CHEMICAL AND BIOCHEMICAL INDICATORS IN THE CHARACTERIZATION OF POLLUTED WATERS FROM THE BAHLUI RIVER, IASI CITY SECTOR

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Abstract: The alteration of physical, chemical and biological properties of water due to natural or atrophic factors makes it improper for daily use. The chemical composition of water from the Bahlui river is determined by the structure and composition of soil and rocks from the reception basin, by the climatic conditions, the amount of wastewater (domestic and industrial), by the sampling area etc. The results of physical-chemical investigation revealed that indicators as turbidity, pH, fixed residue, residue at 180^{0}C, residues calcinated at 550^{o}C şi 900^{o}C, ammonia concentration, phosphate concentration are over the normal standardized limits. The concentration of oxidable compounds in the Bahlui river water is far over the maximum admitted limits.

INTRODUCTION

The source of Bahlui river is the Dealul Mare-Tudora massif, placed in the east of Suceva Plateau, at an altitude of about 500 m, measuring a total length of 435 m. Its hydrographic basin (**fig. 1**) is placed between 47º30' north latitude and 47º03" south latitude (fig. 1).

Figura 1 – The hydrographic basin of Bahlui River (http://ro.wikipedia.org/wiki/Râul_Bahlui)

The Northern limit of the basin is represented by the intersection of the Bahlui and Jijia river and it is delimitated by several villages, as follows: North of Deleni, through Scobinţi, on the east of Cepleniţa, south of the

Coarnele Caprei, through the N-E of Belceşti, through the North of Erbiceni, right through the Romaneşti, on the southern side of Movileni, Popricani, Victoria and it ends at de Holboca. The S-V limit is marked by the intersection of Bahluiului and Bârlad rivers on the south and the Siret river basin. The villages that delimitate the Bahlui basin in the west and south are: Siriţel, Todireşti, Ruginoasa, Heleşteni, Strunga, Oţeleni, Brăieşti, Lungani, Sineşti, Popeşti, Horleşti, Voineşti, Mogoşeşti, Ciurea, Bârnova şi Tomeşti.

The most important physic-geographic component several must be mentioned: the weather, the vegetation, and the soil. Also, the anthropic factor has become more and more important in the formation and evolution of water sources from the Bahlui basin. Land utilization, artificial lakes and ponds, works regarding damming and consolidation of river banks, works on water supply for the population and industries as well as the local transportation network have most definitely influenced the formation, quality and the regime of surface and underground water sources. Today, the Bahlui river basin is considered to be one of the most anthropic basin from Romania. Different studies indicate an high content on organic compounds from residual waters. (Dunca şi colab., 2008; Ciumaşu şi colab., 2008; Neamţu şi colab., 2009)

This work is focused on the evaluation of several pollution markers on water sampled from the Bahlui River between May and October 2009. Several physic-chemical assays were performed (turbidity, pH, fixed residue, residue at 180^{o}C, calcinated residue at 550^{o}C and at 900^{o}C, ammonium concentration, phosphate concentration, CCOCr) on water sampled from there different areas (before, in the and at the exit of the city of Iasi) during three different seasons (spring, summer and autumn).

MATERIALS AND METHODS

Water sampling is a very important step in the analysis process. Samples must be representative and must not suffer any changes in properties and qualities due to defectous sampling, storing or preparing techniques.

River water was sampled in cleaned, dried and tight sealed polyethylene vessels. The vessels were first rinsed several times with the water to sampled then fully filled with the samples. Care was taken not to have any air bubbles trapped inside the vessels.

Water samples were taken in three different seasons: spring, summer and autumn from three different geographical points as follows:

► Beafore the city of Iasi, in the Northern side of the Dacia neighborhood. This is a very representative area as it lies close to the place where Bahlui river enters the city and also close to pharmaceutical production facility belonging to Antibiotice SA (**foto 1A**);

► In the Podu Roş, area, in the middle of the studied river sector (**foto 1B**);

► At 0, 5 km from the Metalurgie neighborhood toward the Dancu neighborhood, area which would indicate the accumulation of pollution agents in the river water due to the influence of the city of Iasi. (**foto 1C**).

Foto 1 – Water sampling points: Bahlui river downstream the Iaşi city (A) Podu Roş area (B) and upstream the Iaşi city (C)

After sampling, the vessels were immediately transported in the lab and kept at 4^{0}C until processing. Usually all measurements were performed after 24 hours from the sampling moment

The water turbidity assay is based mainly on the quantification of light intensity at precise wavelengths using a spectophotometer. (Jakob şi colab., 1989). The turbidity level is directly connected with the light intensity, which diminish due to reflex ion, absorption and scattering phenomena. (efect Tyndall).

The water pH was measured using the electrometric method which records the potential differences due to the variation of pH in samples.

The 105^{o}C dried residue determination implies mainly a gravimetric measurement of the organic and inorganic compounds, by keeping the water samples at the above mentioned temperature until constant weight is achieved.

Because the fixed residue evaluated at 105^{o}C also contains a small amount of crystallsation water, the drying process was continued by keeping the samples at *180^{o}C* in order to evaluate the residue abtained at this temperature using gravimetric methods. (Mănescu şi colab., 1978).

The determination of calcinated residues at 550^{o}C was performed by heating the sample at 550^{o}C and weighting the resulting residue. In the heating process, all organic compounds and some of the volatile inorganic compounds are eliminated (Mănescu și colab., 1978).

The determination of calcinated residues at 900^{o}C was performed basically as the previously described technique, onlty that the sample was heated (Mănescu şi colab., 1978).

The assay for total ammonia content consists of a colorimetric determination using al alkaline di-potassium tetraiodomercuriate solution. The ammonia reacts forming an characteristic yellow-orange color. The total amount of ammonia was expressed using a ammonium chloride standard calibration curve

The Phosphate concentration assay is based on the reaction of ammonium molibdate with the phosphate ions, forming the ammonium phosphor-molibdate. The latter compound can be transformed by a organic or inorganic reducing agent to a characteristic blue compound and can be used to evaluate the amount of soluble phosphate. A calibration curve was build using potassium phosphate (Artenie şi Tănase, 1981).

The chemical oxygen consumption (CCOCr) is based on the ability of K2Cr2O7 to react in acid condition with the reducing compounds from water. The excess of K2Cr2O7 is further titrated with Mohr reagent using the feroine as an indicator (Mănescu şi colab., 1978).

RESULTS AND DISCUSSIONS

Water turbidity dinamics

Water turbidity is caused by the presence of fine organic and inorganic particles. These particles form an suspension in water which can sediment in time. Cloudy water is of an important epidemiologic danger as the particles can function as vectors and support for pathogens.

Our results show that the turbidity depends on both the area as well as on the season when the river water was sampled. (**fig. 2**). In spring the water from the Podu Ros area, in the middle of the investigated river length proved to have the smallest turbidity value. For both the others sampling areas (upstream and downstream the city of Iasi) the turbidity values are close. This could be explained due to the fact that as the river flows through the city, it takes different polluting agents. Also, as it is spring, the water level is high and banks washing phenomena might take place.

In summer, the curve describing the turbidity dynamics is different. The highest value could be observed for the water sampled at the river entry point. As the river flows through the city, the turbidity decreases reaching it minimum at the rivers exiting point. This high value observed upstream the Iasi city could be due to some recent precipitations in the area. The dynamics of turbidity is basically the same in the three investigated points for both summer and autumn. The most significant difference in the absolute turbidity values is in autumn, when the precipitations are abundant.

From a seasonal point of view, in spring and summer could be recorded the smallest turbidity values. I it obvious that in spring this is due to the fact that snow was scarce, and consecutively, the amount of particulated matter brought by the snow-melting water was poor.

The same thing applies also for summer, when precipitations in form of rain was scarce as the whole Moltova region suffered from an excessive drought.

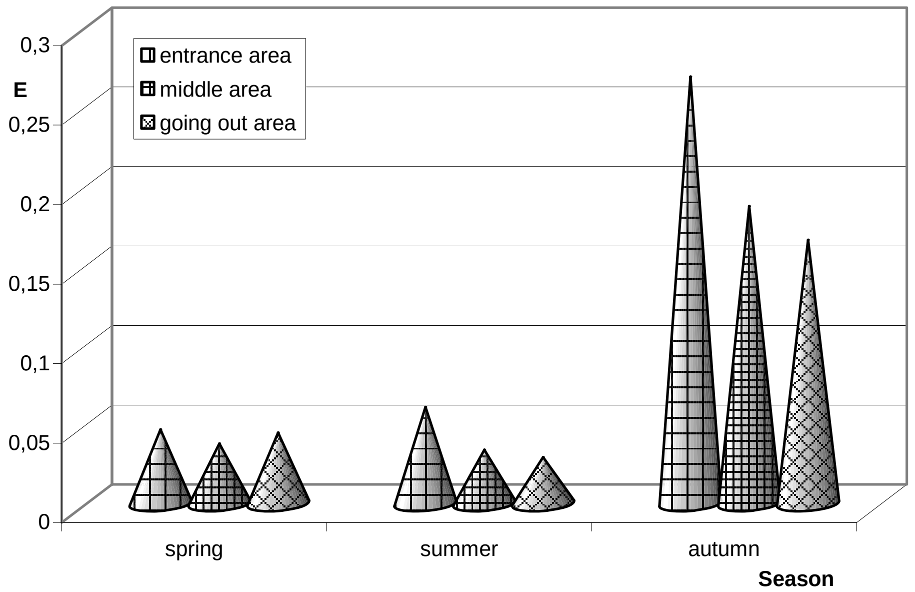

Figura 2 – The variation of water turbidity of Bahlui river samples from three different locations and seasons.

From the above figure one could observe that generally the water turbidity is constant all over the river length passing through the city of Iasi, due probably to the dry whether in the area

Water pH

The pH of water samples from Bahlui river varies great with the sampling season As it can be observed in (**fig. 3**) in spring the pH value is much higher then the recorded value for the other two seasons, with an obvious alkaline character. The mean value recorded for this season (8,02) can be due to chemical residues spills from the Antibiotice SA production facility

In summer, as the vegetation grows, the photosynthesis process is intensified and water solubilized CO2 is consumed. An important source of acidity is this way neutralized and the pH value of water returns towards the neutral area (mean 7,82).

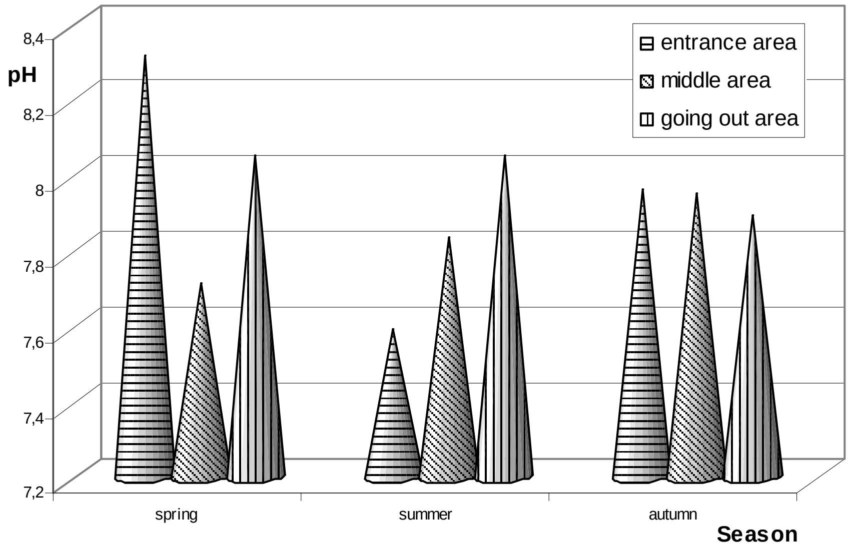

Figura 3 – pH variation of the Bahlui River water in three different seasons and locations

The water pH does not varies significantly with the geographical position from where the samples were taken, as the mean value is approximately constant between 7,83-7,99. The highest recorded value could be observed downstream the city of Iasi, as the river collects various basic componds. The smallest value could be found in the Podu Ros area, in the middle of the city, probably due to the fact that several smaller rivers merge with the Bahlui River, a dilution process taking place. Also, one important observation is the fact that overall the pH of Bahlui river water is outsite the admitted values of 5,5-7,4 for river waters (acordin to STAS 1342-910).

As a conclusion, the Bahlui River is highly polluted and cannot be used as a source for drinking water, neather for humans or animals.

Fixed residue dynamics

The fixed residue obtained at 105^{o}C represents the total amounts of non-volatile organic and inorganic substances from the water

The results show that in spring, in the all the three selected area from the investigated river length this indicator does not varies significantly (fig. 4). In summer, an increase in the recorded values could be observed for the up- and downstream sampling areas. This is due to the fact that along the studied river length, several tributary smaller rivers dilute the main river (fig. 5). In autumn, the fixed residues evaluated at 105^{o}C vary considerable along the investigated river length (**fig. 6**). At the rivers entry point into the city, the high recorded levels are probably due to rain waters which wash the agricultural fields. In the middle of the city, in the Podu Ros area, the value of this indicator is slightly lower, due to the dilution effect caused by all the smaller tributary rivers.

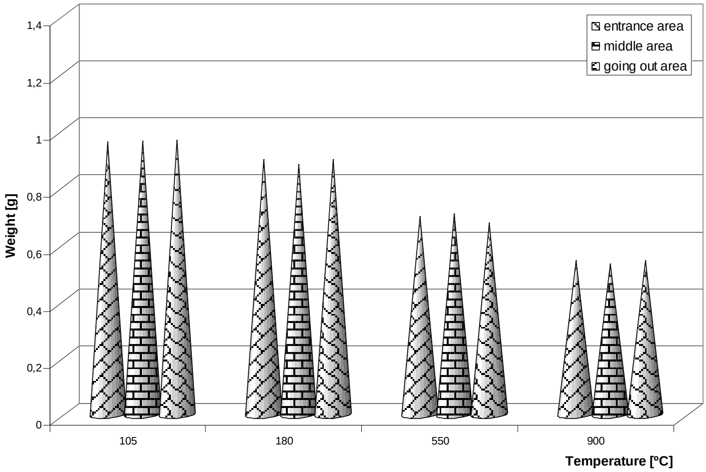

Figura 4 – The variation of fixed residues at different temperatures in the water samples from the three areas along the Bahlui River in spring.

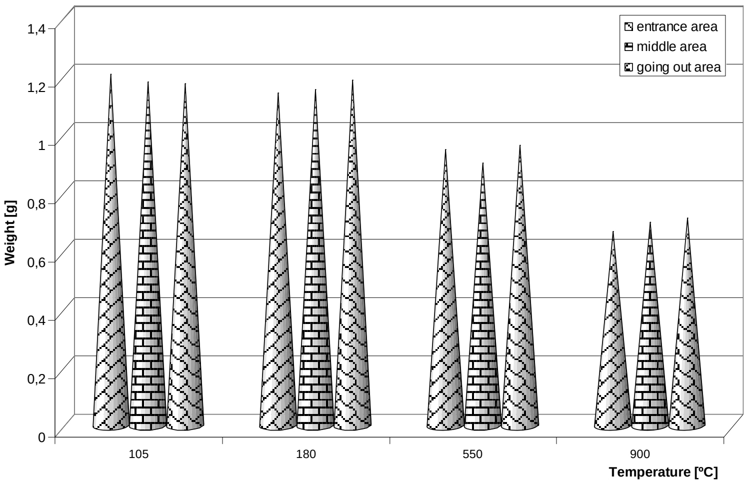

Figura 5 – The variation of fixed residues at different temperatures in the water samples from the three areas along the Bahlui River in summer.

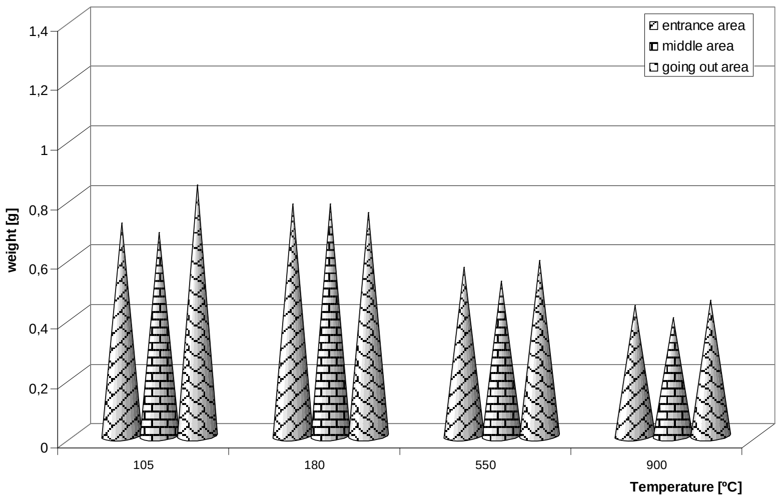

Figura 6 – The variation of fixed residues at different temperatures in the water samples from the three areas along the Bahlui River in autumn.

In order to completely remove the water from the solved compounds, the samples were further heated at 180^{o}C.

The graphical representation of the results indicates that in spring the variation of fixed residue is not significant (fig. 24). In summer as the river flows through the city and takes various organic and inorganic compounds, a slight increase of this parameter could be observed.(fig. 25). In autumn, the values f this parameter is almost unchanges along the river length, with a slight increase upstream the Iasi city, most probably due to heavy rains recorded in that time period The variation of fixed residues at different temperatures in the water samples from the three areas along the Bahlui River in spring.
(Fig.26).

The porcelain capsules containing the fixed residue were further calcinated in order to remove the organic and inorganic volatile compounds. In spring, the fixed residues are slightly increased compared in the Podu Rosu area compared to the other two sampling points (**fig. 4**). In summer, the same slight increase could be observed in the entry and exiting points of the river from the city (**fig. 5**). In autumn, a high value could be observed after the city of Iasi, probably due to edefective waste management in the riverside production facilities (**fig. 6**).

After keeping the samples at 550ºC in the capsules some traces of a black compound could be found, possibly organic carbon. The temperature was further increased at 900ºC in order to complete the calcinations process. The values obtained after this step indicate high amounts of ash in spring, when the precipitations were scarce (**fig. 4**) and a constant decrease up to autumn when the rich rains significantly change the amounts of solved compounds (**fig. 5**). Comparing the recorded values for the water turbity in the three seasons, one could easily observe the low levels in spring and summer. This is due in spring to the fact that smow was scarce and, therefore the water from snow melting was reduced. The same explanation applies for the summer period, when a severe drought was recorderd on the Moldova territory.

The highest amount of soluble compounds could be recorded in the middle of the investigated river length, in Podu Ros area indicating the clear negative effect that the city has on the river through the water side production facilities.

The admitted amount of fixed residues is 325 mg/l, far more then our recorded data, which means that the Bahlui river can accommodate a diverse aquatic wild life with a high productivity.

Ammonia concentration dynamics

The results regarding ammonia concentration in relation with the sampling season show a clear increase in the autoumn. (**fig. 7**). This could be explained only if we consider that the mineralization of animals and plants debris could be a ammonia source. Also, waste waters with high ammonia concentration could be a cause of this fenomenon.

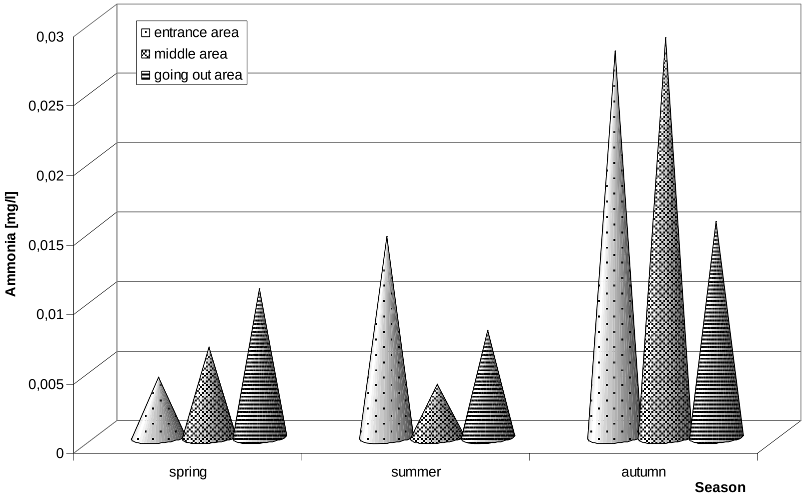

Figura 7 –
Ammonia concentration dynamics in the Bahlui river water samples from three different locations and seasons

The presence of ammonia in water samples during spring and summer is due to fertilizers and pesticides usage which are brought in by rain water. The possibility that although the river banks soil contains an high amount of ammonia, the scarce precipitations did not allow for the ammonia to reach the river must also be considered. In spring, an increase in the ammonia levels as the river flows through the city could be observed. The values recorded at the rivers entry point are very low, most probably due to the lack of precipitation upstream the city.

The values recorded at the rivers entry point into the city are very low, possibly due to the lack of precipitations upstream the city. In the middle of the city the recorded values fall in an average area, indicating a slight accumulation of ammonia containing substances. The highest recorded were recorded downstream of the city, as the heavy rain in the sampling period have washed the surrounding agricultural fields and contaminated the water with high amounts of ammonia.

In summer the Bahlui River brings large amounts of ammonia which correlated with high temperatures lead top the eutrophisation phenomenon, fallowed by a decrease of the solved oxygen, especially in the middle area. .

In summer the amounts of ammonia in the entry and middle area are the highest recorded on our experimental model. The mean recorded values (0,02 mg/l) are far from the maximum admitted limits (0,296 mg/l), values at which the water might be considered incompatible with aquatic wild life.

Phosphate concentration dynamics.

The graphical representation of the results according to the sampling season (**fig. 8**) clearly shows the drop in phosphate concentration from spring to autumn, probably due to the usage in agriculture of fertilizers and pesticides containing phosphorus. The high amount of phosphate found in the river water in summer is a matter of concern as these compounds are part of the eutrophication phenomenon.

If the recorded data is analyzed related to the sampling season, one could clearly see that in spring the amounts of phosphates recorded at the rivers entry point into the city is extremely high, compared with the other areas. Also in this area a clear eutrophication process could be observed.

In summer the amounts of phosphates are lower and continue to drop close to zero. The smallest amounts recorded are in the middle are, due to the dilution process. In autumn a clear and important drop of the phosphates concentration from the entry point toward the exit point could be inferred. As in this season phosphorus-based products are no longer used in agriculture and the precipitations were abundant, the recorded level was low to zero.

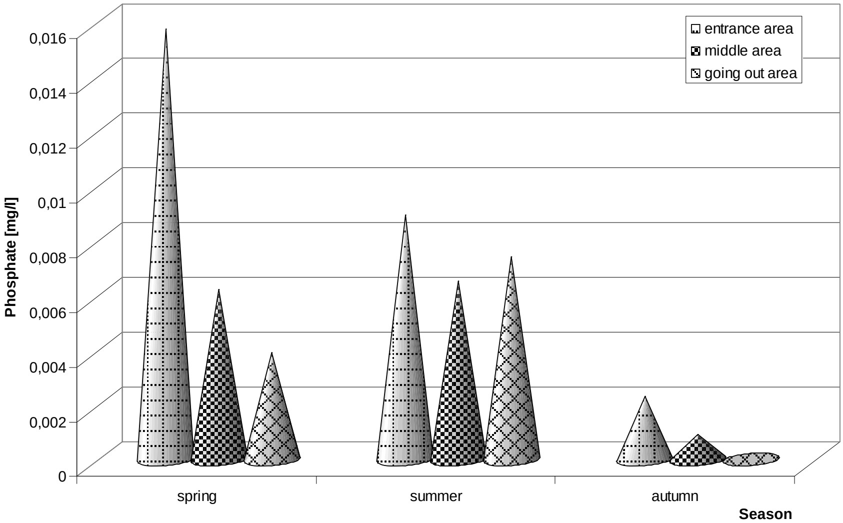

Figura 8 – Phosphorus centration dynamics in the Bahlui river water samples from three different locations and seasons

The mean recorded levels of phosphates along the investigated river sector of 0.0057 mg/l. are low compared to the maximum admitted levels according to STAS(4,468 mg/l).

Thereby we can conclude that the phosphorus pollution level is low on the Bahlui river and it does not represents an danger for the aquatic flora and fauna. .

CCOCr levels variation

Overall, the results regarding the oxidable ccompounds from the water indicate their presence in different amounts al along the experiment (**fig. 9**).

From a seasonal point of view, high levels of this marker could be recorded in summer and autumn. This is most probably due, in spring to snow-melting water arriving into the river and bringing large amounts of vegetable debris. In autumn the increase in oxidable compounds is due to the decomposition of animal and plant debris as well as due to industrial spills.

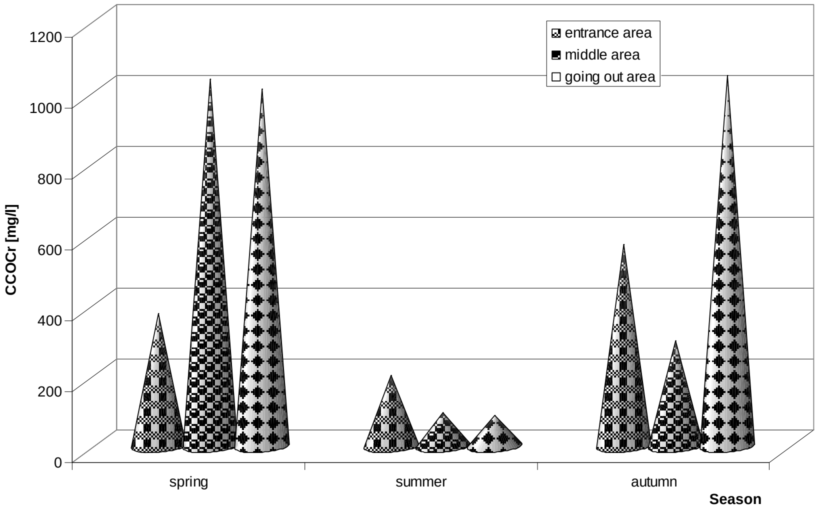

Figura 9 – The CCOCr variation in the Bahlui river water samples from three different locations and seasons

From a sampling area point of view, the results show, in spring, an significant increase in the CCOCr levels in the middle and downstream areas.

In summer, the CCOCr levels are dropping as the river flows through the city. On the other hand, in autumn the levels are much higher with a maximum as the river leaves the city. The results obtained for CCOCr in the water samples from Bahlui river are over the standard admitted value(26,8 mg/l), so the water is highly polluted.

CONCLUSIONS

The water turbidity varies according to the season as well as the levels of precipitations. The highest recorded level of turbidity was in autumn due to large amounts of rain which brought into the river large amounts of various compounds.

The pH-ul of Bahlui River does not varies significantly, being permanently in a slight basic domain. The recorded values for this indicator fall into the admitted interval according to the standards.

The recorded fixed residue values are lower then those reported by standards. The highest values for this indicator were recorded in summer, probably due to spills of organing an inorganic compounds from the surrounding companies.

The ammonia concentration in the investigated river sector are far lower then the admitted standards.The highest values were recorded in spring and summer ammonia-containing fertilizers are intensive used and carried by the rain-water into the river.

Phosphates levels are under the maximum admitted limits. Nevertheless, the high levels recorded in summer correlated with the high temperatures are a real matter of concern, being the main factor in the eutrophication process.

The CCOCr parameter indicates a high level of pollution of the Bahlui river The highest amplitudes of the values are recorded in spring due to the snow-melting water which brings various debris and pollutants.

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