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ENVIRONMENTAL ASSESSMENT OF NITROGEN COMPOUNDS IN THE SURROUNDINGS OF A FERTILIZERS INDUSTRIAL PLANT

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ABSTRACT. The present study was conducted in the proximity of a chemical plant from Târgu-Mureș (Romania), where nitrogen-based fertilizers were produced. The quality of the environmental components was assessed in terms of general physico-chemical parameters and the content of nitrogen dissolved ions (NO_3^-, NO_2^-). The nitrate content in soil varied depending on the distance from the source and land use at sampling point. The nitrite content was correlated with possible transformations from the nitrate forms. For water, special attention should be paid to the nitrate content from the industrial effluent, which in one sample proved to be higher than the national legislation.

Key words: *nitrogen-based fertilizers, surface water pollution, soil pollution*

INTRODUCTION

Soil N is an essential component for the normal development of plants and crops. Because soil organic N can be lost due to plant removal, leaching or volatilization, the use of nitrogen compounds was developed (Jenkinson, 2001). In the natural N cycle, the input, transformation, and output of N were found in an equilibrium, but the intensive use of nitrogen fertilizers has conducted to significant drainages of nitrates or nitrites into surface and underground water (Peigne and Girardin, 2004).

Nitrogen compounds contamination of soil and surface or underground water is a well-known environmental problem, mostly associated to urbanized and agricultural areas (Soldatova et al., 2017; Jang and Liu, 2005). In order to support the worldwide need for food, nitrogen-based fertilizers were used in agricultural activities from many countries, and the excessive use of these products has led to environmental contamination. Thus, agricultural activities represent an important source for nitrogen compounds contamination known even from the past (Commoner 1970; Madison and Brunett, 1984). The need for fertilizers has led to the development of high-capacity plants, which now represent another source for nitrogen compounds contamination, especially due to industrial effluents (Kanu and Achi, 2011; Madhav et al., 2019).

The contamination with nitrogen compounds in Romania was evaluated also in other studies (Lupei et al., 2014; Rotaru and Răileanu, 2008), indicating that this is an environmental problem linked to industrial platforms. The presence of these contaminants was observed in various environmental compounds, such as soil, surface water and underground water.

The present study aims to analyze the quality of soil and surface water in the surroundings of a chemical plant from Târgu-Mureș, Romania. The activity of the plant consists in the production of nitrogen-based fertilizers. The quality of the environmental components was assessed in terms of nitrogen dissolved ions (NO3-, NO2-) content and correlated with the physical-chemical parameters.

MATERIALS AND METHODS

The study area was located in Târgu Mureș city (Romania), nearby an industrial plant which produces nitrogen-based fertilizers, rich in nutrients like nitrogen, phosphorus, potassium, calcium, sulphur, magnesium, boron and zinc. The nitrogenous fertilizer plant consisted of three main producing plants (ammonia, nitric acid and ammonium nitrate). In the last two years, because of the increase price of the energy, several high energy consumers from the older installations had been temporarily shut down. The activity of the fertilizer plant may have an impact on the atmosphere through emissions of ammonia, nitrogen oxides and particulate matter (EPA-Mureș). According to the legislative requirements and the environmental authorization, the plant owner performs determinations of specific contaminants (ammonia and nitrogen oxide) imissions into the atmosphere, at fixed self-monitoring points. There were several periods (e.g., 2003) when slight exceedances of the allowed value for the average daily ammonia concentration were recorded in the monitoring points (EPA-Mureș). Over time, the owner of the fertilizer plant has made significant investments in equipment modernization to reach the best practices in fertilizers manufacturing, in order to reduce the possible impact on the environment and inhabitants' health.

The interest for a clean environment is given by the population living areas and the agricultural fields found in the proximity. For this reason, 10 soil samples (P1 – P10) were collected from 5 cm depth (after vegetation removal) (figure 1), and one reference sample (P Martor) was collected from an area considered to be unaffected by the industrial activity. Their distance from the industrial source varies and they are placed on the main wind directions (ENE), except the reference sample.

Since the Mureș River is located at 300 m in the northern part of the industrial platform, 5 water samples were collected for the study (figure 2). The water sampling points are located at approximately 500 m from each other. Two industrial effluents were found in the field, so a water sample was collected from each discharging point (P Dev and P Dev Ep). The reference water sample (P Martor) was collected upstream from these two dispersion points, while the other two samples (P1 and P2) were collected downstream.

Fig. 1. *Study area with soil sampling points (P1 – P10)*

Fig. 2. *Study area with water sampling points*

Soil samples were collected by a stainless steel hand auger and transferred to polyethylene bags, while water samples were collected directly in clean plastic bottles. All the samples were transported to laboratory at a constant temperature (4ºC) and in the absence of light.

The physico-chemical parameters (pH, redox potential (Eh), electrical conductivity (EC), total dissolved solids (TDS) and salinity) were determined using a portable multiparameter (WTW Multi 350i, Germany). For the soil samples, the physico-chemical parameters were measured in the aqueous extract of soil/water (5:1 ratio), which was obtained according to SR ISO 10390:1999 protocol.

To determine the dissolved ions, the water samples were previously filtered through filter paper, followed by ultrapure water (0.055 µS/cm; 18.2 MΩ/cm) dilution to reach electrical conductivity below 100 µS/cm. For soil samples were used the aqueous extracts of soil/water (5:1 ratio) (LAQUA, 2015). The content of anions (NO_3^-, NO_2^-) was assessed using an ionic chromatography system (IC 1500 Dionex).

RESULTS AND DISCUSSION

Soil samples

The $N\text{-}NO_3^-$ content in soil ranged between 1.6 and 72.1 mg/kg (figure 3). Some of the analyzed soil samples (P1, P2, P6 and P9) had a low content of $N\text{-}NO_3^-$ (<10 mg/l) (LAQUA, 2015). Most of the soil samples had a $N\text{-}NO_3^-$ content between 10 and 50 mg/kg, which is considered the amount required in soil for specific crops, although nitrate content can fluctuate widely depending on soil water movement (LAQUA, 2015). Based on nitrate content, soil sample P3 corresponds to a high content of $N\text{-}NO_3^-$ (>50 mg/kg) (LAQUA, 2015). P3 and P4 samples were taken from a neighborhood of houses, and the sampling points are found at the highest distance (more than 1,2 km) from the chemical plant. Since gardening activities are taking place in the proximity of P3 and P4 sampling points, the nitrate content might be correlated to fertilizers usage. In the case of P7 and P10, the situation is quite the opposite, because these sampling points are found the nearest to the industrial platform, collected from agricultural fields. The nitrate content in these samples was almost 7 times higher than the reference, while the other soil samples

(P5, P6, P8, P9) taken from the same type of soil use revealed similar nitrate content as the reference sample (P. Martor). Several studies have indicated that uncontrolled leaching from different sources (e.g., waste storage, industrial effluents etc.) might be responsible for nitrate accumulation into the soil (Kanu and Achi, 2011; Madhav et al., 2019).

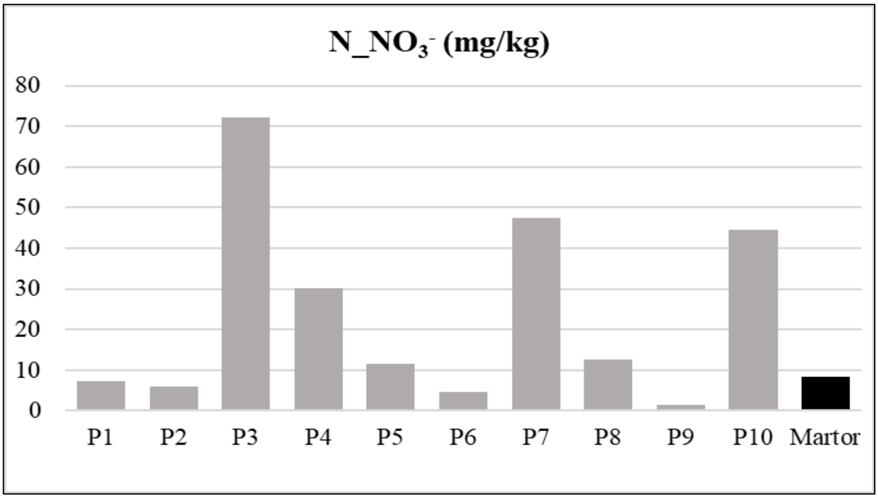

Fig. 3. *Content of N-NO_3^- in the analyzed soil samples*

The presence of nitrate in soil implies various discussions. First, is important to mention that nitrate can be present in soil from mineralization of the organically bound nitrogen originating from crop residues, soil organic matter and organic manures or as a consequence of intensive use of nitrogen-based fertilizers (Jenkinson 2001). Additionally, human activity can lead to nitrate contamination. Regardless the source of nitrate, leaching is the main environmental threat.

There are studies (Robson, 1989) which highlighted the fact that usage of nitrogen-based fertilizers can be associated with soil acidification. Compared with the analyzed physical-chemical parameters (table 1), indeed most of the sampling points with increased nitrate content (P3, P7 and P10) revealed a pH varying between 6 – 6.6, indicating the acidification of soil, while the other samples had a neutral to slight alkaline pH (7.1 – 7.6). The reducing conditions of the analyzed soil samples do not enhance the presence of nitrate, which tend to increase if redox potential is higher than 300 mV (Dayo-Olagbende et al., 2022). Some researchers (Patriquin et al., 1993) found a direct correlation between EC and the nitrate content. A similar trend was found in the present study too. The values for EC and TDS were higher in the samples with high nitrate content (P3, P4, P7 and P10), situation which in is favor for nitrate leaching considering also the acidic pH in these investigation points.

Table 1. *General physico-chemical parameters of the soil samples*

Soil sample	pH	ORP (mV)	EC (µS/cm)	TDS (mg/l)	Salinity (‰)
P1	7.1	+9.8	111.8	73	0.0
P2	7.5	-15.5	77.9	51	0.0
P3	6.6	+35.7	280	182	0.1
P4	7.8	-34.3	329	214	0.0
P5	7.3	-1.7	114.1	72	0.0
P6	6.2	+62.6	70.6	46	0.0
P7	6	+71.0	134.5	89	0.0
P8	7.1	+9.5	98	64	0.0
P9	7.2	+0.8	70.5	46	0.0
P10	6.1	+66.7	140.7	92	0.0
Martor	7.6	-19.6	129.8	84	0.0

Under anoxic conditions, nitrate can be reduced to nitrite by the process known as denitrification (Wrage et al., 2001). Nitrite concentrations were revealed in P4 and P10 (figure 4) previously found with high nitrate content. Other samples also revealed nitrite accumulations (P1, P2, P6 and P8) similar with the reference point (Martor), while in other samples (P3, P5, P7 and P9) it was absent (figure 4). The presence of nitrite in soil can be associated to transformations from the nitrate form, since all the soil samples were characterized by the presence of nitrate. Nitrite was not identified in P3 and P7, even though these samples had elevated nitrate content. Since the soil samples were collected from 5 cm depth, and the soil pH features acidic conditions, it can be assumed that, leaching at higher depts might have occurred due to soil water transport of nitrate (Pilegaard, 2013).

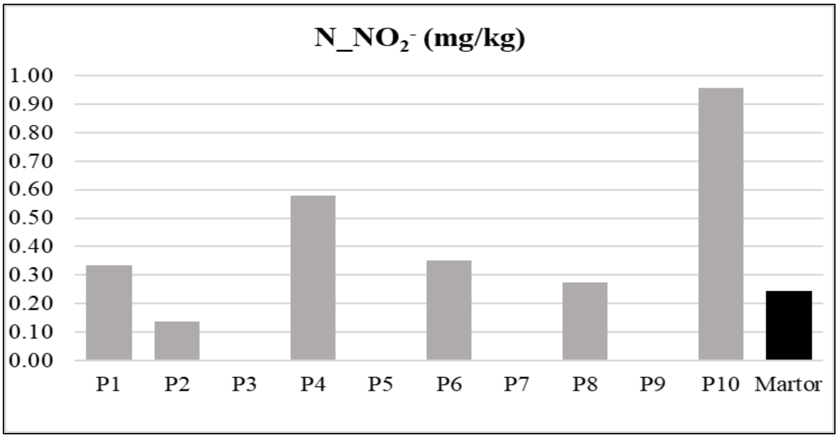

Fig. 4. *Content of N-NO_2^- in the analyzed soil samples*

The presence of nitrite in soil samples poses health threats for the inhabitants living in the study area. Nitrite poisoning was correlated with infant methemoglobinemia and different reactions at stomach or lungs level, including cancer (Serio et al., 2018). For these reasons, the water content of nitrates and nitrites was subjected to environmental legislation.

Water samples

Furthermore, the nitrate concentrations in water samples are listed in figure 5. The industrial effluent from sampling point P DEV EP had a considerably low content of nitrate, which might prove the efficiency of the wastewater treatment from the fertilizer plant. An alarming exceeding of the Romanian national threshold for industrial effluents release in water bodies (Decision 352/2005) was observed in P DEV, the water sample collected at the discharging point of one of the industrial effluents coming from the industrial platform. Despite the high content of nitrate from the effluent point (P DEV), due to high dilution, the nitrate level from Mureș River upstream and downstream from discharging point, was low and did not reach a significand increase. Based on the nitrate level from Mureș River in the proximity of fertilizer plant, the water corresponds to I[st] quality class (a very good ecological status) (Order 161/2006). The nitrite content was below the detection limit in all the analyzed water samples.

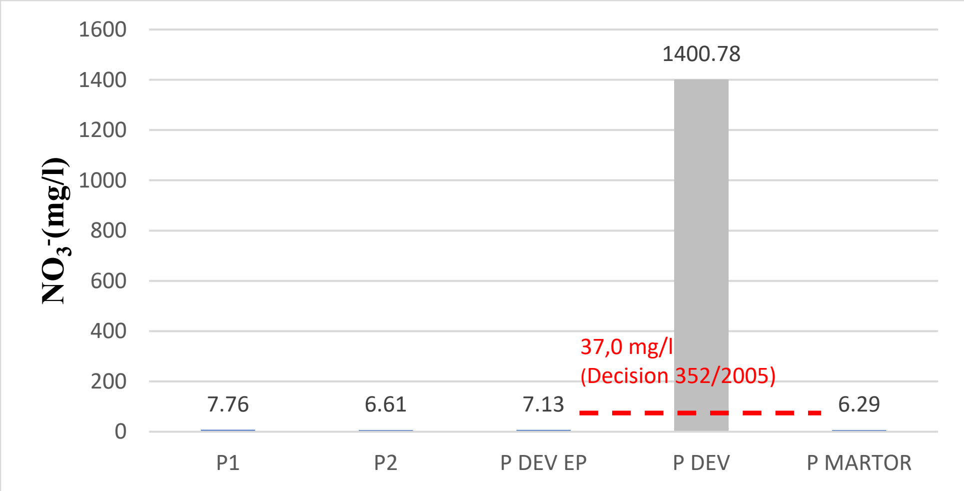

Fig. 5. *Nitrate content in the analyzed water samples*

Correlated with the physical-chemical parameters (table 2), the water pH has not indicated an acidification of the environment as in the case of soil. Even in the water sample with critical nitrate content (P DEV), the pH indicated a neutral feature of the surface water. No significant fluctuation was identified in oxido-reduction conditions, the ORP ranged between -22,1 and +11,2 mV. Except sample P DEV, all the samples indicated similar water quality in terms of electrical conductivity, total dissolved solids, and salinity.

Table 2. *General physico-chemical parameters of the water samples*

Water sample	pH	ORP (mV)	EC (µS/cm)	TDS (mg/l)	Salinity (‰)
P1	7.6	-22.1	243	158	0.0
P2	7.4	-12.3	223	145	0.0
P1 DEV EP	7.3	-5.5	219	142	0.0
P DEV	7.1	+11.2	2106	1398	0.0
P MARTOR	7.3	-7.8	221	144	0.0

CONCLUSIONS

Nitrate compounds under the form of nitrate and nitrite were identified in the soil of the analyzed area. Most of the analyzed soil samples had a N-NO_3^- content suitable for crops. Only one soil sample proved to have a high nitrate content. The N-NO_2^- content was correlated with nitrate transformation, and possible leaching into the soil depth. Since agricultural activities are taking place in some parts of the investigated area, it is difficult to indicate the real source of nitrate presence in soil. As a consequence, no direct correlation can be identified between the air emission generated by the fertilizers plant and the nitrate and nitrite content found the soils located in the proximity area.

For water, most relevant samples were represented by the industrial effluent discharging points. One of the industrial effluents had a low content of nitrate, while the second industrial effluent had a high nitrate content, exceeding the limit imposed by Romanian national legislation. However, the high content of nitrate has not generated a decrease of the surface water quality in the Mureș River due to significant dilution upstream and downstream the discharging point. A supplementary investigation is needed to identify if there was an accidental release of contaminant in the river and to identify the remedial measures.

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