Geological Quarterly, 2003, **47** (1): 91–96

Laboratory methods of estimating the retardation factor of migrating mineral nitrogen compounds in shallow groundwater

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Mikołajków J. (2003) — Laboratory methods of estimating the retardation factor of migrating mineral nitrogen compounds in shallow groundwater. Geol. Quart., **47** (1): 91–96. Warszawa.

The retardation factor (*R*) is a measure of the ground's ability to restrain the migration of particular nitrogen species. It shows how many times the migration of the substance is subjected to adsorption slower than the actual speed of water flow in the pore spaces. Analysis of this factor is described for the two main forms of mineral nitrogen in groundwater, nitrate and ammonium ions, in soils typical of the area of the Kurpie outwash, in northeastern Poland. Retardation factor values have been determined by laboratory static methods, for various concentrations of these ions in water. For most soil types, the retardation factor values for nitrates, determined for various concentrations of these ions, show little variation. For soils developed from outwash sands the results obtained fall between 1.98 and 4.74; for outwash sands — 1.17– 2.68; for clayey sands — 2.75–6.94; and for sandy clays — 7.4–26.54. The highest values 16.31–42.53 were obtained for sands enriched in iron oxides and hydroxides. A substantially higher variation in the retardation factor is shown by ammonium ions. The values determined vary between 9.4–41.4 for outwash sands, 37.6–84.8 for sands enriched in ferruginous oxides and hydroxides, 72.5–327.4 for sandy soils, 466–1043 for clayey sands and 2326–3772 for sandy clays.

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Key words: unsaturated zone, groundwater, nitrogen compounds migration, nitrogen compounds adsorption.

INTRODUCTION

Regional degradation of groundwater quality caused by an excess of nitrogen compounds is common in agricultural lands. Among the nitrogen species occurring in such areas, nitrate ions and to a lesser extent also ammonium ions have the greatest influence on the water quality and dominant mineral nitrogen migration (Vrba and Romijn, 1986). Other nitrogen forms present in groundwater of agricultural areas are nitrites and organic nitrogen. In some specific situations e.g. following over-fertilising by organic fertilisers, nitrites and organic nitrogen may be considerably abundant (Bagińska, 1993), but usually these compounds are of minor significance. This is because organic nitrogen migrates slowly and nitrite is rapidly oxidised to nitrate, depending on the kinetics of the nitrogen cycle (Witczak and Adamczyk, 1995).

Adsorption is the main process influencing the migration of particular components in groundwaters. In the case of nitrogen biofill compounds, biological processes are also important (Chapelle, 1992). It is difficult to evaluate precisely, which of these processes is decisive in restraining the migration of nitrogen compounds into groundwater. In a humus layer, microbiological processes may be of most importance (depending on the season and on biological activity). Below this layer, in both unsaturated and saturated zones, the importance of biological processes decreases and ion exchange plays a predominant role.

The retardation factor (*R*) is one of the coefficients that describe the migration abilities of particular components in groundwater. It shows how many times the migration of the substance subjected to adsorption slower than the actual speed of water flow in pores (Deutch, 1997). The retardation factor can be evaluated by laboratory methods, determining the adsorption isotherms of the migrating substances, or by field observations of the speed of substance migration.

The average intensity of nitrate adsorption is described as low, and the retardation factor ranges between 1 and 2. The adsorption intensity of ammonium ions is described as medium or high, and the retardation factor is variously estimated, but usually a value of few up to a dozen or so is accepted (Witczak and Adamczyk, 1995).

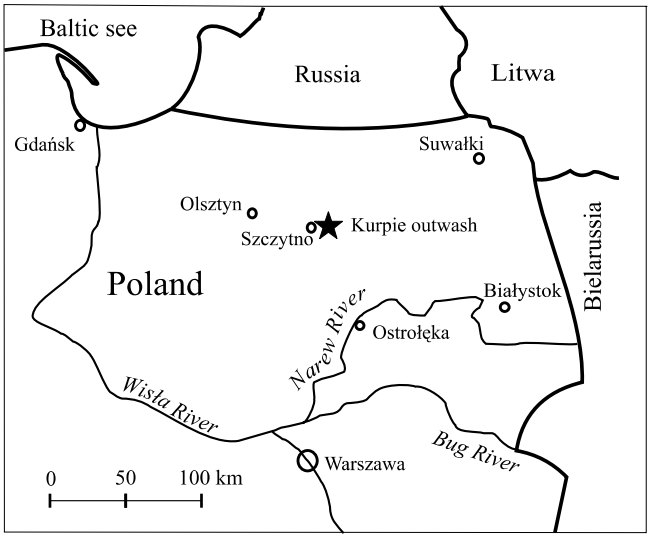

Fig. 1. Location of the studies area

MATERIALS AND METHODS

Adsorption of nitrate and ammonium ions has been studied using a "static method" (Osmęda-Ernst and Witczak, 1991) in order to determine the retardation factor for four soil types occurring in the unsaturated and saturated zones of the area of the Kurpie outwash, northeastern Poland (Fig. 1): outwash sands, clayey sands, sands enriched in ferruginous compounds (oxides and hydroxides) and sandy clays. In order to describe the phenomena taking place in the unsaturated zone, typical soils of this area have also been studied: brown soil, podsolic soil and boggy soil. Field observations of nitrogen compound migration in the unsaturated zone have also been made.

In the deposits studied (clayey sands and sandy clays of the Kurpie outwash) illite is the dominant clay mineral. In sands enriched in ferruginous compounds (iron content *ca*. 4%) goethite is the dominant ferruginous compound together with isomorphic ferruginous oxides and hydroxides indistinguishable by Roentgen methods (Table 1).

In order to evaluate the retardation factor of particular grounds, the specific adsorption of nitrate and ammonium ions has been studied. Adsorption isotherms were determined using a static method. For each soil sample, balance concentrations of nitrate compounds in the soil and in water for 5 different concentrations of nitrate nitrogen (between 1–50 mg $N\text{-}NO_3$/l) and for 6 concentrations of ammonium nitrogen (between 1–50 mg $N\text{-}NH_4$/l) were determined. Concentrations in the solution after obtaining the balance between the solution and the solid phase were determined using ion-selective electrodes, while concentrations in the soils were determined on the basis of the nitrogen mass balance. Results obtained by this method were interpreted using Freundlich, Langmuir and linear formulas describing the adsorption isotherms (Deutsch, 1997).

In all cases of nitrate adsorption and in most cases of ammonium, the best match was obtained for the Freundlich isotherm, described by the formula:

$$C_{ads} = K^F \times C_{aq}^{1/n}$$

where: C_{ads} — balance concentration of the studied compound in the ground; C_{aq} — balance concentration of the studied compound in the water; K^F and n — coefficients of the Freundlich adsorption isotherm.

The Freundlich adsorption isotherms, calculated using such method for selected soils from the Kurpie outwash area are shown in Figure 2 (nitrate) and Figure 3 (ammonium).

Substitute distribution coefficient (determined using the Freundlich isotherm) K_d^F for a given value of balance concentration of ion adsorbed in the solution equals (Osmęda-Ernst and Witczak, 1991):

$$K_d^F = \frac{K^F C_{aq}^{1/n}}{C_{aq}} = K^F C_{aq}^{(1/n-1)}$$

For the distribution coefficient determined on the basis of the adsorption isotherm, the retardation has been defined as (Apello and Postma, 1993):

Table 1

Selected parameters of the soils and soil investigated

Soil type	PH/H_2O	PH/KCl	Humus [% dry mass]	CEC [cmol(+)/kg]	Coefficient of permeability [m/sec]	Active porosity	Storage coefficient	Bulk density [g/cm^3]
Brown soil	7.3	6.9	2.43	5.9	4.6×10^{-5}	0.25	0.2	1.52
Podsolic soil	4.8	4.0	5.1	8.6	7.16×10^{-5}	0.28	0.21	1.45
Boggy soil	6.1	5.4	17.6	17.1	2.74×10^{-5}	0.22	0.17	1.27
Outwash sand	7.1	6.2	0	0.1	1.9×10^{-4}	0.32	0.23	1.67
Outwash sand enriched in Fe	6.3	5.7	1.2	0.4	1.23×10^{-4}	0.30	0.21	1.68
Clay sand	7.2	6.4	0.1	17.8	1.18×10^{-6}	0.1	–	1.89
Sandy clay	7.0	6.1	0	20.16	1.02×10^{-8}	0.035	–	1.98

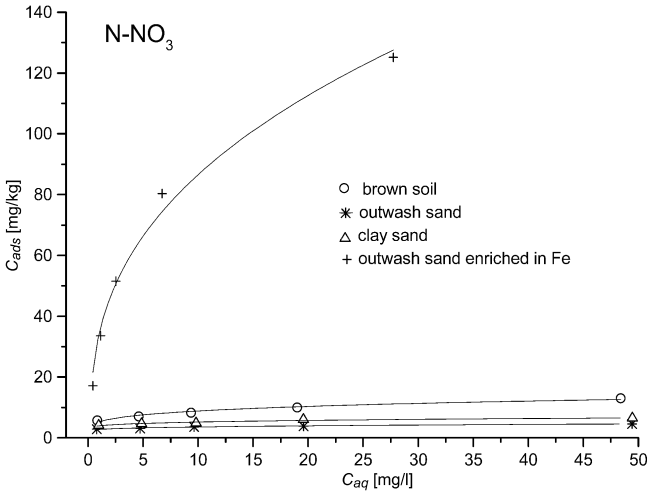

Fig. 2. Freundlich adsorption isotherms of N-NO_3 for selected groups and soils

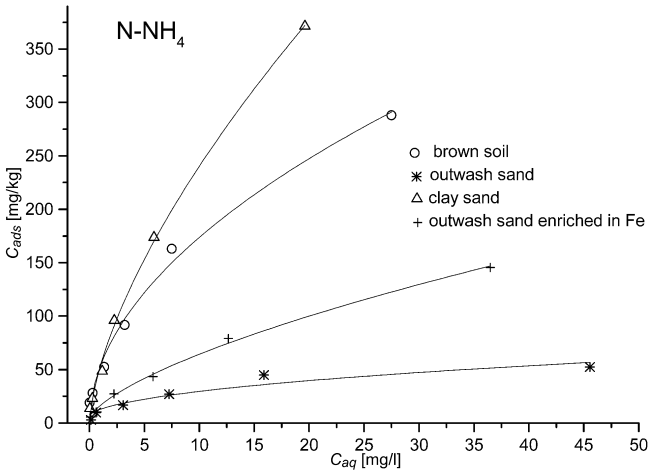

Fig. 3. Freudlich adsorption isotherms of N-NH_4 for selected grounds and soils

$$R = 1 + \frac{\rho_d}{n} K_d^F$$

where: ρ_d — bulk density of the aquifer (kg/dm^3); n_0 — active porosity.

RESULTS

The retardation factor (R) of nitrate and ammonium migration has been determined for various concentrations of these ions, found in the area of the Kurpie outwash, with average and extremely high values of fertilisation. The determined coefficients of adsorption isotherms and retardation factors for soils and grounds occurring in the unsaturated zone and for various concentrations of nitrate and ammonium ions are shown in Tables 2 and 3).

In the case of nitrate ions, the adsorption processes below a soil layer do not play a significant role in restraining the migration. The local occurrence of a layer enriched in ferruginous oxides and hydroxides is discernible in meadow areas. With pH close to natural (for infiltrating waters in the are astudied, *ca.* 6), the nitrate adsorption in this zone rises more than 10 times (Table 2). Although this zone has a limited thickness (*ca.* 10–20 cm), the effects of its influence are evident in the chemical composition of waters infiltrating into the unsaturated zone and into the groundwater, where the nitrate concentration is significantly lower than in other areas.

If the unsaturated zone is composed entirely of outwash sands, the adsorption of ammonium ions below the humus soil zone is of little importance in restraining their migration (Table 3). This is indicated also by a very low total cation exchange capacity (CEC) in sandy soils of the unsaturated zones (Table 1).

The occurrence of clay minerals in the unsaturated zone (clayey sands and sandy clays) substantially increases the am-

Table 2

Coefficients of adsorption isotherms and retardation factors determined for nitrate ions

Soil type	Sorption isotherm coefficient		Correlation	Retardation for concentration of N-NO_3 in water		
	K^F	$1/n$		10 mg/l	20 mg/l	50 mg/l
Brown soil	5.22	0.23	0.86	6.39	4.16	2.56
Podsolic soil	4.29	0.26	0.88	5.04	3.42	2.23
Boggy soil	6.25	0.25	0.87	7.42	4.81	2.92
Outwash sand — average/(min-max)	0.93 (0.65–1.14)	0.36 (0.24–0.45)	0.90 (0.85–0.94)	2.11 (1.59–2.68)	1.71 (1.35–2.15)	1.40 (1.17–1.69)
Outwash sand enriched in Fe	35.04	0.38	0.83	48.07	31.63	18.35
Clay sand	1.81	0.24	0.87	6.94	4.51	2.75
Sandy clay	3.27	0.14	0.81	26.54	15.07	7.40

Table 3

Coefficients of adsorption isotherms and retardation factors determined for ammonium ions

Soil type	Sorption isotherm coefficient		Correlation	Retardation for concentration of N-NH_4 in water		
	K^F	*1/n*		10 mg/dm^3	20 mg/dm^3	50 mg/dm^3
Brown soil	53.68	0.51	0.90	327.37	149.33	106.61
Podsolic soil	36.30	0.58	0.92	188.98	96.62	72.47
Boggy soil	152.51	0.80	0.85	888.40	639.10	556.49
Outwash sand — average/(min-max)	7.42 (7.23–7.74)	0.44 (0.35–0.48)	0.90 (0.87–0.92)	39.72 (38.73–41.39)	16.72 (14.25–18.49)	11.67 (9.45–13.20)
Outwash sand enriched in Fe	14.96	0.64	0.95	84.78	47.93	37.57
Clay sand	55.14	0.65	0.93	1043.15	594.32	466.51
Sandy clay	66.67	0.79	0.94	3772.62	2690.95	2326.56

monium ion adsorption. The adsorption values obtained for this ion in clayey sands and sandy clays are much higher than in the humus zone. Ammonium nitrogen washed out from the surface soil layer is retained in horizons containing large amounts of clay minerals.

COMPARISON OF LABORATORY RESULTS WITH FIELD OBSERVATIONS

The results of retardation factor determinations using laboratory methods are only estimated values. This is an effect of the study methods, based on assuming the achievement of adsorption balance between the solution and the solid phase. In natural conditions this state is rarely achieved during water flow. In spite of this shortcoming, the results obtained give an idea of the scale of the ongoing processes and of adsorption values in particular soil types. A partial confirmation of the results obtained comes from field observations of the variability of mineral nitrogen compound concentrations in the shallow aquifer of the Kurpie outwash (Mikołajków, 1999).

Two typical profiles of the Kurpie outwash unsaturated zone were studied:

— outwash sands *ca*. 2 m thick;

— fluvioglacial sands, clayey sands and tills *ca*. 3.8 m thick (including clayey sands and sandy clays *ca*. 1.7 m thick).

During the studies of nitrogen compound contents in shallow groundwaters that were collected by piezometers and wells, very distinct seasonal concentration variations were observed, connected with the inflow of infiltrating waters which, contain nitrogen washed out from the soils. Over a period of a year, in arable land areas, the recorded concentrations of nitrates were between 5–200 mg/l (annual average — 40 mg/l). The concentrations of ammonium ions were recorded between 0.05–0.9 mg/l (annual average — *ca*. 0.17 mg/l). Concentration changes in particular sample points, which could be unequivocally correlated with intensive infiltration, reached 20–40 mg NO_3/l and 0.2 mg NH_4/l. The greatest concentration variations of nitrate and ammonium nitrogen in groundwater was recorded following inflow of infiltrating meltwaters. A second period, during which a substantial rise of ammonium ion concentrations in infiltrating water took place, was during autumn rains in areas where cow dung was used for fertilisation (Mikołajków, 2001).

In the area of outwash sands a higher content of nitrate ions was recorded in groundwaters after *ca*. 25 days, while the maximum concentration of ammonium ions was recorded 4–5 months after the use of fertilisers. This shows that the retardation factor of ammonium ions in outwash sands is 6 times higher than that of the nitrate ions.

In the case of nitrate in groundwater below the clays, no distinct rapid concentration change was recorded which would suggest inflow of infiltrating water with increased amounts of nitrates. The period during which elevated contents of these ions in the groundwater were detected started about one month later than in the outwash region and lasted practically over the whole summer. The most probable cause of the observed character of concentration variations is a different timing of meltwater inflow, resulting from heterogeneous composition of the unsaturated zone, and a much slower water flow through poorly permeable ground. The observed time of nitrates flow through the aeration zone also points to minor retardation of the migration of these ions.

During the time of observations the concentrations of ammonium stayed at a level of 0.1–0.15 mg/l, despite much higher amounts of fertilisers containing ammonium being used than in the outwash area. No distinct changes of ammonium concentrations in groundwaters have been recorded. This indicates intensive adsorption and substantial retardation of ammonium migration in ground with high contents of clay minerals (illite).

CONCLUSIONS

Two basic features of the unsaturated zone determine the threat of contamination of shallow groundwater by mineral nitrogen compounds — filtration properties, on which the flow speed of the infiltrating waters depends, and the adsorption properties, determining the value of migration retardation. The chemical composition of the infiltrating water is formed in the biologically active soil layer. Below this layer, the possibilities of migration of the main nitrogen species occurring in ground-

water (nitrate and ammonium ions) are governed mainly by adsorption processes.

Because of insufficient verification of the results of laboratory studies in the field, the obtained values of retardation factor (Tables 1 and 2) should be treated as estimated values only. They allow, however, to evaluate the threat of polluting a shallow aquifer by mineral nitrogen compounds in agricultural areas with a variable composition of the aeration zone. Thus, there is only very small migration limitations of these compounds in areas where the aeration zone and the shallow aquifer are entirely composed of sands. In these areas both rapid water flow and the low retardation factor values indicate that the nitrogen which has left the biologically active zone penetrates very easily into groundwaters.

The value of the nitrate retardation factor (R) for various concentrations of this ion in water, determined in the laboratory, indicates little variation and does not exceed 5. Slightly higher values were obtained for tills, while the highest values were received for sands enriched in ferruginous oxides and hydroxides. In these deposits, and when the waters pH is below 6, the retardation factor even exceeds 40. This suggest the possibility of the phenomenon of anion nitrate adsorption, which has not been studied previously and recognised in Polish climatic conditions. In specific geological and hydrogeological situations of some parts of the Kurpie outwash, horizons enriched in hydrated ferruginous oxides and hydroxides occur, showing adsorption abilities with respect to nitrates. Such adsorption may cause retardation of nitrate migration. In the area studied such conditions occur mainly on meadows, where nitrogen load is not high, unlike the situation in the heavily arable lands contaminated. The existence of a poorly permeable layers with a high content of clay minerals, slows down the migration of nitrate ions, but has little influence on the total amount being washed into the groundwater.

A distinctly greater variation with respect to ground conditions is shown by the retardation factor of ammonium ions. The values determined by laboratory methods range from 10 for outwash sands to more than 3000 for sandy clays. This is true mainly for all poorly permeable deposits with high content of clay minerals, in which adsorption of ammonium cations takes place and strongly retards their further migration.

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