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RESEARCH ON THE INFLUENCE OF SOIL AMENDMENTS AND LIVESTOCK MANAGEMENT ON SURFACE WATER QUALITY FROM TELEORMAN COUNTY

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Abstract

These studies are the point to the proposal of solutions to minimize the risk of methemoglobinemia in infants or of other diseases or chronic fluid in adults, which may be caused by the presence of these nutrients in the waters described. The research has been done in 3villages (Măldăieni, Roşiori de Vede, Peretu). For each research site, based on soil, surface/wells and manure samples were determined: the type and soil texture and supply status with major nutrients, soil reaction, fertilizers and pesticides, surface/wells quality, quantities and quality of manure from fresh and fermented samples. The samples were taken of surface water and from the well simultaneously. Surface water quality varies from class II quality close to class III. Water fountain concentrations of nitrogen forms, in all samples analyzed, were very close or exceed of maximum admissible values. Testing the significance of differences observed between the average values of the samples from the sites of research was done with the Student test for each analyzed compartment.

Key words*: amendments, soil structure, surface and wells water.*

INTRODUCTION

Methaemoglobinaemia is diagnosed when the percentage of methemoglobin exceeds 1% of the normal hemoglobin in which the ferric ion was ionized in the heme group to the ferric ion. (Tudor, 2009). Methaemoglobinaemia is characterized by the inability to bind oxygen to hemoglobin with functional anemia and lack of oxygen release to tissues. The classic presentation of methemoglobin is cyanosis in the presence of normal pulmonary oxygen pressure, with chocolate cholesterol that does not become pink by exposure to oxygen (Costache, 2016). Symptoms are proportional to the methemoglobin level and include skin color changes and blood color changes at levels up to 15% (Denshaw-Burke, 2017). As levels rise above 15%, neurologic and cardiac symptoms arise as a consequence of hypoxia. Levels higher than 70% are usually fatal. The application of excess chemical fertilizers in this area combined with poor manure management and lack of sewerage leads to a load of nitrates in surface and fountain water with negative effects on the health of the consuming population (Chirilă, 2012).Infants are most affected by drinking nitrate rich water. Although the maximum admissible limit is 50 mg/l, pediatricians recommend a maximum concentration of 25 mg/l or a safe source of water. Considering the complexity of the issues that the topic involves, in the present study the concentrations of different forms of nitrogen in the surface water and the fountain water (if there are nutrients) were determined in order to assess their vulnerability to pollution with nitrates or nitrites. These studies have been corroborated with soil analyzes, with quantitative and qualitative assessments of manure used as natural fertilizer or those derived from free-range cattle on herds, in order to minimize the risk of methaemoglobinaemia in young infants or other waterborne or chronic diseases at adults, which could be caused by the presence of these nutrients in the abovementioned waters.

MATERIALS AND METHODS

For the present study, a designated area was chosen from Teleorman County, comprising 3 localities that are part of the Vedea catchment area. These are: Măldăieni, Roşiori de Vede and Peretu. In all localities, sewerage and drinking water supply are poor, but for all, communal dwellings are used for grazing cattle.

The research has been done in the whole locality, and took soil samples to determine the type and soil texture and soil supply status with major nutrients (N, P, K). Based on these results and knowing the types of main crops and livestock structure of economic, at villages level, recommendations were made about avoiding the risks of pollution of surface water by nitrates from agricultural and livestock activities. The data on the distribution of the current sources of pollution of the surface waters with manure from the agro-zootechnical sector and especially from cattle were obtained on the basis of direct observations and data from the County Office for Pedology and Agrochemistry.

The structure of the exploited animals, by age and species category, but especially of the bovine species, is presented synthetically, for all three localities, as well as the recommended amendments (the relief, structure, texture and soil reaction are similar).

Working methodology for surface and well water samples: sampling was done using quantitative methods. The conservation and processing of water was performed using STAS methods. For each operational site samples of surface water were taken from 3 regions of the commune, respectively from the upstream side - the part located at the entrance of the communal water, upstream, at the exit of the river from the commune (downstream) and from the central part of the commune, on the water line. Fountain water was sampled from wells located in the city, near the surface water harvesting points.

Analysis of NH_4^+ ion. The "indophenol blue" reaction was used to determine the ammonium ion. The principle of the method is that the phenol reacts with ammonia in the presence of an oxidizing agent (such as sodium hypochlorite, sodium isocyanurate) and forms, under alkaline conditions, a colored compound absorbing the radiation at l = 660 nm.

Analysis of the NO_3^- ion. For the determination of the nitrate ion, the spectrophotometric method using the salicylic acid chromogenic agent was used. Although this method is time-consuming and subjected to interference from organic matter and nitrite ion, for samples of water analyzed, it has yielded good results due to its low content in interfering compounds.

Analysis of NO_2^- ion. Principle of the method: nitrite reacts with sulphanilic acid in the acidic environment resulting diazonium salt coupled with 2 naphthylamine to form a red colored azo compound.

Harvesting of manure samples was: for the chemical analysis of solid slurry, 10 individual samples were taken from each site surveyed. In the case of these solid fertilizers, the individual samples mixed to obtain an average sample, the values obtained from the mean sample analysis characterizing the chemical composition of the entire batch of fertilizer from which it was sampled (Budoi, 2000). For the chemical determinations of the chemical composition of manure from dairy farms as well as those from individual households, the content of ammoniacal nitrogen, nitric nitrogen and total nitrogen was determined. Total nitrogen determinations were made using the Kjeldahl method, for fertilizers known to have a low nitrate content and the Cope modified Kjeldahl method for nitrate fertilizers.

Description of operational sites

From the point of view of the surface waters, on the Măldăieni cadastral territory there are no flowing waters with a permanent flow. The depth of the ground water varies depending on the relief, thus, on the plain and slopes over 10 m, in valleys deeper at 1.5-6.0 m.

Of the total surface (7284.53 ha), 7089.31 ha are occupied by agricultural land, 68.17 ha pastures, 114.16 hectares of vineyards and 12.89 ha of unproductive land. The area cultivated with cereal grains is 3872 ha. As far as the application of fertilizers is concerned, 890 t have been applied at the level of Măldăieni commune. Of the 890 t, 608 t were nitrogenous fertilizers, 281 t of phosphate and 2 t of potash. No natural fertilizers were applied. Of the pesticides, 5 kg of insecticides, 64 kg of fungicides and 182 kg of herbicides were applied, of which 222 kg for maize.

In Măldăieni there are 395 cattle, of which 369 cows and heifers and 26 calves 0-6 months, which are raised in the households, but they also use the communal settlement for early spring free stabbing until late autumn.

The territory of Roşiori de Vede belongs to the water catchment area of the Vedea River with variable flow (very low in summer and higher spring when snow melts), good water for irrigation and drinking for animals. The groundwater level ranges from one relief to the other, being lower in the plain (> 10 m) at shallow depth in the meadow (3-5 m on flat forms and 1.5-3 m on depression forms). Of the total surface area (5902 ha), 5407.51 ha are occupied by agricultural land, 416.18 ha, pastures, 26.33 ha of vines, 10.12 ha of orchards and 41.86 ha of unproductive land. At the level of Roşiori de Vede, the area cultivated with cereal grains is 3564 ha. As far as the application of fertilizers is concerned, 798 t have been applied at the level of Roşiori de Vede on an area of 7513 ha. Of the 798 t, 596 t were nitrogenous fertilizers and 201 t phosphate. No natural fertilizers were applied. Also, 1266 kg insecticides, 2659 kg fungicides and 2557 kg herbicides were applied, of which 241 kg for maize. There are 630 cattle in this locality, of which 458 cows and heifers and 145 calves 0-6 months, which are raised in the households of the population, but they also use the communal harbor for early free spring stabbing and until late autumn. Within the cartographic territory of Peretu, the hydrographic network has the shape of a tree, by the affluence of the tributary network, being characteristic of a region with a flat structure.

For the whole meadow, the water of these rivers plays the role of regulator of the ground water table, which varies from 1.5 to 4 m. Of the total surface area (6207 ha), 6114.37 ha are occupied by agricultural land, 44.48 ha, pastures, 48.08 hectares of vineyards and 0.07 ha of meadows. At the level of Peretu commune, the area cultivated with cereal grains is 3784 ha cultivated. In this locality there are 211 cattle, out of which 180 cows and heifers and 31 calves 0-6 months, which are grown in the households of the population, but they also use the communal settlement for early free spring stabbing until late autumn. Among the wheat grain species in all localities, corn, wheat, durum wheat, barley, barley and spring and autumn oats are grown, and as oily plants, sunflower and rape. Vegetables, as well as fodder, are mostly grown in their own grazing, on relatively small surfaces, and those for the seed are grown only by commercial companies.

RESULTS AND DISCUSSIONS

Results on soil reaction and nutrient status

In Măldăieni locality, the soil reactivity - is strongly and moderately acidic - on 51% of the area (3726 ha), surface to be adjusted with calcium carbonate ($CaCO_3$) - 4 t/ha, to correct the reaction; weakly acidic and neutral on 47% of the area (3426 ha) - favorable for the growth and development of plants; slightly alkaline - on 2% of the surface (150 ha), surface to be treated with phosphogypsum - 6 t/ha, to correct the reaction. The state of supply of assimilable phosphorous soils (P mobile) - is considered to be poorly supplied on 10% of the area (728 ha), on average 25% of the area (1821 ha) and well and very well supplied on 65% of the area (4734 ha).The state of supply of the soils with assimilable potassium (K mobile) - considered medium on 10% of the surface (728 ha) and good and very good on 90% of the area (6556 ha).The state of natural nitrogen fertility - is poorly supplied on 22% of the area (1602 ha), on average 78% of the area (5682ha).

In the Roșiori de Vede locality, the soil reaction - strongly and moderately acidic - on 45% of the surface (2656 ha), surface to be fined with calcium carbonate ($CaCO_3$) - 4 t/ha, to correct the reaction; weakly acidic and neutral on 51% of the area (3010 ha) - favorable to plant growth and development; slightly alkaline - on 4% of the surface (236 ha), surface to be treated with phosphogypsum - 6 t/ha, to correct the reaction. The state of supply of soils with assimilable phosphorus (P mobile) - is considered to be poorly supplied on 33% of the area (1948 ha), on 40% of the surface (2361 ha) and well and very well supplied on 27% of the area (1593 ha). The state of supply of soils with assimilable potassium (K mobile) - considered medium on 12% of the area (708 ha) and good and very good on 88% of the area (5194 ha). The state of natural nitrogen fertility - is poorly supplied on 58% of the area (3423 ha), on average 42% of the area (2479 ha). The state of supply of soils with assimilable phosphorus (P mobile) - is considered to be poorly supplied on 33% of the area (1948 ha), on 40% of the surface (2361 ha) and well and very well supplied on 27% of the area (1593 ha).

In Peretu, the soil reaction - is moderately acidic - on 3% of the surface (187 ha), surface to be fined with calcium carbonate ($CaCO_3$) - 4 t/ha, to correct the reaction; slightly acidic and neutral on 97% of the area (6020 ha) - a favorable reaction to the growth and development of plants.

The state of supply of soils with assimilable phosphorus (P mobile) - is considered poorly supplied on 27% of the surface (1676 ha), 47% of the area (2917 ha) and well supplied with 26% of the area (1614ha).The state of supply of soils with assimilable potassium (K mobile) - considered medium on 36% of the area (2234 ha) and good and very good on 64% of the area (3973 ha). The state of natural nitrogen fertility - is poorly supplied on 40% of the area (2482 ha), on average 58% of the area (3600 ha) and very good on 2% (125 ha).

Results of surface and well water samples.

In the determinations made in the study, the concentrations of the biogenic elements: ammonium, nitrates, nitrites, phosphorus, were reported at the maximum admissible concentrations accepted by the legislation in force (Law 311/28.06.2004 and Law 458/2002) fountain and the specifications in Order 161/16.02.2006 regarding the quality of surface water. These concentrations are summarized in Table 1.

Table 1. Maximum admissible concentrations

Indicator	M.U.	Well water	Surface water class quality I	II	III	IV
$N\text{-}NH_4$	mg N/l	0.5	0.4	0.8	1.2	3.2
$N\text{-}NO_2$	mg N/l	0.15	0.01	0.03	0.06	0.3
$N\text{-}NO_3$	mg N/l	11.2	1	3	5.6	11.2

The results of the chemical analyzes for surface and well water from operational site 1 are shown in Table 2.

Table 2. Calculated statistic valuables for operational site 1

	Surface water			Well's water		
$N\text{-}NH_4$ (mg N/l) n=3	**Upstream**	**Middle**	**Downstream**	**Upstream**	**Middle**	**Downstream**
X	0.84	0.846667	0.853333	0.416667	0.406667	0.423333
Sx	0.005774	0.003333	0.006667	0.006667	0.012019	0.003333
s	0.01	0.005774	0.011547	0.011547	0.020817	0.005774
c.v.%	1.190476	0.68191	1.353165	2.771281	5.118851	1.36382
$N\text{-}NO_2$ (mg N/l) n=3	**Upstream**	**Middle**	**Downstream**	**Upstream**	**Middle**	**Downstream**
X	0.029667	0.029667	0.030667	0.153667	0.15	0.152333
Sx	0.000667	0.001202	0.001202	0.000333	0.000577	0.000667
s	0.001155	0.002082	0.002082	0.000577	0.001	0.001155
c.v.%	3.892249	7.016852	6.788041	0.375716	0.666667	0.758009
$N\text{-}NO_3$ (mg N/l) n=3	**Upstream**	**Middle**	**Downstream**	**Upstream**	**Middle**	**Downstream**
X	3.44	3.353333	3.45	9.996667	9.89	9.98
Sx	0.028868	0.052387	0.026458	0.074461	0.055076	0.095394
s	0.05	0.090738	0.045826	0.12897	0.095394	0.165227
c.v.%	1.453488	2.705896	1.328283	1.290133	0.964549	1.655582

There is a slight increase in ammoniacal nitrogen concentration in surface waters, but these concentrations do not change the class of river segment quality (2nd class). For fountain water, the concentration of this parameter is within normal limits, but it is notice that the downstream concentrations are higher than upstream determination values, most probably due to diffuse source of pollution ($N\text{-}NH_4$). In case of $N\text{-}NO_3$ and $N\text{-}NO_2$ ions can be observed a decrease of concentration from upstream to downstream. The results of surface and well water chemical analyzes from operational site 2 are shown in Table 3.

For surface water, the recorded values of the parameters analyzed fall within the CMA for Class II. The results of the chemical analyzes for surface water and wells from operational site 3 are shown in Table 4.

For the first operational site, surface water falls in the second category of quality and well water parameters are within the maximum limits. If operational sites 2 and 3 class surface water remains unchanged, although a slight increase of the concentration parameters from one site to another.

Table 3. Calculated statistic valuables for operational site 2

	Surface water			**Well's water**		
N-NH$_4$ (mg N/l) n=3	**Upstream**	**Middle**	**Downstream**	**Upstream**	**Middle**	**Downstream**
X	0.8698	0.853333	0.8623	0.423333	0.433333	0.436667
Sx	0.005774	0.003333	0.005774	0.003333	0.003333	0.003333
s	0.013	0.005774	0.011	0.005774	0.005774	0.005774
c.v.%	1.162791	0.676582	1.162791	1.36382	1.332347	1.322176
N-NO$_2$ (mg N/l) n=3	**Upstream**	**Middle**	**Downstream**	**Upstream**	**Middle**	**Downstream**
X	0.030667	0.030667	0.031333	0.154	0.153	0.154
Sx	0.001202	0.001667	0.000882	0.000577	0.000577	0.000577
s	0.002082	0.002887	0.001528	0.001	0.001	0.001
c.v.%	6.788041	9.41332	4.875081	0.649351	0.653595	0.649351
N-NO$_3$ (mg N/l) n=3	**Upstream**	**Middle**	**Downstream**	**Upstream**	**Middle**	**Downstream**
X	3.46	3.436667	3.463333	9.98	9.973333	10.14667
Sx	0.020817	0.003333	0.020276	0.095394	0.103976	0.079652
s	0.036056	0.005774	0.035119	0.165227	0.180093	0.137961
c.v.%	1.042067	0.167997	1.014019	1.655582	1.805741	1.359672

Table 4. Calculated statistic valuables for operational site 3

	Surface water			**Well's water**		
N-NH$_4$ (mg N/l) n=3	**Upstream**	**Middle**	**Downstream**	**Upstream**	**Middle**	**Downstream**
X	0.86	0.86	0.866667	0.44	0.446667	0.45
Sx	0.005774	0.005774	0.003333	0.005774	0.003333	0.003333
s	0.01	0.01	0.001774	0.01	0.005774	0.005774
c.v.%	1.162791	1.162791	0.666173	2.272727	1.292575	1.322176
N-NO$_2$ (mg N/l) n=3	**Upstream**	**Middle**	**Downstream**	**Upstream**	**Middle**	**Downstream**
X	0.031333	0.031	0.033	0.154	0.153667	0.154667
Sx	0.000882	0.001528	0.000577	0.000577	0.000333	0.000333
s	0.001528	0.002646	0.001	0.001	0.000577	0.000577
c.v.%	4.875081	8.534682	3.030303	0.649351	0.375716	0.373287
N-NO$_3$ (mg N/l) n=3	**Upstream**	**Middle**	**Downstream**	**Upstream**	**Middle**	**Downstream**
X	3.463333	3.466667	3.476667	10.14667	10.09667	10.16
Sx	0.020276	0.008819	0.023333	0.078811	0.054874	0.086217
s	0.035119	0.015275	0.040415	0.136504	0.095044	0.149332
c.v.%	1.014019	0.440632	1.16245	1.345308	0.941339	1.469802

Table 5. Testing the significance of observed differences between the mean values of nitrogen in surface water and fountain water ($t_{4;0.05}$=2.776; $t_{4;0.01}$=4.604; $t_{4;0.001}$=8.610; $t_{4;0.2}$=1.533)

N-	Surface water									Well water								
NH$_4$	Upstream			Middle			Downstream			Upstream			Middle			Downstream		
Spec.	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3
S1	-	2.45	2.45	-	1.41	1.41	-	0.76	0.76	-	0.89	2.68	-	2.14	2.14	-	2.83*	2.83*
S2		-	0		-	0		-	0		-	2.83*		-	0		-	0
S3			-			-			-			-			-			-
N-	Surface water									Well water								
NO$_2$	Upstream			Middle			Downstream			Upstream			Middle			Downstream		
Spec.	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3
S1	-	0.73	1.51	-	0.49	0.49	-	0.45	0.45	-	0.5	0.5	-	3.67*	3.67*	-	1.89	1.89
S2		-	0.45		-	0		-	0		-	0		-	0		-	0
S3			-			-			-			-			-			-
N-	Surface water									Well water								
NO$_3$	Upstream			Middle			Downstream			Upstream			Middle			Downstream		
Spec.	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3
S1	-	0.56	0.66	-	1.59	1.59	-	0.4	0.4	-	0.14	1.38	-	0.71	0.71	-	1.34	1.34
S2		-	0.11		-	0		-	0		-	1.34		-	0		-	0
S3			-			-			-			-			-			-

Regarding the analysis of well water, for the first operational site, the values are close to the maximum allowable, but at sites 2 and 3, increases in these concentrations upstream and downstream concentrations exceeding the maximum admissible even in the case of nitrites. These observations are supported and conducted statistical tests (Student). Note the significant differences in the concentrations of ammonia nitrogen in water fountain between all operational sites, both on the upstream and downstream sector. In case of nitrites values Student test detected significant differences between S1 site and sites 2 and 3 in the middle.
In ecology, practice higher values of α (20%) to minimize the probability of degradation observed when it exists. Such an event affects not just a few individuals, but an entire community or the entire life of a community, so this strategy is the right solution (Dragomirescu, 1998). Using this level of significance, slight differences between the concentrations of ammonia nitrogen and nitrates, between first site and the other two sites, in the case of the surface water and between the concentration of ammonia nitrogen and nitrite, in the case of well water.

Results of slurry analysis.
Cattle manure is the cheapest and most complex fertilizer for soil fertilization. Bovine manure improves soil structure, promotes propagation of useful microorganisms and activity, increases the water retention capacity of the soil, causing large increases the yield per hectare (Georgescu, 1983).
For the quantitative assessment of manure, the following parameters were considered as the basis of calculation (Georgescu, 1983):
average weight of a dairy cow - 550 kg;
- feces per day and head - 25 kg;
- kg of urine per day and per head - 13 kg;
- feces kg + urine per day and per head - 38 kg;
- complex fecal density + urine - 0.8 kg/l;
- volume of feces + urine per day and head - 0.0475 m^3 (Tables 6, 7).

In fresh manure, the concentrations of nitrogen-containing forms ($N\text{-}NH_4$, $N\text{-}NO_3$) are lower than in manure, and in nitrogenous debris nitrogen losses due to oxidation-reduction processes occur in the mass manure during the fermentation process.

Table 6. The amount of solid and liquid manure obtained for all operational sites from cows and heifers

Site	Dairy cows	Solid manure (kg)	Liquid manure (l)	Solid manure (kg)	Liquid manure (l)
		24 hours		1 year (average 180 days in shelter)	
1	369	9225	4797	1660500	863460
2	458	11450	5954	2061000	1071720
3	180	4500	2340	810000	421200

Table 7. The amount of solid and liquid manure obtained for all operational sites from calves

Site	Calves 0-6 months	Solid manure (kg)	Liquid manure (l)	Solid manure (kg)	Liquid manure (l)
		24 hours		1 year (average 90 days in shelter)	
1	26	312	130	28080	11700
2	145	1740	725	156600	65250
3	31	372	155	33480	13950

In the fresh manure, concentrations of the relevant types of nitrogen ($N\text{-}NH_4$, $N\text{-}NO_3$) is smaller than in the case of manure, and the normal semifermented records the loss of nitrogen due to of oxidation-reduction to occur in the manure mass during fermentation.
This explains the phenomena occurring biodegradable waste mass in the fermentation process when microorganisms work is very intense, so the rate of nitrification phenomena - denitrification (Man, 1989).
For each site, the results were collated and solutions and recommendations, aimed at compliance with: storage accordance manure on concrete platforms with surfaces and storage capacity sufficient to maximum surface fertilization with manure within the limit of 170 kg nitrogen/hectare, periodic evaluation of the status of soil fertility, avoid use well water in infants and vulnerable (in sites which surpassed the maximum allowable concentrations), recommendations for use of public water supply and connection to sewer .

CONCLUSIONS

From the circumstances described in the sites in which the activity of the locals (growth of animals does not comply with the EU regulations, the use of pasture, the improper use manure, vegetable intensive and empirical in terms of technology, etc.) explain these concentrations and the presence of nitrite in water fountain.

Along with the lack of technology in households and a better information regarding the hazard of nitrates in the water fountain, the social component also has a high share of pollution of surface water because sewage ineffective or lack thereof, and because refusal of the population to be connected to the public water supply and sanitation.

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