Status of Water Quality Parameters along Haraz River

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Received 20 Jan. 2013;	Revised 20 May 2013;	Accepted 25 May 2013
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ABSTRACT: Water samples have been collected from key parts of Haraz River along different points and analyzed for various water quality parameters during winter and spring season. Effects of industrial wastes, municipal sewage, fish farming and agricultural runoff on river water quality have been investigated. The survey was conducted on along the Haraz River (185 km) from near its headwaters at the Polour, foot of Mount Damavand toward the Caspian Sea in Sorkhrood area. It lies between longitude of 35°522 and 45°52 and 36°152 . In this study eight stations were selected, depending on the quality of surface water and effluent entering points from industrial and commercial areas and population density in coastal rivers. 120 samples were taken from these stations and analyzed. Analysis performed as standard methods for the examination of water and wastewater. This study involves determination of physical, biological and chemical parameters of surface water at different points. The river was found to be highly turbid in the middle and lower parts of the river. But BOD and fecal colliform concentration was found higher in the dry season. The minimum and maximum values of parameters were Conductivity 400 -733.33 μ s, DO 8.48 and 12.8 mg/L in stations 5 and 6 respectively, BOD5 1.31 and 3.54 mg/L, COD 8 and 38.67 mg/L, total nitrogen 2.124 and 3.210 mg/L. The results analyzed statistically and used for this river data bank and recommendations for the water authorities.

Key words: Conductivity, BOD, COD, DO, Haraz River

INTRODUCTION

The quality of surface water within a region is governed by both natural processes (such as precipitation rate, weathering processes and soil erosion) and anthropogenic effects (such as urban, industrial and agricultural activities and the human exploitation of water resources) (Jarvie et al., 1998; Liao et al., 2007; Mahavi et al., 2005; Nouri et al., 2008; Pejman et al., 2009). Most important environmental problems in river water quality are eutrophication, acidification and emission dispersion where non point source pollution has become increasingly important within the last decades (Rode and Suhr 2007; Pejman et al., 2009). Human activities are a major factor determining the quality of the surface and ground water through atmospheric pollution, effluent discharges, use of agricultural chemicals, eroded soils and land use (Niemi et al., 1990). Rivers in watersheds with substantial agricultural and urban land use experience increased inputs and varying compositions of organic matter (Sickman et al., 2007) and excessive concentrations of phosphorus and other nutrients from fertilizer application and watershed releases (Easton et

al., 2007). The effective, long-term management of rivers requires a fundamental understanding of hydromorphological, chemical and biological characteristics (Shrestha and Kazama, 2007; Ballantine *et al.*, 2010).

Area of the Haraz drainage basin is more than 1100 km2. Gradient for Haraz River is 13/1000 from the mountain boundary to the north of Amol's city, and it is 7/1000 in the area of Amol's city (MWWO, 1987; Roushan, 1996; Solaimani et al., 2005; Afshin, 1994; Ziaabadi et al., 2010). In Investigation of Haraz river pollutants, three hydrometric stations called Panjab, Karesang and Sorkhrood were chosen. This study indicated, the quantity of DO, BOD, COD, NH3, EC, Turbidity, Color and number of Coliforms were more than the standard limits, which might be caused by environmental changes and by the wastewater flowing into the river. An increase in rainfall in autumn leads to an increase in the quantity of BOO, EC, ms, TSS, NO3, and P04 (Karbassi and Kalantari, 2007; Nielsen et al., 2003; Lane et al., 2008). Aquaculture has been growing in the past decade. Fish farming activities in Haraz Riverside currently accounts for over one third of all fish consumed by human (FAO, 2004). This high

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growth fish farming in the river resulted intensification of aquaculture system and environmental problems. The environmental problem related to the increased fish production in aquaculture is growing to be more serious (Pillay, 2004). Quantity and quality of waste produced by fish aquacultures depends on production system and feed quality and operation and maintenance methods. These aquacultures usually produce solid and dissolved waste, particularly carbon, nitrogen and phosphorous (Cripps and Bergheim, 2000). Solid waste mainly originates from uneaten and/ or spilled feed by the fish and from the feces. Dissolved waste is coming mostly from metabolites excreted by fish (through gill and urine). Accumulation of these pollutants deteriorates water quality in the river system (Amirkolaie et al., 2005; Amirkolaie, A.K., 2008; Fellows et al., 2009). Discharge of the fish aquaculture waste forms a major environmental concern because they can cause eutrophication of receiving water such as lakes and rivers (Chipps and Bergheim, 2000).

The most important urban areas are Amol (population 230,000), there are no waste water collection and treatment facilities in the project area. In most of the cities and villages in this area waste water is discharged in absorbing wells. In some areas, gray water is discharged into the rivers. In Amol's city, the gray water including household and that from municipal activities is discharged into the Haraz River at different discharge points. The amount and quality of urban and rural waste water is not being measured regularly. The household consumption of water is about 200 l/capita/day and the conversion coefficient for waste water is 90%. So, the per capita production of waste water in these cities is about180 l/day. The dominant crop is rice. Water from the fields is commonly released between mid-august to early September. Before this, when paddy fields are water logged, the effluent seeps through to the shallow groundwater. Agricultural waste water contains high levels of phosphate, nitrogen, potash, and pesticides. Since the sub-surface waters in the area have not been surveyed completely, the exact amounts of fertilizer and pesticide infiltrated are not known. Although the amount of industrial waste water is less than urban and agricultural effluents, it is important because it contains a variety of materials that are potentially hazardous. In the middle lands, there are a few industries, but no detailed information about the quality or quantity of discharge of waste water. As mentioned earlier, most of the industries are located around the big cities and along the main roads in the lower lands. The humidity of municipal waste is reported to be about 70-80%. This is quite critical because such amount of humidity can cause a high amount of leachate produced by wastes that, in turn, can increase soil and water pollution. Due to inadequate studies and field testing, there is no information about the quality of leachate produced in this area. However, based on the average determined for the waste leachate produced in Iran, the amount of BOD5 is about 20,000-30,000 mg/l.

MATERIALS & METHODS

In this study, spatial variations of water quality index in Haraz River Basin were evaluated using statistical techniques. Determination of physicochemical parameters was performed from 8 sampling sites up to down of the river. The survey was conducted on Haraz River in Tehran to Amol's route. Haraz River Basin area is located in the Mazandaran Province and north region of Iran (Fig.1). Haraz River originates from Alborz mountain ranges and flows into the southern coast of the Caspian Sea (Keramat Amirkolaie, 2008). Haraz River originates from Alborz Mountain and passed from the middle of Amol City then branched to multi small river and water canal, follow to the Caspian Sea in sorkhrood area (MWWO, 1987). It lies between longitude of $35^{\circ}522$ and $45^{\circ}52$ and latitude of 35°452 and 36°152, Haraz River has a length of 185 km with a discharge of $940 \times 106 \text{ m}3/\text{y}$ (in 2006). The width of river ranges from 50 to 500 m at different locations. (Pejman et al., 2009). The catchments area of river is about 4,060 Km2 with average precipitation of 832 mm/y (Karbassi et al., 2008). The Haraz River is a major source for agriculture activities particularly in downstream basin areas (Pejman et al., 2009).

In this research sampling site selection criteria include natural conditions, as well as human activities. Station 1, represents the conjunction of two streams of Emamzadeh Hashem and Lar Dam outlet. Natural condition where neither agricultural nor industrial activities, but commercial activities can be found. Stations 2, 3, 4 and 5 are mostly affected by agricultural, as well as aqua culture. Stations 6, 7 and 8 are affected by river sand mining activities and almost all types of the pollutant from residential, agricultural and to the lower extent, industrial activities. The sampling stations selected for the project was shown in Fig.2. Determination of river Discharge (Q) obtained from archive record of the area water works organization. Geographic position of all points of field study performed by GPS Model GEKO 310.

Water quality data collected, during two seasons (winter and spring). 120 water samples were taken for the parameters. Water samples were collected from the 8 stations for 2 seasons of Haraz River. Then, collected samples were kept in a 2 L glass bottles cleaned with dishwasher detergent, rinsed many times with distilled water and finally soaked in 10 % nitric acid for 24 h,



Fig. 2. Sampling sites selected for the project

finally rinsed with ultrapure water. All water samples were stored in insulated cooler containing ice and delivered on the same day to laboratory and all samples were kept at 4 °C until processing and analysis. A range of water quality index tests were performed in the field studies (8 sampling stations) including: pH, total dissolved solids (TDS), total solids (TS), biological oxygen demand (BOD), chemical oxygen demand (COD), electrical conductivity (EC), dissolved oxygen (DO), water temperature (T), nitrate (NO_3) , total phosphate (T-PO₄), orto-phosphate(O-PO₄), chloride (CI⁻). The mean results are summarized in different figures. Samples were tested for different parameters in accordance with standard methods for the

examination of water and wastewater, 2005 (APHA, 2005). The temperature, pH and DO concentrations of the water were measured on-site by a thermometer, pH and DO meter (using portable electrode devices). The BOD5 was determined by the Winkler azide method and TS were determined gravimetrically at 105°C (APHA, 2005). NO₃ and T-PO₄ were analyzed by Brucine Sulfanilic Acid and ascorbic acid method (using HACH DR2800 spectrophotometer), respectively. Turbidity was determinate by the nephelometric method (using HACH 2100AN turbidimeter) (APHA, 1998).

RESULTS & DISCUSSION

Secondary standards are "non-enforceable guidelines regulating contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water" (USEPA, 2006). The difference between total phosphate (P<0.049) and orthophosphate (P<0.007) in upstream and downstream fish farm has been significant. This difference is evident in the middle of the field. Net variation in phosphate and total phosphorus of the first farm were recorded 13.19 kg/ day and 21.99 kg / day (100 tons production), second farm, 7.95 kg / day and 15.08 kg / day (80 tons production), and the last farm 2.28 kg/day and 3.63 kg / day (40 tons production), respectively. Organic phosphorus was calculated in first farm 40% (700m up to distance), second farm 47% (300m up to distance) and the last 40% (6000m up to distance). It seems that these changes should be related to farming distance, production, feed type that caused to increase of organophosphorous load in the river. A mean flow of Haraz River in different years, Karesang station indicated in fig. 3. As the figure show, the mean flow of the river is often between 20 until 40 cubic meters per sec.

The statistical analysis of some basic water quality parameters indicated in Table 1.Mean±SD, sample variance, minimum and maximum of basic water quality parameters of different stations, displayed in the Table 1.

The concentration of DO in studied stations was 10.78 (st.3) to 11.88 ppm (st.8). Minimum DO determine 8.48 ppm in station 5. Maximum DO consider 12.8 ppm in station 6 in the winter situation. The DO status, displayed in the fig. 4 is the mean of three time sampling.

There is not a significant difference in BOD5 of samples between stations (P-value<0.05). Minimum of BOD5 was 1.306667 ppm in station 1 and the maximum was 3.54 ppm in station 6(fig.5).

There is not a significant difference in COD of samples between stations (P-value<0.05). Minimum of COD was eight ppm in station 4 and the maximum of COD was 38.66667 ppm in station 3(fig.6).

Total phosphorus of the stations in three stages sampling were about a uniform level and there is not a significant difference in phosphorus of samples between stations in cold and warm conditions (Pvalue<0.05). Mean of TP was varying from 0.188 in station one until 0.313 ppm in station 3 that the high digit related to the concentration of restaurant and commercial shops in up-stream of the river. Minimum ortho phosphorus was 0.011 ppm in station 8, and the maximum was 0.096 ppm in station four (fig. 7).

The concentration of Chloride was 19.5 in station 2 to 40.8 ppm in station 8 (fig.8). Chloride concentration increases from the origin to the downstream river and



water years Fig. 3. Mean flow of Haraz River in differeny years, Karesang station

	C4 - 12	C1 4	C 73	6 73 2	- - -	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	5	r	0 75
parameters	Stauons	26.1	DL 2	51.3	N.4	51.5	3 L 0	SI. 7	SI.8
	Mean	11.23	11.12	10.9	10.9	10.67	11.4	11.18	11.78
	Sample Var.	0.655	0.224	0.102	1.668	3.899	2.074	2.393	0.025
DO	Min	10.72	10.56	10.56	9.46	8.48	9.92	9.44	11.6
	Max	12.16	11.4	11.2	11.84	12.32	12.8	12.4	11.9
	Count	9	9	9	9	9	9	9	9
	Mean	19.33	8.83	38.6	8	13.3	15.3	11.57	14.17
	Sample Var.	121.33	11.08	16.33	13	1.33	2.33	1.56	10.58
COD	Min	12	S	35	5	12	14	10.7	11
	Max	32	11	43	12	14	17	13	17.5
	Count	9	9	9	9	9	9	9	9
	Mean	1.31	3.05	3.15	3.35	2.22	3.54	3.15	3.47
	Sample V ar.	0.5525	0.0705	1.6165	0.7745	3.2812	5.1268	0.154	2.096
BOD5	Min	0.48	2.9	2.24	2.56	0.8	1.8	2.7	2.4
	Max	1.92	3.36	4.6	4.3	4.26	6.1	3.4	5.12
	Count	9	9	9	9	9	9	9	9
	Mean	2.125	2.98	2.44	2.69	2.54	2.87	3.21	2.81
_	Sample V ar.	0.0829	0.09048	0.2626	0.4399	0.414	0.0262	0.2353	0.607
NT	Min	1.807	2.809	1.93	1.93	2.124	2.735	2.73	1.925
	Max	2.369	3.33	2.955	3.103	3.284	3.053	3.7	3.4
	Count	9	9	9	9	9	9	9	6
	Mean	1.6	1.168	1.37	1.49	1.57	1.579	1.72	1.6
_	Sample V ar.	0.003	0.003	0.01	0.036	0.001	0.014	0.102	0.401
NO_3	Min	1.56	1.112	1.264	1.29	1.549	1.459	1.353	0.873
	Max	1.667	1.23	1.464	1.667	1.603	1.695	1.93	1.97
	Count	9	9	9	9	9	9	9	9
	Mean	0.107 ± 0.078	0.0837 ± 0.065	0.126 ± 0.085	0.1403 ± 0.106	0.114 ± 0.092	0.14 ± 0.137	0.105 ± 0.127	0.120 ± 0.109
	Sample V ar.	0.006	0.004	0.007	0.011	0.008	0.0189	0.016	0.012
0-P	Min	0.034	0.024	0.066	0.064	0.03	0.049	0.013	0.011
	Max	0.19	0.154	0.223	0.261	0.213	0.298	0.25	0.23
	Count	٥	0	٥	0	٥	٥	٥	٥

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Fig. 5. Haraz River BOD5 in different stations



Fig. 6. COD of Haraz River in different stations



Sampling Seations Fig. 7. Haraz River TP and Ortho-P in different stations



Fig. 8. Haraz River Chloride in different stations

Caspean sea, shows th different sources of pollution enter the river. The mean chloride concentrations were less than its secondary standard issued bt EPA.

Total nitrogen was varying from minimum mean 1.925 in station 8 until maximum mean 3.330 ppm in station 2(fig.9). The maximum nitrate consider in stations one and five. Declining trend in concentration of nitrogen towards the bottom of the river and Caspean Sea is a sign of nitrification and nitrification in the water path. The concentration of Ammonium was 0.002 to 0.035 ppm in the cold season, but this parameter was 0.015 to 0.224 ppm at the middle of spring.

Conductivity of the water implies the presence of soluble forms, and more conductivity is the sign of high presence of ions. Conductivity related to the soluble forms of solids directly. The mean conductivity (EC) in studied stations was varying from 390 micromohs/cm in station 2 until 670 in stations 2 and 8 (fig.10).

The PH of the samples in different stations was 7.65 to 8.1. Temperature (T) of the water samples in different stations in winter season was 4 to 6.2 and this was 9.2 to 10.7 at the middle of spring.

TSS concentration from 6 in station one increased to 242 ppm at station eight. This increasing indicated the pollutants entering to the river. Figures 11 and 12 show the average of 4 heavy metals (Fe, Mn, Zn and Cr) in different stations in Haraz river. As the fig. 11 show, the concentration of Fe in the middel of the study line (st. 4, 5 and 6) is more than the upper and lower part, that is due to crowding of commercial centers and also fish farming in the river side. Also, the concentration of Fe in all stations is more than standard limit of drinking water (0.3 ppm), but this value have not any problem for agricultural usage. This concentration can have more problems for all usages of the river (industrial, household, commercial). Althogh the concentration of other investigated heavy metals (Mn, Zn and Cr) have no problem. Although the concentrations of of other investigated heavy metals (Mn, Zn and Cr) in river water have not any problem for industrial, municipal, agricultural usage, but rather shows that the concentration of heavy metals in river affect business operations, commercial activities and the nearby river's pollution. The figs 11 & 12 show this event.

Density (No./m²) and Biomas (mg/m²) of Bentic Organisms in Haraz River displayed in the fig. 13. As the fig. 13 show, the Biomass index in stations 3, 4, 5 and 6 is more than other stations that the reason of this event can be presence of fish farming density in adjacent of these stations. Usually these fish farming discharge the effluent to the river without wastewater treatment or uncomplete treatment. Also the figure show the density of bentic organisms is the same as biomass index. As we move towards the Cspian Sea and far away from fish farms, density of benthic organisms in the rivers will be less.

There is substantial data to show pollution within the non-point source cultivated run-off (pesticides, fertilizers, herbicides) as well as point source pollution from small industries and workshops. Pollution of downstream rivers and the southern Caspian Sea coastal area is very high in the province. An agricultural activity due to excessive use of chemical pesticides and fertilizers has increased in the province. It is hoped that the pollution-related toxins have declined significantly in the future due to subsidies of agricultural section. roundwater flow direction is similar to the Haraz River. The direction of flow is from south to north. The hydraulic gradient of the groundwater is high (10-15 per thousand) in the southern parts, and the water table contours are close to each other. Near the sea, these distances reach their



Fig. 9. Haraz River TN and NO3 in different stations

Water quality management







Different Sampling Stations

Fig.13. Density (No./m2) and Biomas (mg/m2) of Bentic Organisms in Haraz River

maximum and the hydraulic gradient in the coastal plains of the Caspian Sea reaches values less than 2 per thousand. Water table elevation close to Amol is less than 18m. The water table falls during some parts of the year, but is recharged during winter and returns to the original level after the rainy season (MWWO, 1987; Roushan, 1996; Solaimani *et al.*, 2005).

CONCLUSION

The research showed that commercial and fish farming activities along the Haraz River cause the river pollution that need to monitor regularly. Also the result showed that we need to prevent the flow of agricultural, urban and industrial wastewater and other decentralized wastewater into the river in order to have an optimal management for Haraz River. Result of principal component analysis and factor analysis evinced that, a parameter that can be significant in contribution to water quality variations in river for one season, may less or not be significant for another one. Unfortunately current monitoring of river pollution is highly inadequate, so it is impossible at this stage to establish a clear personification of the specific water pollutants and the extent of the problem. At present, the amount of solid and liquid wastes is increasing in rural areas in the river margins. At the end, it should be mentioned that we need to prevent the flow of agricultural, urban and industrial wastewater and other decentralized wastewater into the river in order to have an optimal management for Haraz River. Also we need to have a serious control on the huge fish farming effluents that located at the Haraz riverside. Based on the findings of present investigantion we recommend that:-

Industries should be organized and controlled in specific zones in river margins. Solid and liquid

industrial waste should be controlled by a computer system and monitore by the environmental protection organization.

All fish farms located in the margins of rivers, should be controlled by the environmental protection organization.

Permanently, fixed and mobile stations on the river should be sampled and analyse to record the results. All analysis and monitoring results and records of all previous works should be covered by the Geographic Information system (GIS).

Support the expansion of educational efforts by providing the schools special programs and resources that encourage students to be proactive in the protection of the environment.Continue to raise awareness through volunteer programs, educational presentations, and media campaigns so that residents adopt behaviors that protect water quality.

Increase water quality monitoring activities as well as data analysis and response to provide increased protection of our lakes from pollution, particularly sediment, which is becoming an increasing threat as the areas around the lakes continue to experience rapid development.

Non-governmental organizations and public institutions should be invited to help for monitoring of the environmental problems.

Wetlands should be develope in riversides to flood control and slow down water flow.

Improved water quality-vegetation slows down the flow of water and allows sediments to drop to the bottom. Ninety percent of these sediments are absorbed by the wetlands. If not absorbed, sediments would create problems when they moved on to other bodies of water. Wetlands support fishing, hunting, recreation, and bird observation and economic development.

ACKNOWLEDGEMENT

This research supported financially by the Mazandaran Environmental Protection Organization. The authors are especially grateful to Mazandaran University of Medical Sciences.

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