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Nitrates(V) in loess soils modified by weather conditions (preliminary data of a model experiment)**

P. Gliński[1], Z. Stępniewska[2], U. Kotowska[3], and A. Borkowska[3]*

[1]Institute of Environmental Protection Engineering, University of Technology, Lublin, Nadbystrzycka 40a, 20-618 Lublin, Poland
[2]Environmental Protection Institute, Catholic University of Lublin, Kraśnicka 102, 20-718 Lublin, Poland
[3]Institute of Agrophysics, Polish Academy of Sciences, Doświadczalna 4, 20-290 Lublin 27, Poland

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A b s t r a c t. In a model experiment (anaerobiosis) with full saturation of soil samples with water and their incubation at 5, 10 and 20°C during 0-60 days, nitrates(V) concentration in soil solution, Eh and pH in soil sediment were determined. For the investigations 12 samples from loess soils representing surface-humus horizons were taken from various parts of 4 eroded slopes in a small river catchment near Lublin, Poland. Differentiation in nitrates concentrations in the range of 0-1.563 mg dm^{-3} was found, depending on the temperature and time of soil sample incubation, and also on the place of sampling along the catchment and on the slope.

K e y w o r d s: nitrates(V), Eh, pH, loess soils, anaerobic conditions

INTRODUCTION

Nitrogen is one of the most mobile bioelements in soil which undergoes many transformations (nitrification, denitrification, ammonification, fixation from the air) caused by specific groups of microorganisms (Paul and Clark, 2000). Organic forms (plant residues) are the source of nitrogen which, under the biological processes, can be transformed into inorganic forms *eg* NO_3^- as follows:

$$\underset{-3}{NH_4^+} \rightarrow \underset{-1}{NH_2OH} \rightarrow \underset{+1}{NOH} \rightarrow \underset{+3}{NO_2^-} \rightarrow \underset{+5}{NO_3^-}$$

NH_4^+ released during the decomposition of organic matter and not used immediately by microorganisms is rapidly transformed into NO_3^- which can be:

– reduced by microorganisms to free N_2 or totally reduced to NH_4^+ (in anaerobic conditions),
– absorbed by microorganisms,
– leached.

Nitrate(V) form, being easily dissolved in water, is mobile and can be transported in soil. This process was simulated with the use of various models *eg* SWACROP or AWIMO (Dijkstra and Hack-ten Broeke, 1995; Rijtema and Kroes, 1991).

Nitrate(V) losses from agricultural land were identified as a significant source of nitrate(V) in drinking water supplies (Macdonald *et al*., 2005).

The intensity of nitrogen transformation, apart from the properties of a given soil, depends on its moisture status, Eh, pH and temperature (Colbourn and Harper, 1987; Gliński *et al*., 2000; Kralova *et al*., 1992; Mansfeld, 2004; Patrick and Jugusjinda, 1992; Tiedje *et al*., 1984; Yu Tian Ren, 1985). This paper, which is a part of a wider research program concerning physicochemical conditions of soil elements mobility (Gliński, 2004; Gliński and Dębicki, 1999), presents the results of nitrates(V) concentration, Eh and pH in homogenous loess soils (soil samples) flooded with water and incubated at various temperatures (5, 10 and 20°) during 1-60 days.

MATERIALS AND METHODS

The object of the study was eroded loess hill slopes at 4 localities (Motycz, Snopków, Baszki and Pliszczyn) near Lublin, along the the Ciemięga river catchment. The catchment is located on 200-230 m a.s.l. and has an area of

*Corresponding author's e-mail: anetao@ipan.lublin.pl
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157 km^2. It length is 41 km. First two localities are situated in the upper part of the catchment which is of gentle relief. The two others characterize the lower part of the catchment with strong undulating relief. The soils (Haplic Luvisols and Eutric Cambisols) are formed of typical silty deposits of loess containing, in their upper horizons, 1.74-5.42% of organic matter, with specific surface area of 31.84-70.95 m^2 g^{-1}, pH 6.6-8.1 and N-NO_3^- in soil solution from 0.438 to 1.563 dm^{-3} (Table 1).

For the investigations, 12 samples were taken from three places on the slopes at 4 localities (Motycz, Snopków, Baszki, Pliszczyn). They represented surface-humus (0-20 cm) horizons. Soil samples were placed in glass vessels, flooded with distilled water at the ratio of 1:2.5 (15 g soil+ 37.5 cm^3 water), covered, and incubated at 5, 10 and 20°C. In the course of incubation, at different time intervals (days), nitrate(V) concentration in the soil solution was measured with the use of spectrophotometer FIA-Star 5010 (Application Note ASN 110-01/92) and the values of Eh (Gliński and Stępniewski, 1985) and pH – potentiometrically in soil sediment with the use of combined electrodes and PIONer Radiometer instrument.

The chosen conditions of long lasting full water saturation of loess soils at various temperatures appear in south-east Poland.

Analysis of variance by the least significant difference test (95% LSD-test) was performed to determine whether a significant difference existed ($p<0.05$) between means of locality, means of temperature and means of place on slope at different temperatures. All statistical analyses were performed with the Statgraphics Plus 5.1.

RESULTS

Mean nitrates(V) concentration (from the sum of all 204 treatments) was 0.208 mg dm^{-3} at mean values of Eh 298 mV and pH 7.2 (Table 2).

Taking into consideration the place of soil sampling at the 4 localities (M, S, B, P), lower nitrate(V) concentrations in soil solution were found in the lower, most eroded, part of the catchment (B = 0.147 and P = 0.177 mg N-NO_3^- dm^{-3}) than in the upper part (M = 0.237 and S = 0.272 mg dm^{-3}) (Fig. 1). Opposite tendencies were found with Eh values – higher in the lower part (318 and 303 mV) and lower (292 and 281 mV) in the higher part of the catchment (Table 2).

Soil reaction (pH) was rather even (7.1-7.6 for S, B and P) except for a lower value (6.6) for M in the upper, less eroded, part of the catchment where upper horizons were farther from loess deposits with basic reaction (Table 2). The

T a b l e 1. Granulometric composition and some properties of examined soils

Locality	Place on slope		Particle size distribution (%, dia in mm)						OM (%)	$S^*_{H_2O}$	$S^*_{N_2}$	pH_{H_2O}	N-NO_3^- (mg dm^{-3})
			1-0.1	0.1-0.05	0.05-0.02	0.02-0.005	0.005-0.002	<0.002		(m^2 g^{-1})			
Motycz (M)	1	Upper	27	12	35	13	3	10	1.74	35.07	7.06	6.6	0.902
	2	Middle	10	13	46	20	4	7	1.87	31.84	6.39	7.5	0.725
	3	Lower	8	12	48	20	7	5	5.42	70.95	8.63	7.4	1.563
Snopków (S)	1	Upper	7	15	56	3	17	2	3.08	47.24	6.80	7.9	0.926
	2	Middle	6	14	57	17	2	4	2.40	40.93	9.53	7.7	0.703
	3	Lower	22	18	50	7	1	2	5.08	55.69	6.65	7.9	0.966
Baszki (B)	1	Upper	6	9	53	21	3	8	2.28	36.78	15.31	8.1	0.516
	2	Middle	4	13	50	20	5	8	1.94	40.44	10.88	7.1	0.648
	3	Lower	8	14	58	13	2	5	2.72	35.36	8.97	7.6	0.648
Pliszczyn (P)	1	Upper	1	10	62	19	1	7	2.63	40.58	12.35	7.5	0.515
	2	Middle	8	12	53	19	1	7	2.51	33.72	6.61	7.8	0.438
	3	Lower	13	15	47	19	1	5	3.48	34.70	5.25	8.1	0.449

OM – organic matter, S* – specific surface area measured with H_2O and N_2 adsorption, N-NO_3^- in soil solution at 20°C.

T a b l e 2. Mean values of nitrates(V), Eh and pH at different temperature connected with soil sampling in localities and on the slope

Factors	Stand and temperature	Treatments	$N\text{-}NO_3^-$ (mg dm^{-3})	Eh (mV)	pH
Locality	Motycz	n=51	0.237	292	6.6
	Snopków		0.272	281	7.3
	Baszki		0.147	318	7.1
	Pliszczyn		0.177	303	7.6
Slope	1	n=68	0.216	322	7.4
	2		0.177	311	7.6
	3		0.232	262	7.4
Temperature	5°C	n=84	0.096	305	7.4
	10°C	n=72	0.118	283	7.3
	20°C	n=48	0.539	309	7.0
All results (n=204)			0.208	298	7.2

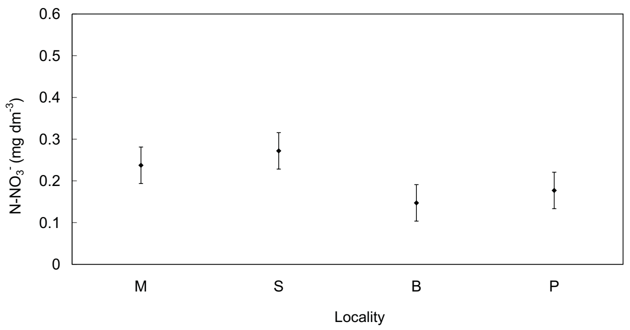

Fig. 1. Nitrates(V) concentrations in soils of various localities of the Ciemięga catchment.

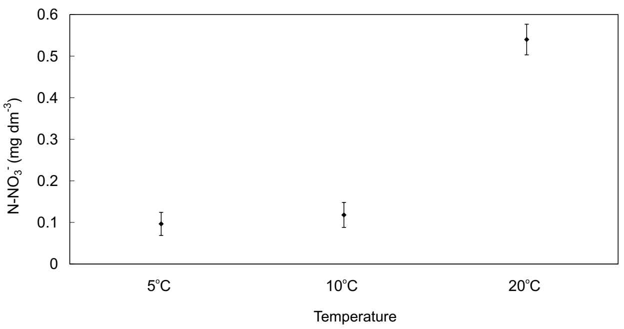

Fig. 2. Nitrates(V) concentrations in soils of the Ciemięga catchment at different temperatures.

lowest values of Eh (262 mV) appeared in the lower part of the slopes, higher in the middle part (311 mV), and the highest (322 mV) in the upper part (Table 2).

A significant correlation was found between nitrate(V) concentration in soil solution and temperature (Fig. 2). Nitrates(V) concentrations was the highest at 20°C (0.55 mg $N\text{-}NO_3^-$ dm^{-3}) in comparison to concentrations at 5°C (0.1 mg $N\text{-}NO_3^-$ dm^{-3}) and 10°C (0.15 mg $N\text{-}NO_3^-$ dm^{-3}).

Mean values concerning nitrates(V) concentrations in soil solutions from 3 places on 4 slopes (Table 2) are higher at the lower places (0.232 mg dm^{-3}) than in two higher places (0.177 and 0.216 mg $N\text{-}NO_3^-$ dm^{-3}). These tendencies are more pronounced when we examine them in relation to temperature (Fig. 3).

In lower temperature, 5°C, nitrate(V) concentration in soil solution gradually decreased along the slope from its upper to lower part. At 10°C this decrease was stopped on the level of middle and lower parts of the slope, and at 20°C the highest nitrate(V) concentrations was found at the lower part of the slope in comparison to its other parts.

The temperature of incubation modified microbial processes in soil samples, mainly those rich in organic matter at the base of the slopes.

Temperature and time of incubation caused a decrease in nitrates(V) concentration (Fig. 4) to a value characteristic for a given temperature (30 days at 5°C and 3 days at 20°C and no change at 10°C) with systematically lowering Eh values. Near the end of incubation there was an increase of the nitrate(V) concentrations at all temperatures. No relation was found between nitrates(V), pH and soil organic matter content.

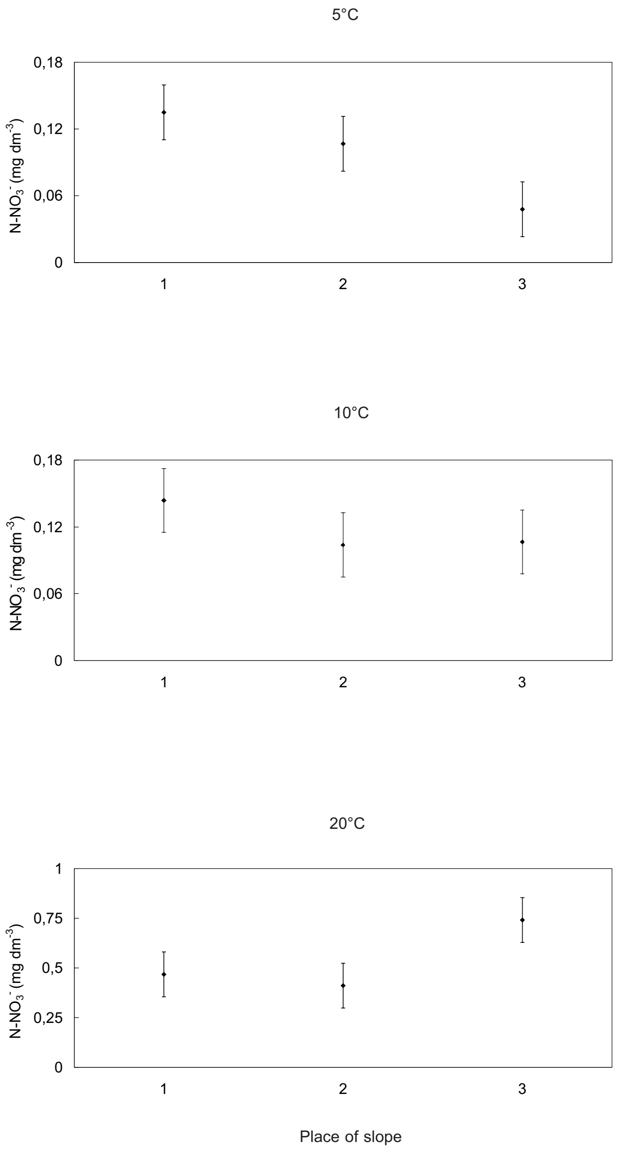

Fig. 3. Nitrates(V) concentrations in soils at various places on slope of the Ciemięga catchment at different temperatures.

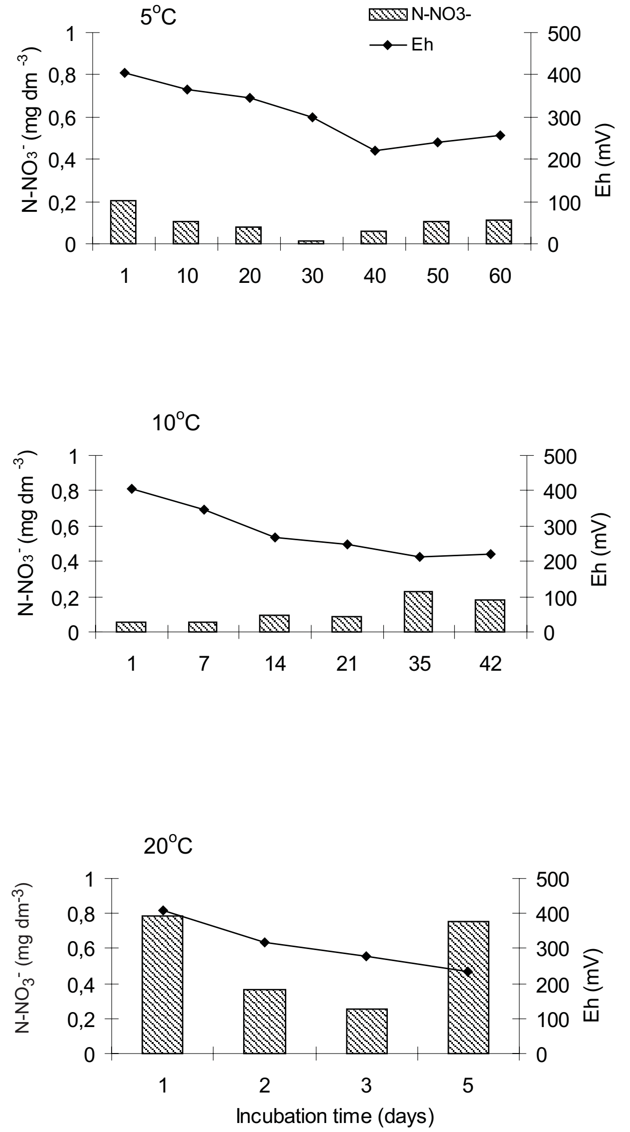

Fig. 4. Nitrates(V) concentrations and Eh changes during incubation of soil samples from the Ciemięga catchment at different temperatures.

DISCUSSION

The purpose of the investigations carried out was to determine the behaviour of nitrates(V) in conditions of soil saturated with water and incubated at various temperatures which had to simulate possible weather conditions of longer duration of rainfall at a given temperature close to that assumed in the experiment. The investigations were performed on samples of soils susceptible to reduction (Gliński and Stępniewska, 2005; Stępniewska, 1988), such as loess soils. These soils are homogenous in their composition but easily undergo erosion processes which modify their properties in vertical and horizontal plane (Gliński and Dębicki, 1999; Gliński and Turski, 2002).

Model conditions of flooding soil samples with water created favourable conditions (Eh<400 mV at pH about 7) for the reduction of oxidized forms of nitrogen (N-NO_3^-) (Patrick and Jugusjinda, 1992). It was confirmed during the incubation time of soil samples when nitrates(V) concentration in soil solution decreased by about 50% of the initial value.

The mentioned modification (variability) of homogenous loess soil cover influenced nitrate(V) concentration in soils dependent on the place of sampling along the catchment, showing a tendency of the concentration to decrease from the upper, less eroded, to the lower, most eroded, part of the catchment.

Differentiation in nitrate(V) concentration was also connected with the place of soil sampling on the slope. Samples taken from the middle (eroded) part of the slopes showed, in some localities, less nitrates in comparison to samples derived from the upper and lower parts of the slopes.

Generally, we can state that the differences found in nitrates(V) concentration in soil solution are caused mainly by soil moisture and temperature conditions assumed in the experiment, being a reflection of possible weather conditions for the examined area. Variation in nitrate(V) concentrations in soil along the catchment and along the slopes resulted from erosion processes modifying properties of surface layer of the soil, mainly their chemical composition.

$N\text{-}NO_3^-$ concentrations found during the experiment appeared to be considerably lower than those (11.3 mg $N\text{-}NO_3^-$ l^{-1}) established for ground waters by Nitrates Directive of the European Community No. 91/676/EEC from 1991 accepted by Poland in 2002.

CONCLUSIONS

1. Analytical data obtained allowed us to draw some conclusions and tendencies which show a possibility for directed changes of nitrates(V) concentrations that could exist in loess soils of eroded areas, caused by atmospheric conditions (excess of rain and variation in temperature) and also by differentiation in soil cover.

2. Homogenous soils, such as those found from loess deposits, change their properties due to erosion processes, also concerning nitrate(V) concentrations in the range of 0-1.563 mg dm^{-3}.

3. These changes are more pronounced in soil incubated at different temperatures than in places of soil sampling in the area of small river catchment.

4. The assumed experimental conditions, close to natural weather conditions, allow the results obtained to be used for the evaluation of chemical hazards to the natural environment.

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