Study on the Seasonal Variation of Nitrogen Nutrients Content from Ialomita River Hydrographic Basin

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This study aim to investigate the seasonal variation of nitrogen nutrients from Ialomita river basin and the relationships between the nutrient content and other water quality parameters, such as: pH, water temperature, conductivity, and dissolved oxygen from 2004 to 2008. The anthropogenic impact of Ialomita River can be shown via high nitrogen nutrient content. The water quality of the river is worst in the cold seasons and an improvement is visible in the warm seasons.

Keyword: inorganic nutrients, nitrites, nitrates, ammonium determination, surface waters

Any element or chemical compound which contributes to the organism metabolism is considered as nutrient. The nutrient term refers, generally, to the chemical species that contain nitrogen and phosphorous (non-nitrogen nutrients). In the category of inorganic nitrogen nutrients may be included the following chemical species: nitrites, nitrates and ammonium.

The nitrogen is an essential element for the plants growing process, the plants nitrogen necessary is being covered by absorbing the nitrogen species from the water. The living organism uses the nitrogen to procure and develop some essential compounds, such as proteins, DNA, RNA, hormones and enzymes [1]. Because the living organisms are not able to use the simple nitrogen forms (nitrites, nitrates and ammonium) have to develop complex forms of nitrogen (amino acids and nucleic acids) and take their adequate nutrients amount from plants and other animals.

Environment pollution sources with nitrogen compounds are natural and anthropogenic sources. Natural sources of pollution are permeable geological formation, but the principal are the anthropogenic sources, point sources and non-point ones. The major non-point sources of nitrogen contamination are commercial fertilizer and animal manure, and the point sources are from industrial sources and municipal sewage sludge.

The major nitrogen polluter is agriculture because, to produce constant crop yields, inorganic nitrogen fertilizers and / or animal manure (organic fertilizers) are used in excessive [2].

The responsible for the major negative effects of water pollution with nitrogen nutrients, eutrophication process, are inorganic forms (NH_4^+, NO_3^- and NO_2^-) resulted from human activities. This algal bloom process and excessive growth of aquatic plants appears when higher quantities of nitrogen compounds than plants need are introduced in aquatic ecosystems. Some of the ecological and toxicological effects of the eutrophication are taste and odour of the water, reduction in water column transparency, phosphorus release from sediments.

Another negative effect of aquatic ecosystem enrichment with nitrogen nutrients is acidification process. The major acidifying pollutants in surface waters are nitrogen oxide (NO), nitrogen dioxide (NO_2) and sulphur dioxide (SO_2). After complex chemical reactions these gaseous pollutants forms sulphuric acid (H_2SO_4) and nitric acid (HNO_3). The wet and dry atmospheric deposition of these acids increases the concentrations of sulphate ions (SO_4^{2-}), nitrate ions (NO_3^-) and hydrogen ions (H^+) in aquatic ecosystems [3]. The adverse effects of acidification process on aquatic ecosystems are decreases of *p*H values, nutrient cycling can be inhibited, bioaccumulation of trace metals in fish [4].

The concentrations of ionized ammonia (NH_4^+) and unionized ammonia (NH_3) are dependent on the pH and temperature values of the water. The unionized ammonia is more toxic than the ionized form (NH_4^+) at alkaline *p*H values. Laboratory studies have showed the acute and chronic toxicities effects of unionized ammonia to the aquatic animals and it have been estimated and recommended the water quality criteria for short-term exposures (0.05 – 0.35 mg/L NH_3-N) and long-term exposures (0.01 – 0.02 mg/L NH_3-N) [5, 6].

As in the case of unionized ammonia, nitrite ions (NO_2^-) can have negative effects to aquatic animals. The main toxic effects of nitrite ions on aquatic organisms are formation of mutagenic and carcinogenic compounds, such as N-nitroso compounds in the fish blood , the nitrite ions convert hemoglobin in methemoglobin, and similarly, in crayfish the nitrite ions entry in the blood plasma and forms methemocyanin [7]. On the basis of acute toxicity study, the water quality criteria for short term exposures were estimated at 0.08 – 0.35 mg/L NO_2-N [8].

Because nitrate ions do not form unionized species, the nitrate toxicity in aquatic ecosystems is due to nitrate ions. The main toxic effects of nitrate ions on aquatic animals are similar to the nitrate one, the conversion of hemoglobin and hemocyanin to methemoglobin and methemocyanin (incapable forms to carry oxygen). In saline waters the nitrate ions have less toxic effects than in the fresh waters. The maximum level for water quality criteria has been proposed at 2 mg/L NO_3-N [9].

The most serious health effects associated with the contaminated water with nitrate and nitrite are the following: methemoglobinemia (baby blue syndrome) [10], birth defects and spontaneous abortion [11], hypertension and thyroid hypertrophy [12], cancer [13]. The toxic mechanism of the nitrite ions consists in the fact

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that they are absorbed from the digestive system and as soon as they arrive in blood, they form with hemoglobin a strong complex called methemoglobin. Depending upon the hemoglobin blocked percentage, there are negative effects on the living organism health when the percentage is high, anemia effects and cyanosis may occur. When the blocking hemoglobin percentage is over 80% the effect is lethal.

The present work deals with the assessment of the seasonal variation of the main water quality parameters in Ialomita River, which drains one of the major rural, agricultural, urban and industrial areas of Romania and receives a pollution load from both point and non-point sources.

Experimental part

Samples

Water samples were taken using clean polypropylene bottles from different locations, starting from the springs of the river situated in Bucegi Mountains up to the confluence with the Danube River, from the middle stream of the Ialomita River. Sampling and preservation were conducted by standard methods for surface waters analysis [14, 15]. The controlled parameters in the surface water samples were the following: the *p*H, the water temperature (WT), the electrical conductivity (EC), the dissolved oxygen (DO), the nitrate nitrogen (NO_3-N), the nitrite nitrogen (NO_2-N) and the ammoniacal nitrogen (NH_4-N). The data sets were obtained from five water quality monitoring stations, three on Ialomita River and the other two on two of its tributaries, Cricovul Dulce River and Sarata River (fig. 1) under monthly control for over 5 years (2004-2008).

Reagents

All reagents used were of analytical–reagent grade and were used without further purification. All solutions were prepared using bi-distilled water.

Analytical Methods

Methods for nitrogen nutrients determination

Absorption molecular spectrometry method was applied for the nitrogen nutrients determination.

The *ammonium ion* determination is based on the measurement of the absorbance at 655 nm of the blue colored coupling compound formed by the reaction of ammonium ions with salicylate and hypochlorite ions in the presence of sodium nitroprusside [16].

The nitrate ions determination is based on the formation of a nitro benzoic yellow colored complex by reaction with salicylic ions in alkaline medium [17]. In this case the absorbance was effectuated at the wavelength of 415 nm. In the present work it was applied a simplified version of the above mentioned method by reducing the determination time using the same calibration solutions, by keeping them without light and at a temperature of 4°C for 54 days [18].

For the determination of the *nitrite ions* from water samples it was applied Greiss method [19], which uses benzene sulfonamide and α naphtyl amine dihydrochloride (NED) as reagents to form with nitrite ions the diazonium salt (under acidic conditions - phosphoric acid). The absorbance of the resulting red colored compound was measured at 541 nm. According to reference [20] chemical reactions involved in Greiss system are presented in figure 2.

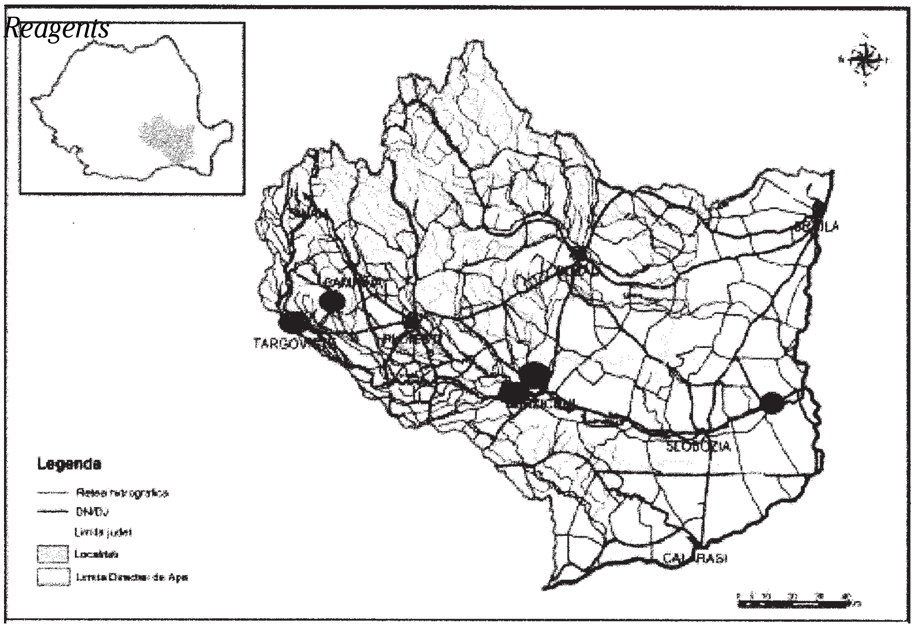

Fig. 1. Map of the studied area showing the surface water quality monitoring stations in the Ialomita River Basin.. 1 - Branesti (Ialomita River); 2 - Amonte Moreni (Cricovul Dulce River); 3 - Cosereni (Ialomita River); 4 - Amonte Urziceni (Sarata River); 5 - Tandarei (Ialomita River)

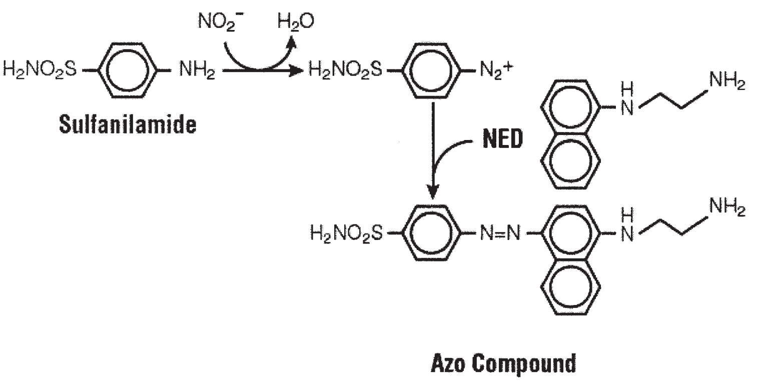

Fig. 2 Chemical reactions involved in the Greiss system

Table 1
WATER QUALITY PARAMETERS, UNITS, LOD, LOQ AND ANALYTICAL METHODS USED DURING 2004-2008 FOR SURFACE WATERS OF IALOMITA RIVER BASIN

Parameters	Units	Analytical standard methods	LOD	LOQ
pH		SR ISO 10523/1997	0.40	1.20
Water temperature (WT)	°C	STAS 6324/1961	0.10	0.30
Dissolved oxygen (DO)	mg/L O_2	SR EN 25814/1999	0.20	0.60
Electrical conductivity (EC)	μS/cm	SR EN 27888/1997	2.00	6.00
Ammonium nitrogen (NH_4-N)	mg/L N	SR ISO 7150-1/2001 [15]	0.010	0.030
Nitrite nitrogen (NO_2-N)	mg/L N	SR ISO 6777/1996 [17]	0.001	0.003
Nitrate nitrogen (NO_3-N)	mg/L N	SR ISO 7890-3/2000 [16]	0.010	0.030

Table 2
SUMMARY BASIC STATISTICS OF WATER QUALITY PARAMETERS AT DIFFERENT LOCATIONS OF IALOMITA RIVER BASIN DURING 2004-2008

Parameters		Station 1	Station 2	Station 3	Station 4	Station 5
pH	Range	6.50 – 8.50	6.70 – 8.00	7.00 – 9.70	7.10 – 9.10	7.40 – 8.50
	Mean	7.25	7.46	7.94	8.11	7.96
WT	Range	1.00 – 24.00	1.00 – 28.00	0.50 – 28.0	2.00 – 23.00	1.00 – 28.00
	Mean	10.13	10.71	12.34	14.18	13.55
DO	Range	7.10 – 12.28	6.38 – 12.30	2.40 – 12.20	4.10 – 14.85	3.80 – 15.96
	Mean	9.959	9.031	8.440	8.650	9.154
EC	Range	283.29 – 516.04	679.6 – 1589.4	637.7 – 1561.4	1179.6 – 2560.3	599.56 – 1400.5
	Mean	384.096	892.568	10.27.42	1933.61	1012.962
NH_4-N	Range	0.01 – 0.923	0.054 – 1.944	0.035 – 2.461	0.017 – 0.673	0.010 – 4.254
	Mean	0.282	0.670	0.563	0.181	0.988
NO_2-N	Range	0.004 – 0.061	0.002 – 0.049	0.004 – 0.323	0.033 – 1.35	0.005 – 0.864
	Mean	0.025	0.023	0.092	0.413	0.148
NO_3-N	Range	0.231 – 3.432	0.03 – 4.516	0.09 – 30.935	0.013 – 0.117	0.181 – 39.084
	Mean	1.615	1.596	2.076	0.047	3.124

All the absorbance measurements were carried out using a Cary 300 Bio UV-VIS spectrophotometer.

Methods for the determination of other water quality parameters

The *p*H, water temperature, electrical conductivity and dissolved oxygen of water samples were determined in situ with a digital electrochemical apparatus, HQD 40 multimeter.

Results and discussions

All the spiked water samples of the Ialomita River Basin were analyzed in duplicate and procedural blank measurements were applied. The standard analytical methods used to collect analytical data for 7 quality water parameters, with their limit of detection (LOD) and limit of quantification (LOQ), the water quality parameters with their units are summarized in table 1.

Table 2 presents basic statistics of the monthly measured parameters at the 5 monitoring water quality stations on Ialomita river during 5 year data set.

In order to interpret the obtained data and to evaluate the water quality the Order 161/2006 [21] from Romanian legislation was used. According to this normative, the water quality assessment is carried out taking into account five quality classes, the limit value for each class being the maximum acceptable value for the respective quality class. The Class I represents reference conditions or background concentrations, the Class II represents the target value (reference objective) for water quality and represents also the quality condition for protection of the aquatic ecosystems, and the Classes III – V are on the "non-complying" side of the classification scheme and their limit values are usually 2-5 times the target values.

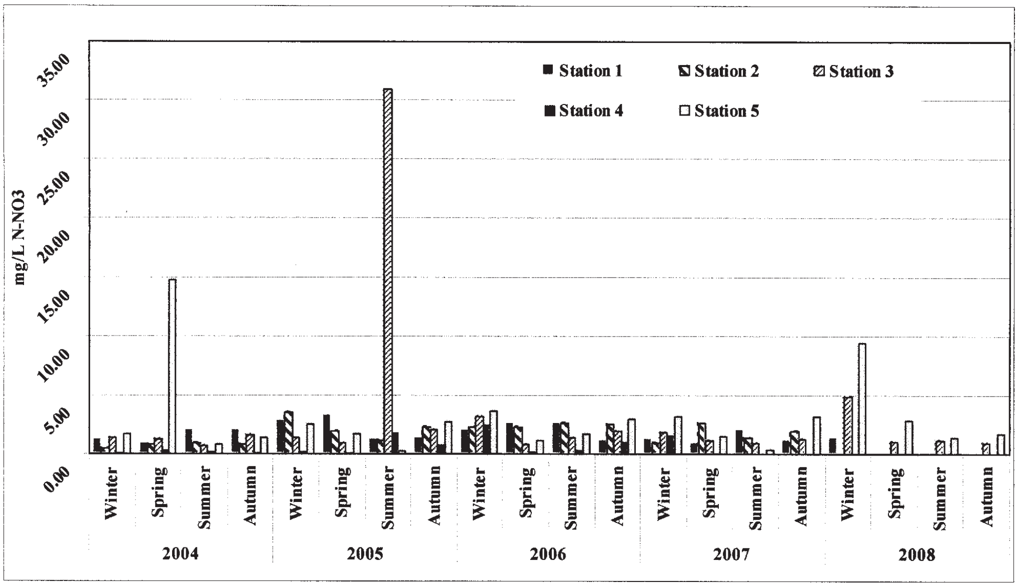

Fig. 3. Seasonal variation of nitrate nitrogen in Ialomita River Basin

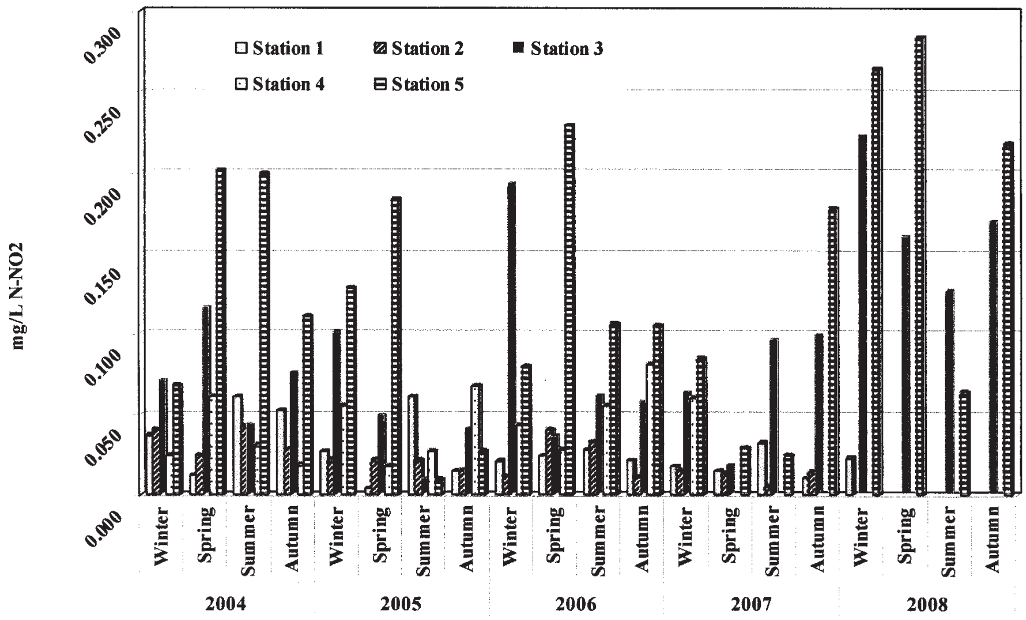

Fig. 4. Seasonal variation of nitrite nitrogen in Ialomita River Basin

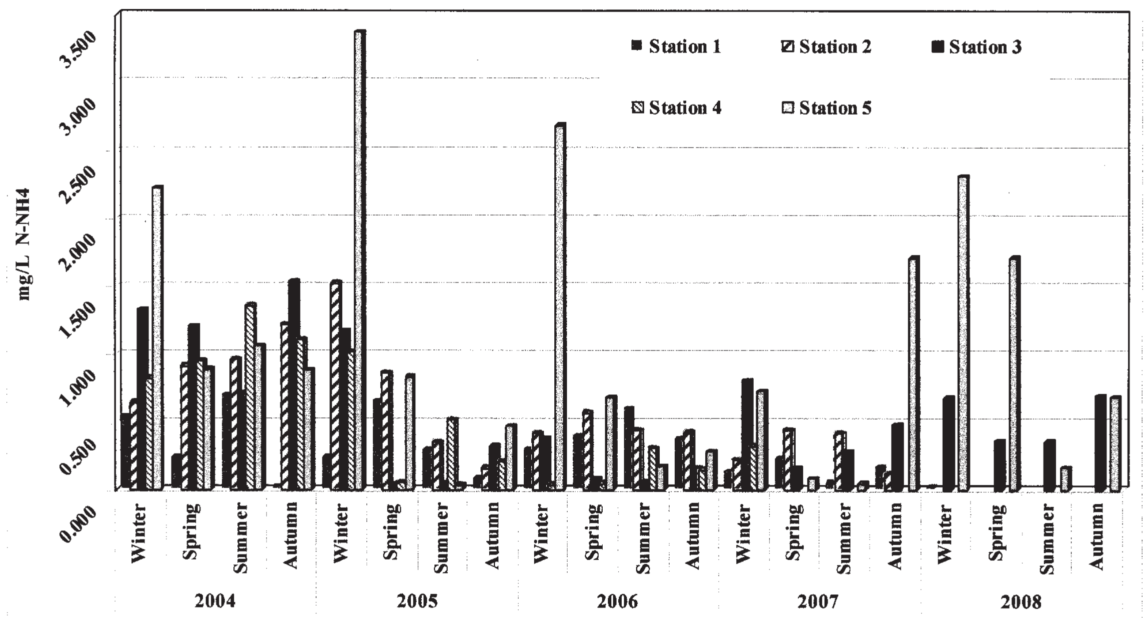

Fig. 5. Seasonal variation of ammonium nitrogen in Ialomita River Basin

The seasonal distribution of nitrogen nutrients during 2004-2008 allows to asses the water quality of Ialomita River in this period of time. From the nitrate-N concentrations presented in figure 3, it can be seen that the variation range for the studied period was 0.013 mg/L N-NO_3 (station 4, spring 2005) – 39.084 mg/L N-NO_3 (station 5, spring 2004). Spatial pattern shows an increasing line from monitoring sites located in the upper part of the river to the site located at the confluence with the Danube. From the temporal point of view, it can be noticed that in spring 2004 and in summer 2005 relative higher nitrate-N concentrations were recorded in station 5, respectively in station 3.

For nitrate-N, distribution of monitoring data into quality classes indicates that a higher number of data (170) belongs to the first two reference classes and only 23 are within the Class III and V respectively.

Nitrite-N concentrations presents a variation range of 0.002 mg/L N-NO_2 (station 2, summer 2007) – 0.864 mg/L N-NO_2 (station 5, spring 2008) – figure 4. In terms of temporal variation, no relevant trend is visible for this indicator. Unlike to nitrate-N water quality classification is worse for nitrite-N, because a very high number of data are in Class IV (68) and only a few in Class I (14).

According to the set of values reported (fig. 5), seasonal variation of ammonium-N concentrations is higher in 2004 for all five stations. In station 5, the last one up to the confluence with the Danube River, the concentrations of ammonium-N are constant higher than the other four stations mostly caused by non- or insufficiently treated waste waters.

Water quality classification indicates for ammonium-N that most of data (106) classify water quality in Class I and only a few in Class III (31), in Class IV (27), respectively in Class V (only 4).

Considering the other four water quality parameters that were monitorized, two of them, water temperature and conductivity, are not standardized according to the Order 161/2006.

In the case of *p*H only two values are higher than 8.5 units (table 2) and those are in winter 2004, respectively in autumn 2006 at station 3, respectively station 4.

According to the set of values reported (table 2), the concentrations of dissolved oxygen from all five monitoring stations more than 75% are in quality class I and II. Only in station 1-Branesti , all of the data for dissolved oxygen are in the first two quality classes, showing in this way that the anthropogenic impact at this station is very low.

Conclusions

The present contribution allowed to establish the variation of inorganic nitrogen nutrients and other water quality parameters in Ialomita River Basin from 2004 to 2008.

$N\text{-}NH_4$: decreasing temporal profile from 2004 to 2008, with most of data in reference condition (Class I); in correlation with oxygen demand indicators, ammonium levels showed the impact of untreated or insufficiently treated wastewaters mainly from municipalities.

Water quality classification is worst for $N\text{-}NO_2$ than for ammonium and nitrate, the majority of data in the "non-complying side" (Class III and IV) is noticed.

$N\text{-}NO_3$: spatial pattern showed an increasing line from monitoring sites located in the upper part of the river to the site located at the confluence with the Danube; distribution of monitoring data into quality classes indicated that a higher number of data was characteristic to reference condition and met quality target than the one within the Class III and V respectively.

Water temperature and conductivity are not standardized *p*H: only two values are higher than 8.5 units of *p*H.

Dissolved oxygen: at station 1 all the data are in the first two water quality classes, and for the other four stations only few values are in quality class IV or V.

According to the water quality parameters that were discussed in this paper it can be observed that station 3 is one of the most polluted monitoring station because it is situated in a very high developed agricultural area, and another station that is also polluted is station 5, but in this case pollution is caused by the municipal waste waters from Slobozia and Tandarei cities that are insufficiently treated. On the other hand from this five stations that were monitorized the most unpolluted station is station 1-Branesti, because it is situated in the mountain area were the anthropogenic impact is very low.

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