Nitrate and ammonium transformation and redox potential changes in organic soil (Eutric Histosol) treated with municipal waste water**

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A b s t r a c t. The dynamics of nitrogen forms in soil irrigated with municipal waste water was studied in order to determine its effect on soil redox potential. The soil (Eutric Histosol) was planted with a mixture of grasses, and irrigated 10 times per year with waste water purified by a two-step (mechanical and biological) treatment with a dose optimal for the plants, or doubled. Simultaneously, control soil (not flooded) with plant vegetation was studied. It was found that redox potential was influenced by nitrate (V) nitrogen in plots irrigated with municipal waste water at the optimal irrigation dosage for the plants and with double the optimal dose. Irrigation with waste water resulted in a decrease of Eh value in the whole soil profile, causing a reduction of redox potential value below the level of +200 mV, especially in lower horizons, corresponding to dissimilative reduction of nitrates (V) to the forms of N_2O and N_2.

K e y w o r d s: redox potential, biogene, irrigation, hydro-botanical treatment plant

INTRODUCTION

Water plays a very special role in the mutually related processes that take place in ecosystems, constituting a fundamental, necessary for their functioning, abiotic element of the environment. Soil is the fundamental acceptor of wastes generated in nature (Fashchevsky and Fashchevskaya, 2003). Wastes purification utilizing the soil and plants is the result of complex processes – chemical, physical, physico-chemical, biochemical – that take place in the aeration and saturation zone.

Nitrogen compounds occurring in municipal and industrial water can cause serious effects such as deoxidation due to nitrification, ammonia poisoning and biomass excessive growth. Because of the above effects intensive studies including the removal of biogenic substances from waste water (Obarska-Pempkowiak, 1991) and the use of soil and plants in hydrobotanical waste water treatment plants (Richardson and Davies, 1987) have been carried out in recent years. Nowadays, in Poland there are about 40 waste water treatment plants of this type.

Studies of processes occurring under the conditions of intensive irrigation of soil and plants, among others willow (*Salix Americana*) and grass, with municipal waste water from the 'Hajdów' waste water treatment plant were carried out in 1997-1999 in Lublin (Report, 1998). Intensive periodic irrigation of soil caused an increase in redox processes. The intensity of the processes was evaluated based on changes and current values of redox potential which is one of more important parameters used to describe soil solution and its oxygen conditions (Stępniewska, 1988; Stępniewska *et al.*, 1997).

The values of pH of soil water were in the range of 6.85-8.8 and those of pH of waste water from 6.5 to 8.4 (Report, 1998), so the conditions for nitrification and denitrification processes were favourable.

The aim of the paper was to compare changes of redox potential in soil with changes of concentrations of nitrate (V) and ammonia nitrogen in soil water during irrigation of mixed grass cultivations. The comparison was aimed at evaluation of the influence of nitrogen forms on redox potential values at different depths of soil.

METHODOLOGY OF STUDIES

The experiments were carried out in the Bystrzyca River Valley in the area of about 8 ha, divided into 7 equal plots. The area of one plot was covered with grass mixture. Every plot was divided into 3 subplots (A – control, B – with an optimal irrigation dose for the plant, C – with double the optimal dose).

To evaluate ammonia and nitrates (V) nitrogen concentrations in soil solutions, ceramic drains for soil water sampling were installed at depths of 10, 30, 50, 70 and 100 cm on each subplot. Measurements of nitrogen forms concentrations were conducted on a FIA-star 5010 /TEKATOR/ spectrophotometer.

Redox potential (Eh) at the above depths was measured with platinum electrodes using a calomel electrode (NEK) as reference, and an Orion Model 401 meter. Taking into account temperature fluctuations, adjustments of reference electrode potential were made assuming for the temperatures of 10, 15, 20 and 25°C the values equal to 254, 251, 247 and 244 mV, respectively.

Waste water from the 'Hajdów' used for the irrigation of mixed grass showed rather stable basic physiochemical parameters (Report, 1998). Concentration of nitrogen forms, especially ammonia and nitrate (V) nitrogen, was more variable. Concentrations of NH_4^+-N and NO_3^--N were in the range of 1.1-7.1 g m^{-3} and 20.2-38.4 g m^{-3}, respectively (Report, 1998).

Treated waste water can supply the soil with biogenic substances in quantities corresponding to intensive fertilization. The optimum irrigation dose of 600 mm (grass) supplied the soil with at least 180 kg N, 30 kg P, and 110 kg K ha^{-1}, and the quantities of nitrogen, phosphorus and potassium amounted to 270, 45, 167 kg ha^{-1}, respectively. On the subplots irrigated with double the optimum dose, the quantities of fertilizers were twice as much.

RESULTS AND DISCUSSION

Nitrogen transformations in field irrigated with waste water after 2nd stage of treatment

Transformations of the ammonium form

The highest average concentration of ammonium form in the first year of the experiment on the control plot covered with grass mix was found at the depth of 30 cm (0.96 g N m^{-3}), and the lowest at 100 cm (0.16 g N m^{-3}) (Table 1). Distinctly lower concentration of ammonium ion in the surface part of the soil profile (10 cm) could be related to more intensive uptake of ammonium N by the root system of the grasses.

Waste water irrigation in the single and double doses had its reflection in the content of the ion analyzed in soil solutions taken from plots B and C. The addition of waste water caused an increase in the concentration of ammonium ion to 3.87 and 4.82 g N m^{-3}, respectively for plots B and C for the depth of 10 cm *ie* almost four- and five-fold as much as the native concentration of ammonium form in the control plot (Fig. 1). A somewhat lower increase was observed at depths below 10 cm in the soil profile. In the initial stage of waste water effect on the soil and the grasses only a slightly

Table 1. Average concentrations of nitrogen forms and values of Eh in control plots (A) for grass mix in the first year of the study

Depth (cm)	NH_4^+-N (g m^{-3})	NO_3^--N (g m^{-3})	NO_3^--N/ NH_4^+-N	Eh (mV)
10	0.24	4.9	20.41	491
30	0.96	7.98	8.31	474
50	0.88	3.46	3.93	420
70	0.31	2.95	9.51	54
100	0.16	2.49	15.56	-86
Average	0.51	4.35	11.54	270
Drainage water	0.41	2.33	5.68	-

higher concentration of NH_4^+-N was observed at the depth of 10 cm; at the other depths the concentration of ammonium ion was very much similar in both plots. Considerably greater differences in the concentration of the ion under analysis were observed on the second day from flooding, especially at depths down to 30 cm.

The decrease in the concentration of ammonium ion at the lower dose of waste water results, among other things, from the process of nitrification, its fixing in the sorptive complex of the soil, and immobilization by plants and microbes.

Figure 2 presents the balance of NH_4^+-N transformations in the period from the 3rd hour to the 7th day after irrigation with waste water, expressed in the form of reduction or increase in the amount of the analysed ion, in absolute values.

Analysis of the results presented indicates that the effectiveness of the reduction decreases with depth, which is undoubtedly related with the lower biological activity in the deeper parts of the soil profile.

An important factor in the process of ammonium ion sorption was the dosage of waste water applied, where a greater reduction in the amount of NH_4^+-N was observed in the case of the double dose, especially at the depth of 10 cm. The tendency decreased with the increase of depth.

Concentration of ammonium ion in drainage water under grass mix is presented in Fig. 3 with relation to waste water dosage. A higher concentration of the NH_4^+-N ion was noted in plot (B), where it remained on a fairly stable level from the 3rd hour after irrigation till the second day. The concentration of NH_4^+-N dropped nearly by half on 7th day from irrigation. This fact may be related to the distinctly higher index of filtration of plot (B) as compared to that of plot (C). In the case of the latter, the concentration of ammonium ion in the drainage water remained stable on a relatively high level for a period of seven days. The higher level of the NH_4^+-N ion in the drainage water with relation to the control varied within the range from 3- to 1.5-fold.

However, taking into consideration the amount of NH_4^+-N ions introduced with the waste water, their concentration in the drainage water dropped from 3- to 6-fold.
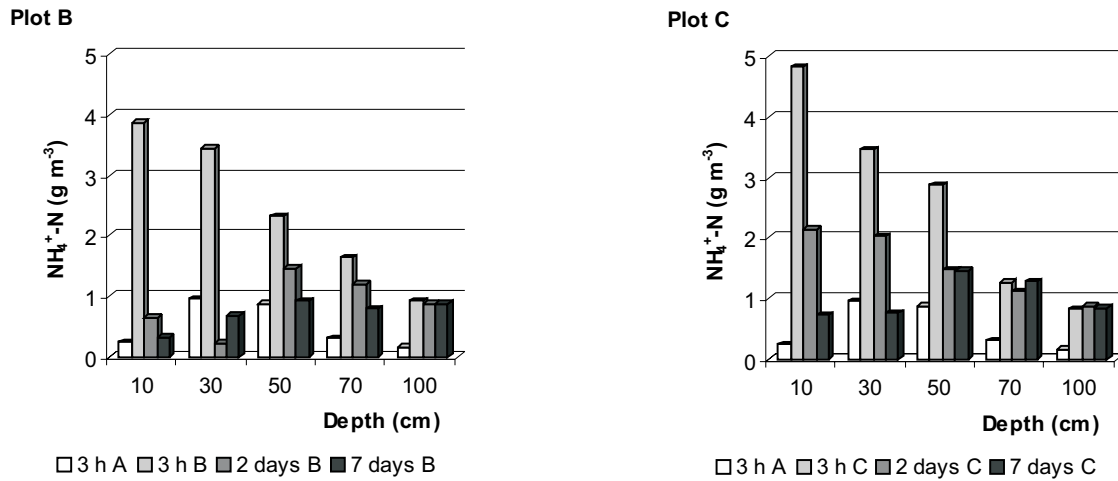
Plot B

Plot C

Fig. 1. NH_4^+-N concentrations in soil solution during 7 days after flooding under grass mixture in a control plot A and as dependent on the waste water dose (single – B and double – C).
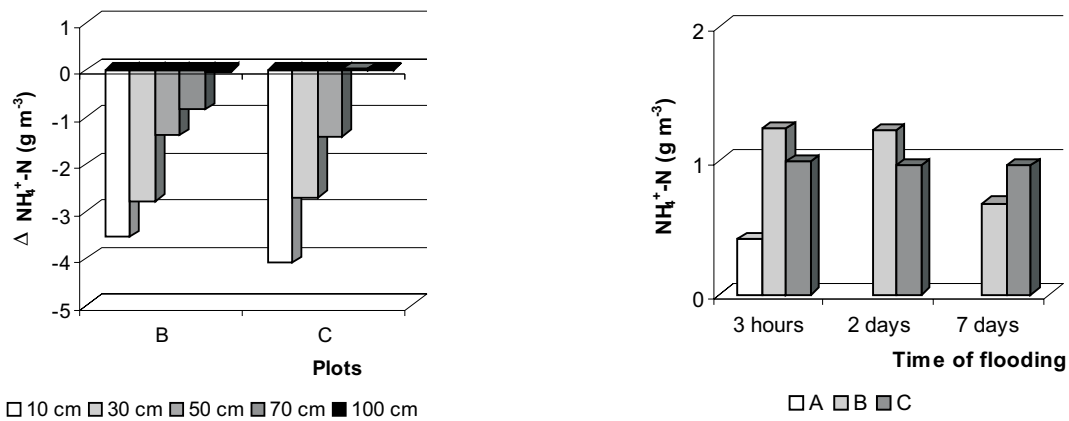

Fig. 2. Changes in NH_4^+-N concentrations in soil solution expressed like a decrease or increase after 7 days after flooding under grass mixture as dependent on the waste water dose (single – B and double – C).

Fig. 3. NH_4^+-N concentrations in drainage water during 7 days after flooding under grass mixture in a control plot A and as dependent on the waste water dose (single – B and double – C).

Transformations of nitrate (V) form

Figure 4 illustrates the distribution of nitrate (V) form concentration within the whole soil profile with relation to waste water dosage. The native content of nitrates (V) varied from 2.49 to 7.98 g N m^{-3}, respectively for the depths of 100 and 30 cm (Table 1). Somewhat lower concentration of NO_3^--N occurred at the depth of 10 cm (like in the case of the ammonium form), which should be ascribed to intensive development of the root system of the grasses in that part of the soil profile, especially in the first year of cultivation.

The application of waste water affected the dynamics of transformations of nitrate (V) nitrogen irrespective of the dosage (Fig. 4). Comparison of NO_3^--N concentration within the whole period of waste water effect on the soil and

plants, as well as in the soil profile between single and double dosage, suggests that in the case of the grass mix the amount of nitrogen (V) introduced does not play any significant role in its transformations.

Figure 5 presents the balance of nitrogen transformations between the 3rd hour and the 7th day from irrigation, expressed in the form of reduction or increase in the amount of nitrate (V) ion, in absolute values. Analysis of the results presented indicates that the reduction in the amount of nitrate (V) ion decreased with depth in the soil profile in plot B and was much higher than in plot C.

Figure 6 presents the concentration of NO_3^--N in the drainage water with relation to waste water dosage. The mobility of nitrates (V) caused that already after 3 h from the moment of waste water application their maximum
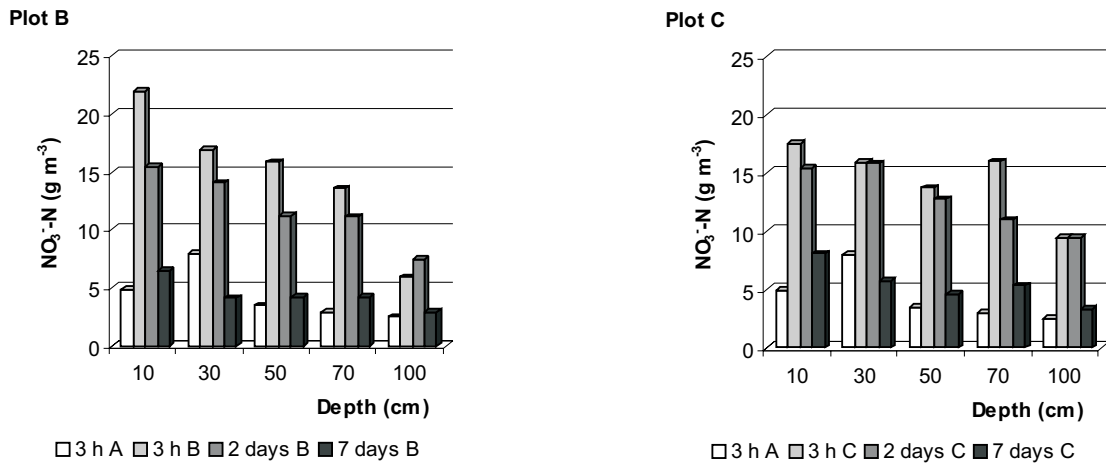
Fig. 4. NO_3^--N concentrations in soil solution during 7 days after flooding under grass mixture in a control plot A and as dependent on the waste water dose (single – B and double – C).
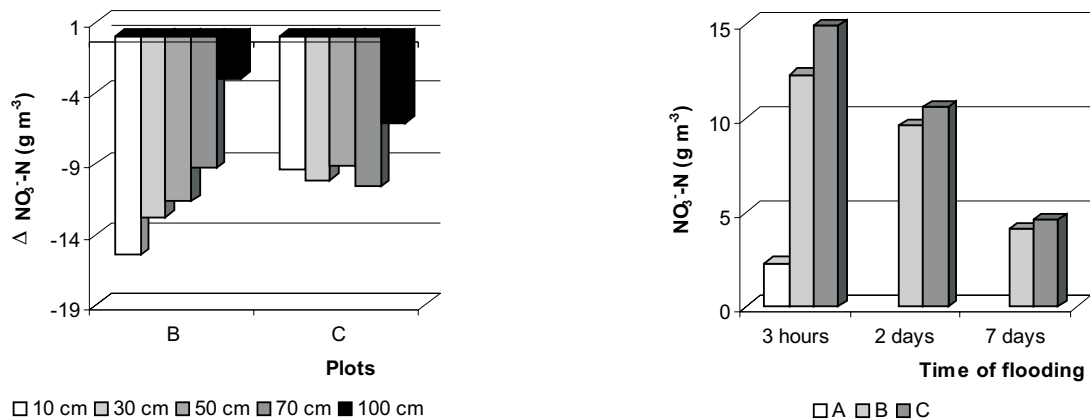
Fig. 5. Changes in NO_3^--N concentrations in soil solution expressed like a decrease or increase after 7 days after flooding under grass mixture as dependent on the waste water dose (single – B and double – C).

Fig. 6. NO_3^--N concentrations in drainage water during 7 days after flooding under grass mixture in a control plot A and as dependent on the waste water dose (single – B and double – C).

concentration was observed, proportionally to the amount of waste water applied. On day seven of the experiment, the concentration of NO_3^--N dropped three-fold, and taking into consideration the amount of nitrates introduced with the waste water, the concentration of NO_3^--N decreased by a factor of six.

Dynamics of redox potential changes

Introduction of waste water to the soil in amounts causing its total flooding results in radical changes in the water-air relations in the soil. As shown by research by

numerous authors (Gliński and Stępniewski, 1985; McKenney *et al.*, 2001), under the conditions of soil flooding with water exhaustion of oxygen occurs within several hours, resulting in a variety of changes in the soil. In particular, the redox potential of the soil decreases, with the drop of Eh values below +300 mV being caused by reduction of the soil and successive activation of redox couples other than the O_2/H_2O system *eg* NO_3^--N/NO_2^--N (Gliński and Stępniewski, 1985).

As a result of oxygen content in the soil decrease below 1% (v/v), anaerobic microorganisms begin to dominate over aerobes. Gliński and Stępniewski (1985) conclude that soil

flooding with water causes a gradual drop of redox potential until a certain fairly stable level is reached. The rate of the decrease and the value of Eh depend on the intensity of the process of reduction, determined by temperature and by the content of easily decomposable organic substrate and of oxidized inorganic compounds functioning as acceptors of electrons, including nitrates (V).

Figure 7 presents the change of redox potential after 3 h, and after two and seven days from the application of the single and double irrigation doses in fields under grass mix. Redox potential in the control soil profiles was stabilized down to the depth of 50 cm and varied within the range from about +400 to +500 mV *ie* in the range of aerobic oxidation of carbon (Tate, III, 1995).

On the second day after flooding the soil with waste water, for both the single and double dosage, in most of the analysed soil horizons down to the depth of 50 cm the phenomenon was observed of fairly rapid increase in the redox potential value reversing to a decrease by the seventh day from flooding. The rapid decrease after flooding could be related to high microbial activity that is always accompanied by fast depletion of oxygen in the environment and a drop of Eh before the microorganisms can adapt to anaerobic conditions and the system involving the NO_3^--N/NO_2^--N pair of electrons (next in line after O_2) can activate. This phenomenon occurs most frequently when the soil gets flooded following thorough drying.
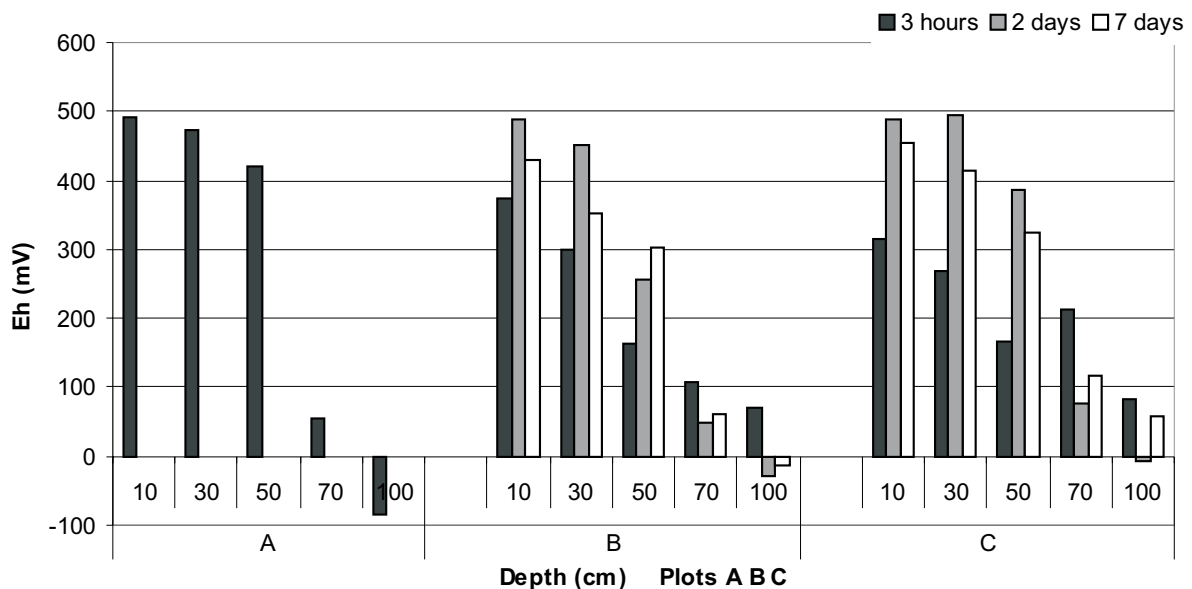

Fig. 7. Redox potential value in various profile depths as dependent on the waste water dose (A – control, B – single dose, C – double dose), time after flooding (3 h, 2 and 3 days) under grass mixture.

At depths below 50 cm the value of Eh rapidly drops, reaching negative values. Such a drastic drop of the redox potential is related with the appearance of ground water table at the depth of 50-60 cm. That is why the values of Eh at the depths of 70 and 100 cm were relatively low and varied from about +60 to -90 mV.

Irrigation of the fields with the single and double doses of waste water resulted in a change of the redox potential. Analysis of changes in the aeration status in plots A, B, C down to the depth of 50 cm on the 3rd h showed a lower value of Eh in the combinations with irrigation than in the control plot (A). Generally, it can be stated that the value of redox potential, at the 3rd h from irrigation, decreased with depth in all the objects studied. The decrease in the lower part of the profile depended more on the ground water table than on the waste water applied.

Thus, in the case of fields with grass mix, in the profile down to the depth of 50 cm (except for field 6B at 50 cm), there was no distinctly observable phenomenon of reoxidation, so important for proper development of the root systems of plants grown.

Concentration of nitrates (V) versus redox potential in the soil irrigated with single and double dose of waste water after 2nd stage of treatment

Soil flooding may cause a gradual decrease of redox potential until a certain relatively stable level is reached. The rate of the decrease and the minimum value of Eh depend on the intensity of processes of reduction, determined by temperature and the amount of easily available organic

substrate, and on the amount of bioreducible inorganic compounds which are acceptors of electrons (nitrates, three- and four-valent manganese compounds, iron oxides). The presence of such compounds maintains redox potential on a certain constant level which *eg* in the case of nitrates, is from +100 to +200 mV (Bailey and Beauchamp, 1971; Gliński and Stępniewski, 1985).

In parallel to analysis of concentration of nitrate (V) ions, data concerning the redox potential were collected and an attempt was made at determining the correlation between the concentration of nitrates (V) introduced with the single and double doses of waste water and the value of the redox potential. The relations obtained are presented on the example of average values of NO_3^--N concentration and values of Eh measured in the fields in the first year of the irrigations (Fig. 8).

concentration. At seventh day of experiment, the process of reoxidation, especially in higher part of horizons, could influence redox potential more than nitrate content (Fig. 8). Włodarczyk (2000) found that with a decrease in the content of nitrates within the range from about 100 to approximately 10 mg NO_3^--N kg^{-1}, redox potential value decreased from 250 to 190 mV. For mineral soils, the limit value which is accompanied by a clear decrease in Eh value is the level of approximately 100 mg NO_3^--N kg^{-1}. It is to be supposed, therefore, that below +400 mV the decrease in NO_3^--N concentration was caused by the process of denitri- fication. Literature reports indicate that the beginning of the process of denitrification in various soils occurs at different values of Eh, sometimes below +200 mV (Kralova *et al*., 1992; Van Cleemput and Patrick, 1974; Włodarczyk, 2000).
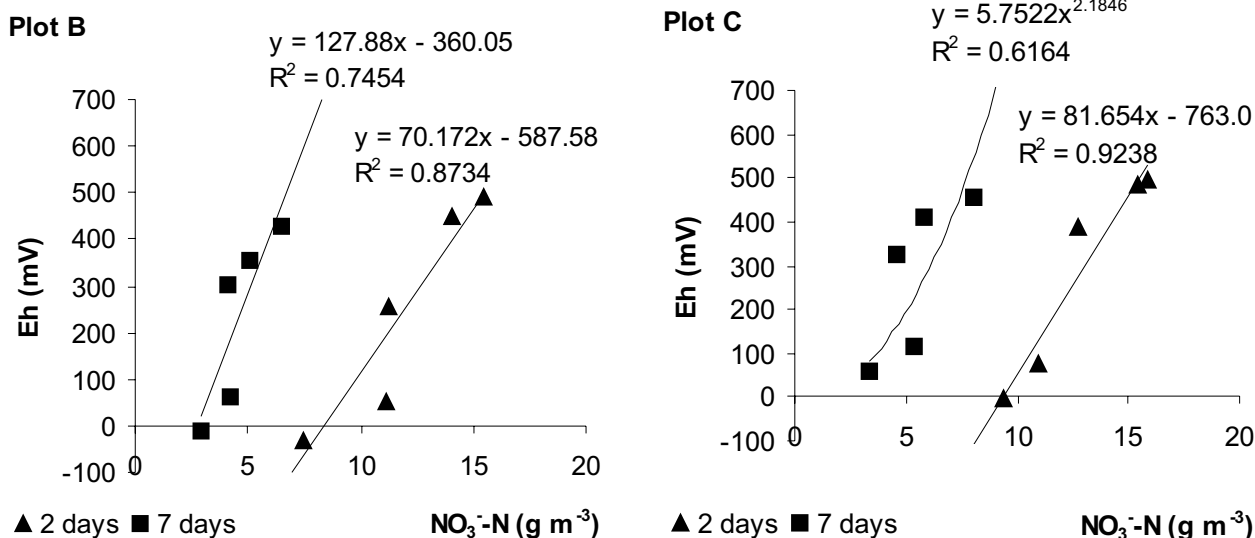

Fig. 8. Redox potential value after 2 and 7 days after flooding versus NO_3^--N concentration and waste water dose (B – single dose, C – double dose) under grass mixture.

The relationship is described by two mathematical functions: linear (y= a + bx) and power (y = ax^b). In all the cases analysed the functions are positive, which means higher concentration of NO_3^--N is accompanied by a higher value of Eh.

A higher coefficient of determination was observed in fields irrigated with the double dose of waste water (C). Analysis of the diagrams presented shows that up to two days from waste water application in all the cases analysed the value of Eh held at the level of +200 mV within the range of NO_3^--N concentrations of 12-20 g m^{-3}. With high soil moisture, nitrate content could protect the soil against the process of reduction. In the case of soil flooding with waste water, there occurred a restriction of oxygen influx, first of all in the surface horizons. In that situation the presence of nitrates affected the value of Eh proportionally to their

Under favourable conditions (min. low Eh value, available organic matter), nitrates (V) entered the path of dissimilative reduction, where the final product was the ammonium ion, periodically increasing its concentration in the soil profile, especially in its lower horizons.

The data presented in Fig. 9 show the effect of depth on the value of Eh. Statistical analysis of Eh values in the function of depth showed their close correlation. The dependence is described by linear function (y = a + bx). In all three plots under analysis the functions are negative, which means that redox potential decreases with depth. In all cases the coefficient of determination R^2 is close to 0.9 or even higher, which, with five replications, gives significance at the level of 0.001.
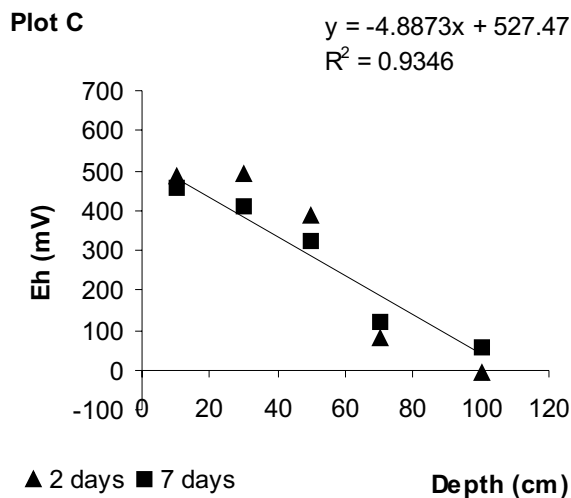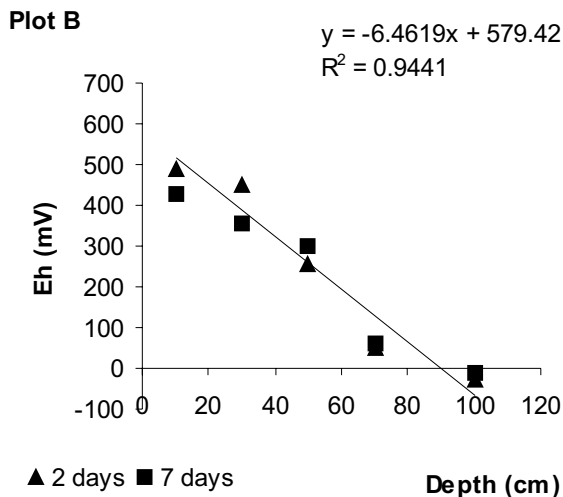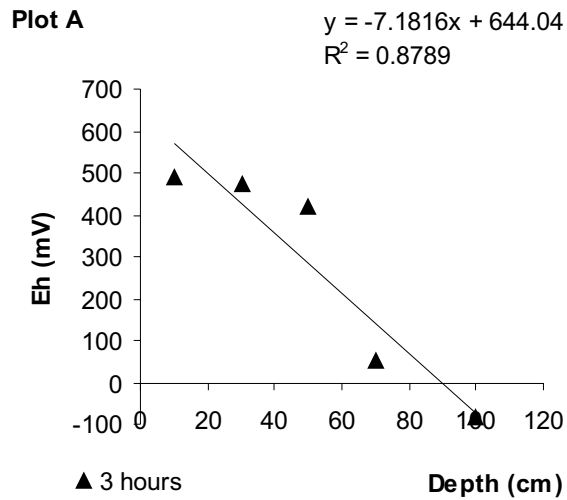
Fig. 9. Redox potential value after 3 h, 2 and 7 days after flooding versus depth of profile and waste water dose (A – control, B – single dose, C – double dose) under grass mixture.

CONCLUSIONS

1. Decrease in the concentration of NH_4^+-N and NO_3^--N ions in the soil profile indicates that grass mix can be used in the process of waste water purification.

2. In a great majority of cases discussed, the concentration of NO_3^--N in drainage water did not exceed 15 g N m^{-3}, which meets the requirements imposed by the European Union.

3. The best aeration conditions were found down to the depth of 30 cm, where Eh values held about +300 mV, with the possibility of nitrifiers development; below the depth of 50 cm redox potential decreased to a value permitting the development of denitrifiers.

4. A significant relationships has been shown between the redox potential and nitrogen transformations taking place in a soil irrigated with waste water after 2nd stage of treatment.

5. A significant negative effect of waste water dosage on redox potential was observed, especially in the case of the double dose, causing the reduction of redox potential value below the level of +200 mV, corresponding to dissimilative reduction of nitrates (V) to the forms of N_2O and N_2.

6. Waste water application in the single dose may provide a valuable source of nitrogen in the cultivation of plants for industrial purposes.

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