

DETERMINING AMMONIUM AND NITRATE POLLUTION OF THE OLT RIVER BASIN IN RM. VALCEA INDUSTRIAL AREA

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ABSTRACT

Surface water is an important source of water in many parts of the world. Agriculture constitutes the largest user of the resource, consuming about 70% of all freshwater supplies on a global scale. The quality of surface water is sensitive to the contaminants originated from industrial and agricultural chemicals. This work aims to investigate the levels of ammonium and nitrates in the Olt River Basin, waters that supplies the industrial area of Rm. Valcea town. The water samples were collected during 4 consecutive months, from November 2012 to February 2013, the chemical parameters studied ranging between 7.3 mg/l and 43.9 mg/l for nitrates and, respectively, from 0.02 mg/l to 2.56 mg/l for ammonium. There are high nitrate concentrations in the entire basin indicating pollution, higher in the agricultural area than in the industrial part. Olt River and the industrial waters have higher ammonium concentrations than Olt tributaries. The chemical characteristics of these samples enable to establish the water quality and to classify them in the appropriate quality standard. Considering that the levels of both species in the surface water are high, future continuous monitoring of their respective levels is required.

Keywords: *nitrogen species, pollution, river basin, surface water.*

1. INTRODUCTION

Determination of nitrogen species in surface water is usually an integral part of basic water quality assessment since their concentrations are general indicators of the nutrient status and the degree of organic pollution of any affected water body. Nitrogen inorganic compounds are essential plant nutrients, but in excess amounts they can cause significant water quality problems. Found in several different forms in terrestrial and aquatic ecosystems, nitrogen forms include ammonia (NH_3) dissolved as ammonium (NH_4^+), nitrates (NO_3^-), and nitrites (NO_2^-) [Heaton T.H.E., 1986; Battaglin W.A., et. al., 2001].

This paper aims to determine the level of ammonium (NH_4^+) and nitrates (NO_3^-) in surface water on a defined area along the Olt River basin, the industrial area of Rm. Valcea town. The knowledge of the amount of nutrients in surface water of Olt River basin, the main tributary of Danube River, is essential since high loads can be toxic to aquatic organisms. Together with phosphorus, nitrates in

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excess amounts can accelerate eutrophication of streams, lakes and reservoirs within the basin, causing dramatic increases in aquatic plant growth and changes in the types of plants and living organisms [Segal-Rozenhaimer M., 2004].

The natural level of ammonium or nitrate in surface water is typically low (less than 1 mg/L); in the effluent of wastewater treatment plants, it can range up to 30 mg/L. Under certain conditions, at concentrations higher than 10 mg/L, the nitrates can cause hypoxia (low levels of dissolved oxygen) and can become toxic to warm-blooded animals [Reinhardt M. et al., 2006].

The distribution and transport of nutrients within the waters of Olt River basin can be influenced by any factors including watershed characteristics and nutrient sources.

Nitrate is a common contaminant of water closely associated with agricultural activities, the primary source for nitrate in surface waters being from fertilizer use. Being an extremely soluble form of nitrogen, nitrate can readily move with soil water toward plant roots to be taken up by them. Fertilizer nitrogen that is not taken up by plants can leach its way into the soil in the form of nitrate. Another potential source of nitrate leaching to the surface water that deals with farming is the storage of manure. The amount of nitrogen released depends on the type of manure, application rate and method, and consecutive years of application. The nitrate ion (NO_3^-) is dissociated in the aquatic environment, and consequently nitrate toxicity to aquatic animals is due to nitrate ions [Burkart M.R. et al., 1999; Broshears R.E. et al., 2001].

In natural surface waters, ammonia which is a product of microbiological activity is seen as indicative of sanitary pollution. It is rapidly oxidized by certain bacteria to nitrite and nitrate, a process that requires the presence of dissolved oxygen. Being a source of nitrogen, ammonia is also a nutrient for algae and other forms of plant life contributing thus to overloading of natural systems and causing pollution [Freney J.R. et al., 1983]. The ionized ammonia (NH_4^+ - ammonium) and un-ionized ammonia (NH_3), the main toxic form of ammonia, are interrelated through the chemical equilibrium:



In surface water, ammonium concentration can vary for several reasons like upstream discharge of high nitrate or ammonium sewage effluent, leaching from agricultural land during storm conditions, discharge of farm or industrial effluents and(or) seasonal effects [Ging P.B. et al., 1996].

2. MATERIALS AND METHODS

The study was carried out by systematic collection of surface water samples from Olt River and its main tributaries in the industrial area of Rm. Valcea Town. The sampling started on Olt River at Calimanesti town and ended on Olt River at Ionesti, including all the main tributaries: Govora, Bistrita, Topolog, Luncavat Rivers. The main industrial discharge points are at Priza Olt and Govora River.

Surface water quality monitoring uses standardized national sampling protocols to help ensure the scientific validity and relevance of the water data collected and analytical methods are available for detecting, measuring nitrate and ammonium ions [GD 100/2002].

Sample collection and storage. The samples were taken during the study period, from November 2012 to February 2013, from 11 selected sampling points (Table 1). Standard methods were used for collection and analysis of surface water samples [ISO 5667-10, 1992]. The water samples were collected in clean glass bottles, which were rinsed with de-ionized water and stored to the laboratory for up to 24 h, at 4°C, to retard the microbiological activity as well as the rates of possible physical and chemical reactions.

Table 1. Measured values of nitrate (NO₃⁻) and ammonium (NH₄⁺) in water samples, with sampling location

Sample code	Sampling location	Sampling location description	Nitrate (NO ₃ ⁻) (mg/L)					Ammonium (NH ₄ ⁺) (mg/L)				
			Mean	SD	Min	Max	Median	Mean	SD	Min	Max	Median
S1	Olt - Calimanesti	0.5 km downstream from the Turnu dam and 0.3km upstream from the Jiblea dam	27.4	7.04	17.8	34.6	28.6	1.21	1.20	0.10	2.56	1.09
S2	Olanesti - Rm.Valcea	-	17.5	3.96	14.2	23.2	16.3	0.23	0.18	0.02	0.45	0.22
S3	Olt - Rm. Valcea	Rm. Valcea dam	14.3	6.01	8.5	22.2	13.3	0.74	0.90	0.02	1.92	0.51
S4	Olt - Priza Olt (upstream)	9 km downstream from the Rm. Valcea - South dam and 0.5 km upstream from the Raureni dam	13.0	6.86	7.3	22.9	10.9	0.68	0.89	0.12	2.00	0.31
S5	Olt - Priza Olt	industrial waste water duct	29.4	12.54	11.3	39.8	33.2	0.65	0.69	0.02	1.50	0.55
S6	Olt - Priza Olt (downstream)	9 km downstream from the Rm. Valcea - South dam and 0.5 km upstream from the Raureni dam	18.7	2.98	14.3	21.0	19.7	0.35	0.09	0.28	0.46	0.32
S7	Govora - Babeni	discharge of industrial waste water	15.6	4.80	11.5	20.9	14.9	0.30	0.21	0.10	0.57	0.26
S8	Bistrita - Babeni	-	17.0	2.89	14.6	21.1	16.2	0.27	0.22	0.10	0.58	0.20
S9	Topolog - Galicea	-	22.1	7.63	12.2	30.3	23.0	0.27	0.08	0.18	0.36	0.28
S10	Luncavat - Otesani	-	25.5	16.50	10.4	43.9	23.8	0.33	0.25	0.20	0.70	0.22
S11	Olt - Ionesti	3.5 km downstream from the Galicea dam and 3.5 km upstream from the Ionesti dam	23.0	6.77	17.7	32.3	21.1	0.71	1.13	0.03	2.40	0.20

Sample analysis. The nitrate and ammonium concentrations in samples were determined by colorimetric method, using a UV-VIS spectrophotometer type

SPECORD 250. The quality control analysis has been tested using Certified Reference Material.

Ammonium analysis method - Ammonium reacts with hypochlorite ions generated by the alkaline hydrolysis of sodium dichloroisocyanurate to form monochloramine. This reacts with salicylate ions in the presence of sodium nitroprusside at pH around 12.6 to form a blue compound. The absorbance of this compound is measured spectrophotometrically at the wavelength 660 nm and is related to the ammonium concentration by means of a calibration curve.

Nitrate analysis method - The analysis is based on the reaction of nitrate with sodium salicylate in a sulphuric acid medium, which formed yellow colored salts of nitrosalicylic acid. The absorbance of this compound is measured spectrophotometrically at the wavelength 415 nm and is related to the nitrate concentration by means of a calibration curve.

All the results, for ammonium and nitrate concentration are expressed in mg/L.

3. RESULTS AND DISCUSSION

The nitrate (NO_3^-) and ammonium (NH_4^+) levels in the investigated surface waters expressed in mg/L are summarized in Table 1 and Figure 1, as means, limits, standard deviations and medians. The values for nitrate (NO_3^-) concentration range between 7.3 mg/L and 43.9 mg/L, while for ammonium (NH_4^+) from 0.02 mg/L to 2.56 mg/L.

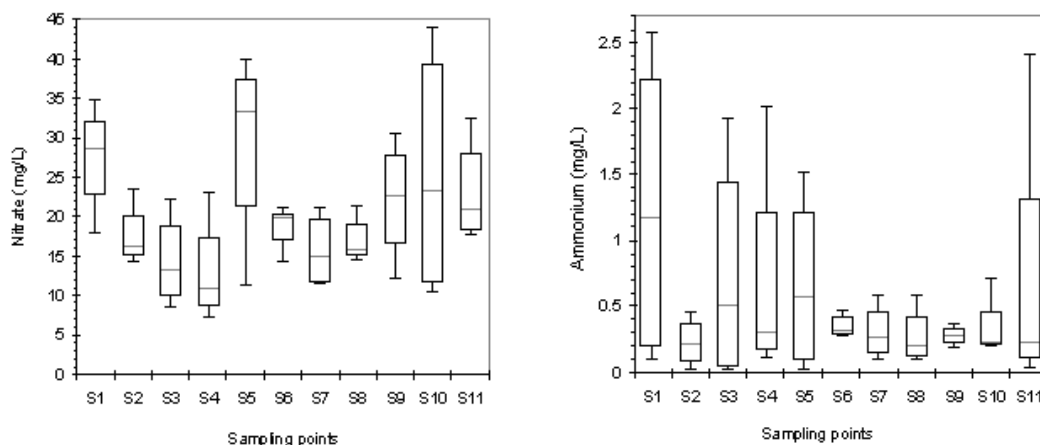


Figure 1. The range of variation for nitrate and ammonium levels in the Olt River Basin within the 11 sampling points

The obtained values for nitrate concentrations in the investigated samples are within the limits imposed by the national and international regulations. Maximum value for nitrates in surface water [GD 100/2002 which transposes the European Directive 75/440/EEC] and in groundwater [GD 53/2009 that transpose European Directive 2006/118/EC] is 50 mg NO_3^- /l. Natural levels of nitrate in surface waters seldom exceed 0.1 mg/l, but waters influenced by human activity

normally contain up to 5 mg/l with levels over 5 mg/l indicating pollution by animal or human waste or fertilizer runoff [Kohl D.H. *et al.*, 1971]. All the collected samples exceed 7.3 mg/l nitrate, indicating pollution. Also, taking into account the mean nitrate concentrations, all the sampling points can be attributed to class V water quality (bad ecological state) [O 161/2006], when the water quality decreases with its number, the worst class being V. Higher nitrate concentrations (between 10 and 43.9 mg/l) can be observed for S1, S5, S9-S11 sampling sites. These sites represent the entrance and exit points for the studied basin. Smaller concentrations (7.3-24 mg/l) were found at S2-S4, S6-S8 locations that are the middle sampling locations of the study area. These values indicate that agriculture is a more important source of pollution with nitrate than industry in the Rm. Valcea area.

The results for ammonium concentrations in the investigated samples are below the limits (maximum admissible limits of 2 mg/L in surface water) imposed by GD 100/2002 which complies with the European Directive 75/440/EEC, with the exception of S1 in January, S4 in February and S11 in February. Higher ammonium concentrations can be observed for S1, S3, S4, S5 and S11 sampling locations where four locations were dams and one is an industrial discharge (the industrial discharge duct from Priza Olt - S5). Also, for these sites the range of values is significantly higher showing big variations in time. On the other hand, six sampling locations had low ammonium concentrations, from which four locations have stream water (S2, S8-S10), one is an industrial discharge (S7) and one is near a dam (S6). It is common that nutrient concentrations to be lower in rivers downstream from reservoirs than in the reservoirs because of uptake of nitrogen by aquatic plants followed by decomposition to ammonia, denitrification and accumulation of phosphorous associated with sediment in reservoirs, phenomena that increase the ammonium concentration [Kendall C., 1998]. Mainly Olt River, with the exception of S6 point, has higher ammonium concentrations than its tributaries.

The ammonium's mean concentration of these samples can be used to determine the water quality and to classify it in the appropriate quality standard [O 161/2006]. The sampling points S2 and S6-S10 are corresponding to class I (very good ecological state), sampling points S3-S5 and S11 can be attributed to class II (good ecological state) and S1 can be set as class IV (week ecological state).

Nutrient concentrations in streams and reservoirs along the Olt River basin can vary seasonally due to specific changes related with growth and decay of vegetation [Mattraw H.C., Elder J.F., 1984], change (i.e. increase) in temperature with effects on aquatic plants growth in reservoirs, nitrification of ammonium and nitrate [Ehlke T.A., 1978], seasonal applications of fertilizers, rainfall, and pollution factors. The distribution of ammonium and nitrate for surface water samples collected between November, 2012 and February, 2013 period was plotted by sampling period (Figure 2). For ammonium, the sampling period doesn't influence the concentrations, the sample location being the most important factor. The nitrate concentrations are better distributed with the sampling period, indicating stability in time for the values. Since all the sampling months were cold, an increase in concentration of the nutrients during warmer and fertilization periods

is expected, since this study will continue over a longer period of time of at least one year.

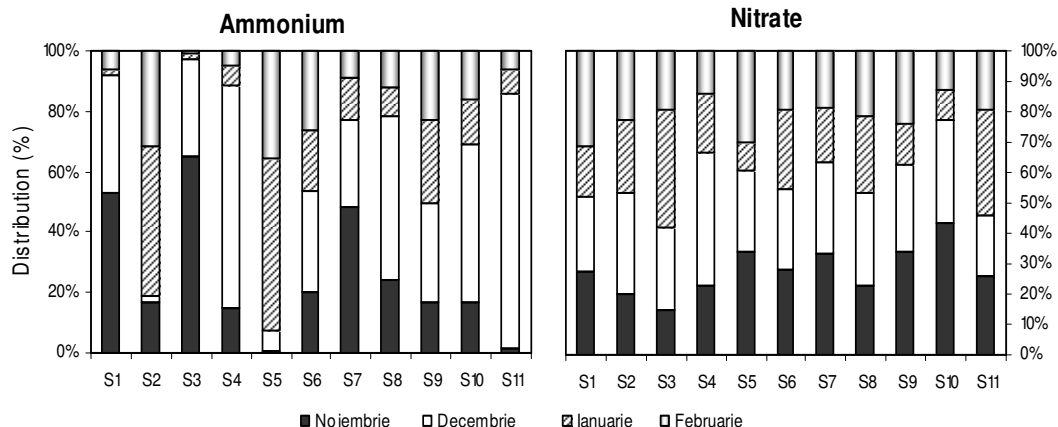


Figure 2. Seasonally variation of nitrate and ammonium in the Olt River Basin within the 11 sampling points

4. CONCLUSION

In order to prevent pollution in the earliest possible stages, the state of contamination must be constantly monitored and prevention measures for the contamination of surface waters must be taken by having a more efficient and environmentally friendly chemical industry and agricultural activities.

Generally, the levels of nitrate and ammonium in surface waters samples are subjected to variability since they are governed by factors such as seasonal/climatic variations, soil over which it flows, nature and rate of sewage and industrial effluent discharges into it and the sampling point.

With few exceptions the measured values for the nitrate and ammonium concentrations were within the limit allowed by the national and international regulations.

The sampling sites of the Olt River Basin in Rm. Valcea area were found to be polluted with nitrate, having a water quality of class V (bad ecological state). The presence of nitrate ions in the investigated samples can be associated with the industrial (chemical industry) and agricultural activities, when the agriculture is a more polluting factor than the industry.

Taking into account the ammonium concentrations, Olt River sampling points located in or near dams and industrial sources have higher concentrations than Olt tributaries with stream waters, due to ammonium formation in stationary waters. In contrast with the nitrate pollution, the ammonium concentrations classify the majority of the wasters as having a very good (class I) and good (class II) ecological state.

This work is a pilot study for a further investigation of Olt River basin waters in the Rm. Valcea industrial area by means of nitrogen isotopes.

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