A PRELIMINARY INVESTIGATION OF TOTAL ORGANIC CARBON VARIATION IN INFLUENT AND EFFLUENT OF ISFAHAN (IRAN) WATER TREATMENT PLANT, URBAN NETWORK AND FELLMAN WELLS

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Summary – In this work a series of total organic carbon (TOC) analyses were carried out to analyse the influent and the effluent of a water treatment plant providing Isfahan city in Iran. Other analyses were focused on the determination of TOC in the urban network and Fellman wells (in Isfahan and Dehaghan cities), in order to compare the water quality soon after the treatment with that of circulating water in the city network. Since it supplies water treatment plant, TOC content of Zayandeh-rood River was also compared with the treated water. The obtained results revealed that there were significant differences between TOC content of effluent of water treatment plant and that of the urban network (made with eight different points). In this project all the samples were withdrawn during 2005. It is worth noting that the analyses were carried out with a high precision combustion-infrared method with a confidence limit lower than 0.05. The mean of TOC in Isfahan and Dehaghan Fellman wells were 0.7 and 2.6 $mg.l^{-1}$, respectively. The mean of TOC in influent of water treatment plant during June, July and September were 0.703, 1.148, 1.513 $mg.l^{-1}$ respectively which after treatment process reduced to about 0.7 $mg.l^{-1}$. In conclusion it can be said that during the summer with higher consumption of water and increase in vaporizing surface waters, we have accumulation of organic compounds and therefore we have increase in TOC content of various waters.

INTRODUCTION

The Islamic Republic of Iran, with an average annual rainfall of 240 mm is counted among the arid and semi arid countries of the world. Isfahan is one of the main industrial cities that is located in the center of Iran and it had an average annual rainfall of about 203 mm in 2005 (FIG. 1).

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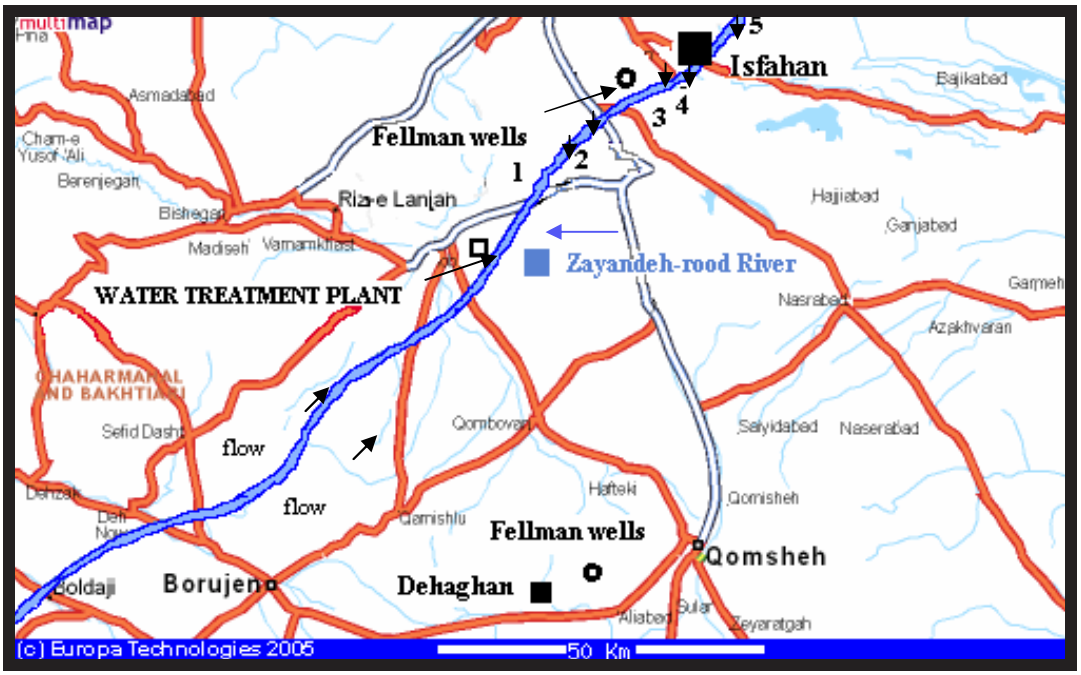

FIGURE 1 – The regional map of investigated water basin area.

The presence of organic compounds in water is an important factor affecting water quality. Continuous discharge of pollutants in water receiving resources causes an increase in their concentration in critical periods, and can be very dangerous for the health of consumers.

The raw water required for Isfahan Water Treatment Plant is taken from Zayandeh-rood River with a normal load of about 350,000 m^3/day. Discharge of flooding waters into the river can cause many problems for the treatment process. Changes in the pressure of urban water network due to the fluctuation in consumption of water can also cause leakages of potable water or presence of many pollutants. TOC tests provide an easy and fast method for determination of organic pollutants in water, and in particular, the accurate analysis of the TOC values is important to check the quality of water resources, such as surface, drinking and various fine waters. In the absence of TOC investigations, other very expensive tests would be needed, in order to determine the nature and concentration of the present organic materials, and in particular, of organohalogenated compounds (produced during the chlorination treatments) and to examine the colour, the taste and the odour of water.[1,2] According to the latest data, the maximum level of TOC in treated waters has been generally reported to be below 2 $mg \cdot l^{-1}$.[3] An overdose would cause digestion and neural perturbations in human body. In FIG. 2 all the possible forms of carbon, that can be found in water, are schematized. It is worth noting that TOC includes purgeable organic carbon (i.e. volatile compounds) and non-purgeable organic carbon (i.e. particulate and dissolved compounds). In the first step of TOC analyses, inorganic carbon mainly carbonates giving rise to a separation from the organic carbon in the samples. In the second step, extractable particulate and dissolved organic carbon are separated using aeration, temperature and other methods.[4,5]

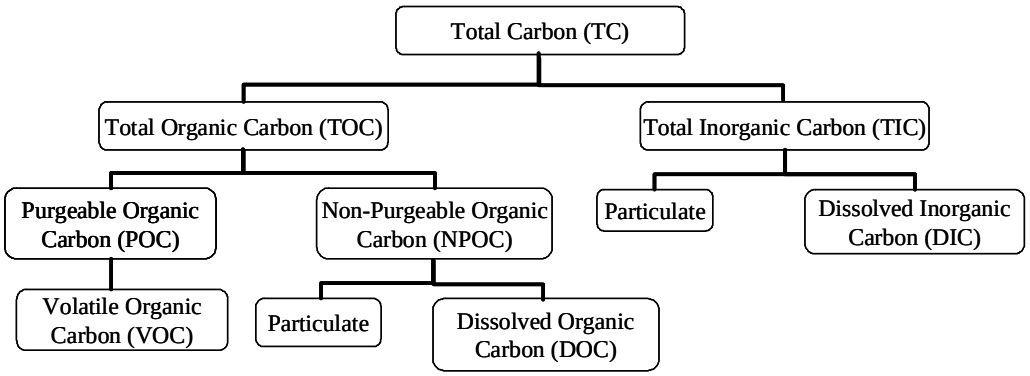

FIGURE 2 – Diagram showing a classification of total carbon present in aqueous matrixes

In most water samples the amount of total inorganic carbon (TIC) is several times higher than TOC. A particular care is needed to remove the interference of TIC: some parameters are needed to be set to provide accurate TOC determination. So far no elimination of purgeable organic carbon (POC) was carried out. The amount of non-purgeable organic carbon (NPOC) can be determined by measuring total organic carbon. In most surface and ground waters the ratio between volatile organic carbon (VOC) and TOC is negligible, so TOC concentration can be replaced, in almost the whole cases, with NPOC determination. If we assume that there is no volatile matter in water, the amount of TOC and NPOC is closely equal.

The separated fraction of TOC depends on some experimental conditions and on the type of used supplies, such as: temperature of samples, amount of ionic compounds, rate of gas flow, type of defusing gas, dimensions of separating cell and amount of separated volume.[6-8] We used the same experimental conditions during the determination of VOC and NPOC of the same samples. In this way we obtained comparable results, although the experiments were carried out in different laboratories.

There are three methods for TOC determination:

a) Combustion-Infrared Method. An aliquot of the sample is vaporized and the organic carbon is oxidized to CO_2 and H_2O. The CO_2 from oxidation of organic and inorganic carbon is transported to the carrier-gas streams and is measured by means of a non-dispersive infrared analyzer.

b) Persulfate-Ultraviolet Oxidation Method. Organic compounds are oxidized to carbon dioxide by persulfate in the presence of ultraviolet light. The CO_2 produced may be measured directly by a non-dispersive infrared analyzer, reduced to methane and measured by a flame ionization detector, or chemically titrated.

c) Wet-Oxidation Method. In this method samples are acidified, purged to remove inorganic carbon, and oxidized with persulfate in an autoclave at temperatures from 116 to 130 °C. The resultant carbon dioxide is measured by non-dispersive infrared spectrometry.[6-8]

In the present paper, TOC variations in influent and effluent of Isfahan water treatment plant, urban network and Fellman wells of Isfahan and Dehaghan cities (FIG. 1) in spring and summer of year 2005 were investigated by using the method “a”. Fellman wells are very deep and are considered as a backup for supplying drinking water in critical conditions. At the bottom of these wells there are many horizontal tunnels inside which polymeric perforated cylinders for filtration of water are located.

EXPERIMENTAL

Sulfochoromic acid, phosphoric acid, sulfuric acid and hydrochloric acid (purchased from Sigma-Aldrich) and high quality organic free water were used for the analyses. The following solutions were used: a stock solution of TOC was prepared by dissolving 2.1254 g of anhydrous potassium biphtalate $C_8H_9KO_4$ in 1 l extra pure water. This solution was then diluted as necessary and used to prepare appropriate standards for each TOC assay run (FIG. 3); samples were preserved by acidification to pH=2 with H_3PO_4 or H_2SO_4; an inorganic carbon stock solution was prepared similarly by dissolving 4.4122 g of anhydrous sodium carbonate and 3.497 g of sodium bicarbonate in deionized water. This solution was used for preparing appropriate standards for TIC assay run.[6]

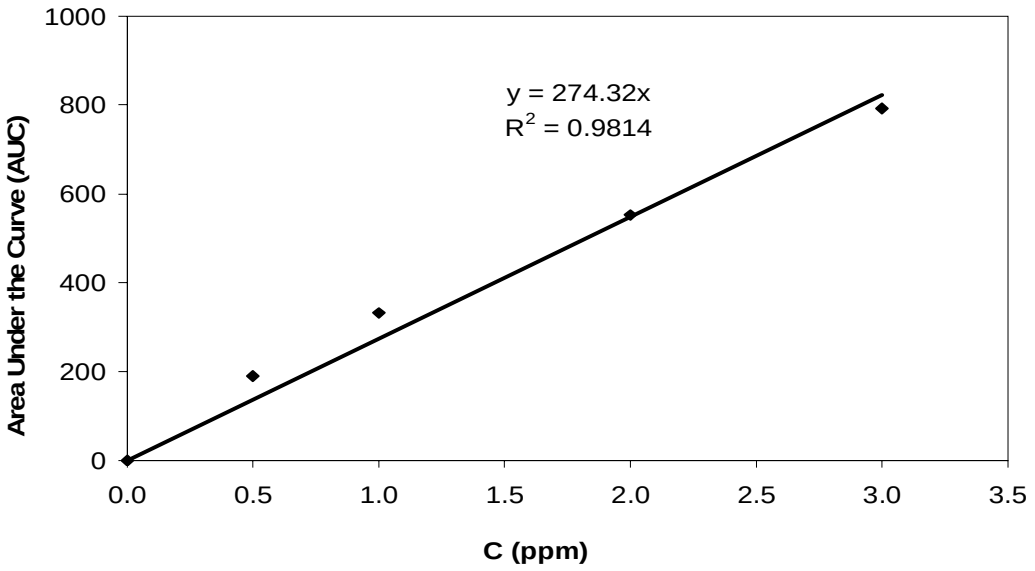

FIGURE 3 – TOC standard calibration curve for analysis of water samples.

The analyses were carried out by a TOC analyzer “Skalar Holland” model and a “TOC V-CSH” model.

Sampling was performed in different locations of city water network, Zayandeh-rood River, influent and effluent of a water treatment plant and Fellman wells. Subsequently the samples were held in dark bottles with TFE-lined stoppers. Before sampling these bottles were rinsed with sulfochromic acid and double distilled water and then they were sealed with aluminium foils. Finally they were annealed in a furnace at 450-550 ˚C for 2-3 hours. Sampling was carried out in grab method and then the pH was adjusted to 1-2 using phosphoric acid. These bottles were hold in ice and analyzed as soon as possible.

The samples were homogenized with magnetic stirrer and diluted as necessary. A 200 µl aliquot of prepared samples were introduced into heated reaction chamber by using a jet Hamilton injector. The chamber was packed with cobalt oxide as an oxidative catalyst and heated up to 680 °C.[6,9] In this condition organic compounds contained in injected water were cleaved. In fact, organic substances were transformed into CO_2 and H_2O thanks to gaseous O_2 or pure air passing over the catalysts. The subsequent course of this gaseous mixture through a helical and cooled

column caused the condensation and the separation of water. In this way gaseous CO_2 was measured by an IR detector and the total carbon contained in the sample was hence gained from this value, which is, of course, proportional to total carbon (TC). Finally the TOC contained in the sample was calculated as a difference between TC and TIC.[10,11]

RESULTS AND DISCUSSION

FIG. 4 shows the average values of TOC concentration of influent raw water of Isfahan treatment plants in a period of three months. As shown in the figure, TOC values depend strongly on the season in which the samples were withdrawn, but in all cases the concentrations are below the maximum level of TOC in treated waters (2 $mg \cdot l^{-1}$).

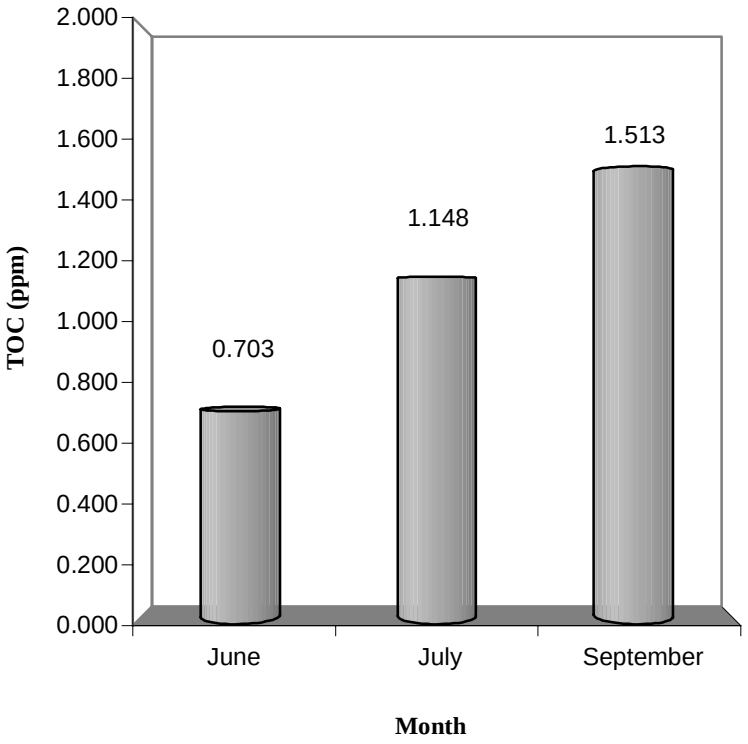

FIGURE 4 – Average values of TOC concentration of influent water in the treatment plant during June, July and September 2005.

FIG. 5 shows the average values of TOC concentration of effluent of water treatment plants of Isfahan city in three months. The values are obviously lower on respect to those found for the influent samples (see FIG. 4), due to the purification carried out in the plants. It can be also noticed that the values are very similar each other, indicating that the plant worked properly throughout all months.

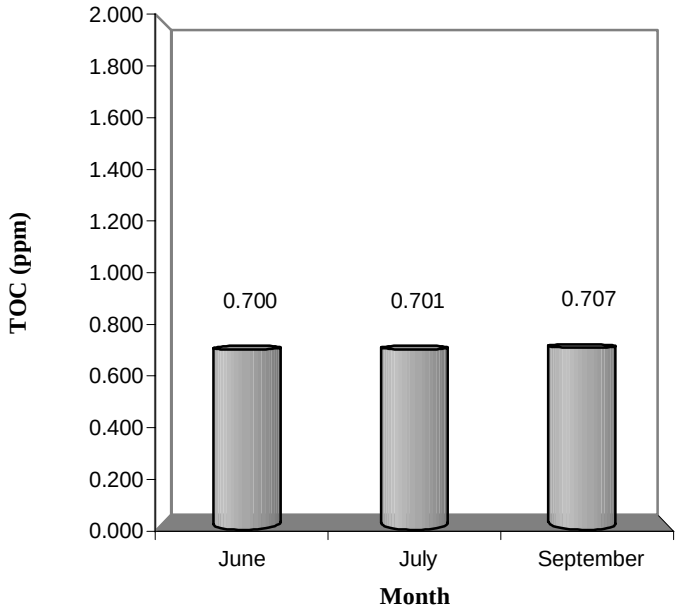

FIGURE 5 – Average values of TOC concentration of effluent of water treatment plants during June, July and September 2005.

Sampling and analysis of forty samples from raw and treated water reveal that treatment process can reduce the mean of TOC of raw water to about 0.7 $mg \cdot l^{-1}$ (Table 1).

TABLE 1 – Statistical parameters of TOC values for forty different samples in influent and effluent of Isfahan water treatment plant (SD: standard deviation; CV: coefficient of variation).

	Influent			Effluent		
	June	July	Sept	June	July	Sept
Mean	0.703	1.148	1.513	0.700	0.701	0.707
SD	0.098	0.134	0.149	0.136	0.099	0.104
CV	0.139	0.116	0.098	0.194	0.142	0.147

FIG. 6 reports the average values of TOC concentration of Fellman wells (Dehaghan) in a rural place. Because of the presence of organic substances derived from agricultural activities in the ground water of this region, the resulted values are higher than those allowed.

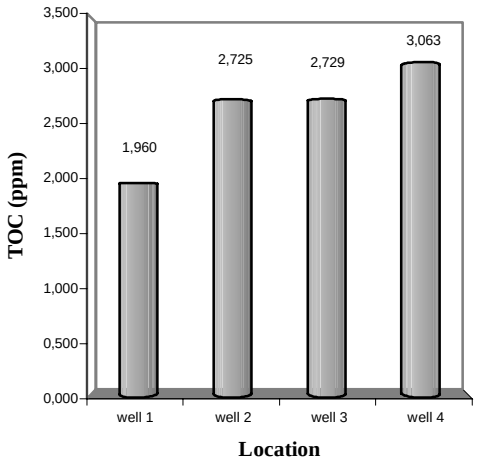

FIGURE 6 – Average values of TOC concentration of outlet water of Fellman wells in Dehaghan during April 2005.

FIG. 7 shows the average values of TOC concentration of Fellman wells in Isfahan city. It is worth noting that the figures are very variable depending on seasons and regions. These strong differences could be due to quite dissimilar climatic conditions.

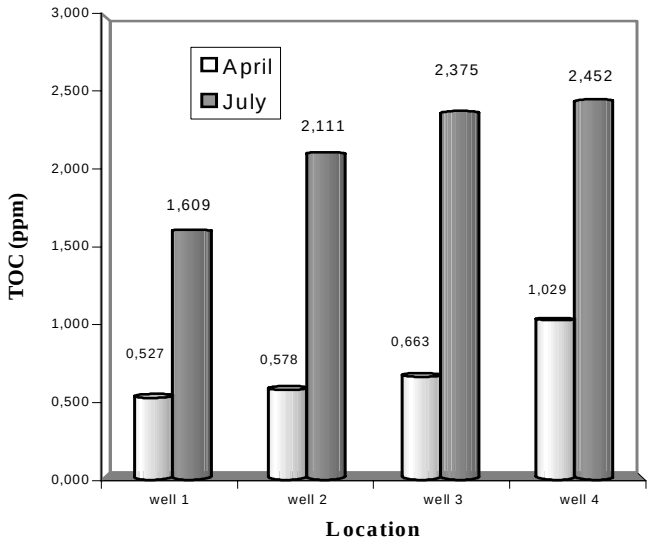

FIGURE 7 – Average values of TOC concentration of outlet water of Fellman wells during April and July 2005.

FIG. 8 shows the average values of TOC concentration of Iranian mineral water. TOC concentration is very low in such water samples and, consequently, this water is more suitable for drinking purposes in comparison with other kinds of water.

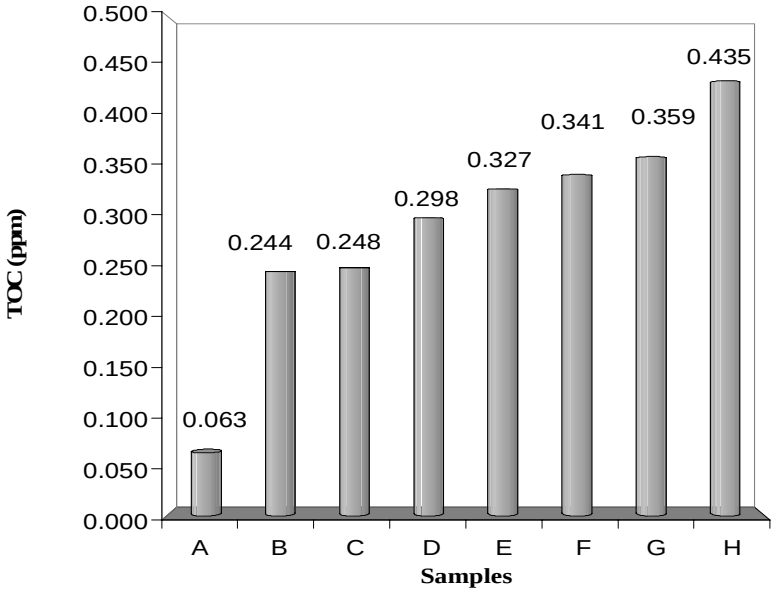

FIGURE 8 – Average values of TOC concentration in different mineral waters packaged in Iran during April 2005.

FIG. 9 shows the average values of TOC concentration of samples withdrawn from Zayandeh-rood River water in Isfahan city during May and September 2005. There are significant differences between the amount of TOC in surface waters of the Zayandeh-rood River and that of water network.

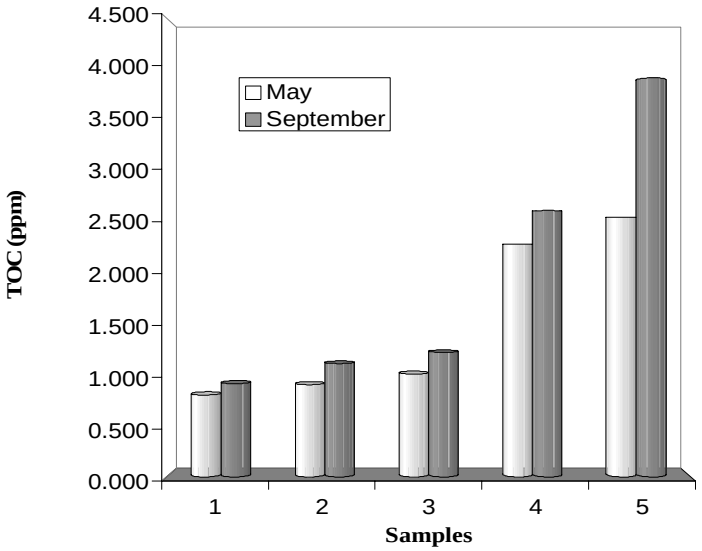

FIGURE 9 – Average values of TOC concentration of Zayandeh-rood River water in five different points during May and September 2005.

FIG. 10 shows the average values of TOC concentration of water network of Isfahan city during April and September 2005. It can be observed that in some periods the amounts of TOC slightly exceeded the allowed concentration. These findings can be explained by considering possible infiltrations of organic pollutants in the water network due to various discharges, whose

extent is variable. It is worth noting that many TOC figures reported in FIG. 10 are higher than those reported for the effluent water deriving from the water treatment plant of Isfahan city. This finding suggests the presence of defects along the line and/or infiltrations of waste water. Moreover dilution caused by raining water could be responsible for the lowest values.

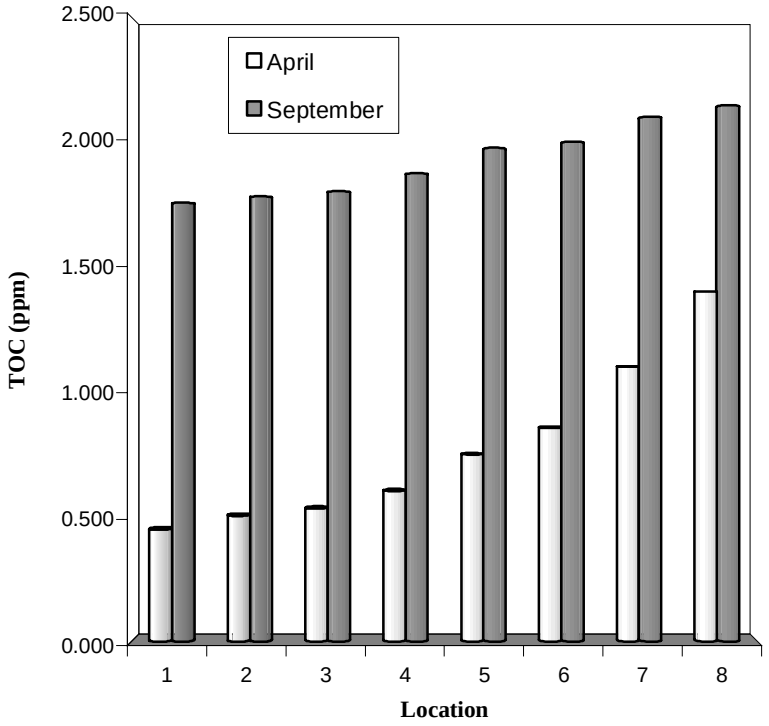

FIGURE 10 – Average values of TOC concentration of network water in eight different points during April and September 2005.

CONCLUSIONS

The knowledge of TOC values throughout a long time in urban and rural water resources is very important for the benefit of consumers. In this work it was reported that the TOC values in network water were lower than the limit values, while the examined rural waters showed the highest values, probably due to the presence of organic species used in agricultural activities.

The following main conclusions can be drawn from our findings:

a) The TOC variation in different seasons in Zayandeh-rood River was about 0.1 to 1.4 $mg \cdot l^{-1}$. This variation in TOC concentration was lower in spring and higher in summer due to differences in temperature and atmospheric conditions and this could affect the raining levels.

b) Variation in average values of TOC concentration of influent in water treatment plant during different seasons and the nearly constant value of 0.7 $mg.l^{-1}$ in effluent reveals that this treatment process didn't have any effect on a costant part of the TOC.

c) The TOC differences between network water and Zayandeh-rood River water in Isfahan city (Iran) during spring seasons was negligible (0.4-0.6 $mg \cdot l^{-1}$) while it was higher during summer (0.8-

1.8 $mg \cdot l^{-1}$). So using this surface water for supplying drinking water in warmer seasons implies higher risk of forming halogenated organic compounds during disinfection process in water treatment plant.

d) The TOC differences between network water and the effluent of water treatment plant in Isfahan city were significant. The mean value of this variation was 0.7 $mg \cdot l^{-1}$ in spring and 1.6 $mg \cdot l^{-1}$ in summer. This aspect can be justified by taking into account possible technical defects along the connection lines, causing infiltrations of Fellman wells water and of various wastes into treated network water.

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