be determined as follow (Nikanorov, 2004; Margaryan, 2009):

$$RFSQTI = 31.536 \cdot \sum_{i=1}^{n} W_i \overline{C_i} \qquad (1)$$

Where W_i is the river water flow during i time period (m^3/sec); C_i is average concentration of the hydrochemical parameter during i time period (mg/dm^3), RFSQTI's unit is tons by year.

For monthly calculation it becomes:

$$RFSQTI = 2.592 \cdot \sum_{i=1}^{n} W_i \overline{C_i} \qquad (2)$$

In this case RFSQTI's unit is tons by month.

If there are no any data about concentration of subject hydrochemical parameter (or the hydrological data of river), the Index value can be calculated as comparison with analog river for the flux amount of the same substance. It could be determined as follow (Nikanorov, 2004; Margaryan, 2009):

$$RFSQTI = \frac{RFSQTI_a \cdot W}{W_a} \qquad (3)$$

Where W is the river water flow of the study river and W_a– for analog river (m^3/sec); $RFSQTI_a$ is calculated for analog river.

The analog-river is the river comparable or semi-comparable discharge and geochemical region of flow with the study river. This kind of RFSQTI's determination is indicative, and it could become more accuracy if the analog-river will be chosen not only as comparable with river flow, but also comparable with hydrochemical content (Nikanorov, 2004).

When the anthropogenic impacts on water body are significant, they should be calculated and excluded from the (1) equation. It can be achieved by anthropogenic component of the RFSQTI and determined as follow (Nikanorov, 2004; Margaryan, 2009).

$$RFSQTI_a = RFSQTI_p - K_B \cdot RFSQTI_f \qquad (4)$$

Where $RFSQTI_a$ is the anthropogenic component of flux amount of subject substance for relevant period, $RFSQTI_p$ is the total amount of flux amount of the substance for relevant period, $RFSQTI_f$ is the background amount of flux amount of the substance, K_B – correction factor for the difference of water flow during the study and background periods.

The background period, in this case, is determined as the time, when were absent any antropogenic influence on river's hydrochemical regime or their impact was uncertainty. Mostly, that time period is considered up to 1980, because of the human impact on natural water resources was extremely increased in the coming years (Margaryan, 2009).

The relative error of calculation of RFSQTI for (1) and (2) is determined according to assumptions of the theory of errors.

It was determined as follows (Nikanorov, 2004):

$$S_{C_i} = \sqrt{S_{W_i}^2 + S_{K_i}^2} \qquad (5)$$

Where S_{Ci} is the relative error for RFSQTI calculation for i time period, S_{Wi} – the relative error of determination of river flow for i time period, S_{Ki} – the relative error of determination of average concentration of transferring substance for i time period.

The relative error for determination of river flow (S_{Wi}) is approximately 10%, in the case of determination method was defined as "velocity-area" with using of hydrological turntables, which was the mostly used method in practice.

The relative error of determination of average concentration of transferring substance is determined as follow (Nikanorov, 2004):

$$S_{K_i} = \frac{1}{\overline{C}} \sqrt{\frac{\sigma_B^2 + (\overline{C} \cdot \nu_a)^2}{n}} \qquad (6)$$

Where σ^2_B – standard deviation of the time series of the average concentrations in the river section; C- the average concentration of transferring substance for i time period, v_a – relative error of the method of analysis, n – the number of water samples for i time period.

Summarizing, absolute error ($\Delta RFSQTI_i$) for RFSQTI calculation for i time period was determined as follows (Nikanorov, 2004):

$$\Delta RFSQTI_i = \pm RFSQTI_i \cdot S_{G_i} \qquad (7)$$

The suggested new model (RFSQTI) in the present study has a computer based calculation in MsExcel program based on Margaryan et al. (2009). The scripts in Excel resolve the Equations (1, 4, 5,6 and 7) considering the input variables which are river flow, concentration ranges of transferring substances, relative error of the method of analysis, and etc.

Sampling

Hydrological and hydrochemical measures

The investigations took place in a fixed point in Marmarik River Basin, upstream Hanqavan village (Figure 2). The sampling point was located near the river source, where there are no major anthropogenic influences on the basin (Observation stations, 2003). So, it was considered as a water body with natural hydrological regime.

The hydrological observations of Marmarik River were performed during the 2000-2013 in the Meteorological Station of “Armenian State Hydrometeorological and Monitoring Service” SNCO (№57 sampling point, on Figure 1) (Observation stations, 2003). The observation consisted of river runoff using hydrological turntables methods (Sargsyan, 2006).

The hydrochemical observations of Marmarik River were performed during 2006-2013 in the sampling point, at about 0.5km upstream of Hanqavan village (№57 sampling point, on Figure 1) by “Environmental Impact Monitoring Center” SNCO (Observation stations, 2003). The water sampling were made 6-7 times per year, mainly from April to November, according to ISO 5667-1 (2006). From the water samples the Mineralization and Total hardness was determined.

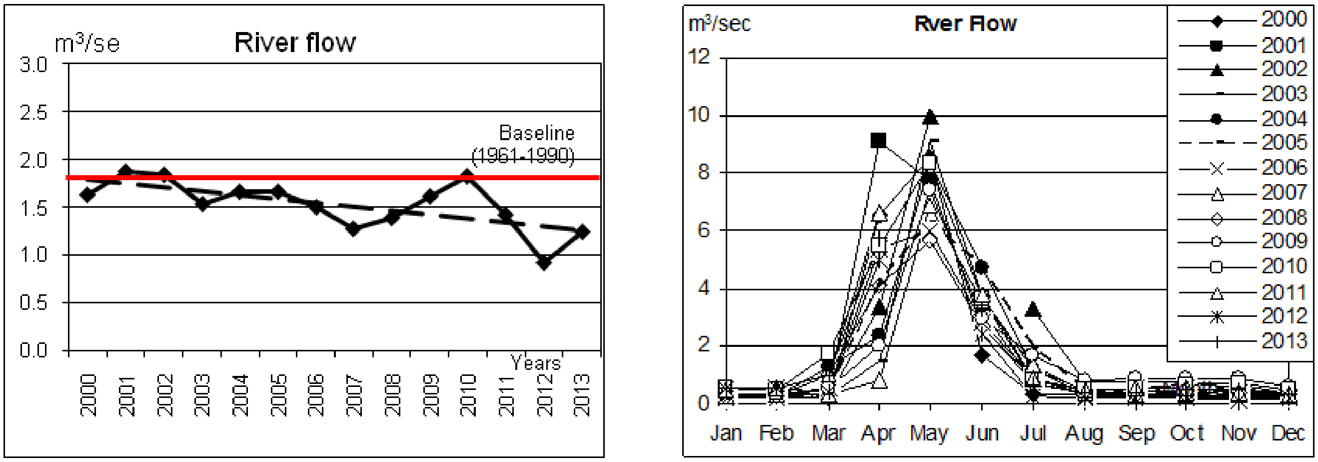
The mineralization of the river water were determined as the sum of major light ions (calcium, manganese, potassium, sodium, sulphate, chloride, bicarbonate) (Fomin, 2000). The total hardness of water was determined as the sum equivalents of calcium and manganese ions (Standard methods for the examination of water and wastewater, 1998). The concentrations of calcium, manganese, potassium and sodium were determined by ICP-mass spectrometric methods on ISO 17294-2 (2005) via Elan 9000 device.

Concentrations of sulphate and chloride were determined by ion-chromatography method according to ISO 10304-1 (2007) via Dionex 1000 device. The concentrations of bicarbonate in water samples were determined by Turbidimetric method on GOST 20806-228:069 (02)-77 (Guidance on chemical analyses of surface wtare, 1977).

RESULTS AND DISCUSSION

Assessment of changes in hydrological regime of Marmarik River Basin

Marmarik River flow data (Figure 2) reveal the inter-annual variability, which observed during the period



(a) (b)

Figure 2. Long-term hydrological observation results for Marmarik river, during the period 2000-2013, (a) annually changes of river flow and (b) monthly changes of river flow.

2000-2013. The hydrological measurements showed that the river flow was decreased. The River flow was reduced by 1.3-1.5 times during the 13 years of study. The reduction in the river flow was likely caused by change in the air temperature and precipitation.

The Figure 2b shows monthly average changes of the river flow over the entire period of observation (13 years). It shows seasonal variation in river flow, with minor deviation over the time. The comparison of study results with historical data (Hydrological Year Books, 1969-2013) in Figure 2a showed that climatic parameters, especially air temperature, evaporation and precipitation, changes effect not only on annual changes of river flow, but also on Marmarik River flood period. The river's flood period became about a month early in relation to baseline values of 1961-1990. If in the future the river flood observed on May, in the present, it observed on April.

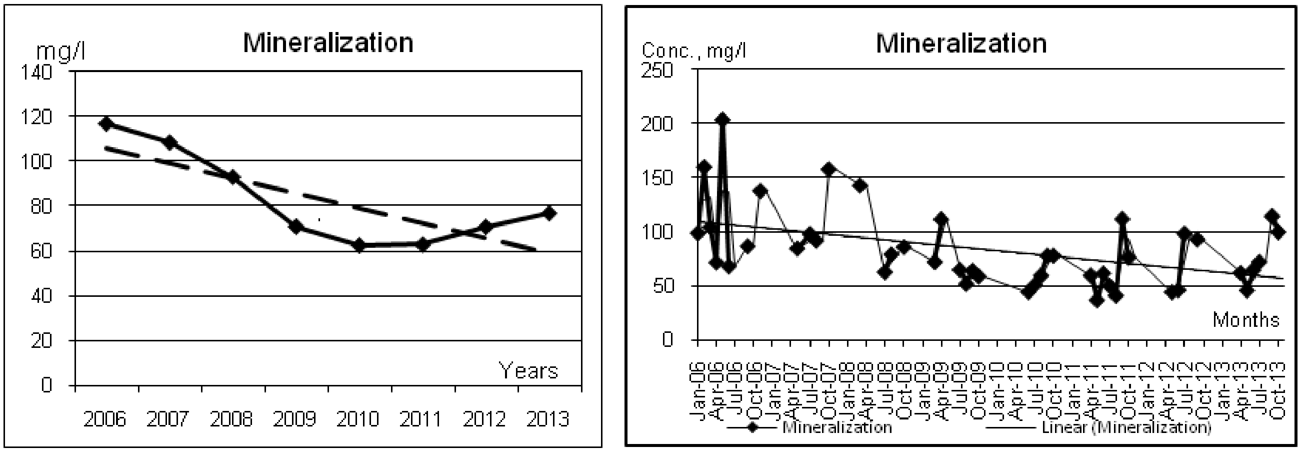
These hydrological regime changes of Marmarik River may influence dramatically on water use in the entire area of the river basin. The reduction and highly unequal seasonal distribution of river flow will inevitably affect on water supply and water demand and lead the water shortage for irrigation and recreation water use. The change of river's flood regime may also impact on agriculture. Natural and climatic conditions of Marmarik River basin allow cultivating a limited number of crops: wheat, late-ripening potato, vegetables in small quantities (e.g. cabbage) and forage crops. Thus, the April is not perfect time for these crops cultivation and irrigation: the soil is not enough warm, the fields don't need to be irrigated, due to high precipitations.

Assessment of the hydrochemical regime of Marmarik River Basin

Long-term hydrochemical studies of Marmarik River have shown that the mineralization of the river was falling down (Figure 3a, b). The mineralization reduced in 1,5-1,8 times over the last 8 years. Generally, the highest mineralization were observed in October and November (in autumn), when the streamflow of Marmarik have been on minimal level. Meanwhile, total hardness of the water were increased by straight line, which was the opposite to water mineralization trend (Figure 4a, b).

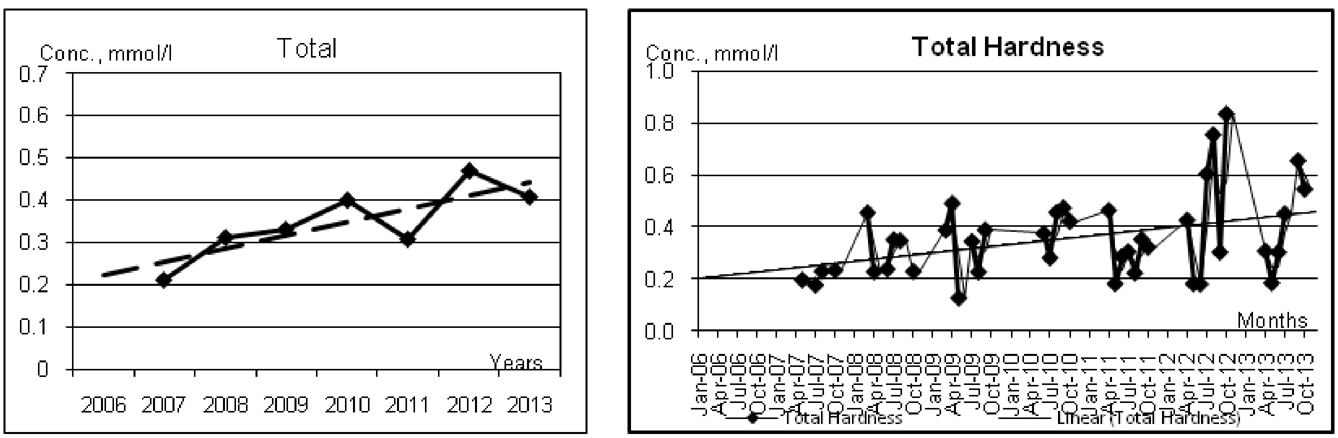
However, the Figures 5a and b says that trend of the total hardness increase was 1.28 times higher than mineralization reduction. The total hardness of Marmarik River water was increased by 2 times in the last 8 years. The highest values of total hardness, as well as mineralization, were observed during low streamflow level, basically in autumn. In general, when the river has mostly groundwater supply, the concentrations of calcium, magnesium and sulfate ions in river water are higher than concentrations of other general ions (Alekin, 1970; Sadovnikova et al., 2006). Otherwise, in the case of surface supply of river, the concentrations of sodium, potassium and chloride ions are dominated. Thereby, these kinds of seasonal changes of mineralization and total hardness of Marmarik River are the result of changes of the river supply sources.

The anthropogenic influence in river and extensive geological changes of this region during 13 and more years were not registered, which leads to consider that the changes of Marmarik River supply sources might be as the result of global climate change (Hydrological Year Books, 1969-2013; Chilingaryan et al., 2002). The climatic change of this region has caused some deviation in hydrological regime of the river in relation to baseline of 1961-1990 (Hydrological Year Books, 1969-2013). If, the majority part of the river supply source was surface water in the past, nowadays, the river feeds basically on groundwater source. So, the river feeds on groundwater source got higher on 10% (became 37-47%



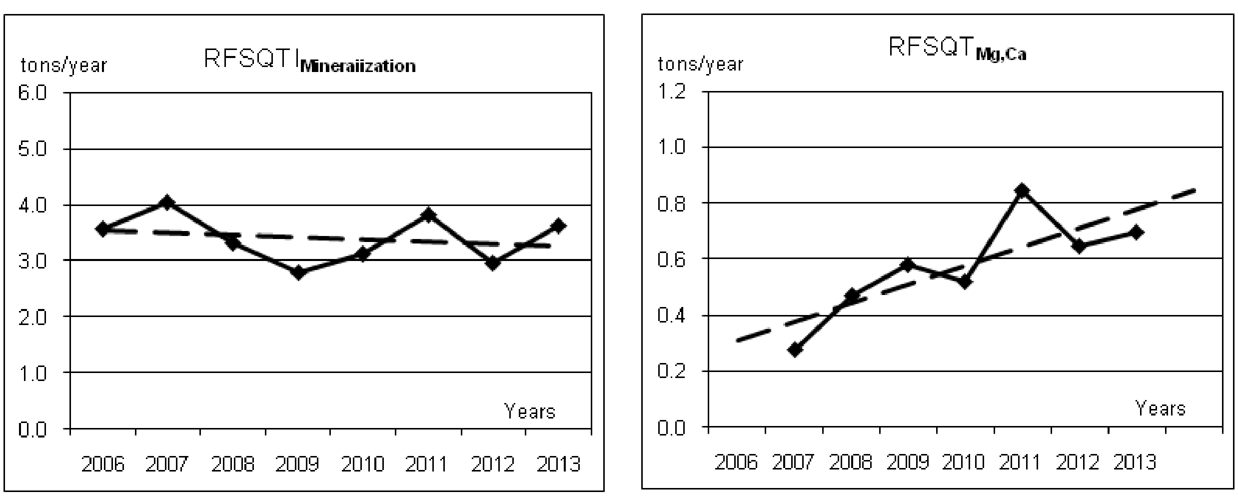
(a) (b)

Figure 3. Long-term monitoring data of Mineralization for Marmarik river, during the period 2000-2013, (a) annual and (b) monthly changes.



(a) (b)

Figure 4. Long-term monitoring data of Total hardness for Marmarik river, during the period 2000-2013, (a) annual and (b) monthly changes.



(a) (b)

Figure 5. The River Flow Substance Quantity Transfer Index (RFSQTI) data for Marmarik River Flow, during the period 2000-2013, (a) RFSQTI values for Mineralization and (b) RFSQTI sum values for Mg and Ca.

except on 27% (Chilingaryan et al., 2002)), because of rainfall shortage in summer and autumn.

Due to this kind of hydrological regime deviation of Marmarik River, the hydrochemical regime also suffers. As a result, the concentrations of chloride, sodium and potassium ions decreased, which cause the reduction of mineralization, despite of increasing of concentrations of calcium, manganese and sulfate ions. The trend of latest ones concentrations growth is more than reduction of concentrations of chloride, sodium and potassium ions. These cause the increase of salinity of river, which is serious environmental challenge that will be able to have destructive impact on the river basin ecosystem.

The statistic shows, that 2.1% of annual amount of water intake in Marmarik River is used for irrigation (Chilingaryan et al., 2002). Thus, the increasing of heavy ions concentration in river water will be, inevitably, effect on acceleration of soil salinization process in entire area of the Marmarik River Basin.

Climate change impact assessment on Marmarik River Basin via RFSQTI

To investigate of correlation between river flow, mineralization and total hardness changes for Marmarik River, it is necessary to combine the river's hydrological and hydrochemical data. For this propose it was offered to use RFSQTI model. It was determined the transferring amount of mineralization, Mg and Ca through RFSQTI model by Marmarik River flow for 2006-2013 (Fig. 5). The RFSQTI values for Mg and Ca were added. As a background concentrations for the hydrochemical parameters the monitoring data for baseline period the 1982-1990 were considered (no older hydrochemical data are available) (Hydrochemical Year Books, 1982-2013) (mineralization was 216 mg/l (RFSQTI=12tons/year), Total hardness was 0.3mmol/l ($RFSQTI_{Mg,Ca}$=0.13tons/year)).

Based on the assessment result, the slightly reduction of RFSQTI values for mineralization were observed, that means 92.5% of mineralization reduction in the river water (Fig. 3a) depends on the reduction of river flow and remaining 7.5% is caused by other reasons. The correlation between monthly data of river flow and mineralization showed the direct relationship: the mineralization is reduced in parallel with the river flow. The low concentrations for mineralization in the river water were coincided with river flow low values, and vice versa. Thus, it turns out that mineralization of the river did not change and the observed variations were natural adaptation example of climate change, aims to stabilize to hydrochemical regime for new reduced streamflow of the river. In this case, it would have not been appeared any negative impact on the river basin ecosystem. However, the RFSQTI calculation results for total hardness (Fig. 5b) have shown the high impact on hydrochemical regime of river due to river flow reduction. During process to adapt to new kinds of climate parameters (more precipitation, high evaporation, less streamflow), the river's ecosystem also seeks to maintain water balance. As a result, the river is starting to feed more from groundwater sources. These are causing to increase of total hardness in water of the river. The monthly variations of mineralization and total hardness concentrations in the river also approved that there is the process of change of river's feeding type. If the main sources of supply for Marmarik River were melting water and atmospheric precipitation in past (about 55%) (Chilingaryan et al., 2002), now the underground supply became dominate. As a result the concentrations of heavy ions, such as Mg and Ca, were increasing (increase in total hardness) and light ions, such as Na, K, Cl, were decreasing (reduce in mineralization) (Hydrochemical Year Books, 1982-2013).

Based on the RFSQTI assessment for total hardness, the content of heavy ions in river water increased in 2,5 times due to slight changes of the river flow in only last 7 years. The flux mineralization amount for mineralization was reduced by 2 times and the flux amount of sum equivalent amount of manganese and calcium was increased by 4.4 times in relation to baseline of 1961-1990 ((Hydrological Year Books, 1969-2013; Hydrochemical Year Books, 1982-2013).

CONCLUSION

Due to climatic changes there were observed the slight reduction of mineralization and river flow for Marmarik River, as well as the increase in the total hardness was recorded over last 8 years. The RFSQTI assessment results showed that the flux mineralization and sum equivalent for Mg and Ca amounts were several times changed in relation to baseline of 1961-1990. These changes explained by the changes of the river's sources supply types. As a result, the salinity of the river water is increasing, that may lead the poor water quality for water supply and irrigation. The reduction of river flow and increase in total hardness in the long-term period leads the water shortage and usage of poor water quality in the entire area of the Marmarik River. Moreover, water quality and quantity changes of the Marmarik River will have high impact on riverine ecosystem: change the biodiversity of river due to heavy ions concentration increase, deconstruction of ecosystem.

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