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Original Article

Water Pollution by Nitrates from Agricultural Sources

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Abstract

The paper presents the results obtained after analyzing water from village wells of Văceni Teleorman concerning the pollution caused by nitrates from agricultural sources. It shows that from the total number of 22 wells studied in October 2014, in 14 of them (63%) there were recorded values of the nitrates content above 100 mg/l, in 4 of them (18%) were registered values ranging from 50-100 mg/l, values exceeding the maximum permissible limit of 50 mg/l, which make the water unsuitable for consumption, and only in 4 of water sources analyzed, the values were below the limit of 50 mg/l and meet the requirements to be classified as drinking water. At the samples tested in February 2016, a rate of 62.96% from the 27 wells analyzed, the nitrates concentration exceeded 100 mg/l and is required to be prohibited from use of water as drinking water. Only a rate of 7.40% from the analyzed cases, the water was within the maximum acceptable limits of nitrates concentration for drinking water. Within the range of 50 -100 mg/l, there were a rate of 18.18% of analyzed wells in the year of 2014 and a rate of 29.63% in the year of 2016. The manure from animals of households from Văceni village annually produces about 2577 kg of nitrogen

Keywords: water pollution, vulnerable areas,nitrates pollution

1. Introduction

The main factor that transforms almost totally and irreversible the renewable resources in non-renewable resources is pollution. When one of the natural resources is seriously affected by pollution, it may be considered that the degradation of the environment has been caused, with long-term consequences that are difficult or impossible to assess and reclaim [2].

Water is a natural resource that is vital, vulnerable, renewable and limited, and which need a proper management in order to be bequeathed to future generations [11]. Although agriculture is the food source for thousands of years for the mankind, it was turned into a pollution source both to human health and the environment as a result of intensive practices and ignoring its negative effects.

Agriculture can have significant and extended effects on water quality and aquatic ecosystems. Agricultural pollution is difficult to attribute only to a certain source and varies in space and time. Given the difficulty of attribution, except for animal wastes and pesticides, most of the public policies addressing agricultural pollution are based on incentives for voluntary emission reduction [1].

Lack of sanitation in villages, together with sewerage degradation in towns significantly contributes to pollution of groundwater and is

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difficult to judge which is the main source: the human wastes or the animal husbandry wastes.

Agriculture consumes about 85% of the total freshwater globally used. Nutrient management in sustainable agriculture must be balanced between agronomic, economic and environmental factors [6]. The main water pollutants are plant nutrition elements, organic matter, and pathogens originating from livestock wastes. Potential pollutants of secondary importance can be the smell and the color [11].

As regards the nitrate pollution of waters, four main pollution sources are delimited:

- nitrates from manure and household wastes mineralization;
- nitrates from uncontrolled or poorly controlled fermentation of wastes and wastewater from livestock;
- nitrates from chemical fertilizers;
- nitrates from mineralization of humus [2].

The nitrogen as nitrate is found naturally in the environment as part of the nitrogen cycle. However, the human interventions have greatly increased the nitrate concentrations in groundwaters and surface waters. This has had a severe impact on aquatic ecosystems and gave rise to humans and animals health concerns. Therefore, identification of nitrates sources is very important for maintaining the water quality and to achieve the sustainability of our water resources [5].

2. Material and Method

Vulnerable areas and potentially vulnerable areas were determined by ICPA together with the National Administration "Romanian Waters" considering the provisions of HG 964/2000 on the approval of the Action Plan for water protection against pollution caused by nitrates from agricultural sources in the Romanian legislation transposing the Directive Council of Europe 91/676/EEC.

Action Plan for water protection against pollution caused by nitrates has the following objectives: to reduce water pollution caused by nitrates from agricultural sources; Nitrates Pollution Prevention; streamlining and optimizing the use of chemical and organic fertilizers containing nitrogen compounds.

Water samples were collected from households wells and surface waters in Văceni village during October 2014 and February 2016. Water samples analysis was performed with the probe Hydrolab DS5 Water Quality Multiprobes for determining water quality indicators. Thus, the nitrates content (NO3-), the ammonium content (NH4+), the amount of dissolved oxygen, the amount of chlorophyll, temperature, pH, salt content and the sampling depth were determined.The multiparameter probe determines and measures the above mentioned analyzed parameters at the moment of water sampling.

During October 2014, a number of 22 samples from wells and one sample from the surface waters were collected.

During February 2016, a number of 27 samples from wells and 3 samples from the surface waters were collected

3. Results and discussions

In the year of 2000, it was approved the Resolution no. 964 regarding adoption of the Action Plan for water protection against pollution caused by nitrates from agricultural sources.

According to HG no. 100/2002, for the surface waters to be classified as 1st category, the nitrates concentration must be lower than 25 mg/l for indicative concentrations and lower than 50 mg/l for exceptional climate and geographical conditions. For waters falling in the categories 2nd and 3rd, the nitrates content should be less than 50 mg/l. The Guidelines for drafting reports on the Nitrates Directive by the Member States propose introducing of an intermediate class of 40-50 mg/l for groundwaters and surface waters in order to reflect the evolution of a zone "that presents an exceeding risk on a short period of the standard" [3].

Intensive agriculture has a negative effect on the growth of nitrates content in water, and the researches in this field estimated that annually are released into water over one million of tons of nitrogen affecting surface waters, but also the groundwaters [7].

Studies conducted on groundwaters in Vitoria - Gasteiz area (Basque Country) followed up the evolution and leaching in time of the nitrates concentrations from fertilizers into the soil solution. The average concentration of nitrates increased from 50 mg NO3- /l during the year of 1986 up to 200 mg/l during the year of 1995, which represents an increase of approximately 20 mg of NO3-/year.

Nitrates pollution of groundwaters is the result of abusive utilization of fertilizers. Thus, 964 kg of NO3-/ha has leached into the groundwaters, which account for 87% of nitrates applied to the soil as fertilizer in the studied period [9].

[9] Conducted a study to quantify the effects of the Nitrates Directive on pollution by nitrates (NO_3) of groundwaters and surface waters, as well as on emissions of ammonia (NH_3), nitrous oxide (N_2O) oxides of nitrogen (NOx) and dinitrogen (N_2) into the

atmosphere. There were simulated two scenarios: with and without application of the Nitrates Directive. For the N emissions calculations were used the model MITERRA-Europe at the regional level within the EU-27 for the period of time between 2000-2008.

The total loss of Nitrogen calculated for agriculture within the EU-27 was: 13 Mton of N in 2008, in the form of N_2 (53%), NO_3 (22%), NH_3 (21%), N_2O (3%) and Nox (1%).

By implementing the Nitrates Directive, the total emissions have decreased, in the EU in the year of 2008 than without Nitrates Directive implementation, by 3% for NH_3, 6% for N_2O, 9% for NOx and 16% for N loss to groundwaters and surface waters.

Implementation of the Nitrates Directive decreased the N losses both in groundwaters and surface waters, and also decreased the gas emissions into the atmosphere.

Since nitrogen is one of the major pollutants by leaching into the groundwater, [8] studied the contamination process and the spatial distribution of the nitrates concentrations into the groundwaters, in a typical high-yield agricultural area in northern China, in order to draw the guidelines on the management and pollution control, as the nitrates pollution of groundwaters could be directly linked to management practices.

Nitrates pollution of the soil and groundwaters is higher in vegetable crops and orchards than in cultivated land with cereals.

Nitrates concentrations within the 0-30 cm soil depth for vegetables crops
and orchards were 1.2 times higher than those on cultivated land with cereals as a result of the application of high doses of fertilizers.

The premise of obtaining higher yields of crops by applying nitrogen fertilizer has led to increases of the nitrates content in soil and to groundwater pollution [4].

One of the main sources of water pollution by nitrates is the storage of manure in improvised platforms located near the water sources, the uncontrolled fermentation or poorly directed of wastes and wastewaters from livestock because in most households the animal stables were located near the wells. Another source of water pollution is represented by the nitrates from fertilizers and the nitrates coming from humus mineralization.

Water samples were collected from wells located in Văceni village, which belongs to the Draganesti-Vlasca commune, Teleorman County.

The cadastral territory of the Draganesti-Vlasca village covers an area of 10330 hectares, of which 425 ha are urban land and 9905 ha is outside town land. Văceni village covers an area of 50.5 ha. Animals number in Văceni village are as follows: 20 cows, 8 horses, 15 goats and 20 sheep.

The nitrogen amount from manure was determined according to the calculation program of the Code of Good Practices (Table 1) and the following quantities of nitrogen/year resulted:

Table 1. Nitrogen from the farm yard manure

Animals category	Number of animals	The amount of nitrogen applied to land by animal species		The total amount of nitrogen applied to land at farm level and by animal species		The total amount of nitrogen from mature manure applied to land at farm level	
		Solid kg N/an	Liquid kg N/an	Solid kg N/an	Liquid kg N/an	Solid kg N/an	Liquid kg N/an
Dairy cows	20	40	44.36	800	887.20		
Horses	8	46.54	-	372.32	-	1689.72	887.20
Goats	15	15.88	-	238.20	-		
Sheeps	20	13.96	-	279.20	-		

Animal manure from households annually produces a total amount of nitrogen of approximately 2577 kg.

The results of analyses performed in the year of 2014 as shown in Table 2 show that from the total number of 22 wells studied, 14 of them (63.64%) were recorded values of the nitrate content above 100 mg/l, in four cases (18.18%) values ranged between 50-100 mg/l, values which exceed the maximum permissible limit of 50 mg/l, making the water improper for consumption. Only at 4 of water well sources analyzed the values ranged below the limit of 50 mg/l and meet the requirements for water to be fitted as drinking water. Values below 25 mg/l were recorded only in one sample and which fits within the 1st category of quality.

Ammonia nitrogen content in all cases studied exceeded the maximum permissible value of 0.5

mg/l, and above 70% of those showing values higher than 3 mg/l.

mg/l, representing 9% of samples; 2nd class - 13%; 3rd class- 27%; 4th class - 27% and 5th class - 22%.

The total content of salts for drinking water in Romania must range between 800 and 3000 mmhos (STAS 1342-91).

Values in this range were recorded at 27.27% of the cases analysed, values between 3000-4000 mmhos at 13.64% of the analysed cases, values between 4000-6000 mmhos at 4.91% of the analysed cases, at 13.64% of the analysed cases the values ranged between 6000-10000 mmhos, and values above 10000 mmhos at 4.55% of the analysed cases.

The analysis carried out in February 2016 (Table 4) have shown that from 27 wells analysed, a number of 17 wells had a nitrate content above 100 mg/l, representing 62.96%, 8 samples had values between 50-100 mg/l (29.63%), and values of 25-50 mg/l were found within just two samples.

From the total number of analyzed wells only in 7.40% of these the water meets the quality requirements for nitrates content.

The ammonia nitrogen content exceeded the maximum permissible limit of 0.5 mg/l only in 5 cases (18.52%), the remaining 22 samples showed values below 0.5 mg/l (81.48%).

Dissolved oxygen (Table 5) in water measured in mg/l fits in the following classes:

- 1st class - over 7 mg/l, representing 7.41% of the samples;
- 2nd class - 22.22%;
- 3rd class - 22.22%; 4th class IV - 6.66% and 5th class - 30%.

The total content of salts, with values in the range 800-3000 mmhos, were recorded at 59.26% of the analyzed cases, values between 3000-4000 mmhos were recorded at 29.63% of the analyzed cases and values between 4000-6000 mmhos of the analyzed cases 7.4%.

Water temperature varied from 12.07 to 14.81°C in the year of 2014 and between 8.73-11.57°C in the year of 2016.

According to the Order no. 1146/2002 of MAPM, the temperature is not normalized. Water pH ranged from 5.32 to 8.43 in the year of 2014, and from 7.26 to 8.24 in the year of 2016.

The pH must be ≥6,5 - ≤9,5 according to Law no. 552/2002. It has been found during the measurements that only one water sample had a pH value below 6.5.

Dissolved oxygen (Table 3) in water measured in mg/l fits in the following classes: 1st class - over 7

The concentration of nitrates in surface waters had very low values, and they were between 8.25 and 10.11 mg/l in both 2014 and 2016.

The ammonia was within the permissible limits, the values ranging between 0.22 and 0.48 mg/l.

4. Conclusions

The interpretation of the results found lead to the following conclusions:

Nitrates content with values above 100 mg/l of the analyzed samples showed a slight decrease, from 63.64% of a total number of samples recorded in the year of 2014, to 56.66% of a total number of samples recorded in the year of 2016.

For values found between 50-100 mg/l, there was an increase from 18.18% of a total number of samples recorded in the year of 2014, to 29.63% of a total number of samples recorded in the year of 2016.

The water samples, falling below the maximum permissible limit of 50 mg/l, decreased by 10.71% in the year of 2016 when compared to the year of 2014.

As for the ammonia, there was a decrease in values of the analyzed samples, in the range of 1-5 mg/l, from 95.45% in the year of 2014 to 3.33% in the year of 2016.

In the year of 2014, none of the analyzed water wells did not fit below the maximum allowed limit for drinking water.

In the year of 2016 there was a very significant decrease of the ammonium ion concentration so that 81.48% of the examined cases, the values were below 0.5 mg/l.

Values of oxygen concentration greater than 7 mg/l were found only at two wells both in the year of 2014 and of 2016.

The total content of salts in the range of 4000-6000 mmhos decreased from 40.91% in the analyzed samples in the year of 2014 to 7.40% in the year of 2016.

Values above 6000 mmhos were found in 18.18% of the analyzed samples in the year of 2014, whereas in the year of 2016 such high values have not been found.

The values fitted within the admissible limits increased from 27.27% in the year of 2014 to 59.26% in the year of 2016.

It is recommended to supply with drinking water the village and at the same time to build a sewerage system and a wastewater treatment plants.

Table 2. The degree of pollution with various chemicals of the common water sources in Vaceni village, Draganesti-Vlasca communa (February 2014)

No. crt.	Location				Tempe-rature (^{0}C)	Chemical measurements						Sampling depth (m)
	Village	N	E	Altitude (m)		Salts (mmhos)	O_2 diz. (mg/l)	NH_4 (mg/l)	NO_3 (mg/l)	pH	Clorophyll (mg/l)	
1.	Văceni	4407061	02553801	94	12.84	2.914	7.47	3.62	>100	6.93	0.00	10.00
2.	Văceni	4407011	02553633	93	13.21	2.792	5.04	3.81	>100	6.83	0.03	3.638
3.	Văceni	4406901	02553210	97	13.08	4.810	3.55	4.87	>100	6.88	0.00	9.754
4.	Văceni	4406829	02553132	95	12.94	3.432	6.06	4.81	>100	7.04	8.39	7.055
5.	Văceni	4406497	02553299	86	14.13	4.300	5.30	3.09	>100	5.32	0.00	6.522
6.	Văceni	4406723	02553354	95	13.07	10.23	4.24	0.72	15.21	8.43	0.00	>10
7.	Văceni	4406942	02553950	94	13.10	3.539	5.23	1.76	>100	7.21	0.00	>10
8.	River	4408109	02556151	83	15.74	9.845	4.68	0.48	9.35	8.77	5.61	0.746
9.	SCDA	4407800	02555609	95	12.07	2.232	3.40	1.64	84.52	7.03	0.00	-
10.	Văceni	4407030	02553725	93	12.76	3.006	6.56	2.38	>100	6.81	0.09	>10
11.	Văceni	4407125	02553542	93	13.16	2.626	5.70	3.06	67.12	7.0	0.09	>10
12.	Văceni	4406827	02553528	90	14.39	1.969	7.22	4.27	35.24	7.27	0.00	8.264
13.	Văceni	4406705	02553242	94	13.69	2.326	5.43	2.06	66.41	6.90	0.02	>10
14.	Văceni	4406798	02552390	88	14.81	4.595	6.51	3.49	>100	6.98	0.55	>10
15.	Văceni	4406581	02553097	96	13.85	6.283	4.56	4.62	>100	6.71	0.00	>10
16.	Văceni	4406541	02553491	95	13.88	5.440	3.36	4.11	>100	6.78	0.00	>10
17.	Văceni	4406620	02553506	98	14.06	5.382	4.62	3.13	67.21	6.96	0.00	5.331
18.	Văceni	4406743	02553389	98	14.21	6.300	3.14	4.08	>100	6.77	0.00	>10
19.	Văceni	4406724	02553560	99	13.88	5.081	4.23	4.08	42.66	6.63	0.00	>10
20.	Văceni	4406621	02553673	99	13.60	5.860	4.33	2.71	38.66	6.87	0.06	6.548
21.	Văceni	4406721	02553718	98	13.19	5.310	3.83	4.07	>100	7.03	0.00	>10
22.	Văceni	4406744	02553840	102	13.44	6.010	5.16	3.84	>100	6.88	0.00	>10
23.	Văceni	4406898	02553846	93	13.67	5.856	4.38	3.16	>100	6.84	0.12	>10

Table 3 Framing the parameters of the drinking water in quality classes in wells of Vaceni village during the year of 2014

NO_3 (mg/L)			NH_4 (mg/L)			O_2 (mg/L)				Salts (mmhos)		
Interval	No. of samples	%	Interval	No. of samples	%	Class	Interval	No. of samples	%	Interval	No. of samples	%
>100	17	62.96	0-0.5	22	81.48	I	>7	2	7.41	<800	1	3.70
50-100	8	29.63	0.5-1	4	14.81	II	6-6.9	6	22.22	800-3000	16	59.26
25-50	2	7.40	1-2	1	3.33	III	5-5.9	6	22.22	3000-4000	8	29.63
<25	-	-	2-3	-	-	IV	4-4.9	2	6.66	4000-6000	2	7.40
			3-4	-	-	V	<4	9	30.00	6000-10000	-	-
			4-5	-	-					>10000		

Table 4. Framing the parameters of the drinking water in quality classes in wells of Vaceni village during the year of 2016

NO_3 (mg/L)			NH_4 (mg/L)			O_2 (mg/L)				Salts (mmhos)		
Interval	No. of samples	%	Interval	No. of samples	%	Class	Interval	No. of samples	%	Interval	No. of samples	%
>100	14	63.64	0-0.5	-	-	I	>7	2	9.09	800-3000	6	27.27
50-100	4	18.18	0.5-1	1	4.55	II	6-6.9	3	13.64	3000-4000	3	13.64
25-50	3	13.64	1-2	2	9.09	III	5-5.9	6	27.27	4000-6000	9	40.91
<25	1	4.55	2-3	3	13.64	IV	4-4.9	6	27.27	600-10000	3	13.64
			3-4	8	36.36	V	<4	5	22.73	>10000	1	4.55
			4-5	8	36.36							

Table 5. The degree of pollution with various chemicals of water sources from Vaceni village, Draganesti-Vlasca communa (February 2016)

No. crt.	Location				Tempe-rature (^0C)	Chemical measurements						Sampling depth (m)
	Village	N	E	Altitude (m)		Salts (mmhos)	O_2 diz. (mg/L)	NH_4 (mg/L)	NO_3 (mg/L)	pH	Clorophyll (mg/L)	
1	Văceni	4407149	02553766	95	11.57	1878	5.491	0.50	95.52	7.30	0.584	0.514
2	Văceni	4407187	02553668	94	11.45	208	2.657	1.13	>100	7.29	0.715	0.720
3	Văceni	4406973	02553631	93	11.23	1341	1.983	0.70	81.38	7.26	0.380	3.638
4	Văceni	4406912	02553229	97	11.19	1462	1.789	0.68	>100	7.35	0.293	9.752
5	Văceni church	4406852	02553537	93	11.14	1602	11.540	0.43	>100	7.42	0.113	4.523
6	Văceni	4406996	02553307	94	10.92	2304	6.711	0.32	>100	7.36	0.234	>10
7	Văceni	4406833	02553158	95	10.01	2661	3.022	0.34	92.87	7.78	0.321	7.055
8	Văceni	4406513	02553286	86	11.18	3095	2.649	0.28	>100	7.71	0.218	6.521
9	Văceni	4406711	02553344	95	10.83	4378	2.198	0.18	23.48	8.24	0.162	>10
10	Văceni	4406842	02552999	95	10.11	3081	2.692	0.42	>100	8.08	0.261	6.824
11	Văceni	4406793	02552902	95	9.96	2786	4.661	0.38	>100	7.93	0.112	>10
12	Văceni	4406550	02552931	96	10.22	3006	2.785	0.41	>100	8.16	0.117	>10
13	Văceni	4406506	02553321	95	11.47	2941	5.221	0.67	>100	7.08	0.263	0.718
14	Văceni	4406621	02553673	99	11.33	4321	4.603	0.29	>100	8.11	0.201	6.547
15	Văceni	4406744	02553840	102	11.31	2969	6.721	0.44	>100	8.18	0.310	>10
16	Văceni	4406924	02553979	94	8.73	1595	9.102	0.38	>100	7.38	0.241	>10
17	Văceni waterlogging in arable land	4406892	02553961	94	9.22	2170	5.562	0.92	6.88	7.34	0.503	-
18	Lake near Research Station	4408075	02556092	83	8.66	562	13.072	0.29	10.11	8.01	0.123	0.810
19	River	4408123	02556134	83	8.56	413	5.481	0.22	8.25	8.23	0.112	0.792
20	SCDA	4407812	0255631	95	10.12	2989	2.654	0.38	87.25	7.56	0.119	-
21	Văceni	4407041	02553741	93	11.17	2409	5.434	0.48	89.12	7.38	0.134	>10
22	Văceni	4407139	02553561	93	10.89	1972	5.558	0.36	77.34	7.28	0.287	>10
23	Văceni	4406842	02553532	90	11.42	2434	6.213	0.21	42.78	7.39	0.349	8.254
24	Văceni	4406783	02552421	88	9.77	3256	5.879	0.68	>100	7.87	0.234	>10
25	Văceni	4406556	02553479	95	10.21	2978	6.563	0.43	>100	7.62	0.214	>10
26	Văceni	4406602	02553501	98	10.63	2546	6.925	0.31	72.45	7.46	0.192	5.329
27	Văceni	4406731	02553398	98	10.93	3435	5.819	0.41	>100	8.01	0.212	>10
28	Văceni	4406726	02553551	99	10.28	3091	6.213	0.39	51.69	7.78	0.198	>10
29	Văceni	4406721	02553709	98	9.98	3456	5.906	0.41	>100	7.98	0.176	>10
30	Văceni	4406879	02553839	93	10.36	3629	6.215	0.36	>100	8.11	0.149	>10

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