

Nitrate contamination of groundwater in the Republic of Lithuania

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In many countries nitrate contamination of groundwater has become a serious ecological problem and Lithuania is no exception. In fact, irrational, unbalanced development of the economy coupled with specific geological and climatic conditions have led to nitrate contamination on such a scale that it has become the object of interest for specialists of neighbouring countries.

Contamination is worst in the vicinity of fertilizer factories and intensely manured agricultural land. Excessive nitrogen concentrations, typically as nitrates, are common in unconfined groundwater which is vulnerable to direct contamination from the land surface and the atmosphere. In deeper aquifers, apparently relatively isolated from surface pollution, ammonium is prevalent. Nitrogen contamination of groundwater shows a clear increasing tendency with time.

Nitrogen compounds are not necessarily stable. They can be affected by various biochemical reactions. In these reactions, interconversion between nitrates, nitrites and ammonium can occur, as well as denitrification (i.e. loss to the atmosphere as nitrogen gas). Thus, groundwater can purify itself from such contamination with time.

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Introduction

Groundwater is the sole source of drinking water in Lithuania (summary map - Fig. 1). This is due to several factors; groundwater resources are very large (Juodkazis 1989, Juodkazis & Klimas 1991), there is abundant available recharge (annual precipitation averages from 540 to 930 mm), and geological conditions are favourable (the thickness of sedimentary rock cover varies from several hundred metres to two kilometres or more).

The upper aquifers are composed of glacial (e.g. Samogitian and Baltija Hills, Middle Plain - Fig. 1) and glaciofluvial sands and clays (e.g. Coastal lowland, Southeast Plain). Beneath these one can also find other fresh groundwater aquifers. It is calculated that potential fresh groundwater resources are around 3.2 million m³/day in Lithuania (Juodkazis 1989). Extensive surface water resources (rivers, lakes) also exist, but in many places these are polluted and not suitable for water supply.

During the past 30 years hydrogeologists have also investigated groundwater quality, and it is clear that groundwater is threatened by extensive pollution (Kondratas & Mikalauskas 1973, Mikalauskas 1976, Klimas 1979, Klimas 1990). Especially worrying is the threat posed to groundwater by nitrogen compounds (Zabulis 1988, Klimas 1990a, Klimas 1991), particularly by nitrates. Particular sources of

intensive nitrogen contamination are industry (e.g. Jonava factory for nitric fertilizers) and agriculture (e.g. large pig-breeding farms).

The studies of the current, and earlier, authors (Kondratas & Mikalauskas 1973, Klimas & Paukštys 1990, Klimas 1991) show that nitrogen contamination of groundwater is occurring over practically the whole territory of Lithuania. This phenomenon is largely due to regional pollution sources; i.e. atmospheric pollution and agricultural activity. The effect of the former is not great; only 5-10 % of groundwater contamination may be explained by atmospheric deposition ('acid rain'). The remaining 90-95% is the result of agricultural activity. The prominence of agricultural pollution is due to several factors. Firstly, during the past 50 years, an unbalanced agriculture, occupying an area of some 3.6 million hectares, has been developed. Increased crop-yields have been achieved almost purely by the use of mineral fertilizers, applied by aircraft with little attention being given to the actual requirements of the crops (fertilizers were spread both in autumn/winter and in spring). Typical applications have been around 299 kg active fertilizer per hectare. It has also been common practice to spread manure on the fields in wintertime. During the snowmelt floods, the manure-laden run-off became a source of contamination for surface- and groundwater alike.

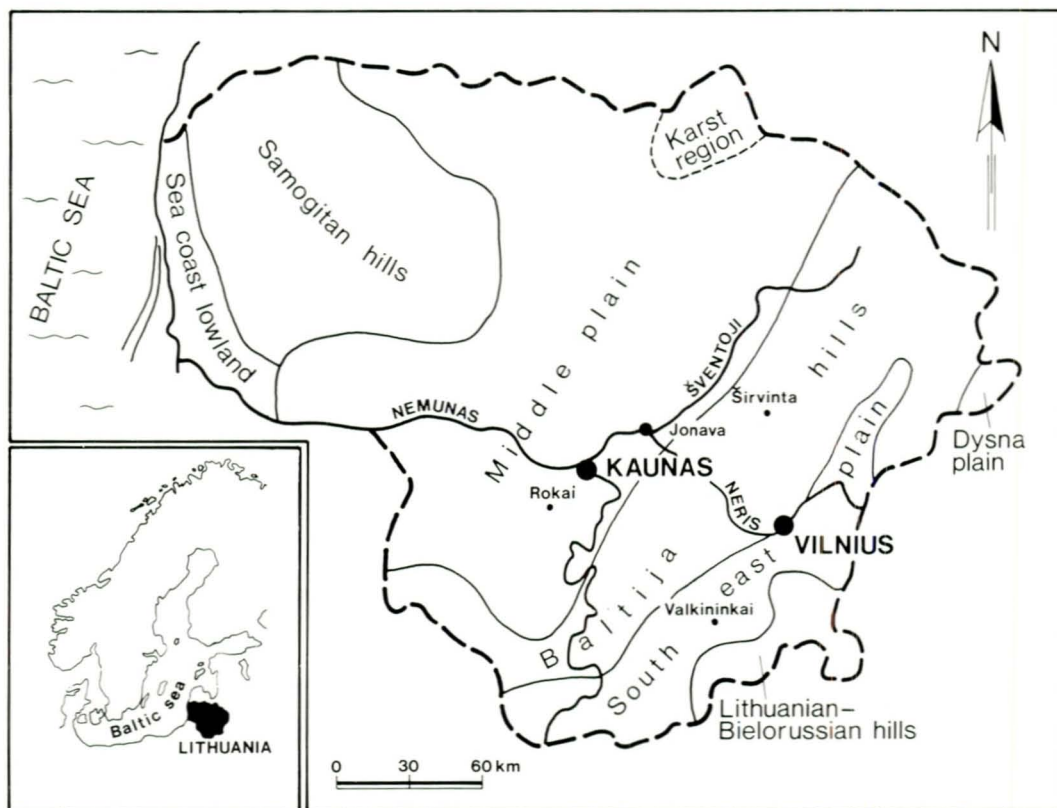


Fig. 1. Location map, showing the main geomorphological elements of Lithuania.

Nitrate contamination of groundwater is a source of concern the world over, e.g. in Great Britain (Foster et al. 1985), Czechoslovakia (Vrba 1985), India (Handa 1983), Republic of South Africa (Heaton et al. 1985), U.S.A. (Hallberg 1987) and Poland (Kowalik 1987). In many countries, it is observed that the nitrogen content of groundwater is increasing with time. The rate of increase has been determined in Belgium (de Smedt & Loy 1983), Denmark (Overgaard 1985) and Germany (Such 1985). It is noted that unconfined groundwater, having a direct connection with the atmosphere, is typically being contaminated by nitrates (Krainov et al. 1989). Reduced nitrogen species (ammonium and nitrite) are only found in unconfined groundwater at the centre of intensively contaminated areas (Klimas & Kadunas 1983, Zabulis 1988). The reduced species may, however, accumulate in deeper aquifers as a result of the reduction of nitrates (Botcher & Strebel 1985, Klimas 1990a, Klimas 1991).

The aim of this paper is to demonstrate the

extent of nitrogen contamination of groundwater in Lithuania, its lateral and vertical distribution, and the distribution of oxidised and reduced nitrogen species in the groundwater.

Nitrogen contamination - common features

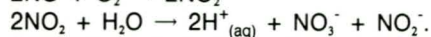
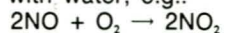
Groundwater contamination by nitrogen may be local (point-source) and regional (diffuse source). Sources of local contamination may be associated with:

- (a) towns and industry: sewerage systems, domestic and industrial waste disposal, stores of industrial and raw materials, anthropogenic deposits and others.
- (b) agriculture: stores of fertilizers and chemicals, silos, manure storage, large farms, settlements.

As regards regional contamination there are two possible sources: polluted atmospheric

deposition and agricultural activity. Burning of fossil fuels and some fertilizer factories contaminate the atmosphere with nitrogen compounds. In agriculture, organic and mineral fertilizers are the main source of nitrogen contamination (Gustafson 1983, Such 1985, Gerhart 1986, Scheffer & Walther 1988, Zabulis 1988).

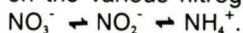
Nitrogen is a chemical element of variable oxidation state. In groundwater it may be found in the form of dissolved gases (NH_3 , N_2 , N_2O , NO , NO_2 , N_2O_3) or ions derived therefrom (nitrates (NO_3^-), nitrites (NO_2^-), and ammonium (NH_4^+)). Many of the gaseous nitrogen compounds are relatively soluble in water without being particularly reactive (N_2 , N_2O , NO), although on oxidation, they may react readily with water, e.g.:



Ammonia reacts with water to form a basic solution, i.e.:



but the greater part often remains in the solution in the form of dissolved ammonia (Krainov et al. 1989). Two main factors, oxygen and organic material, control the state of nitrogen in groundwater. The most stable form of nitrogen in oxidised environments is nitrate. In a closed system, dissolved oxygen is rapidly used up in the oxidation of organic material, whereafter oxygen from other dissolved species (e.g. SO_4^{2-} or NO_3^-) is consumed. The reduction of nitrates and nitrites to ammonium occurs after (i.e. at a lower Eh) reduction of iron and manganese oxides, but before (i.e. at a higher Eh) the reduction of sulphate to sulphide (Krainov et al. 1982). Bacterial activity is intimately involved in all the transitions between the various nitrogen species, i.e.



During the course of such transformations, a certain portion of nitrogen is liberated as nitrogen gas (N_2), i.e., the total amount of nitrogen in the system decreases due to the processes of biodegradation and biodestruction (Bottcher & Strebel 1985, Wolff et al. 1985, Trudel et al. 1986, Ronen et al. 1987, Zabulis 1988). The geochemical environment, as defined by the redox potential (Eh) and acidity (pH), determines the distribution of the various nitrogen species in groundwater (Krainov & Schwetz 1987). As the transformation reactions are equilibrium reactions, all three species (NO_3^- , NO_2^- , NH_4^+) are usually found, to a greater or lesser

degree, in groundwater at different pH and Eh values (Krainov et al. 1989, Klimas 1991).

The mechanism of the transport path of nitrogen compounds down to groundwater is rather complicated (Gustafson 1983, Gerhart 1986, Thiery & Seguin 1986, Scheffer & Walter 1988b). The main biochemical transformations take place in the soil. The amount of nitrogen leached out of the soil depends on many factors: climate, soil-type, quantity of fertilizers, their type and time of application, agricultural practice, etc. Biotransformation processes continue in the unsaturated zone, and some denitrification may occur, returning part of the nitrogen to the atmosphere. Thus, the concentration of nitrogen compounds in the unsaturated zone decreases with depth. Also, infiltration of sewage into the ground by means of septic tanks, infiltration plants and liquid manure spreading fields is commonly practised as a means of treating sewage effluent, and it has been shown that the majority of pollutants, including nitrogen, can reach the water table (Klimas 1988b). The infiltrated water initially contaminates the surface layer of the unconfined groundwater. The groundwater velocity, horizontal & vertical dispersion coefficients and hydraulic conductivity of underlying strata determine the further lateral and vertical spreading of the contamination (Klimas 1990c).

A phenomenon commonly observed in connection with local and regional groundwater contamination by nitrogen is that of vertical and lateral geochemical zonation (Zabulis 1988, Krainov et al. 1989). Typical of vertical zonation is a decrease in nitrates with depth and a corresponding increase in ammonium. In instances of regional contamination of deeper confined aquifers, the offending species is typically ammonium, derived from reduction of nitrate. In the case of local contamination a contrary picture has been observed; in the centre of intensive contamination, ammonium is usually dominant in near-surface groundwater, with nitrates becoming more common further from the centre. All these cases can be documented by concrete examples from Lithuania.

Methods

In all of the following hydrochemical investigations, standard analytical methods have been applied; pH and Eh have been measured in the field, and other parameters in the laboratory following preservation and storage of samples. Pilot studies of local groundwater contamination were

Table 1. Some indices of the unconfined groundwater quality in the region of the Jonava nitric fertilizer factory. Note that concentrations of nitrate and ammonium are referred to in mg NO₃⁻ or NH₄⁺/l throughout the paper, rather than mgN/l.

Unconfined groundwater sampling point (sampling depth, m)	Number of observation wells	Number of samples	Water quality indicators (arithmetic mean)				
			pH	Eh (mV)	NO ₃ ⁻ mg/l	NO ₂ ⁻ mg/l	NH ₄ ⁺ mg/l
Background groundwater quality (6 - 12 m)	3	30	7.2	130	0	0	0.2
Below the factory's ammoniac water reservoirs (6 - 8 m)	14	25	9.3	170	475	60	3000
Below the factory's emergency storage ponds (8 - 10 m)	5	15	7.5	400	19	0.15	2.1
Region of polluted precipitation (10 - 12 m)	7	40	7.4	400	46	0.03	1.2

carried out at specially equipped observation areas (Jonava nitric fertilizer factory, three pig-breeding farms, the karst region of North Lithuania, etc.)

For the studies of regional pollution of unconfined groundwater, some hundred drilled wells, and approximately one thousand dug wells were sampled. Intermediate confined and deep confined groundwater chemistry studies are based on the sampling results from approximately 3000 drilled wells.

Nitrogen compounds were analysed in the laboratory using standard methods such as Nesslerization and colorimetry.

Local contamination

The Jonava factory for nitric fertilizers is an example of especially intensive local industrial contamination of groundwater by nitrogen compounds (Klimas & Kadunas 1983, Klimas et al. 1988). The factory is built at the intersection of the valleys of two large rivers: the Neris and Sventoji (Fig. 1). Here, in the upper part of the geological section, alluvial sand and gravel deposits dominate. The total thickness of these sediments is typically 15-20 m. The deposits contain a saturated zone which is typically 5-12 m thick. Among the sources of groundwater contamination one can name (Table 1):

- emergency flows from ammoniac water reservoirs and infiltration of contaminated ammoniac-rich water from emergency ponds.
- infiltration of contaminated precipitation.

In the region of the factory's storage reservoirs and ponds, contaminated infiltration waters

mix with confined groundwater which discharges in the locality. The latter naturally has a small content of dissolved solids, but the contaminated mixture discharging into the valleys of the above-mentioned rivers is best described as a highly mineralized water, containing especially high levels of ammonium and sodium (cations) and nitrate, chloride and bicarbonate (anions). In the vicinity of the factory, precipitation is contaminated by ammonia, leading to a nitrate concentration in unconfined groundwater some tens times higher than the background level. The process of nitrification of ammonium begins in the atmosphere, continues in soil, and is completed in the aeration zone (Klimas & Zabulis 1984).

Large cattle-breeding and pig-breeding farms are the legacy of collective agriculture in Lithuania. During the past 15 years, more than 40 such farm-complexes have been built. The capacity of the pig-breeding complexes is around 12,000 - 54,000 pigs per year. The manure accumulated here is removed using water, and the resultant liquid manure is spread on fields. Due to poor technology, great quantities of liquid manure accumulate on the fields. In winter and spring, fields of a limited area are intensively manured (up to 700-1100 kgN/ha) when soils are still saturated. In this way, unconfined groundwater can be severely contaminated (Zabulis 1988).

Table 2. Chemical composition of unconfined groundwater below the manured fields of some pig-breeding farms. TDS = total dissolved solids, C_{org} = organic carbon.

Location (Aquifer)	Number of observation wells	Sampling depth (m)	Chemical composition of groundwater, mg/l				
			TDS	C _{org} dissolved	NO ₃ ⁻	NO ₂ ⁻	NH ₄ ⁺
Valkininkai (sand, thick unsaturated zone)	21	10-13 m	400 [300-1200]	10 [9-26]	15 [7-710]	0.2 [0.1-0.3]	1 [0.3-7]
Rokai (sand, thin unsaturated zone)	14	1-3 m	700 [400-2200]	39 [17-61]	450 [10-900]	1 [0.1-2]	3 [0.4-12]
Sirvinta (sandy loam)	9	5-7 m	1300 [200-2000]	45 [11-64]	30 [5-300]	2 [0-3]	30 [2-35]

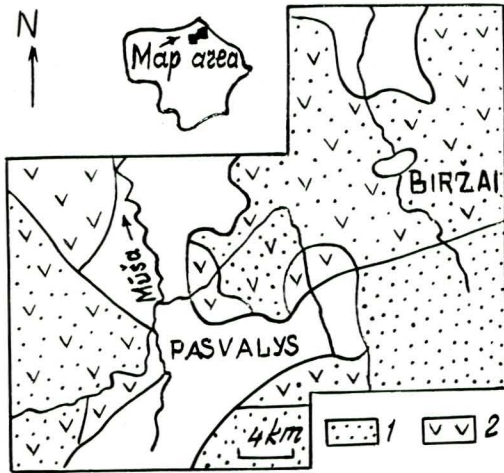


Fig. 2. Trends in pollution of karst groundwater in Lithuania. 1—areas in which karst water was already polluted by nitrogen compounds in 1978-1979; 2—areas in which indices of nitrogen pollution increased by more than a factor of two during a 10 year period.

excessive nitrate concentrations. Even further down-gradient, denitrification and dilution lead to an eventual attenuation of nitrate concentrations (Zabulis 1988).

The territory of North Lithuania possesses an outcrop area in excess of 1000 km² of gypsiferous Upper Devonian deposits (Paukstys 1991). The upper part of these strata is karstified. Recharge of groundwater typically occurs via the direct infiltration of precipitation on the outcrop area, and karst water discharges into small local rivers. In these gypsiferous rocks, a calcium sulphate groundwater, with a moderate dissolved solids content (2000 - 2500 mg/l) is typically found. Upper Devonian sands and sandstones underlying these gypsiferous strata typically contain fresh groundwater. Groundwater within a large area (about 400 km²) of the gypsiferous deposits is, however, wholly or almost wholly unprotected from surface contamination, and is therefore being intensively polluted by organic materials or

Table 3. The chemical composition of polluted groundwater in the karst region of North Lithuania.

Aquifer (Sampling depth, m)	Some indices of chemical composition, mg/l (except Eh, pH)									
	TDS	Ca ⁺⁺	Mg ⁺⁺	SO ₄ ⁼	Cl ⁻	Eh(mV)	pH	NH ₄ ⁺	NO ₂ ⁻	NO ₃ ⁻
Phreatic, sandy loam (borehole) (10-15 m)	352	61	27	32	12	<100	6.8	120	<0.01	2
Phreatic, dolomite (dug well) (10-15 m)	1063	154	64	101	135	330	6.9	<0.1	<0.01	180
Phreatic, dolomite (borehole) (20 m)	392	30	31	8	5	150	7.6	30	<0.01	<0.5
Deep confined, dolomite (borehole) (40-60 m)	365	22	31	4	5	120	7.8	45	<0.01	<0.5

The nitrogen in liquid manure is largely in the form of ammonium and organic nitrogen. If (a) the subsoil beneath the manured fields is sandy, (b) the unsaturated zone is thick and (c) the manure application is not very intensive (i.e. less than 300 kgN/ha in total), then the unconfined groundwater may escape excessive contamination. Such contamination as exists is typically in the form of nitrates (Table 2 - Valkininkai). Down-gradient from the manured field, denitrification and dilution by clean infiltration water result in a rapid attenuation of the contamination plume. If, however, the manured fields are underlain by more clayey, fine grained subsoil, with a relatively shallow water-table, and if manuring is intensive, heavy contamination by ammonium and organic material is most typical. Down-gradient, active oxidation of ammonium and organic nitrogen takes place in the groundwater, leading to

nitrogen compounds (Fig. 2). This is due to agricultural activity, particularly the application of mineral and organic fertilizers. Especially highly contaminated groundwater is found in the vicinity of cattle-breeding farms with stores of manure, silos, sewage and manure accumulators and fertilizer storage areas (Klimas & Paukstys 1990) — e.g. the first two rows of Table 3. The areal distribution of contaminated karst water areas shows a regular pattern (Fig. 2), reflecting very well the hydrogeological structure of the karst. The water is most contaminated in local areas of recharge (in interfluves and the upper reaches of small rivers) and least in the zones of discharge of karst water (in river valleys). This simplistic picture is, however, distorted by the abstraction of groundwater (Paukstys 1991).

The karstic groundwater is typically contaminated by ammonium, and the thermodynamic

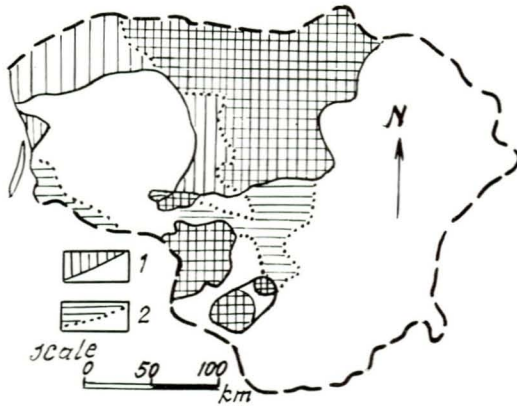


Fig. 3. Unconfined groundwater pollution and soil bonitet in Lithuania. 1—highly polluted unconfined groundwater; 2—soil bonitet in the range 50-100 (of 1st-5th class).

and biochemical stability of that species is consistent with a low redox potential (below 200 mV) and a neutral pH, around 7 (Krainov et al. 1989). In the water from wells in areas where the water has good access to the atmosphere, Eh values are much larger and nitrates prevail.

Regional pollution

Unconfined groundwater

In Lithuania, shallow unconfined groundwater typically exists within Holocene (alluvial, aeoli-

an, marine sand) and Pleistocene (glacial and fluviolacial sand, loam, and sandy loam) deposits. The chemical composition of such waters is very variable. It is, however, possible to show that the level of contamination is two to three times greater below more clayey, poorly-drained areas than below sandier, well-drained plains (Kondratas & Mikalauskas 1973, Klimas 1991). This difference is both directly and indirectly connected with the geology, as it is typically the more clayey areas which are most fertile (soil bonitet of 1st-5th class: note — in Lithuania, 10 classes of soil bonitet are in use) and thus the locations of most intensive agriculture (Fig.3).

In Lithuania, the nitrate concentration in shallow groundwater varies widely, from around zero to several hundred mg/l, but one can state that beneath about one third of the country the nitrate in unconfined groundwater exceeds the permissible drinking water standard (45 mg/l). Only in one eighth of the territory is the concentration less than 10 mg/l (Fig. 4a). Low nitrate concentrations are found only in the Coastal lowland and South-Eastern Lithuanian plains, where the agricultural activity is not intense, and the groundwater resources are large (Juodkazis & Klimas 1991). The organic material content of groundwater is similarly distributed: permanganate oxidation in the regions contaminated by nitrates gener-

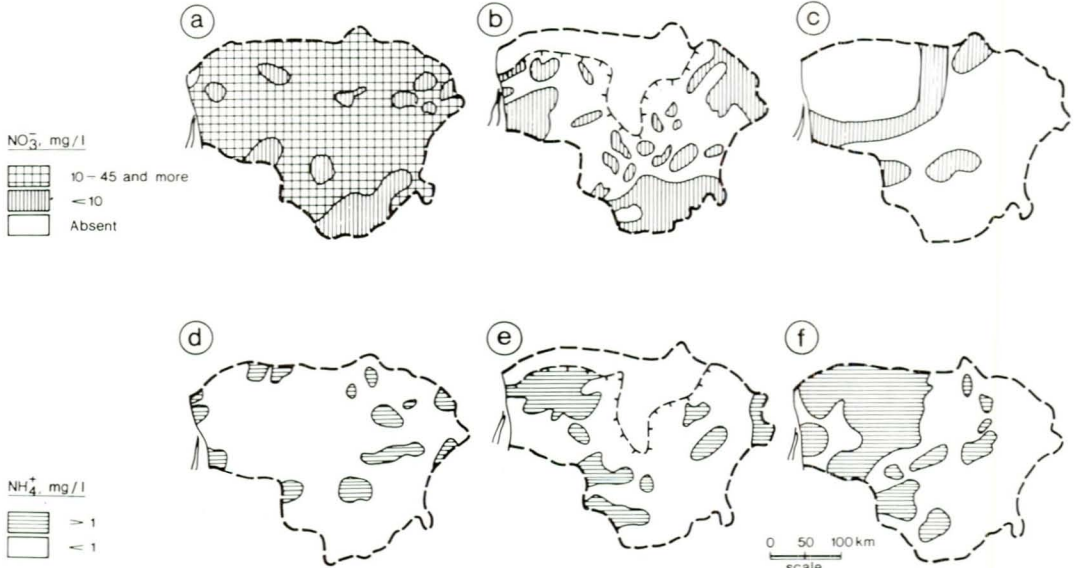


Fig. 4. Nitrate (a, b, c) and ammonium (d, e, f) concentrations in unconfined (a, d), intermediate confined (b, e), and deep confined groundwater (c, f) in Lithuania.

ally exceeds 5 mg/l and in some places it reaches 10 mg/l.

The amount of ammonium in unconfined groundwater is comparatively small; it exceeds 0.2 mg/l over only 10-15% of the territory (Fig. 4d).

Intermediate confined groundwater

This is the transitional type of groundwater between unconfined and deep confined groundwater. It is typically found in intermorainic deposits (Klimas 1991). In Lithuania, one or two such aquifers can typically be found in a vertical section through the Quaternary deposits, but in some places up to five or six can occur. They are usually hydraulically interconnected and may have good hydraulic contact with both underlying artesian water and overlying unconfined groundwater.

Intermediate confined water is commonly only minimally protected against anthropogenic pollution (Klimas 1990a). Therefore, where unconfined groundwater is contaminated, intermediate confined groundwater is generally also contaminated (Fig. 4a and b). It is clear that this occurs where contaminated unconfined groundwater recharges intermediate confined aquifers (i.e. a downward hydraulic gradient from unconfined to intermediate confined aquifers), most frequently in highlands. On the contrary, in plains and river valleys, where unconfined groundwater is sometimes highly contaminated, intermediate confined groundwater usually remains clean because the latter is protected by confining strata and generally by an upward hydraulic gradient.

The contamination pattern for intermediate confined aquifers is shown in Figs. 4b and e. Comparison of the diagrams shows that increased nitrate contents in intermediate confined water are found, not in Middle Lithuania where unconfined groundwater contamination is greatest, but in the marginal parts of the republic, especially in regions of high topography (i.e., in the recharge areas of intermediate confined aquifers). It is clear that the areas of intermediate confined groundwater contaminated by nitrates are much less extensive than those of unconfined groundwater. Nitrate concentrations in intermediate confined groundwater rarely exceed 10 mg/l whereas in unconfined groundwater the value is usually 3-4 times greater.

Comparison of Figs. 4d and 4e indicates that intermediate confined groundwater is

more areally extensively contaminated by ammonium than unconfined groundwater. These areas of ammonium contamination in unconfined and intermediate confined groundwater do not coincide. In intermediate confined aquifers the high ammonium values are found in areas where groundwater is better isolated from unconfined groundwater (limnoglacial plains, moraine dominated areas and the Samogitian highlands — see Fig. 1).

Deep confined (artesian) groundwater

In Lithuania, deep, confined water can be found in deposits of all geological ages, from Cambrian sandstones to Paleogene and Neogene sands (Juodkakis 1989). Such deep confined groundwater is one of the main sources for large, centralised water supplies in Lithuania. Only a small proportion of deep confined aquifers are, however, reliably isolated and protected from surface pollution. In recharge areas (topographical highs) deep confined groundwater is recharged from intermediate confined and unconfined groundwater. Due to intensive exploitation in West and Middle Lithuania, large areas of depressed groundwater head have been formed. Thus, some areas of natural discharge of artesian water have become areas of recharge, creating conditions suitable for the downward migration of polluted water to deeper confined aquifers (Klimas 1979).

Investigations reveal that deep confined water is only contaminated by nitrates to a limited extent (Fig. 4). The few areas of deep confined water with elevated nitrate concentrations do not coincide with areas of unconfined groundwater and intermediate confined water which are highly contaminated by nitrates. Klimas (1991) has noted generally higher concentrations of ammonium in deep confined waters than in intermediate confined or unconfined groundwater (Fig. 4f). The areas in which ammonium concentration exceeds 1 mg/l account for almost 20% of the territory of Lithuania. Ammonium accumulates comparatively well in the isolated deep confined aquifers of West Lithuania but is practically absent in the much less isolated, East Lithuanian, deep confined aquifers. A similar pattern can also be recognised in the distribution of organic material in deep confined water. It thus appears that the low nitrate and elevated ammonium contents typically found in deep confined

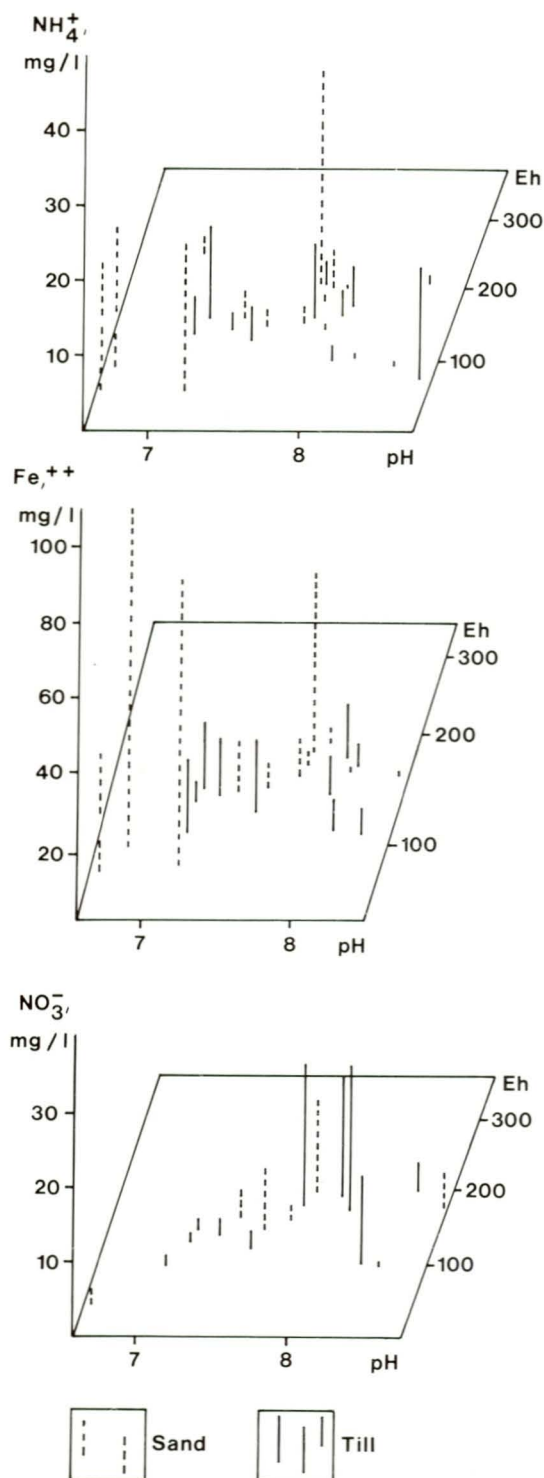


Fig. 5. Eh-pH diagrams for a) ammonium b) iron and c) nitrate in polluted, unconfined Lithuanian groundwater.

groundwater are the result of the chemical reduction of nitrate to ammonium (Klimas et al. 1988, Krainov et al. 1988, Klimas 1991).

Discussion

Investigations of local and regional groundwater pollution by nitrogen compounds in Lithuania reveal regularities in the pattern of contamination and allow one to predict its future evolution.

Redox potential (Eh) and acidity (pH) values reflect the processes of migration and transformation of nitrogen compounds in groundwater. Unconfined groundwater aquifers usually enjoy a good connection with the atmosphere and therefore exhibit high dissolved oxygen levels, commonly up to 7-10 mg/l, Eh typically exceeds +200 mV and pH is around 7. In such water one typically finds a limited range of nitrate concentration (2-10 mg/l). In centres of intensive contamination, practically all the oxygen is consumed by the oxidation of organic contaminants. The amounts of unoxidised organic material and ammonium show elevated values in such situations (see Table 2), and a corresponding reduction in Eh and nitrates (see Table 3) due to biochemical reduction by ammonification bacteria. The values of pH found at such contaminated localities vary widely (Fig. 5). These chemical conditions are especially noticeable in contaminated, unconfined groundwater aquifers occurring in clayey, poorly-drained areas.

Fig. 5 is compiled from studies carried out in fields sprayed with liquid pig-manure (300-600 kgN/ha) covering an area of 150 hectares. Unconfined groundwater is found at a depth of 0-5 m in sand, morainic sandy loam and loam deposits. It can be seen that the level of contamination of unconfined groundwater, composition of the contamination components and the values of Eh-pH of unconfined groundwater found within the comparatively small area vary greatly. A pattern can, however, be identified. Firstly, the nitrate concentration in sandy deposits is distinctly lower than in clayey ones (Fig. 5c). Furthermore, increases in NO_3^- concentrations correspond to increases in Eh and pH. In addition, the concentrations of ammonium and iron show a correspondence, and are related to depressed Eh and pH values. The dependence of ammonium and iron on lithology is not so distinct as is the case for nitrates.

A similar pattern can also be observed in

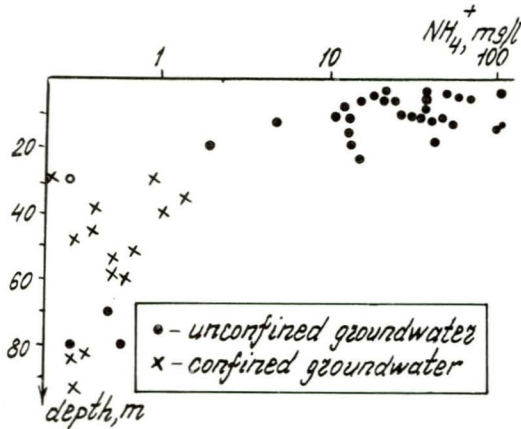


Fig. 6. Ammonium concentrations plotted against depth for the groundwater of the Lithuanian karst region.

the case of regional unconfined groundwater contamination. It has already been demonstrated that nitrate tends to be the dominant nitrogen species in unconfined groundwater in Lithuania. Only in limnoglacial clayey formations can elevated concentrations of ammonium be found (Fig. 4d). One exception, however, is the karst region of North Lithuania where fissured dolomites with interbeds and lenses of gypsum outcrop (Klimas & Paukstys 1990, Paukstys 1991). The groundwater within these is strongly polluted with organic material and contains practically no dissolved oxygen. Redox potentials are typically lowered to 60-180 mV, and iron concentrations can reach 8 mg/l (Paukstys 1991). Generation of methane and hydrogen sulphide can also be observed. Ammonium dominates among nitrogen compounds. The variation of its concentration with depth is presented in Fig. 6.

Fig. 6 demonstrates that in cases of intensive contamination, an inversion of oxidation-reduction zonation can take place: a zone lacking oxygen, with low Eh values, and enriched in ammonium is formed above an oxidised zone (areas 2 on Fig. 2).

On a regional scale, however, a normal zonation (Fig. 4) is typically observed, i.e. an upper, oxidised, nitrate zone over a deeper reduced ammonium-dominated zone. The fact that the amounts of ammonium and organic material in intermediate confined and deep confined aquifers are increasing with time indicates that the phenomenon is really connected with anthropogenic pollution. This increase is described by the following relations (Klimas 1991):

in intermediate confined water
 $NH_4^+ = 0.012 t + 0.411$ ($r = 0.39$)
 $P = 0.131 t + 1.61$ ($r = 0.82$)

in deep confined water
 $NH_4^+ = 0.0405 t - 0.02$ ($r = 0.46$)
 $P = 0.142 t + 0.32$ ($r = 0.75$)

where P = permanganate oxidation mg O₂/l, characterising the amount of readily oxidisable organic material in water
 t = time from the beginning of the analysis (1958) period, in years.
 r = correlation coefficient, significance level 0.5 %.

From these equations it follows that in deep confined water organic material has been present since before 1958 ($P \neq 0$, when $t = 0$), while the process of the accumulation of ammonium has begun later ($NH_4 \approx 0$, when $t \approx 0$). Furthermore, the correlation coefficient for ammonium is half that for organic material. This is presumably due to the instability of ammonium; with access to oxygen it readily oxidises to nitrite and eventually to nitrate.

The exploitation of confined groundwater can greatly alter the geochemical environment within aquifers. It can induce leakage of groundwater of a different chemical composition from strata above and below the exploited aquifer (Klimas 1979). For example:

- (1) water leaking to the aquifer from above is commonly enriched in oxygen and may thus lead to a progressive increase in the nitrate concentration in the exploited aquifer.
- (2) water leaking to the aquifer from above may, however, be strongly polluted with organic material and nitrogen compounds, leading to consumption of oxygen in the exploited aquifer and increasing concentration of ammonium.
- (3) water leaking to the aquifer from below (from deeper horizons) is usually oxygen-poor, leading to decreasing values of Eh and accumulation of ammonium in the exploited aquifer. All these cases can be observed at groundwater works in Lithuania (Klimas 1973, 1991).

Biotransformation of nitrogen compounds, accumulation of unoxidised organic material, and a decrease in Eh can greatly alter the geochemical environment in an aquifer, such that favourable conditions for the mobilisation of toxic microelements (including heavy metals) may be formed in these aquifers (Krainov & Schwetz 1987, Klimas 1988a).

Conclusions

Studies of groundwater pollution by nitrogen compounds have a long history. The information presented in this paper has been collected from groundwater monitoring data and from special hydrochemical maps compiled for individual aquifers. The analysis of this material indicates a complicated and rather ominous view of the pollution of the Lithuanian groundwater environment by nitrogen compounds. On the whole, it coincides rather well with the observations of such pollution in many other countries. Despite the complexity of the processes occurring in the subsurface, certain patterns can be identified in the data:

- 1) Groundwater is contaminated by nitrogen compounds locally and on a regional scale. There are many sources of local pollution, but only two sources of regional pollution – atmospheric pollution and agricultural activity.
- 2) Nitrogen compounds take an active part in biochemical reactions, and their speciation and concentrations in groundwater can vary. Eh and pH conditions are decisive in determining whether nitrate or ammonium is the dominant species.
- 3) Patterns in nitrate and ammonium distribution can be detected. These are expressed as vertical and horizontal zonation of redox potential and nitrogen speciation. In upper aquifer horizons, and in recharge areas of deeper aquifers, nitrates dominate and Eh is typically greater than +200 mV. In deeper aquifers, and especially in their transit and discharge areas, ammonium is dominant in groundwater, with Eh typically less than +200 mV.
- 4) In unconfined groundwater, with a comparatively good connection to the atmosphere and a sufficient amount of dissolved oxygen, nitrate is usually dominant. Only in the

centres of intensive pollution (e.g. manure spreading fields) where microorganisms are not able to oxidise organic material and nitrogen compounds, does ammonium dominate in unconfined groundwater.

- 5) The amount of nitrogen compounds in unconfined groundwater may decrease comparatively quickly due to denitrification, dilution by 'clean' precipitation (infiltration recharge). These processes proceed quicker in sandy deposits and more slowly in clayey deposits. Unconfined groundwater is therefore most strongly polluted by nitrate in the clayey plains region of Middle Lithuania.
- 6) In deeper aquifers where there is an increase in concentrations of unoxidised organic material due to progressive pollution, the groundwater environment becomes steadily more reducing, Eh values fall and nitrate is transformed to nitrite and eventually ammonium. The concentration of ammonium increases with time.
- 7) The increasingly reducing environment in deeper aquifers is one of the main reasons for the accumulation of some metals in groundwater. Major changes in geochemical conditions can be caused by groundwater exploitation. During such exploitation, not only regional groundwater flow patterns, but also hydrochemical zonation are disturbed. Exploitation can thus seriously influence the distribution, concentrations and speciation of nitrogen compounds in groundwater.

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