PRACE GEOGRAFICZNE, zeszyt 103

Instytut Geografii UJ
Kraków 1998

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NITRATE CONTAMINATION OF SHALLOW GROUNDWATER IN THE CARPATHIAN FOOTHILLS (SOUTHERN POLAND)

Abstract: This study, based on a rural area in the Carpathian Foothills, aimed to assess the extent of contamination to a shallow aquifer by nitrates. The aquifer is composed of flysch and molasse sediments deposited during the Alpine orogeny, dominantly fine to medium grained sandstones. Nearly all the sediments are folded, faulted or deformed. This makes the hydrogeology very complicated since there is a lack of continuity and hydraulic connectivity, but the aquifer has been simplified to a single unit approximately 20 m thick. Fine-grained loess overlies the flysch and molasse deposits. This wind blown deposit which was later reworked sub-aqueously, varies in thickness between zero and 15 m. The hydraulic conductivity of the loess is low, so it acts as a confining layer.

The range in nitrate content varied from to zero to almost 90 mg l^{-1}. The WHO limit is 50 mg l^{-1}. Nitrate can cause methemoglobinemia in babies and has been linked to stomach cancer. The highest nitrate concentrations were found in samples taken from wells situated in relatively high terrain. These areas have the lowest loess cover which protects the aquifer from contaminants. The nitrate concentration may also relate to the proximity to septic tanks. In most areas there are no sewage pipes and when a septic tank is placed up flow of a well there is high potential for contamination.

Currently the farming practices in Southern Poland are non-intensive. However Poland is developing very rapidly and practices may change. The potential for contamination by pesticides and other agro-chemicals must be assessed. Through investigating the vulnerability of the aquifer to nitrate contamination, future problems can be predicted and possibly prevented. A vulnerability assessment on this area concluded that the aquifer has very little protection from contaminants where there is no loess cover. Where the aquifer is confined, the aquifer is not very vulnerable to contamination. Recommendations include that farming practices take account of the need to protect drinking water sources and that where septic tanks are the source of pollution, either the tank or the well is re-sited, or an alternative supply is found.

1. Introduction

The foothills of the Carpathian Mountains are populated by a predominantly farming community. Most farms are very small and are used for subsistence rather

Fig.1. Position of study area.

Ryc.1. Położenie obszaru badań.

than commercial purposes. Farming methods are traditional and non-intensive, with low usage of artificial fertilizers and pesticides, thus agriculture is unlikely to provide a source of diffuse contamination to groundwater. Most households obtain water from a shallow hand dug well in their garden. In addition there are scattered public wells for those who do not have their own supply. Increasingly, piped water is available, but many people choose not to take this option because of the expense and their doubts about the quality of this water. However, the shallow wells are often dug close to potential point sources of contamination, such as septic tanks and manure heaps. Contamination from these sources is minimised by the legislation in Poland, but this legislation is not always obeyed, and accidental leaks may occur. There is concern that, as Poland develops, more intensive farming methods may be adopted, posing a greater risk of contamination. It is important to assess the potential effects on the drinking water resources and whether current practices are already rendering the water unsafe for consumption.

The area chosen for geochemical sampling and piezometry was the Stara Rzeka drainage basin. This is located in the foothills of the Carpathian Mountains in Southern Poland, 45 km east of Kraków (Fig. 1). The catchment has an area of 22.24 km^2 and an elevation of between 210 and 360 m above sea level. About forty per cent of the land is forested, with the remainder used as farmland or occupied by small villages. The greatest population density (which is always fairly low) is in the valleys, with the lowest density occurring in the far west and south-east of the catchment where forest dominates. The map (Fig. 2) shows the catchment with sampling points marked.

2. Hydrogeological background

The water bearing strata found in the Carpathian Foothills would not be considered an aquifer by most resource specialists, and are not included as an aquifer on the hydrogeological map of Southern Poland. The aquifer is composed of flysch and molasse sediments deposited during the Alpine orogeny. The sediments were mainly deposited as turbidites, debris flows and slumps, with some pelagic deposition. The sequence is dominated by fine to medium grained sandstones. There are also

Fig. 2. Site map of the Stara Rzeka catchment.

Ryc. 2. Położenie punktów poboru prób wody w zlewni Starej Rzeki.

siltstones, conglomerates and evaporites (gypsum and halite). Nearly all the sediments are folded, faulted or deformed. This makes the hydrogeology very complicated, since there is a lack of continuity and hydraulic connectivity between the small, localised aquifers. For this study, the system has been simplified, with the various stratigraphic units combined as a single aquifer unit.

The aquifer thickness varies rapidly with changes in geology and it is impossible to state the precise aquifer thickness at any point. Information gained from the householders who own and who may have even dug their well showed that wells were generally dug until hard rock was encountered and digging became impractical. Any rock too hard to dig may be considered to have limited permeability and therefore, in the absence of more detailed information, has been presumed to be the base of the aquifer. Estimates based on the information available indicate that aquifer thickness varies from about 10 to 25 m.

The hydraulic conductivity of the sediments is very variable. In the flysch, reported values range from 10^{-4} to 10^{-1} m d^{-1} (Małecka and Murzynowski, 1978). Hydraulic conductivities for the Miocene molasse are probably similar or lower, because the molasse is finer grained but less well cemented. The yield from the sediments is generally low. This is due to a number of factors; in some cases because the hydraulic conductivity is low, but frequently the hydraulic conductivity is relatively high but the strata are discontinuous.

Overlying the flysch and molasse deposits are loess-like sediments. These deposits probably act as a confining layer. Many of the wells investigated were seen to be overflowing, even at relatively high altitudes and the householders questioned often stated that the water in the well rose at the time of digging, indicating artesian conditions. The loess-like sediments have low hydraulic conductivity (around 10^{-3} m d^{-1}), principally due to fluvial reworking after deposition. The thickness of this confining layer varies from 0 to 15 m, being thicker in low lying areas.

The average depth to water, based on measurements at 70 sites was 3 m. Excluding springs, which may originate from shallow throughflow rather than true groundwater, the mean depth to water is 3.4 m.

3. Nitrates in groundwater

There are a number of possible sources of nitrates to the aquifer. These include fertiliser application (including manure) to arable land, discharges from septic tanks, leaks from sewage pipes and ploughing. In Southern Poland, farming methods are non-intensive and there is little application of artificial fertilisers, although a limited quantity of manure is used. There are almost no sewage pipelines in use since most houses have a septic tank. The septic tanks are likely to be a source of contamination to the aquifer, particularly when they are badly installed, old or leaky.

It is important to protect groundwater from nitrate sources because nitrates are extremely soluble, and are commonly not attenuated in the soil or unsaturated zone. In addition, nitrates are relatively stable, have low adsorptivity and high migration capacity. This is particularly true in karst and fractured rock aquifers where transport velocities are usually relatively high (Walther, 1991). Where transport velocities are low, nitrate levels are more likely to be lowered by bacterial decomposition. Nitrate contamination is a particular problem in shallow phreatic aquifers where the distance from source to abstraction point can be very short.

Nitrogen sources from septic tanks are mostly in the form of ammonium-nitrate (75-80%) with organic nitrogen making up the remainder (Hantzsche and Finnemore, 1992). Nitrification below the tank is very efficient at converting these nitrogen sources to nitrates, particularly in a well aerated soil. Some nitrate may be taken up by plants or microbes in the soil but these are considered to be insignificant nitrate sinks (Lance, 1972). Denitrification occurs where the soil has high organic carbon, high moisture and high pH.

4. The nitrate controversy

Nitrate is considered dangerous in drinking water because it can cause methaemoglobinemia (blue baby syndrome) where the concentration of nitrate is greater than 50 mg l^{-1}. This condition is occasionally fatal. There are also concerns that excessive nitrates in drinking water may cause stomach cancer. Some children exposed to high levels of nitrates have slower reflexes and may have slightly retarded bodily growth (Terblanche, 1991). Nitrate in itself is not poisonous but is converted to nitrite in the stomach by faecal organisms. Nitrite can then act as an oxidising agent on haemoglobin, creating methaemoglobin which inhibits the oxygen carrying capacity of the blood. Infants are particularly susceptible to this effect because foetal haemoglobin is more readily oxidised (Kross et al., 1992). Nitrites are suspected of causing stomach cancer by reacting in the stomach with amines and amides to form nitrosamines and nitrosamides which are causative agents for gastric cancer (Dahab et al., 1994). Nitrites are known to cause stomach cancer in rats, but whether this data can be extrapolated to humans is questionable.

Finally, in the midst of the controversy on whether nitrates are harmful or not, new evidence suggests that nitrates in the diet may have a beneficial role. Nitrites in the acidic environment of the stomach are broken down to nitric oxide gas. This gas, in combination with the hydrochloric acid naturally occurring in the stomach, is highly effective in destroying harmful bacteria such as salmonella and shigella (Bonner, 1996). So nitrates in water may actually protect the body against infection.

5. Sampling

Approximately fifty samples were collected from wells, springs and streams. The groundwater samples were collected from shallow, large diameter hand dug wells, which are used mainly for domestic purposes plus occasional farm uses. Some of the wells have small submersible pumps but frequently there is only a bucket on a chain. Although ideally three well volumes should be expelled from the well before sampling, this was not feasible with only a bucket and chain in wells with large volumes. Even when there was a pump, purging the well of tens of cubic metres would have emptied the well and left the household with no water for at least a day. This meant that in several cases the water sampled was not in equilibrium with the aquifer. In many locations however, where a pump was in regular use, it was reasonable to assume that the well had been recently purged. In any case, since the water is being assessed for drinking purposes, it is relevant to know the composition of the water in the state in which it is usually consumed.

Sampling points were chosen to cover as large an area in as much detail as was practically possible. The sampling programme was constrained by the distribution of wells, but where there were no settlements, springs were sampled instead. Often samples were taken linearly along a flowpath in an attempt to asses how the chemical composition of the water changes. In order to quantify the piezometry as accurately as possible, the depth to water was measured in 21 extra sites, along with the electrical conductivity.

6. Piezometry

The topography of the catchment was overlain by a contoured plot of measured water levels in the wells (Fig. 3) to compare elevation with piezometry. The map clearly shows that the hydraulic gradient is controlled by topography. Flow directions are towards the north-east of the catchment, consistent with the surface flow of the

Fig. 3. Plot of approximate piezometry with elevation.

Ryc. 3. Przybliżone położenie zwierciadła piezometrycznego na tle hipsometrii terenu.

Stara Rzeka. The mean hydraulic gradient from the west to the north-east is 0.01 and 0.03 from the south-east to the north-east. Approximately, if a hydraulic conductivity of 6 m d^{-1} an effective porosity of 3 % is assumed, then the groundwater velocity is 4 m d^{-1}:

$$v= \frac{K\, i}{n_e}$$

From Darcy's Law : Q = K A i

where: Q = flow m^3 d^{-1}

K = hydraulic conductivity, m d^{-1}

A = cross sectional area perpendicular to flow, m^2

i = hydraulic gradient (dimensionless)

v= velocity, m d^{-1}

n_e = effective porosity (dimensionless).

The piezometry is strongly controlled by topography, partly due to the relatively low permeability of this aquifer and also because most of the recharge infiltrates through the hills rather than the valleys. These factors create a hydraulic gradient from the hills in the west and south-east to the north-east. Where the loess is present, it acts as a confining layer. Using the calculated velocity of 4 m d^{-1} and the catchment length of 10 km, it is estimated it would take 6.8 years for water to completely flush through the catchment.

7. Nitrate Distribution

Nitrate concentrations show a very wide range from 0 to almost 90 mg l^{-1}. Nitrate concentration does not correlate with any other chemical species. This is primarily because almost all nitrate input is from anthropogenic sources.

A map of nitrate distribution and piezometry was constructed (Fig. 4). From this map it appears that the higher nitrate concentrations are in elevated areas, with the exception of site 7. This may be because the loess cover is thinner in higher areas. Although it appears from the map that nitrates increase with increasing topography, this trend is not statistically significant and needs to be confirmed by further analysis. There are several points to note from the map. Firstly, the pollution is not diffuse but highly localised with very high nitrates at only a few sites. Secondly all the sites (except site 7) with high nitrates are around the edge of the catchment. These areas have the thinnest cover of loess, but they are also the least densely populated. If most of the contamination were coming from septic tanks, then the areas with the greatest density of septic tanks would have the most elevated nitrate levels. This is not the observed trend and highlights the importance of the confining layer. Even where there is a high volume of potential contamination, nitrates are not reaching the aquifer. Either denitrification is occurring during the slow passage though the confining layer, or the water in the aquifer below has travelled from uncontaminated recharge areas, such as the forests to the west and south east of the catchment.

Fig. 4. Plot of nitrate distribution.

Ryc. 4. Koncentracja azotanów.

The thickness of the loess cover is significant because the time taken for nitrates to travel through the relatively impermeable loess is much longer than the travel time through flysch or molasse. A travel time calculated using chloride tracers and by measuring tritium levels has estimated the downward velocity to be 0.3 to 0.4 m per year (Bury, 1995). This very slow velocity would give ample time for the nitrate to be degraded by bacterial action. It is important to take into account that there may be faster pathways through cracks, tree roots and faults.

The high levels of nitrate at site 7 do not fit in with this theory, since it is positioned in a valley where the loess cover should be at its thickest. A sample taken within a few metres of this site (site 38) has low levels of nitrate, indicating that the contamination has not migrated very far. The well at site 7 may be particularly close to a septic tank, or to another source of nitrate contamination.

Both the evidence from the major ion geochemistry and the nitrate distribution highlight the lack of hydraulic connectivity between the lithologic units. Both the sulphate and the nitrate distribution show highly localised peaks. This indicates that groundwater is not moving rapidly through the aquifer and where contamination occurs, it is not likely to migrate rapidly or very far.

In conclusion, there are probably two factors controlling the nitrate distribution; firstly the thickness of the loess cover and secondly the condition and position of septic tanks. Generally where the loess cover is thick, the nitrate contamination is not reaching the aquifer. However there are exceptions to this where the wells are very close to a source of contamination. More work needs to be done to investigate how often high levels of nitrate are found at high altitudes and how many are just randomly scattered throughout the catchment.

8. Potability of groundwater

The groundwater of the Stara Rzeka catchment is generally of very high quality with low dissolved solids and nitrates. However there are a few notable exceptions. One well (site 4) has a high sulphate concentration of 1592 mg l^{-1}, far above the World Health Organisation (WHO) limit of 400 mg l^{-1}. Although this level of sulphate has more affect on the taste of the water rather than major health risks, it is still a cause for concern.

Nitrate levels in the majority of the samples are less than the WHO limit of 50 mg l^{-1} but there are 6 samples (sites 1, 7, 14, 15, 59, 60) with high nitrate concentrations, up to almost 90 mg l^{-1}. Nitrate concentrations at this level probably do not pose a significant risk to health but should be monitored to ensure that they do not rise to a dangerous level. There are several other sites with moderately high nitrate levels, between 10 and 50 mg l^{-1}, sites 3, 8, 12, 16, 38, 39, 40 and 43. Although these concentrations are below WHO limits again they should be carefully monitored.

9. Vulnerability assessments

A number of systems for assessing vulnerability are available. For the Stara Rzeka catchment, the GOD method devised by Foster (1987) was found to be the most appropriate. An assessment using this method found that where the aquifer is protected by loess, it is not susceptible to contamination. Where there is no loess cover, however, the aquifer has a high vulnerability rating. The aquifer is vulnerable in unconfined areas because the depth to the water table is shallow and the lithology is relatively permeable. The vulnerability assessment is supported by evidence from the contaminant distribution which indicated that the unconfined areas are often contaminated in contrast to the confined areas.

10. Recommendations for future research

Many of the conclusions reached by this investigation are based a small number of samples. To confirm the findings of this study it is necessary to undertake extensive monitoring and to analyse samples from more sites. In particular, the sites where high nitrate concentrations were found should be re-sampled a number of times to monitor whether situation is deteriorating or improving. An investigation into the presence of coliform bacteria in the wells would confirm whether the contamination is coming from septic tanks or otherwise.

The control of lithology on hydrogeochemistry could be assessed by comparing more hydrochemical parameters with the nature of the strata from which samples were collected. Initial results show that there may be a control but more samples need to be analysed to confirm whether this is an actual or just apparent relationship.

This project has shown the need to protect groundwater resources even in low-technology rural areas. This is particularly true where the aquifer has no protection from a confining or semi-confining layer. The only way of preventing contamination from septic tanks from reaching the wells would be to resite the well or the tank. If the farming methods become more intensive, then legislation must be adapted to protect high vulnerability aquifers from becoming irretrievably contaminated.

Acknowledgements

The authors wish to thank NERC for providing financial support to Jill Ellis throughout the MSc and TEMPUS for financing the expedition to Poland. Thank-you to the staff of the Jagiellonian University for providing data, instruction and invaluable support, in particular; Wojciech Chełmicki, PhD for supervising the project and his help in providing all the background data for this project; Stanisław Leszczyński, PhD for his advice on the geology of the Stara Rzeka catchment, and the staff and students at the Łazy Research Centre for their time and patience when faced with endless requests for help, these staff include; Mariusz Klimek, MSc, Anna Tutaj, MSc, Mirosław Żelazny, MSc and Danuta Szewczyk. Thanks are also due to the other students on the Hydrogeology MSc course, in particular Mark Hall for his assistance in Poland.

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Skażenie azotanami płytkich wód podziemnych Pogórza Karpackiego

Streszczenie

Celem pracy jest ocena stopnia skażenia azotanami płytkich wód podziemnych w zlewni Starej Rzeki na Pogórzu Karpackim koło Bochni. Azotany zawarte w wodach pitnych stanowią istotne zagrożenie dla zdrowia, zwłaszcza dzieci.

Zbiornik wód podziemnych na badanym obszarze tworzą utwory fliszowe i molasowe, w których dominują drobno- i średnioziarniste piaskowce. Występują ponadto zlepieńce, utwory ilaste i ewaporyty przykryte pylastymi utworami lessopodobnymi o miąższości do 15 m. Liczne deformacje tektoniczne powodują, że warunki hydrogeologiczne odznaczają się znacznym stopniem złożoności i brakiem ciągłości. Dla uproszczenia przyjęto, że wymienione wyżej utwory tworzą jednostkę hydrogeologiczną o miąższości 20 m, przykrytą utworami lessopodobnymi o zmiennej miąższości.

Koncentracja azotanów w wodach podziemnych jest zróżnicowana; od 0 do prawie 90 mg l^{-1} (ryc. 4), wobec wartości dopuszczalnej wynoszącej 50 mg l^{-1} (wg WHO). Najwyższe koncentracje azotanów stwierdzono w wodach studzien położonych w obrębie elewacji terenowych pozbawionych miąższej pokrywy utworów lessopodobnych, mogących izolować wody podziemne od zanieczyszczeń docierających z powierzchni terenu. Wysokie koncentracje azotanów stwierdzono także w sąsiedztwie szamb.

Zakładając wzrost intensyfikacji rolnictwa w przyszłości, można się spodziewać wzrostu skażenia wód podziemnych nie tylko azotanami, lecz także środkami ochrony roślin i innymi substancjami stosowanymi w rolnictwie.