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Conditions of pH and Ionic Composition of Water in a Macrophyte Dominated Reservoir (Hanna Reservoir - Isfahan Province),IRAN

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Abstract: 2/3 of the reservoir surface area was approximately covered with dense populations of Myriophyllum, Ceratophyllum and Potamogeton species. The headwaters of the reservoir were considered as a hard water and had both carbonatic and non-carbonatic hardness. When they were exposed to lentic condition of the reservoir and its intensive photosynthetic activities of macrophyte communities, the bicarbonate ions were absorbed significantly and the pH of water increased to relatively serious levels and calcium carbonate precipitated as subsequontly. These processes caused a significant decrease in calcium and bicarbonate ion concentrations of the water column of the reservoir. Thus, in the headwaters, calcium and bicarbonate ions were dominated and the cationic and anionic ratios in water were in the order of $Ca^{2+}>Mg^{2+}>Na^{+}$ and $HCO_3^{-}>Cl^{-}>CO_3^{2-}>SO_4^{2-}$ respectively. But in the water column of the reservoir, due to above mentioned reasons, magnesium and chloride ions prevailed and ionic status order changed to $Mg^{2+}>Ca^{2+}>Na^{+}$, and $Cl^{-}>HCO3^{-}>CO_3^{2-}>SO_4^{2-}$

Key Words : Ionic composition, pH, Macrophyte, Reservior, Isfahan

Introduction

Classically it is believed that when headwaters reach the basin of the dams and meet lentic condition, the surface of evaporation increases and ionic composition of water usually changes to chloride and sodium ions prevalence (Rippey & Wood, 1985). In soft waters lentic condition and intensive photosynthetic activities cause an undesirable changes in pH values of the water column (Pokorny *et al.*, 1984). But in hard waters, however, lentic condition, even in the case of high photosynthetic pressure, is not able to make significant changes in pH values

(Stumm & Morgan 1970). According to above mentioned hypotheses when lotic water of rivers meet lentic condition of dam basins, the high buffering capacity of the hard water neutralizes the possible photosynthetic proton exchange capacity and pH will not meet significant changes. But in Hanna Reservoir, with rather hard water, significant pH changes were observed by the cageculturist. The pH values of the water increase to undesirable levels especially during summer months when the cages carry maximum fish biomass. Because the pH changes in the reservoir were different from classical knowledge, it is hypothesized that, the ionic composition and changes brought up by development of macrophyte communities, could be the most important cause for this case.

Materials and Methods

The Agh Dagh, Rag Hanna, Dareh Ali, Dela and Morvarid Mountains located in southern part of the Isfahan Province form the Hanna River watershed. The watersheds is located at coordinates of 31° N, 51° W, and is adjacent to south-western part of large central watershed of the Iranian plateau, and is a small portion of very large watershed of Karoon River (Fig. 1). The watershed has high mean altitudes of 2600 meters above sea level extending 40 Km in length and 18 Km in width with a total surface area of 71 square kilometer. Bahmanzad and Chahtal rivers form the head waters of the Hanna River, the former flowing from south-eastern to north-western parts of the watershed and the latter running from north to south and meet each other at 4.5 km west of Hanna village. The headwaters are supplied mainly by many small and large springs in addition by snow melts and in lesser extent by run-offs initiated from heavy rains. The surveyed watershed is a hilly or mountainous region and calcite, conglomerate and marl comprised most components of its rocks, sands and soils (Eskandary, 1993).

Snow is the main component of precipitation in the watershed and raining is usually rare. The fast moving surface run-off, resulted by snowmelt or rain, has significant eroding effect on the rocks and soils of watershed and has washed out different salt components to the headwaters and reservoir. Moreover there were approximately 48675 hectares of non-irrigated and 9000 hectares of irrigated lands in the watershed (Shahmoradi *et al.*, 1987). The irrigated lands lie along the headwaters and include several small and large farms.

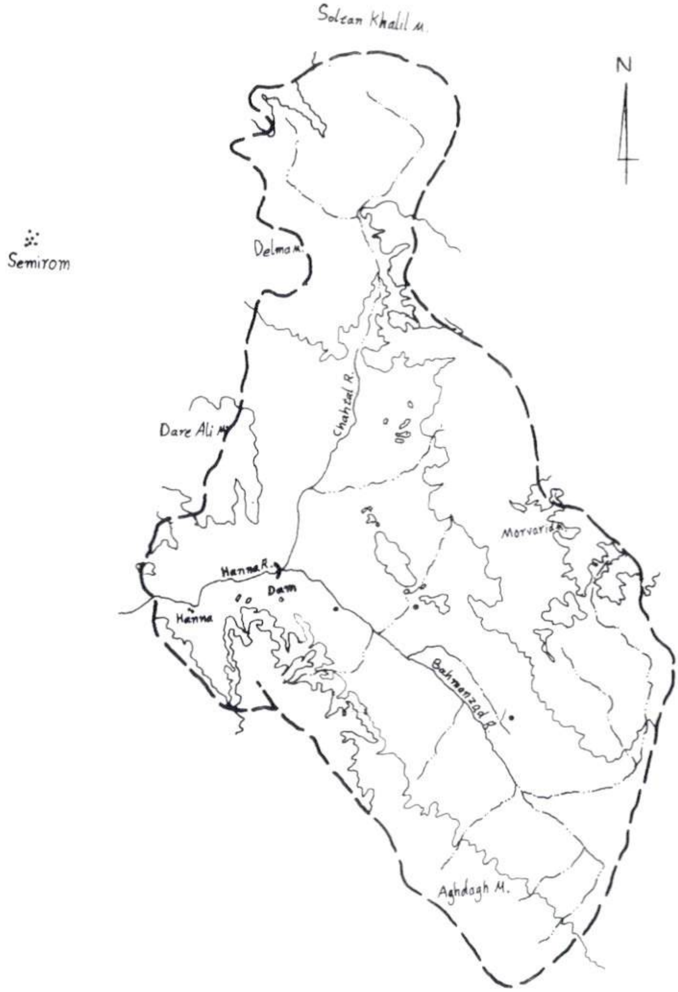

Figure 1: The location of Hanna Dam, Hanna River and the headwaters (1:250000)

During agricultural seasons water from Bahmanzad and Chahtal rivers are directed to the main supplying channel of each farm which irrigates different related patches. Due to relatively high slope of the grounds, the water quickly flows through the patches and ultimately flows down to the same river and washes out additional different chemical components to the headwaters.

The Hanna Dam was constructed and impounded in 1997 on Hanna River at the meeting point of the headwaters, situated at a distance of 30 kilometers from southwest of Semirom town. The dam has 245 meters length, 10 meters width at the top and maximum height of 35 meters. The maximum capacity of the basin is 50 million cubic meters and serves water supply for irrigation of 9000 hectares agricultural lands in Hanna plain. The reservoir has maximum depth of about 30 meters adjacent to the dam, and according to the depth and slope of the bottom it was divided in two parts. The upper large and shallow part, which is permanently served by headwaters and the lower small and deep part situated nearby the dam, and supplies the out flowing waters. The surface area of shallow and large upper part is approximately 8 times higher than deep lower one.

Water samples from Hanna Reservoir and the headwaters have taken in monthly intervals from May 1999 through April 2000. Whole water column samples, in the headwater, the river and shallow parts of the reservoir were taken by P.V.C. tube with 5-cm diameter and in the deep parts of the reservoir by Ruttner bottle sampler. The sub-samples of each sampling site were mixed carefully and adequate amount have been taken to the laboratory for further analysis. Fig. 2 shows the location of sampling sites in the headwaters and in the reservoir. Sites 1 and 2 indicate the headwaters where they reach the reservoir. Sites 3–5 and 6–9 represent the upper and lower parts of the reservoir, respectively and site 10 exhibits the outflow water.

The water temperature and pH values were measured *in situ* at sun- rise and sun set with mercury – glass thermometer and portable pH meter. The concentration of major anions and cations were measured following the standard methods developed by Iranian Environmental Protection Organization (1998). The hydrological data were obtained from the Management Office of Hanna Dam and the climatic data were collected in Shahid Hamzavy meteorological station located at southern part of the Hanna village and managed by Isfahan Center for the Research of Animal Science and Natural Resources. During samplings of summer months limited macrophytic communities were identified by Ekman Grab sampler and then the extent of macrophyte coverage was estimated by planimetery of water counter line map of the reservoir (Olah, 1990). The main taxonomic group of macrophytes were identified according to Raju, 1996 & Terrell and Perfetti, 1996.

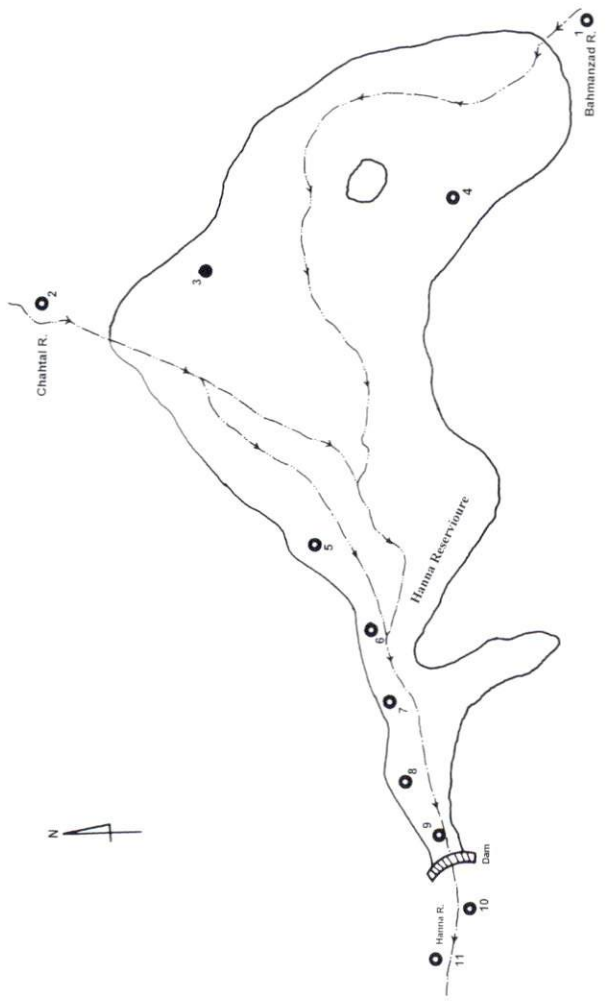

Figure 2: The location of sampling stations in the headwaters, Hanna Reservior and Hanna River (1:20000)

Results

The maximum and minimum values of mean depth, inflow water and surface area of the reservoir were observed in rainy and dry seasons, respectively. The values of outflow and retention time were completely related to agricultural cultivation activities and dry seasons (Table 1).

Table 1: Hydrological data of Hanna Reservoir (Apr. 1999 – Mar, 2000)

Month	Surface area (ha)	Inflow (m3/s)	Outflow (m3/s)	Standing volume (million/m^3)	Retention time (day)	Mean depth (m)	Changes of water level (m)
Apr	870	5.5	0.2	51	2951	5.8	+0.8
May	840	3.2	4.12	47.3	132	5.6	-0.5
Jun	760	3.4	3.8	44.3	135	5.8	-0.4
Jul	665	1.6	4	36.5	105	5.5	-0.9
Aug	620	1.5	3.5	30.6	101	4.9	-0.8
Sep	540	1.2	2.5	26.08	120	4.8	-0.8
Oct	520	1	1.7	23.85	162	4.5	-0.4
Nov	530	2.3	1.5	25.5	196	4.8	+0.3
Dec	600	2.5	0.95	29	353	4.8	+0.6
Jan	650	2.6	0.8	33	477	5	+0.7
Feb	710	3.4	0.7	39.5	653	5.5	+0.7
Mar	890	3.4	0.4	47.9	1385	5.3	+0.7

Source: Management Office of Hanna Dam (unpublished data).

Due to decrease in depth and volume of water in summer and autumn, approximately 2/3 of surface area of the upper shallow part of the reservoir was dried and the shoots of its macrophyte communities were completely exposed to the air.

Rainy season in Hanna district lasted from November to April with monthly precipitation variation of 12 to 105 millimeters. The total annual precipitation recorded 248 millimeter. During the surveying year, Hanna area was very windy, especially in summer months, when there were only three calm days in a month. But in late autumn and whole winter, windy days were significantly reduced (Table 2).

Table 2: Precipitation (millimeter) and wind speed (Nautical mile) in Hanna district (1999).

Month / Parameters	Apr.	May	June	July	August	Sep.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar
Changes in wind speed	4-28	8-28	4-20	4-20	4-28	4-20	4-20	8-28	4-16	4-20	8-16	8-28
Mean wind speed	3.74	6.32	5.74	6.62	8.06	5.16	5	3.73	1.24	2.66	1.24	3.81
Calm Days	10	8	6	3	3	9	19	7	22	15	24	15
Precipitation	40	0	0	0	0	0	0	12	39	105	33	19

Source: Shahid Hamzavy Meteorological Station (unpublished data).

During the year, the mean pH value in the headwaters and in the reservoir fluctuated between 7.8 – 8.5 and 7.8 – 9.5, respectively. From early spring to late autumn the measured mean pH values of the reservoir were higher than headwaters and the highest differences were found in summer months, in contrast with most of the samples of late autumn and winter, the pH of headwaters were higher than reservoir. During the year, pH values of headwater increased almost monthly and reached maximum values in autumn and winter, but pH values of the reservoir showed monthly fluctuations with maximum and minimum values in summer and late autumn, respectively. (Fig. 3).

During spring and summer, daily fluctuations of pH values in reservoir were higher than in the headwaters, but during autumn and winter they were approximately equal in both ecosystems. The maximum daily value difference of 0.8 unit was observed in the reservoir in spring (Fig. 4).

The variations of carbonate concentrations in headwaters were characterized by July minimum and October maximum, in the reservoir they also showed minimum values in July but the maximum concentrations in upper and lower parts of the reservoir were found in October and May, respectively. The variation of carbonate concentrations in out-flowing water and the lower part of the reservoir were similar (Fig. 5).

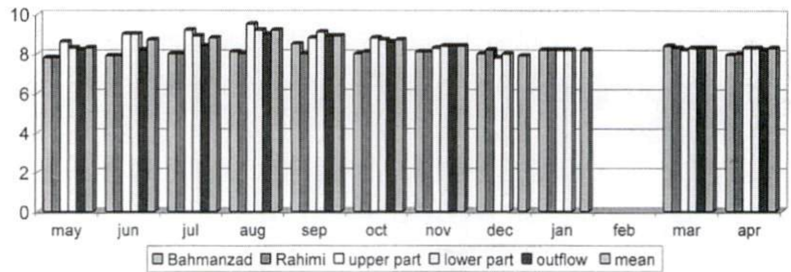

Fig.3: Monthly pH values of Hanna Reservoir(May1999-Apr2000)

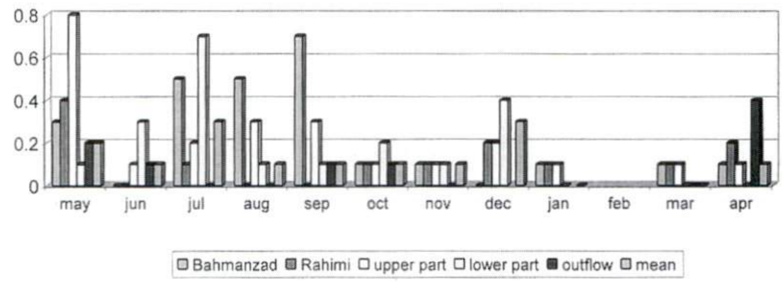

Fig.4:Daily differences of pH in Hanna Reservoir
(May1999-Apr2000)

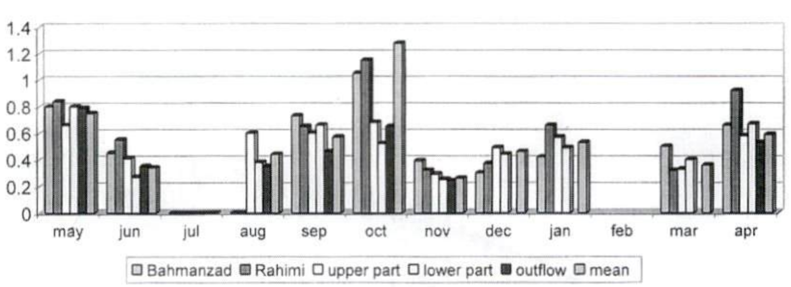

Fig.5:Concentrations of carbonate ions in Hanna Reservoir(meq/l)
(May1999-Apr2000)

The bicarbonate concentrations in most samples of headwaters showed marked fluctuations and were characterized by three maxima in April, October and March and two minima in July and September. But in the water column of the reservoir they exhibited more regulated and modified variations with two maxima in April and May and one minimum in August or September. Outflow however, had marked variation in bicarbonate concentrations with three maxima in April, July and November and two minima in May and August (Fig. 6).

There were significant differences in chloride concentrations between two branches of headwaters. In Bahmanzad River chloride concentration was minimum in April, May and December and was at its maximum in June. But Chahtal River was characterized by quite higher chloride concentrations with two minima in April and July and two maxima in May and September followed by no significant changes in autumn and winter. The chloride concentrations in upper part of the reservoir were higher than lower one, and showed marked monthly fluctuations in both ecosystems. In contrast, the outflow had regulated changes in chloride concentrations, increasing from early spring to late winter with no significant fluctuation (Fig. 7).

During the year in Bahmanzad River the sulfate concentrations were very low and relatively constant, but Chahtal River had higher and more variable sulfate concentration (Fig. 8).

The concentrations of calcium ions in headwaters, reservoir and outflow varied between 2 – 4.2, 0.96 – 2.6 and 1.4 – 2.4 meq/l, respectively. Therefore the reservoir and outflow had always much less calcium ion content than the headwaters (Fig. 9).

From April to August the concentrations of magnesium ions in the reservoir were approximately higher than in the headwaters. But in the rest of the year opposite condition was observed (Fig. 10).

Similar to chloride ions, the concentrations of sodium ions in two branches of headwaters were also not identical. Bahmanzad River was characterized by much lower sodium concentration than Chahtal River. In all samples the sodium content of reservoir was relatively higher than mean values of headwaters.

During the surveying year, the concentrations of sodium in outflow were quite identical with average values of lower part of the reservoir (Fig. 11).

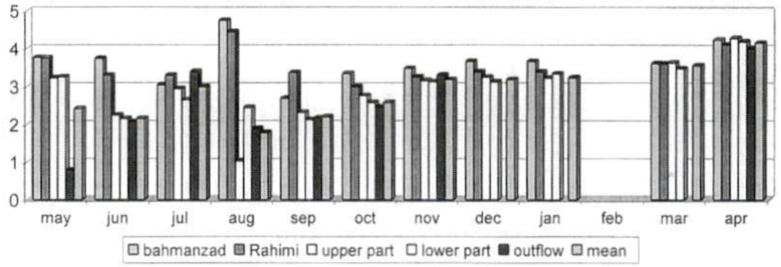

Fig.6:Concentrations of bicarbonate ions in Hanna Reservoir(meq/l)
(May1999-Apr2000)

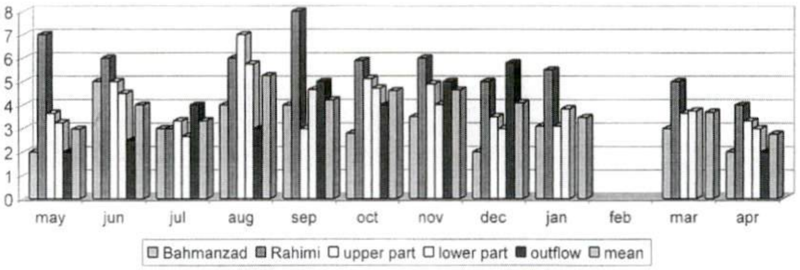

Fig.7:Concentrations of chloride ions in Hanna Reservoir(meq/l)
(May1999-Apr2000)

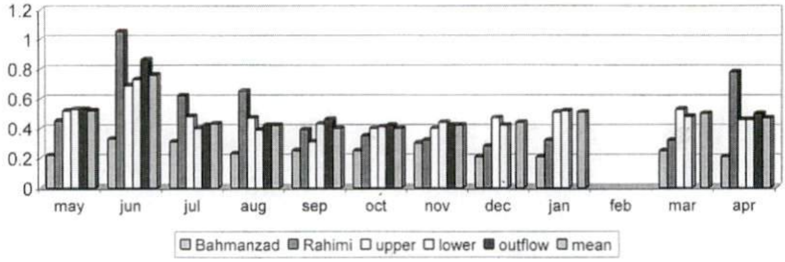

Fig.8:Concentrations of sulfate ions in Hanna Reservoir(meq/l)
(May1999-Apr2000)

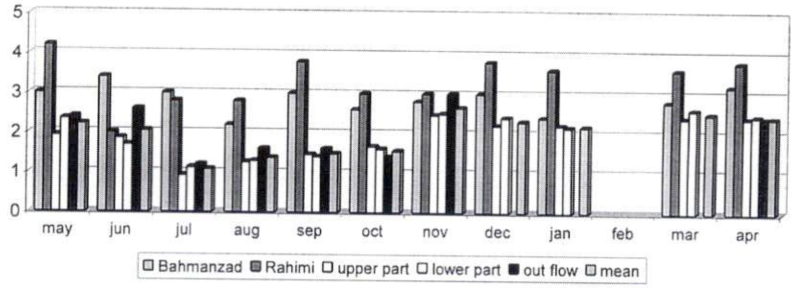

Fig.9:Concentrations of calcium ions in Hanna Reservoir(meq/l)
(May1999-Apr2000)

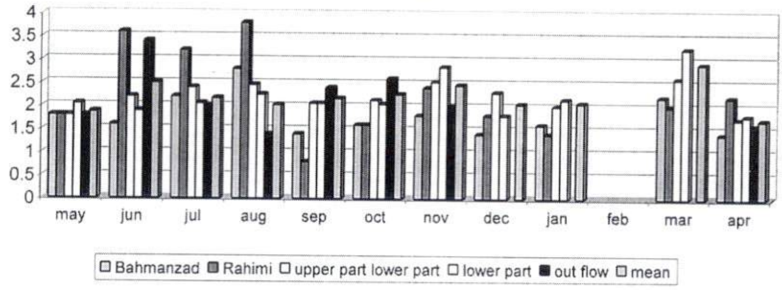

Fig.10:Concentrations of magnesium ions in Hanna Reservoir(meq/l)
(May1999-Apr2000)

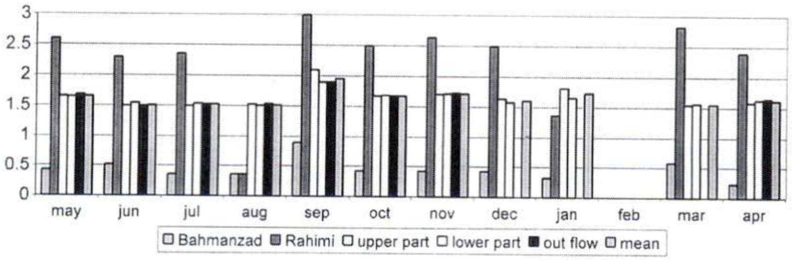

Fig.11:Concentrations of sodium ions in Hanna Reservoir(meq/l)
(May1999-Apr2000)

The ionic ratios varied between different surveyed ecosystems. Ca^{2+}: Mg^{2+} in headwaters and reservoir fluctuated between 1.48 – 1.58 and 0.85 - 0.94, respectively, Ca^{2+}: Na^{+} in Bahmanzad River was 6.33 and it was quite lower in the other surveyed ecosystems, ranging from 1.11 to 1.46. Mg^{2+}: Na^{+} in Bahmanzad River was 4, in Chahtal River was lower than 1 and in different parts of the reservoir it was around 1.3. In all of the examined ecosystems the CO_3^{2-}: HCO_3^{-} and (CO_3^{2-} + HCO_3^{-}): Cl^{-} ratios were lower than 1, but the ratios of (CO_3^{2-} + HCO_3^{-}): SO_4^{2-} were much higher than 1, fluctuating from 5.28 to 16.28. Cl^{-}: SO_4^{2-} were and largely high, ranging between 7.4 – 12.48, and ratios of Cl^{-}: Na^{+}, Cl^{-}: HCO_3^{-}, Cl^{-}: CO_3^{2-} and (Ca^{2+}+Mg^{2+}): (CO_3^{2-} + HCO_3^{-}) were relatively more than 1(Fig. 12).

2/3 of reservoir surface area was covered with dense populations of Myriophyllum, Ceratophyllum and Potamogeton species. The macrophytes had a fast growth in early spring and reached its maximum growth in summer and disappeared in December.

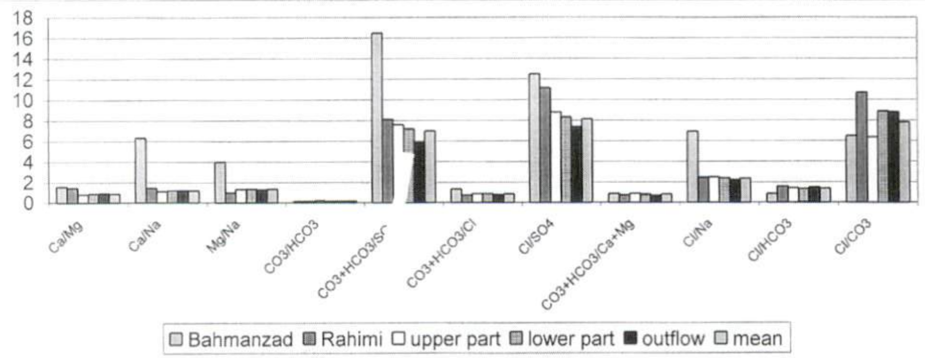

Fig.12:Ionic ratios in Hanna Reservoir(Mar1999-Apr2000).

Discussion

It is more or less a routine to start the discussion on ionic condition of waters (salty or non-salty) with equations such as the following, taken here from " Limnological Analysis" by Prof.R.Wetzel and G.Likens (page 107).

$$H_2O + CO_2 = H_2CO_3^- = H^+ + HCO_3^- \quad \text{pH decreases}$$

$$CaCO_3 + H_2CO_3 = Ca^{2+} + 2HCO_3^- \quad \text{Calcium dissolves}$$

The ionic concentrations in headwaters were high, especially for calcium and magnesium (sharp slope, high calcium content of the bedrock, high rate of erosion due to agricultural activities). Due to high calcium and magnesium concentration of headwaters they turn to harder waters. High hardness was also reported in Siahrood and Haraz rivers, which are exposed, to industrial and agricultural pollution (Rooshan Tabari 1996, 1997). Among anions, the concentration of bicarbonate was highest, followed by chloride and carbonate and the concentration of sulfate was the lowest. In headwaters calcium was the main cation but the concentrations of magnesium and sodium were also high, especially in Chahtal River the concentration of calcium was only 1.5 times more than the concentration of magnesium or sodium. In this river the concentration of sodium ions were higher than magnesium. Therefore in headwaters in addition to calcium and magnesium salts, the sodium salts, especially sodium chloride were also important. One of the most important aspects of aquatic chemistry is the ratio of major ions. If carbonate, bicarbonate, calcium and magnesium ions prevail, then the hardness is carbonatic and its buffering capacity is high. But even in hard water if chloride ions prevail over carbonate and bicarbonate ions, the chloride ions react with calcium and magnesium ions and create non-carbonatic hardness. Because chloride salts do not participate in proton exchange activities, non-carbonatic hardness does not produce buffering capacity in aquatic ecosystems (Stumm and Morgan, 1970). In world scale, the cationic and anionic ratios of rivers are reported as $Ca^{2+} > Mg^{2+} > Na^+ > K^+$ and $HCO_3^- > CO_3^{2-} > SO_4^{2-} > Cl^-$, respectively and the compositions of $Ca^{2+} > Na^+ > Mg^{2+} > K^+$ in volcanic watersheds and $Cl^- > SO_4^{2-} > CO_3^{2-}$ in very soft waters are dominated (Wetzel, 1975). But the characteristic of soils and rocks and perhaps other factor in this watershed significantly change the above-mentioned ionic ratios.. In rivers having watershed with marine deposits and exposed to agricultural and industrial pollution, ionic composition changed to $Cl^{-}>HCO_3^{-}>SO_4^{2-}$ and $Na^{+}>Mg^{2+}>Ca^{2+}>K^{+}$ (Markich & Brown, 1998). Similarly in headwaters of Hanna River, the watershed properties, climatic conditions and agricultural pollution governs the ionic composition of the water.

In the headwaters the sum of equivalens of calcium and magnesium were higher than total equivalent of carbonate and bicarbonate ions. It means that total hardness was more than bicarbonate hardness and bivalent cations could combine to other anions as well, ensuring the existence of non-carbonatic hardness. Because the concentration of chloride anions were significantly more than the concentration of sodium cations, the none carbonatic hardness probably originated from existence of calcium chloride and magnesium chloride salts in the headwaters.

The above mentioned special feature for hardness and ionic ratios of water exerts significant influence on buffering capacity of headwaters. But when they reach the reservoir environment with high photosynthetic activity and related high proton exchange, the bufferig capacity of water drops causing vast annual and daily fluctuations in pH of the reservoir water column.

As mentioned previously, in the headwaters the bicarbonate was the most important anion followed by chloride, carbonate and sulfate but in the reservoir the chloride ions dominated over bicarbonate, carbonate and sulfate. The prevalence of chloride in general is related to increase in area of evaporation (Rippey & Wood, 1985), and photosynthetic activities of phytoplankton and macrophytes (Jones, 1990). When inflow waters, rich in calcium and bicarbonate ions, are exposed to lentic ecosystem of the reservoir with dense populations of macrophytes, the bicarbonate ions are absorbed significantly and pH increases and calcium carbonate precipitates as a subsequence. When the bicarbonate ions are reduced, the chloride ions become dominant (Pokorny *et al.*, 1984). The precipitation of calcium carbonate creates blue–greenish color in the water column of the reservoir (Rich *et al.*, 1971). Moreover the lentic condition of the reservoir caused only prevailing of chloride ions over bicarbonate ones and there were no changes in situation of carbonate and sulfate ions.

In all samples chloride concentrations in headwaters were slightly higher than in the reservoir. Therefor chloride concentrations did not really increase in the reservoir and its prevalence in ionic composition during the period mentioned was a result of vast absorption and reduction of bicarbonate ions through the intensive photosynthetic activities. This finding in Hanna Reservoir is not in agreement with Rippey & Wood (1985), who postulated that evaporation is main reason for prevalence of chloride ion in ionic composition of many reservoirs and lakes not the photosynthetic activities.

There were no significant difference in sulfate concentrations between the headwaters and the reservoir, during the surveying year and also the fluctuation of sulfate concentrations of most samples were not significant. It is well known that in aerated aquatic ecosystems such as Hanna Reservoir sulfate usually is not an essential pathway for energy flow and recycling of nutrient salts (Wetzel, 1975).

The cationic composition of $Ca^{2+}>Mg^{2+}>Na^{+}$ in the headwaters changed to $Mg^{2+}>Ca^{2+}>Na^{+}$ when retained in the reservoir. Increase in photosynthetic activities and pH were the reasons for calcium carbonate precipitation and reduction. In Hanna Reservoir white deposition of calcium carbonate covered vast populations of macrophytes in dried littoral area. Coverage of macrophytes with precipitated calcium carbonate in macrophyte dominated lakes is also reported by Moss (1980).

Due to rain and anthropogenic activities calcium concentrations in the headwaters were rather changeable, but in the reservoir its fluctuations were controlled to some extent by photosynthetic activities.

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