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Nitrogen leakage from different land use types – a comparison between the watersheds of Graisupis and Vardas, Lithuania.

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Preface

This paper was made in order to achieve a master degree in physical geography at the Department of Physical Geography, Lund University, Sweden. Supervisors were Mr Ulrik Mårtensson at the Department of Physical Geography and Mr Antanas Sigitas Sileika at the Lithuanian Institute of Water Management. The paper is directed to anyone with an education in natural science at university level, which can use this study to improve their knowledge about nitrogen leakage from terrestrial systems.

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Key words: Lithuania, nitrogen, conductivity, land use.

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Abstract

Eutrophication problems in the Baltic Sea have drawn attention to the contribution of nutrients from surrounding countries. The problems have attracted considerable attention to non-point source nitrogen pollution of rivers and lakes. The ability to predict nitrogen export from inland sources is essential in order to evaluate the effects of anthropogenic activities, of which the leakage from agriculture is one.

In this study the nitrogen leakage from different kinds of land use is investigated in Lithuania. The overall aim is to develop an easy, fast and cheap methodology, in order to measure nitrogen leakage. Thus, a method used in the Genevad drainage basin, Sweden, was applied (Wickberg, 2000). The latter uses an established relationship between nitrate/nitrite and conductivity in order to count for the nitrogen leakage. Another part of the aim is to present a new method of land use mapping at the Lithuanian Institute of Water Management. The study includes a comparision between the watersheds of river Graisupis, an agricultural region, and river Vardas, in a more hilly part of the country.

In order to carry out the study, land use maps, based on aerial photos from 1995, was created and water samples were collected and analysed. The data material was then analysed and presented with statistical- and GIS- methods. A Digital Elevation Model (DEM) was used together with an application written in Visual Basic 6.0, in order to isolate sub-drainage basins, which were used in the analyse of leakage.

The results show that there is no significant relationship between conductivity and nitrite/nitrate in either of the two watersheds. Thus, the regression equation for these two variables could not be used to count for the nitrogen leakage from different land use classes using the collected conductivity values. This shows that the method used in the Genevad drainage basin is not valid in the study area, and thus the overall aim of the study (easy, fast, cheap) could not be achieved. When instead using the measured conductivity values, in order to observe the leakage of nutritive salts from different land use classes, they show that there is a high leakage from forest in both watersheds. Also, the correlations between the distribution of a specific land use class and the amount of nitrogen in the river, show a small significance only in forests in Graisupis. Thus, forest seems to affect the leakage of nutrients. However, riverine transport of nitrogen cannot only be based exclusively on land use. Other catchment characteristics must also be considered in order to understand the influences from different processes concerning nitrogen leakage.

1. Introduction

The Baltic Sea in northern Europe is a brackish waterbody where eutrophication is considered a serious problem by the surrounding countries. Discharges of nutrients to The Baltic Sea during recent decades have had severe effects on the environment. The most dramatic examples are the death of fish and crustaceans, algal blooms and the expansion of anoxic bottom areas. The development is caused by an increased load of both phosphorus and nitrogen, however recent research has shown that currently it is primarily the supplied nitrogen that is causing the increased primary production that has given rise to the above effects (Leonardsson, 1994). Trend analysis shows that the nitrogen concentration has increased within the Baltic Sea during the last twenty years (Sandén and Rahm, 1993 - in Arheimer, 1998), and the nitrogen load is estimated to be four times higher than it was one hundred years ago (Larsson *et al*., 1985). With these facts in mind it is necessary to limit the transport of nitrogen to coastal areas, and action has to be taken on land in order to improve seawater quality (Leonardsson, 1994).

Human activities may increase the nutrient leakage to lakes, seas and streams, and it is proven that anthropogenic nitrogen emissions to the Baltic Sea come from rivers, atmospheric deposition and coastal point sources. The riverine load represents more than 60 per cent of the total load to the sea (Stålnacke, 1996 – in Arheimer, 1998). In each river, the nitrogen transport reflects specific land-use activities and point sources within the river basin (Arheimer and Brandt, 1998). Some anthropogenic activities cause nutrient leakage from forestry and agriculture, straightened ditches in agricultural areas, lowering of lake surfaces, and failure to clean sewage water from cities and industries (KTH, 1996). The ability to predict nitrogen export from catchments is essential in order to evaluate the effects of anthropogenic activities on the trophic status of streams, lakes and sea areas (Lepistö *et al*., 1994). Solutions of nutrient problems demand catchment-based knowledge of nutrient transport processes, and it is important to identify fundamental key processes for nutrient transport in different settings (Arheimer and Lidén, 1998). Thus, there is a need to reduce the nitrogen load to the marine environment through control of the nitrogen transport in streams (Leonardsson, 1994).

The annual loading of nitrogen to the Öresund, the Belt Sea, the Kattegatt and Skagerak from Sweden, Denmark, Norway and Germany is about 260 000 tons. The nitrogen derives from agriculture (50 %), the atmosphere (30 %) and other sources (20%). The loading from the Baltic States is 1 350 000 tonnes a year and the contribution from agricultural activities is estimated to 40-50 per cent. Lithuania is part of the Baltic Sea catchment. Pollutants reaching water bodies within Lithuania will end up in the Baltic Sea, mainly through the river Nemunas (Sileika *et al*., 1998).

Thus, there is a need to control the nitrogen transport in inland streams and rivers. Normally, most riverine nitrogen originates from non-point sources and thus it is difficult and expensive to construct a satisfactory picture of soil leakage and water transport based only on measurements. Nowadays models are usually applied in these kinds of studies, one example is the HBV-N model. A model is here defined as a mathematical approach to N-transport estimations, and there are a large number of models available (Arheimer, 1998).

1.1 Background

The Helsinki Commission adopted a long-term programme in 1992 with the aim to restore the ecological balance of the Baltic Sea through policy and institutional reforms, institutional strengthening, human resource development and infrastructure investments. This programme, called the Baltic Sea Joint Comprehensive Environmental Action Programme (JCP), is a twenty-year duration project. Through the Baltic Sea Environmental Action Programme the Swedish University of Agricultural Science (SLU) has allocated money from the Swedish government to reduce pollution from agriculture in Estonia, Latvia, Lithuania, Poland and Russia (St. Petersburg and Kaliningrad district). The Baltic Environmental Agricultural Run-off Project Group (BEAROP) was appointed to carry out one part of the programme, which is called the Baltic Agricultural Run-off Action Programme (BAAP). BEAROP consists of a group of experts from SLU, the Swedish Institute of Agricultural Engineering (JTI) and the Swedish Board of Agriculture. The long-term strategy of the BAAP programme is implementation of sustainable agriculture practice in Lithuania through monitoring, demonstration and education activities in two small watersheds and demonstration farms. These watersheds are the rivers of Graisupis and Vardas (Sileika *et al.,* 1998).

Lithuanian Institute of Water Management (LIWM) is part of this BAAP project. This paper was initiated by an initiative of cooperation between LIWM and the Department of Physical Geography in Lund. LIWM is interested in using some of the results and to take part of the methods used in this project. The idea to the project came from a Swedish study in Genevadsån, Halland. In the river of Genevadsån a strong relationship between conductivity and nitrate has been established with statistical methods (Wickberg, 2000). This relationship shows that in Genevadsån the nitrate determine the conductivity value in the river. It could be interesting to examine if this relationship existed, and could be used, anywhere else than in Halland. The overall objective of the study is therefore to examine an easy way to detect nitrogen leakage without using a model, and to improve the knowledge, of both the authors and the readers, of factors affecting nutrient leakage.

The effects of nutrient leakage on lakes and seas – eutrophication - are not discussed in this paper, nor are the problems involved with other nutrients, like phosphor.

2. Aim

Nitrogen leakage comes from both point sources and non-point sources. This paper investigates how land use, which is a non-point source, may affect the leakage. A common problem is that it is expensive to measure and count for the non-point leakage. Therefore the overall aim of this project is to develop and evaluate a fast, easy and cheap kind of investigation to briefly find out how much different kinds of land use affect stream water.

Specific aims

1. The first aim is to suggest a new strategy for land-use mapping at LIWM, using aerial photos and GPS. Land use maps are created for the watersheds of the rivers Graisupis and Vardas.

2. The second aim is to apply the method used in Genevadsån, Halland (Wickberg, 2000) in the watersheds of Graisupis and Vardas, and investigate if it is possible to establish a valid relationship between conductivity and nitrate.

3. If a relationship is found, the third aim is to use this relationship in order to calculate the nitrate leakage using conductivity values collected along the rivers of Graisupis and Vardas.

4. The fourth aim is to show how a different kind of land use affect the amount of nitrogen leaking from terrestrial systems into the two rivers.

3. Lithuania

In this chapter the country of Lithuania is presented. The intention is to get an overview of the geographical information concerning the country. In order to understand the complex of problems concerning the environment it is important to have a brief overview about the history of Lithuania, the country's agricultural development, and its influence on the environment.

3.1 Geographical information

Lithuania is situated between 54°-56.5° Northern latitude and 21°-27° Eastern longitude and has an area of 65.3 thousand km^2, figure 1.1. In the beginning of 1997 the population was about 3.7 million, and 32 per cent of the population were rural. Compared with other countries in Europe Lithuania is sparsely populated, and density of population is only 57 inhabitants per km^2. Farming land occupies 50 per cent of the country, forests cover 27 per cent and urban areas 17 per cent. The largest river basin is that of Nemunas that drains 73 per cent of Lithuania as well as portions of Belorussia, Poland and Kaliningrad District. The Nemunas river basin is a "hot spot" concerning agricultural runoff of nutrients to the Baltic Sea (Sileika *et al.*, 1998).

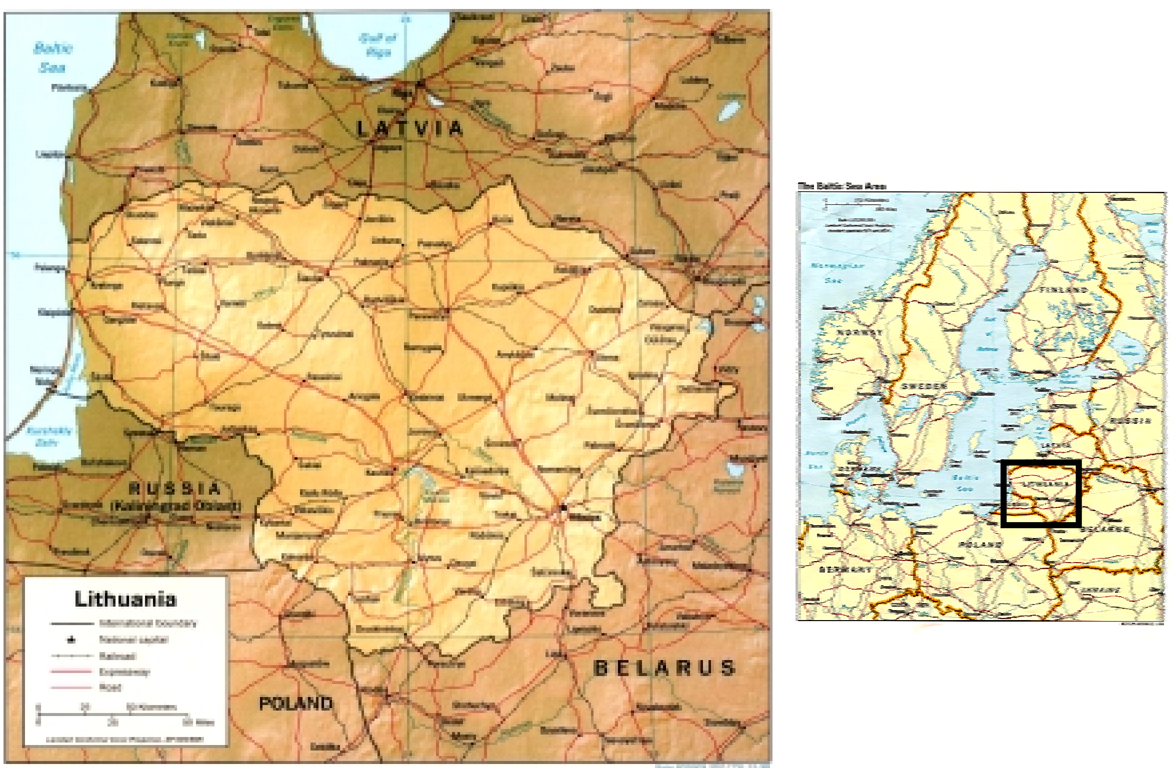


Figure 3.1 *The country of Lithuania and its geographical extent in the Baltic Sea area (Internet 6).*

The average annual temperature is +6°C and the average precipitation is 630 mm year^{-1}. There are differences in climate across the country and it is influenced by both sea and continental factors. The western parts have a warmer and a more maritime climate than the eastern part, which has a cooler and more continental. This makes the climate both a Cfb and a Dfb climate according to Köppen´s climate classification system (Ahrens, 1994). The dominating air masses come from the Atlantic Ocean (National Encyklopedin, 1993).

Lithuania is mainly lowland covered with a thick moraine cover. Sedimentary rocks make up the bedrock and they have no or little influence on the topography. The ice sheet has formed the surface and the lowlands are dominated by fine textured soils in a north-south direction. A glacial valley that has been filled with sand, gravel and stones has formed narrow lowland in the southeast. In some places the sand has formed dunes. A northeastern fraction of the Baltic moraine ridge branches through the eastern and southeastern parts of Lithuania. The terrain is hilly and there are several lakes and depressions. The moraine ridge reaches the highest point of Lithuania, Juozapine, 294 above sea level. The western parts of Lithuania also consist of a slightly undulating landscape and here the soils are deeply leached with low carbonates. The most characteristic soil is soddy podzols (Sileika *et al.*, 1998 and National Encyklopedin, 1993). Just as in Sweden spruce and pine, the latter mainly on sandy soils, make up the dominating forest. Deciduous forests are rare but mixed deciduous forest exists with species like oak, maple, elm, lime, ash and hornbeam (National Encyklopedin, 1993).

3.2 History of Lithuania and its agriculture

The state of Lithuania was established at the beginning of the 13th century. The Grand Duchy of Lithuania was a powerful state in eastern Europe until the middle of the 15th century. The country was later divided several times, and in 1795 the country was allotted to Russia. Lithuania regained independence only after First World War in 1918. In 1922 the agricultural reform started and promoted the establishment of individual farmsteads and created favorable conditions for the development of agriculture (Sileika *et al.,* 1998).

Lithuania was occupied again by the Soviet Union in 1940. After that land ownership was restricted and later economical and physical liquidation of landowners started. In June 1941 mass deportation of private farmers to Siberia began, but German occupation during the Second World War interfered with these processes. Soviet occupation was restored after the end of Second World War, and in 1948 the collectivization process became more rapid. All farming land was transferred into collective and state farms - kolkhozes. From 1965 tile drainage was installed on the area of 2.5 million ha, more mineral fertilisers were allotted and the energy supply was improved. However, even with these measures agricultural production grew very slowly (Sileika *et al.,* 1998).

The crop production in the former Soviet states around the Baltic Sea, including Lithuania, was extremely low compared to other countries in the same area. Input of fertilisers was higher than in the western countries, and the strategies for farming were of lower quality regarding both timing and quantity. This depended partly on bad technology, mismanagement, and central management disregarding local variations. Especially the biological demands on technology were ignored (Carlson *et al*., 1999).

3.2 Agriculture today

The land reform started in 1990, when Lithuania became an independent country, and privatisation started in 1991. During March 1993 previous collective and state farms were transformed into 3760 agricultural companies and enterprises. Some companies went bankrupt and others decided on self-liquidation. About 1000 companies continued farming on 12.6 per cent of the total agricultural land. Agriculture accounts for 21 per cent of the labour force in Lithuania today (Sileika, 1999 and Sileika *et al*., 1998)

Before 1990 agricultural export was an important possibility for producers to sell their products in the East. About 40 per cent of the agricultural products were sold there, and a large part to the former Soviet Union. Agriculture was before 1990 highly dependent on energy and export to former Soviet Union. Nowadays the eastern market is limited because Lithuanian products are too expensive, and there are other risks due to the economic situation in Russia. Since 1989 agricultural production has drastically declined. The agricultural output in 1995, together with crop and livestock production, was 50 to 69 per cent of the production in 1989. However, the decrease of agricultural production has stopped and processes towards stabilisation and development has started after 1995 (Sileika, 1999 and Sileika *et al.*, 1998).

The use of mineral fertilisers declined very much from 1990 to 1994 due to high prices and limited financial possibilities of the farmers to buy them. However, application rates for both fertilisers and plant protection products have increased on all farms since 1995. However, the impact of agriculture on the environment was significant despite the hard economical conditions in the period from 1990. Despite the fact that fertilization rates were lower the crop production did not decline so much, and this shows that the nutrient storage in the soil is large, figure 3.1. This is also confirmed by the fact that nitrogen (nitrate) in surface waters flowing through agricultural regions did not decrease during 1990-1992. In fact, nitrogen content increased five times. Since 1993 surface waters have started to improve, but it is still worse than before 1990. Agricultural production started to increase in 1997 and a there is also a higher load of nitrogen (nitrate) concentration in waters. Nitrogen loading in rivers flowing through agricultural regions is much larger than from waters in non-agricultural regions. Water from agricultural regions contributes significantly to the increase of nutrients in the Baltic Sea (Sileika, 1999).

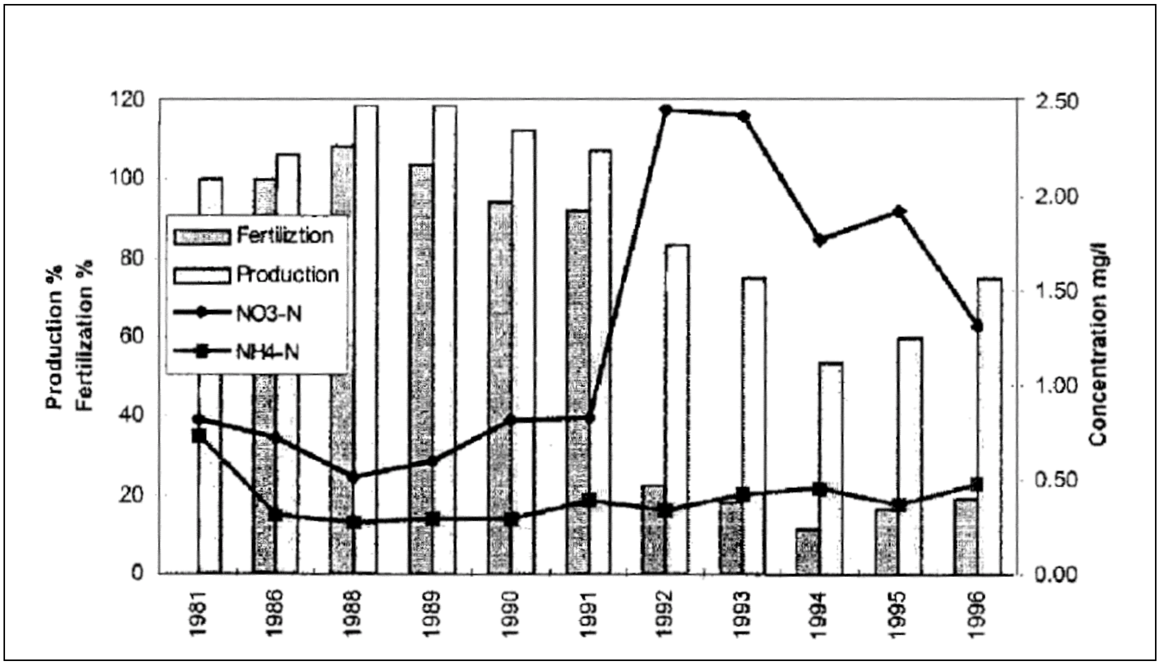


Figure 3.1. *Changes in the agricultural output, the amount of fertilizers used, and the nitrate(NO_3^-) and ammonium(NH_4^+) concentrations in the rivers flowing through agricultural areas (average per year) from 1981-1996. The figure shows that crop production declined much less than fertilisation from 1990 to 1996. This, together with the high nitrate values, shows that the nutrient storage in the soil is large, and that the use is not well balanced (Sileika et al., 1998).*

3.3 Agriculture and environment

Agriculture today in the Baltic Republics and Russia does not utilise the resources on the farms in an efficient and proper way. Today the practices cause pollution of air, soil and water bodies. The technology used is not suited to biological demands in agricultural production, and heavy equipment with unsuitable tyres compacts the soil. This cause severe decreases in harvests. Agriculture needs to be modernised with new machinery and improved knowledge of strategy, handling and maintenance on all sizes of farms (Carlson *et al.,* 1999).

After independence, when the large collective and state farms had been divided into small farms, problems arose. The machinery were to be used on large areas and were not suited for small farms. The farmers started to work with horses again, as 50 years ago, since they could not afford to buy new machines. The main problem today is farmers' lack of financial resources to buy tractors, fertilisers and chemicals. The machines are old and consume lots of fuel. It is also impossible to cultivate land, seed grain and spread manure evenly with old equipment. This affect crop yields to a great extent and could be harmful for the environment. Despite the depression of agriculture there is an unestimated excess of nitrogen load in Lithuanian rivers, which shows that inland nitrogen cycle is very complicated and still little known. Coming increase of agricultural production can have unpredictable consequences on inland water and the Baltic Sea in the near future.

Therefore attention should be made to reduce nutrient losses from different sources of pollution (Sileika *et al.,* 1998).

3.4 Good Agricultural Practice, GAP

According to "State agricultural development programme" agriculture will continue to play an important role in Lithuanian economy in the future. The goal of the programme is to increase livestock and milk production from 1996 to 2005 by 60 per cent and grain production by 32 per cent. To achieve these results there is a need to increase the use of fertilisers five to ten times between these years. If the use of fertilisers, manure handling, soil cultivation and crop rotation will be done in the same way as it was in the former Soviet Union, it could raise additional problems for Baltic Sea. Therefore there is a need to work out a Good Agricultural Practice (GAP), knowledge and technology, and improvement of legislation and regulation to reduce pollution associated with nutrient run-off and ammonia emission from agriculture in Lithuania (Sileika *et al.,* 1998).

GAP implies "successful management of resources for agriculture to satisfy changing human needs while maintaining or enhancing the quality of the human environment and conserving natural resources. The objectives for GAP highlight the importance of reducing dependence on inputs based on fossil fuel and mineral phosphorus, minimizing risks of soil and environmental degradation, and maintaining an increasing trend in per capita productivity and support development of a sustainable agriculture" (Carlson *et al.,* 1999).

To solve these problems in the future the Baltic Environmental Agricultural Run-off Project Group (BEAROP) has been appointed. The Baltic Agricultural Run-off Action Programme (BAAP) focuses on several activities to reduce the pollution from agriculture. For many farmers and officials the BEAROP project has opened the door to a new understanding of agricultural and environmental issues (Sileika *et al.,* 1998).

4. Study area

In this part of the paper the choice of watersheds is explained. The chapter also presents a more precise description of the watersheds like area, land use, soil type and population.

4.1 The watersheds

The choice of watersheds was influenced by the existence of considerable quantities of data for the study area and the interest of LIWM in evaluating the effects of land use on nitrogen recharge to the two rivers Graisupis and Vardas. These two demonstration watersheds have already been established during the Project Interim, headed by BEAROP. Therefore they "provide a good platform for future activities presenting measures leading to sustainable agriculture", as LIWM put it (Sileika *et al.*, 1998). The location of the watershed of river Graisupis is very comfortable for activities because it is close to the main agricultural and scientific institutes, and the area is intensively cultivated and thereby very homogenous. In addition, Vardas is interesting regarding the difference in land-use, soils, and topography, figure 4.1.

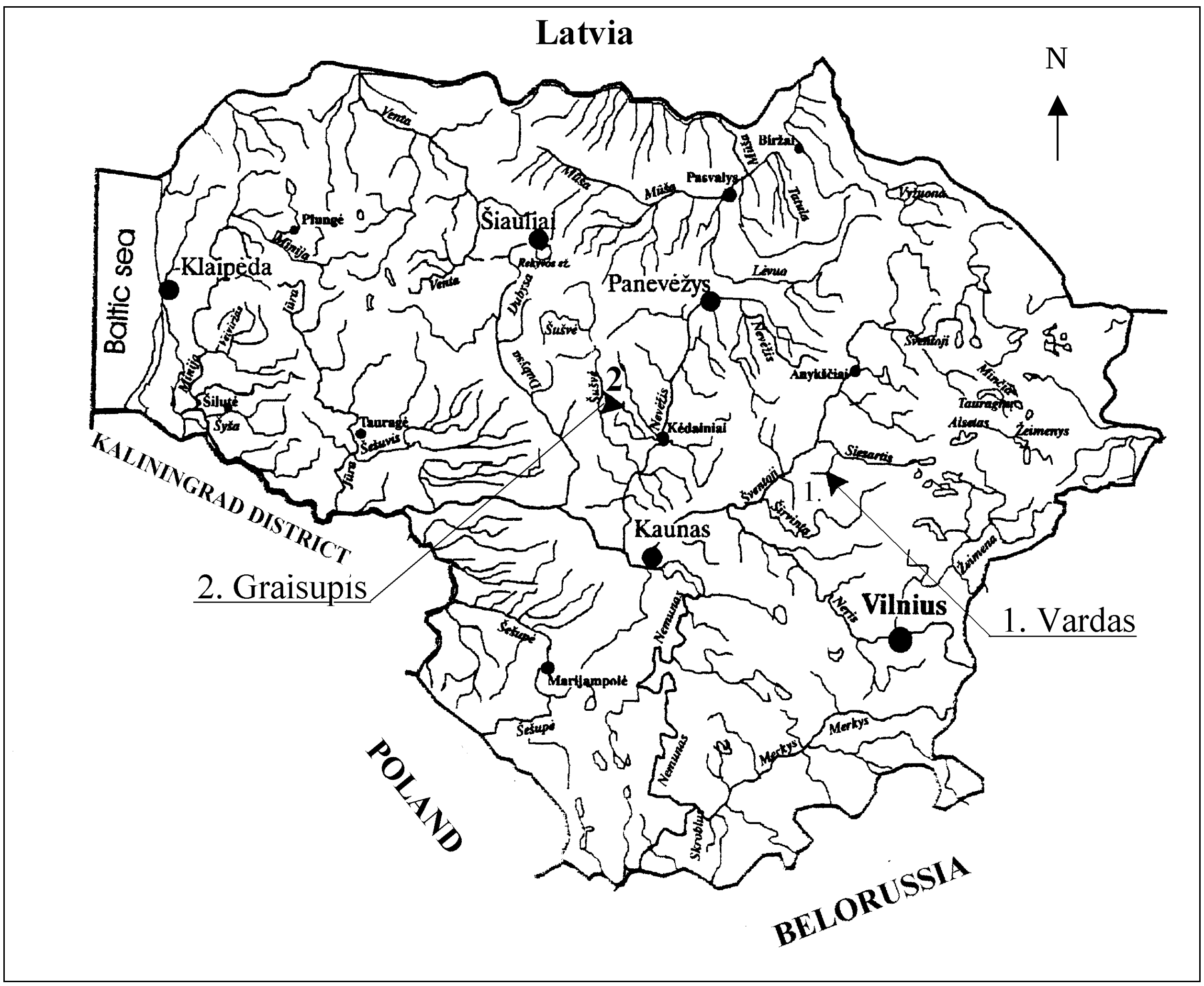


Figure 4.1. *Map showing the two watersheds location in Lithuania (Sileika et al., 1998).*

4.1.1 Vardas

The first watershed is located within Zelva rural community, Ukmergé district, and is part of the hilly area of eastern Lithuania. Vardas is located in the basin of Sventoji, which is second order tributary of river Nemunas. The total length of Vardas is 8.5 km and the total area of the watershed is 7.6 km^2. The watershed consists of many small hills with deep depressions and the river winding between the hills. Average basin slope is 0.73 per cent, and the area is descending from south to north. Most of the watershed has been drained with tile drainage systems. Here, water is less polluted than in Graisupis and conditions for agricultural production is poorer because of poor soils. The area is also more sensitive to soil erosion (Sileika *et al.,* 1998 and Sileika, 1999).

Eastern Lithuania has glacial origin where most of the rocks were carried from the western parts of Finland, Sweden and the Baltic bottom. The quaternary sediment layer reaches a depth of 300 m and consists of sandy loam, sand and moraine sandy loam. The landscape has hills of moraine with small flat bottom depressions and the soiltype is soddy gley. Typical podzol soils are left only on the flat hilltops, and on the slopes there are easily eroded light loam soils. Interhilly depressions have deliuvium and soil with peat. The watershed is situated between 130-180m above sea level (Sileika *et al.,* 1998).

There are 20 family farms and 95 homelands (2-3 ha) located in the area. Thus, the main part persists of private farms and only one of them is cultivated as a company (Sileika *et al.,* 1998). Here pastures constitute the largest part of the land use, and cropland only reaches a small portion. The poor soils and the hilly terrain that is easily eroded explains this distribution of land use. Almost all household farm owners keep animals; 2-3 milk cows, 1-2 heifers, 1-2 calves, 2-3 pigs, and some poultry. The main crops grown here are grass ley, potatoes and fodder beets (Sileika *et al.,* 1998).

4.1.2 Graisupis

The second watershed is situated in Lithuanian middle plain in the central part of Lithuania. It belongs to the Dotnuva rural community, Kedainiai district. The drainage area of the river Graisupis basin is 11.3 km^2, and the river is the second order tributary of the river Nevezis. Nevezis is a tributary of Nemunas, the largest river in Lithuania, which has its outflow to the Baltic Sea. The river of Graisupis is straightened and has a total length of 8.2 km. Most parts of the watershed have been drained by pipe drainage systems. There are no buffer zones on the banks of streams and rivers. Here, fertile soils and flat land surface gives good opportunities for an intensive agricultural production, and half the Lithuanian yield are grown in the region. The watershed lies on a plain that descends from northwest to southeast, and average basin slope is 0.3 per cent. The landscape rises about 62-65 m above sea level. Graisupis lies on Silurian bedrock and the quaternary sediment layers consist of sandy loam, and the main soil type is soddy gley (Sileika *et al.,* 1998 and Sileika, 1999).

There are three large farms in the area, Ausra agricultural company, Lipliúnai agricultural company and the experimental farm of LIWM. Fourteen farms are private, and about 90 are homelands (2-3 ha). The total number of inhabitants is about 190 (Sileika *et al.*, 1998). Cropland constitutes the largest part of land use in the watershed, which is explained by the fertile soils in this area. Pasture only takes a very low part of the distribution. The main crops are sugar beets, grain cereals (barley), and winter wheat. In addition, grass ley is commonly sown. It is common to have some dairy cows because the farmers do not rely on one source of income nowadays, but cattle breeding are not usual here (Sileika *et al*., 1998).

5. Theory

In this chapter the main processes affecting nutrient leakage will be investigated. These processes involve the water transport and flow paths (groundwater and soilwater), chemical transformations of substances in soil and water, and the nitrogen cycle concerning the leakage from terrestrial systems. It is vital to understand how different factors and processes affect the nutrient leakage in order to follow later discussions about the problems in Lithuania.

5.1 Introduction

Research during the last decade has shown that nutrient concentration in water discharge from river basins is a result of several interacting processes. These include exchange between cycles in the terrestrial, aquatic, geological and atmospheric environment. The processes can be categorized into three:

1. Water transport (like transit time and flow paths).
2. Transformation and immobilisation of nutrients (denitrification, sedimentation and adsorption).
3. Nutrient release (for example through mineralisation, weathering, fertilization, atmospheric deposition and sewage effluents).

The influence of different processes varies; because they may be more or less favored by watershed conditions like, land use, physiography, land management, climate or hydrology. Therefore there is a need to emphasize the importance of linking combinations of watershed characteristics to stream-water quality, because this enable further understanding of influences from several different processes (Arheimer and Lidén, 1998).

5.2 Water in streams

Water in a stream is a mixture of groundwater and surface water. When precipitation infiltrates the ground, the groundwater surface rise and the outflow of groundwater increase to the streams. This happens because the groundwater surface then have a steeper slope towards the stream, i.e. the level of the groundwater increase, figure 5.1. The groundwater origin can be studied through the chemical composition of the water, i.e. the conductivity (the ionic salinity of the water). The conductivity is higher in groundwater than in rainwater, because its flow paths through soil and rock chemically influence the groundwater. The superficial groundwater is younger and has existed only for a short time in the ground, and has therefore lower conductivity than the old groundwater at deeper levels. The conductivity of stream water diminishes when the water flow increase, which is explained by more rainwater in the stream caused by the outflow of young and superficial groundwater (Grip and Rodhe, 1994).

Soil water is the water that exists in a soil just above the groundwater surface. The uppermost layer in the soil water area is called the root zone. In the root zone it is determined how much of the infiltrated water that will return to the atmosphere through the uptake in plants, and how much that will percolate down to the groundwater. In the root zone the chemical changes of the infiltrated rainwater takes place (Grip and Rodhe, 1994).

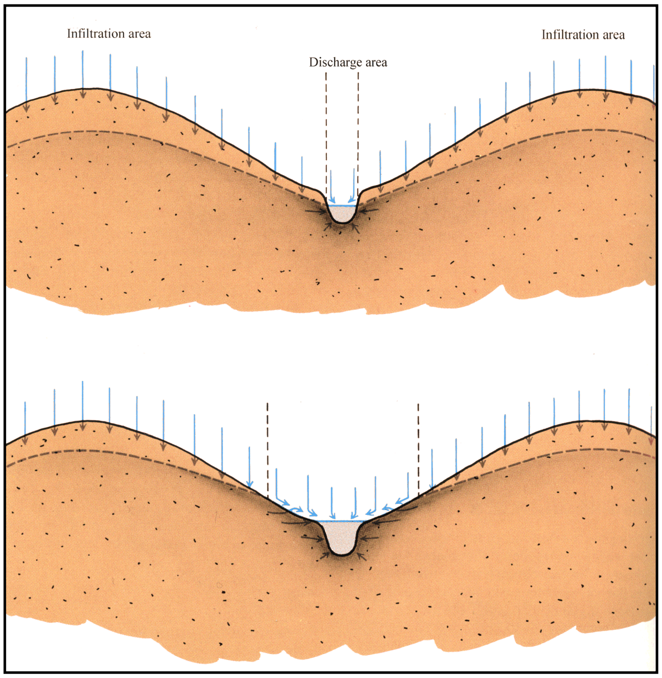


***Figure 5.1**. When precipitation infiltrates, the groundwater surface rises and the runoff increases to the river. This is explained by the increased leaning of the groundwater surface. The intensity of the dark colour shows the size of the groundwater flow (Grip and Rodhe, 1994).*

5.3 Chemical processes in water and soil

5.3.1 Brief overview

Geological and climatological factors primarily determine the environment in lakes and seas, and mostly the geological character of the drainage basin determines the chemical composition of the water. A regional difference of substances in water then depends on, for example, if the soil is rich in calcium or the chemical composition of the soil (KTH, 1996). Chemical substances are also transported to the ground and soil from the atmosphere and from the vegetation in a watershed. The input of chemical substances from the atmosphere to the soil comes from precipitation and deposition of particles. Larger particles can be deposited from the air on the vegetation and directly on the soil surface. Smaller particles cannot sediment on the ground directly, and lots of particles get caught on leaves and needles when the trees filtrate the air. The rain later washes these leaves and needles. Thus, the deposition rate in a forest is larger than in a field due to the deposition of both large and small particles (Grip and Rodhe, 1994).

When it rains the water first infiltrate the top soil layer that consists of decomposed organic matter - humus. This layer of humus consists of many hydrogen- and cations, which out level temporary variations in the composition of the precipitation when the precipitation passes the humus layer. In the root zone, below the humus layer, the minerals of the soil are weathered. This leads to more cations in the soil water. The vegetation uses their roots to assimilate nutrients and water, and when they respire they give off carbon dioxide to the root zone. The carbon dioxide create carbonic acid when it solutes in soil water, which contributes to further weathering when water percolates down to the groundwater. When the groundwater moves through the soil weathering and changes of the minerals occur. Therefore, the amount of ions in groundwater always rises successively. When water finally flows out into the drainage basin certain elements can oxidise and for example iron and calcium can deposit (Grip and Rodhe, 1994).

5.3.2. Elements and chemical substances in soil and water

There are several elements that can leak through the soil profile and contribute to the amount of nutrients in surface waters;

- Sources of sulphur compounds to natural waters include rocks, fertilisers, atmospheric precipitation and dry deposition. Sulphur (S) is supplied to the surface water either as sulphate ions (SO_4^{2-}) or sulphuric acid (H_2SO_4) from precipitation, as sulphate (SO_4) in particles or as sulphur dioxide (SO_2). The most important natural sources in the atmosphere are volcanic activity, sulphur hydrogen (H_2S) from swamp areas and particles from breaking waves. At present time, the atmospheric sources that origin from combustion industries dominate all other sources. Sulphate is also released during geochemical weathering of rocks and soils that contains either sulphides or free sulphur, which are oxidized in the presence of water to form sulphuric acid. This tends to lower pH. Bacteria contribute to the oxidation of sulphides and sulphur, both in soil and in water (Wetzel, 1983 and Grip and Rodhe, 1994).

- Nitrogen (N) is provided to the drainage area mainly as ammonium ions (NH_4^+) for example from the fertiliser industry, nitrate ions (NO_3^-) in precipitation or as nitrogen oxide gases (NO, NO_2) that the vegetation assimilate. Some microorganisms in the drainage area can, through biologic nitrogen fixation, use nitrogen directly from the atmosphere. Even though nitrogen is the atmospheres main constituent, there is always insufficient access of nitrogen as a nutrient in the soil (Grip and Rodhe, 1994).

- Ammonia (NH_3) is an end product from decomposition of organic material. From calcareous rocks, in manure stacks and other basic environments, ammoniac gas can be released into the atmosphere. One of the largest sources of ammoniac today is the fertilizer industry (Grip and Rodhe, 1994).

- The positive basic cations calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), and the negative chloride ion (Cl^-), reach the drainage area through precipitation and dry deposition of salt particles. These ions have reached the atmosphere by breaking waves, wind erosion from land and through combustion. The basic cations are important nutrients in the soil. Other elements do not contribute to the chemical composition of surface- and groundwater in a drainage area as much as the elements mentioned. Decomposed vegetation also supplies nutrients to the soil, which have earlier been assimilated from the root zone (Grip and Rodhe, 1994).

When water percolates through a soil it is exposed to a dramatic chemical change. The rainwater is transformed to soil- and groundwater. The decomposition of organic matter in the ground leads to oxidation where many hydroxyl- (-OH) and carboxyl- (-COOH) groups are created. When the hydroxyl groups in humus give off hydrogen ions they instead bind other cations that exist in soil water. The humus layer in a forest soil is a large magazine of basic cations. It is also a large cation exchanger and has the possibility to out level temporary fluctuations in the composition of precipitation, as mentioned before (KTH, 1996). The soil water concentration of dissolved substances gets higher during evaporation from the ground, because only the H_2O evaporates. The water that then percolates down through the humus layer has therefore a higher concentration of dissolved substances than the precipitation had. Due to the flow of organic acids through the humus layer, the mineral soil below is exposed to strong chemical weathering. This layer is called the leeching zone. When the percolating water pass the leeching zone, where hydrogen ions are consumed in process of weathering, the water becomes less acid and contains more metal cations than when leaving the humus layer. The increment of sodium, potassium, calcium and magnesium can through weathering be in the same order as the atmospheric deposition (Grip and Rodhe, 1994 and Wetzel, 1983).

In the leeching zone the root density, decrease with depth, and at 60 centimetres depth there are few roots left. Through the roots most of the mineralised nitrogen and a large part of other dissolved nutrients are assimilated. These substances will later go back to the soil as litter when the vegetation dies. In this way nutrients circulate in the system (Grip and Rodhe, 1994).

The weathering gets slower in the groundwater zone. Hydrogen ions are used during weathering, and therefore pH rise when the groundwater is older, due to the release of basic cations. Older groundwater therefore has a higher salinity (conductivitiy) than younger groundwater. The water percolating down through the root zone will eventually emerge as surface water in streams. The character of this water changes in time and during periods with a high groundwater level, and a large river flow, groundwater flows out into the river. This groundwater has low pH and low levels of basic cations. On the other hand, when the groundwater level is low, and when the riverflow is low, the groundwater that flows to a stream is older and pH and basic cations are high (Grip and Rodhe, 1994).

5.4 Conductivity

The concentrations of four major cations, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, and four major anions, CO_3^{2-}, HCO_3^{-}, SO_4^{2-}, Cl^{-}, usually constitute the total ionic salinity of the water.

Concentrations of other ionic elements such as nitrogen (N), phosphorus (P), iron (Fe) and numerous other elements are of immense biological importance, but are usually minor contributors to total salinity. The conductivity is closely proportional to concentrations of the major ions - it is a measure of the salinity of the water. Conductivity is a measure of the resistance of a solution to electrical flow, and usually presented in the unit mS/m. Conductivity is temperature dependent, and higher water temperature gives a higher conductivity value, which is about 2 per cent per degree Celsius. It is generally accepted that conductivity has a higher value in nutritious waters than in non-nutritious waters. There is a positive correlation between conductivity and pH, and conductivity rise during acidification of the water (Ekologisk metodik, 1981 and Wetzel, 1983).

The salinity of surface waters is highly variable and depends on ionic influences from the surrounding land, atmospheric sources derived from the land, ocean, human activities, and exchange with sediments within the water body. Three major mechanisms control the salinity of world surface water. These are; weathering of bedrock, atmospheric precipitation and the evaporation-precipitation process, figure 5.2. Over large regions of the temperate zone, in which Lithuania is included, dominance by calcium and bicarbonate ions prevails in surface waters (Wetzel, 1983).

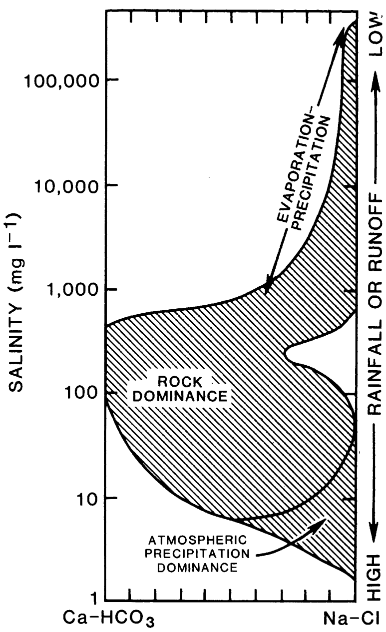


Figure 5.2. *Diagrammatic representation of the general processes controlling the salinity of surface waters of the world (Wetzel, 1983).*

5.5 Nitrogen

Nitrogen (N) has a complicated cycle in the atmosphere - soil - water - vegetation system. The nitrogen cycle includes both an atmospheric gas phase and many biological transformation processes. *Inorganic nitrogen*, ammonia NH_4^+, nitrite NO_2^-, and nitrate NO_3^-, is easily soluble and moveable in soil and water, which results in that inorganic nitrogen is easily removed from soil with groundwater and drainage water. *Organic nitrogen* exists in a large number of organic compounds from amino acids to proteins and refractory humic compounds. It is not that easily soluble and transported as inorganic nitrogen (Wetzel, 1983 and KTH, 1996).

The large nitrogen pool in the atmosphere is in the form of nitrogen gas (N_2). In a non-affected ecosystem nitrogen is fixated from the air by bacteria and lichens. The supply of nitrogen in this way is naturally low in the humid climate region, about 1 kgN $year^{-1}$. Today large sources of nitrogen come from atmospheric deposition and fertilization of both agricultural land and forests. In Sweden about 100 kg ha^{-1} year^{-1} of fertilisers is applied to agricultural land (KTH, 1996). Increased import from fertilisation of the soil system seldom causes increased leakage directly, but instead contributes indirectly to a larger nitrogen pool, and as a result more nitrogen is available for leakage in the long run (Arheimer, 1998).

When nitrogen has reached the soil it is assimilated by vegetation. The amounts of nitrogen circulating in an ecosystem are large, and the litter is decomposed by organisms in the soil in order to form ammonium and is then assimilated by the vegetation again. This internal cycle leaks normally only small amounts of nitrogen in forest soils, 1-2 kg ha^{-1} year^{-1}. The leakage is in the form of nitrate, ammonium and organically bound nitrogen. Larger supplies of nitrogen, especially on agricultural land, contribute to an increased leakage of nitrates from the soil (KTH, 1996).

Losses of nitrogen from the system consist of removal of vegetation, outflow from the basin, reduction of nitrate (NO_3^-) to nitrogen gas (N_2) by bacterial denitrification with return of N_2 to the atmosphere, leaching and permanent sedimentation loss of inorganic- and organic nitrogen-containing compounds to the sediments (Wetzel, 1983 and Arheimer, 1998). Enrichment of fresh waters with nutrients needed for plant growth occurs commonly because of losses from agricultural fertilization, contribution from sewage and industrial wastes, and enrichment via atmospheric pollutants, especially nitrate (Wetzel, 1983).

5.5.1 The Nitrogen Cycle

The nitrogen cycle is divided into several interacting processes. These are (figure 5.3):

- Nitrogen fixation (N_2)
- Ammonification
- Assimilation, and assimilatory nitrate reduction
- Immobilisation
- Mineralisation
- Nitrification
- Denitrification

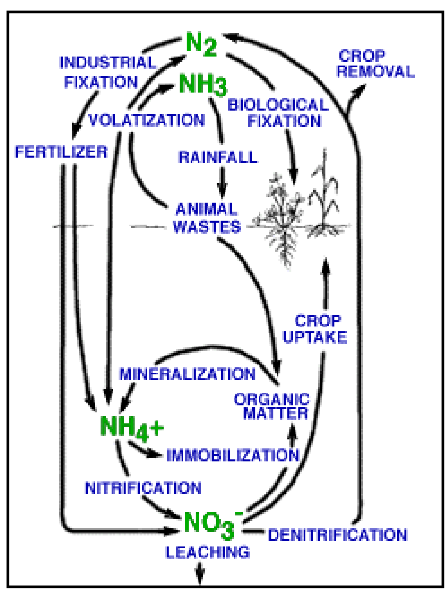


Figure 5.3. *The nitrogen cycle (Internet 3).*

Nitrogen fixation

The amount of nitrogen in soil, and in living and dead organic matter has once been fixated from the surrounding air. Plants cannot use the nitrogen in the atmosphere without the help of nitro fixating bacteria (Wetzel, 1983). These certain bacterial species, both aerobic and anaerobic, carry out the conversion of gaseous nitrogen (N_2) into ammonia (NH_3), which the plants then assimilates (Internet 2). Some vegetation may as well fixate nitrogen, i.e. alder (Wetzel, 1983).

Ammonification

Ammonia (NH_3) is formed in the soil by the decomposition of plants and animals, and by the release of animal waste (Internet 4). The bacteria generate ammonia as the primary nitrogenous end product of decomposition of proteins and other nitrogenous organic compounds (Wetzel, 1983).

Assimilation

Ammonia is present primarily as NH_4^+ ions, and is readily assimilated by plants. It is assimilated into organic compounds inside cells, producing amino groups ($-NH_2$). Nitrogen is one of the major constituents of cellular protoplasm of organisms (Wetzel, 1983 and Internet 2). Plant roots assimilate nitrogen in the form of nitrates, while animals assimilate their nitrogen by eating plants (Internet 4). Nitrate (NO_3^-) is far more common than ammonia, and many organisms can only acquire nitrogen in the form of nitrates. They must reduce nitrate to form the amino groups needed for metabolism, and that is called “assimilatory nitrate reduction” (Internet 2).

Immobilisation

Inorganic nitrogen is used by microorganisms and is changed into organic forms of the same element (Internet 3).

Mineralisation

Mineralisation is the slow release of nutrients from organic material. Mineralisation of dead organic matter means transformation of ammonia (NH_3) to ammonium (NH_4^+) (Arheimer, 1998 and Internet 3).

The biological turnover through mineralisation of dead organic matter and immobilisation determine the amount of mobile nitrogen available. Generally less than 0.1 per cent of the total nitrogen storage in soils exists in mobile forms (Arheimer, 1998).

Nitrification

Only certain bacteria, the nitrifying bacteria, can use ammonia (NH_3) as an energy source. Bacterial nitrification proceeds in two stages:

1. The oxidation of ammonium (NH_4^+) $\rightarrow$ nitrite (NO_2^-), largely by *Nitrosomonas* but also by other bacteria.
2. And by the oxidation of nitrite (NO_2^-) $\rightarrow$ nitrate (NO_3^-), in which *Nitrobacter* is the dominant bacterias involved (Wetzel, 1983).

Generally, nitrification can be defined as the biological conversion of organic and inorganic nitrogenous compounds from a reduced state to a more oxidized state.
Through the products of nitrification, plants receive the components of the "fixed" nitrogen using nitrates in the soil to provide the nutrients they need. Nitrification only occurs when the surrounding environment is aerobic (Wetzel, 1983 and Internet 4).

The overall nitrification reaction:
$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$

Denitrification
Bacterial denitrification is the biogeochemical reduction of oxidized nitrogen anions, concomitant with the oxidation of organic matter. Bacterias in sediment and soils, that can respire anaerobically, perform the denitrification when they feed on the break down of organic material. The bacteria convert nitrate (NO_3^-) to nitrite (NO_2^-). Some anaerobic respiring bacteria can also use nitrite (NO_2^-), converting it further into nitrous oxide (NO), nitrogen dioxide (N_2O), and ultimately nitrogen gas (N_2) (Wetzel, 1983 and Fleisher *et al.*, 1991).

The general sequence of denitrification is:
$NO_3^- \rightarrow NO_2^- \rightarrow N_2O \rightarrow N_2$

The nitrogen gas (N_2) that is released into the atmosphere can only be recycled again through nitrogen fixation (Leonardsson, 1994). Conditions like pH between 4 and 8, temperature greater than $0^{\circ}C$, sufficient NO_3^-, the amount of soil moisture, low O_2 concentration, presence of degradable organic substrate, and a large denitrifier population favors denitrification (Fleischer *et al*., 1991 and Arheimer, 1998). Denitrification is significant in recharge areas below the root zone, especially below the groundwater table where O_2 levels are low, and is therefore considered an important process that can help prevent nitrate contamination of groundwater (Arheimer, 1998). The process is highly temperature dependant and leads to a recess of denitrification during autumn and winter, hence during the same time as percolation and nutrient leakage have their optimums (Andersson, 1986). The more frequent pipe draining in catchments with fewer open ditches may significantly decrease denitrification, as it changes soil moisture, flow paths, and residence time (Arheimer, 1998).

Also the rates of other biochemical transformation processes, like ammonification, nitrification, denitrification, and assimilation, and adsorption on soil organic matter, are influenced by environmental conditions, for example, pH, O_2, soil moisture and temperature as denitrification is (Arheimer, 1998).

5.5.2 Nitrogen retention

On its way from the discharge sources to the sea the nitrogen is included in processes that result in retention of nitrogen, figure 5.4. This takes place through:

1. Denitrification that releases nitrogen.
2. Nitrogen uptake in plants (assimilation).
3. Sedimentation of organic matter.

(Fleischer *et al.,* 1991 and Arheimer, 1998).

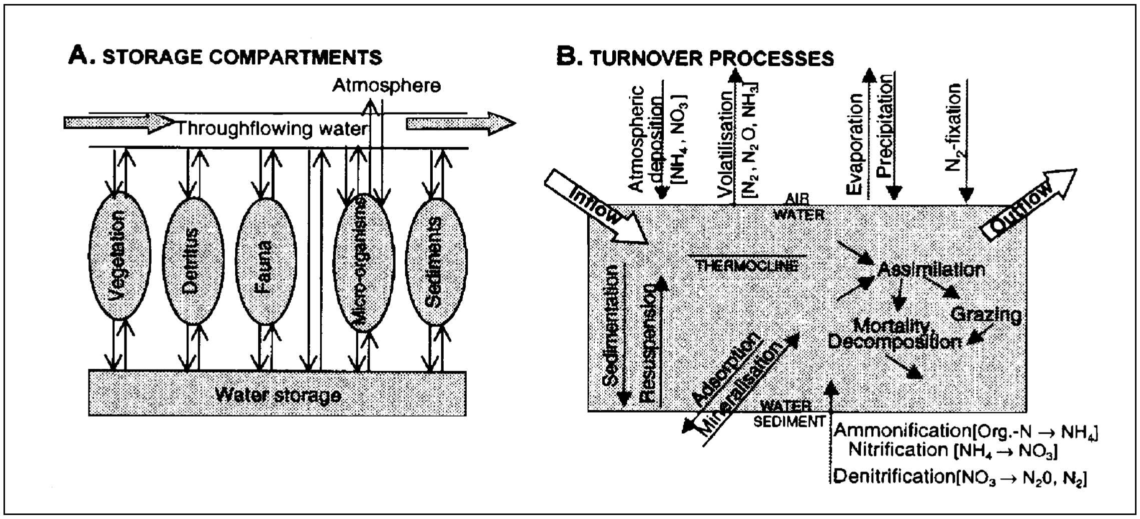


Figure 5.4. *The nitrogen transformation in the aquatic system; a) interactions between transported nitrogen and major storage compartments and b) major turnover processes affecting nitrogen concentration in a water body (Arheimer, 1998).*

Denitrification is the process that most effectively reduces available biological nitrogen from the system. The nitrogen that is denitrified leave as nitrogen gas (N_2) to the atmosphere (Leonardsson, 1994).

During the vegetation season plants *assimilate* nutrients in the water and sediments. Probably is the leaking of oxygen from the plant roots to sediments the most important thing when plants contribute to nitrogen retention. Then ammonia is oxidized to nitrate, which is the primary material in denitrification. Plants also increase the denitrification surface, because denitrification can occur in the dead parts of plants in water (Leonardsson, 1994).

The most important thing for *sedimentation* is that flow velocity is low so that particles in the water can be deposited at the bottom. The particles should avoid turbulation and should stay as sediments in order to make a successful retention. In this way the water is cleaned from particulate bound nutrients that instead will end up in the sediments. The process of sedimentation of organic material is also necessary for denitrification. The organic material then decomposes in the sediments. As a consequence large part of the nitrogen is released and is transported further down the drainage system (Leonardsson, 1994).

Retention is related to temperature, as increasing temperature accelerates all metabolic processes including denitrification and biological uptake, which is reflected in lower summer concentrations of nitrogen. Retention is also related to hydrology, as longer residence time allows more of the nitrogen to be removed from the water. Thus, retention is favored where water is stored in the landscape, as in lakes and wetlands (Arheimer, 1998). If the water discharge is changed, for example through drainage of lakes and wetlands, and straightening and culverting of streams, this result in faster transport of nitrogen to the sea and decreases the chances of retention (Fleischer *et al.*, 1991).

5.6 Nitrogen leakage

From all kind of soils there is a natural leakage of nitrogen, but it varies to a great extent depending on climate, soil type, fertilisers, and the plant community. The leakage varies from year to year depending on climate and rainfall characteristics, and runoff is the main factor affecting the leakage. It is difficult to count for the nitrogen leakage from agricultural land, because it is diffuse and a non-point source if compared with for example sewage water, which is a point leakage. Generally nitrogen is lost through the leaking of nitrate, and the nitrate follows the water movements in the soil (Johnsson and Hoffman, 1996).

Excluding erosion, three conditions have to be fulfilled before any element can be lost from the soil system and leached into surface water. First, the element has to appear in a soil water-soluble form, secondly, mobilization must be larger than retention and thirdly, the element has to be vertically and laterally transported within the soil profile or on top of it. The solubility criteria is the most limiting factor for nitrogen leakage from terrestrial ecosystems since only ammonium, nitrate and a small fraction of the organically bound nitrogen compounds have a high solubility in soil water. Organically bound nitrogen, mainly accumulated in living tissue, detritus and humic compounds, must decompose before it turns into a soil water-soluble form (Löfgren, 1991).

The nitrogen is said to be leaking when it is transported down through the soil and the root zone at about one m depth. The plants can no longer use the nitrogen when it has passed the root zone, and therefore the nitrogen is said to have left the agricultural system. Even different kinds of cultivating practices (i.e. ploughing) can no longer affect the leaking. The nitrogen is then transported deeper down to the groundwater, or through some kind of drainage system, which will end up in ditches and larger streams. During this transport, processes like nitrogen retention occurs, which reduces the amount of nitrogen reaching the stream (Johnsson and Hoffman, 1996).

Water in soil acts as a transport agent of important nutrients for plants. However, plants and microorganisms use only some of the nutrients in the water. The water that reaches the groundwater and streams therefore contains only a fraction of the total amount of nutrients that are found in the soil, i.e it only contains the nutrients that are not assimilated by the plants. The ground is said to be leeched when these remaining nutrients leave the soil together with the percolating water. The soils of humid climate regions are called leeching soils, and the most important natural soils of this region are podsols. Consequently leaking from soils is something that naturally occurs in this climate region. The amount of nutrients in soil that can be leached is also affected by human activities, for example by fertilisation (Andersson, 1986).

5.6.1. Factors controlling the loss of nitrogen from agricultural land and forests

There are a couple of factors that controls the nitrogen losses. Some of these factors can be explained by structural changes in agriculture; for example that the animal stock is more concentrated to larger and fewer places, that the area of grass ley has diminished and is replaced by cereal, and that the turnover of nutrients in agricultural ecosystems has increased through an increased fertilising level (Andersson, 1986). This part of the chapter will focus on the turnover of nutrients and the general factors that regulates this.

Runoff

The amount of runoff and its distribution throughout the year has a large impact on the nutrient leakage. In several investigations strong correlations are found between runoff and nutrient leakage in drainage systems and streams, both in agricultural land and in forests (Kolenbrander, 1980; Brink and Ivarsson, 1985 – in Andersson 1986, and Fleischer *et al*., 1991). Runoff from agricultural land and forests, occurs mainly during the period from autumn until spring due to the high amounts of precipitation during that time of the year (Andersson, 1986).

Precipitation and evapotranspiration determine the total runoff from agricultural land together with, in a short time perspective, changes in the water storage (Andersson, 1986). In summer time, when there is more evapotranspiration, the water is withdrawn from the runoff when plants intercept the water (Grip and Rodhe, 1994).

Soil type

The infiltration capacity of the soil, together with topography, determines the distribution between surface runoff and infiltration. There are large differences in infiltration capacity between different soil types. Fine textured soils have the lowest infiltration capacity and sandy and organic soils have the best. The infiltration capacity can also be affected by agriculture practices, for example by the choice of ploughing technique (Andersson, 1986).

Nitrogen leakage is greater in coarse-textured soils than in clayey soils due to their poorer water retention ability, faster percolation and a less effective nutrient uptake since the root system in such soils is not so deep (Andersson, 1986).

Crops and rotations

There are also differences in nutrient leakage depending on which kind of crops that are grown. The differences are controlled by the length of the growing period, the development of root systems, the yield, the amount of nitrogen in the plants and how easy they mineralise. The most optimal plants, regarding to exchange and minimal loss of nitrogen, are grass ley where the ground is covered all year. Wegener (in Andersson,

1986) uses the following ranking regarding nitrogen leakage from different crops: grass< winter crops< spring crops< sugar beats< potatoes< vegetables.

Crops with a long growing period (grass ley, winter crops and sugar beats) leave less nitrates to the soil than crops with a short growing season (barley, potatoes). These former crops also have deep and large root systems that can use nitrogen from fertilisers more effectively than spring crops and potatoes. Fields with spring crops (like barley) contain lots of nitrate during late autumn. A study conducted in Halland (Andersson, 1986) shows that fields with barley and potatoes have higher nitrate values than other cereals even next spring, and at a depth which makes it impossible for a spring cereal to use the nitrogen.

The amount of nitrogen is almost always low in spring. This is explained by the losses to air and water during the winter (Andersson, 1986). During recent years attempts have been made to sow special crops in periods between ordinary growing seasons. Special crops planted in autumn reduce the nitrogen leakage with 20-30 per cent, which depends partly on the crops uptake of nutrients and partly on lesser runoff due to evapotranspiration. However, during dry autumns the roots of the special crop may not develop, and this results in that the crop does not have time to assimilate the nitrate from the soil. (Gustafson and Torstensson, 1984 - in Andersson, 1986).

Inorganic nitrogen concentrations in stream flow become significantly lower during the growing season. This is caused by increased biological activity during summer, which reduces nitrogen from the water phase. Biochemical processes that may affect the concentration include biological uptake and denitrification. During the growing season, biological uptake probably dominates nitrogen reduction in the root zone, while denitrification may dominate under the root zone and in the terrestrial-aquatic interaction zone near the stream channel. Inorganic nitrogen is also often positively correlated to water discharge in the beginning of an event, but then reaches its peak concentrations before the water flow peak (Arheimer, 1998).

In contrast to inorganic nitrogen, the highest levels of *organic nitrogen* are found during summer. The contribution of organic nitrogen concentrations may be linked to instream erosion and sedimentation processes, which makes the leakage less dependent on the biologic activity of the growing season. Organic nitrogen is also positively correlated to water discharge (Arheimer, 1998).

Fertilisers

The nutrient leakage to water and air in agricultural land is in the long run decided by the balance between fertilisers and the take-away of cereal products in agricultural areas. In most places where there has been an increased fertilising level there is more nitrogen in the soil than is necessary for plant growth. It is generally found that nutrient content of manure is utilised considerably less than the corresponding content in chemical fertilisers, which leads to a higher leakage. Manure, which consists of organic matter, has to be decomposed by organisms (mineralised) in the soil before the nutrients can be used. This leads to a longer and successive release of nutrients in organic manure. It is also easier to spread industrial fertilisers more evenly, and to use the right amount. How much fertilisers that are spread, and in what time, is also very important to consider (Andersson, 1986).

Pipe draining

Pipe draining leads to faster and deeper flowing paths of runoff and results in improved oxygenation, which stimulates the mineralisation of organic material and causes poorer conditions for denitrification. The water in these drainage pipes consists of both groundwater that has been infiltrated from the surrounding land, and of water that has infiltrated arable land. Pipe draining reduces groundwater formation on cultivated land when the infiltrated water flows through the drainage pipes as runoff instead of forming groundwater. This reduces the supply of nitrate to groundwater but increase the nitrate leakage to streams and lakes (Andersson, 1986).

Nitrogen leakage from forests

The conditions that decide the leakage of nitrogen from agriculture are valid also for forests. The largest difference between the two systems is that the vegetation in forests is characterised by many plant species with different root depths, and lots of species live for many years. The natural leakage of nitrogen from forests to surface water is rather low, 0.5-3 kg ha^{-1} $year^{-1}$ in Sweden (Löfgren and Olsson, 1990). High nitrate leakage values are also correlated with high water discharge. There are also much higher losses during shorter periods of events like clear-cutting, storm felling, forest fire, fertilising and ditching. In the first three examples the nitrification is favoured, and the loss of nitrate can be high, when the vegetation uptake of inorganic nitrogen decrease (Löfgren, 1992).

The nitrogen cycle in forested ecosystems involves many gaseous, aqueous and particulate forms of nitrogen, and a large number of complex pathways. Inputs to the system are mainly through atmospheric deposition, N_2 fixation, and fertilisation. Nitrogen transformations take place when soil organic matter is decomposed into organic nitrogen or completely mineralised, forming NH_4^+ that may then be oxidised to NO_3^- by nitrifying organisms (Arheimer *et al*., 1996).

Atmospheric nitrogen deposition

Research has shown that forests affected by high atmospheric nitrogen deposition can loose large amounts of inorganic nitrogen, mainly as nitrate. The atmospheric deposition of nitrogen is in many parts of Europe much higher than the critical load of 3-15 kg N ha^{-1} $year^{-1}$. The critical load is the highest atmospheric deposition of acidifying compounds that will not cause long-term chemical changes with respect to base saturation in the soils. If the atmospheric deposition is higher than the critical load it may lead to “nitrogen saturation” of forest soils, figure 5.5. An increased nitrogen leakage to groundwater and surface water will be one of the consequences if the forests turn nitrogen saturated. The inorganic nitrogen ions of ammonium and nitrate, together with sulfate ions, constitute the major part of the atmospheric input, and the deposition of organically bound nitrogen, mainly in particulate form as pollen, is generally low. Nitrogen is both wet- and dry-deposited. The ions of ammonium, nitrate and sulfate are released by precipitation and are therefore called wet deposition. Other compounds of sulfur and nitrogen reach the ground before they have been solved in water, and this is called dry deposition (Löfgren, 1991 and Statistics Sweden, 1996). Dry deposition is difficult to measure, but it is higher in forests than in open areas and it is higher in coniferous than in deciduous forests. It is evident that the canopy acts as a sink for nitrogen in most forested areas. Throughfall measurements in southern Sweden, of both wet- and dry deposition, showed that in forests it varied between 12-24 kgN ha^{-1} year^{-1}, while deposition on open areas was in the range of 9-15 kgN ha^{-1} year^{-1}. The atmospheric deposition of organically bound nitrogen generally does not exceed 1 kg N ha^{-1} year^{-1}, and it is mainly in particulate form as pollen (Löfgren, 1991).

The total deposition of nitrogen (ammonium, nitrate and organically bound nitrogen) in the Nordic countries is within a range of 2-25 kgN ha^{-1} year^{-1}. Higher deposition rates can occur locally due to local emission sources like intense animal farming (ammonium) or industries. This means that the critical load is exceeded in many areas (Löfgren, 1991).

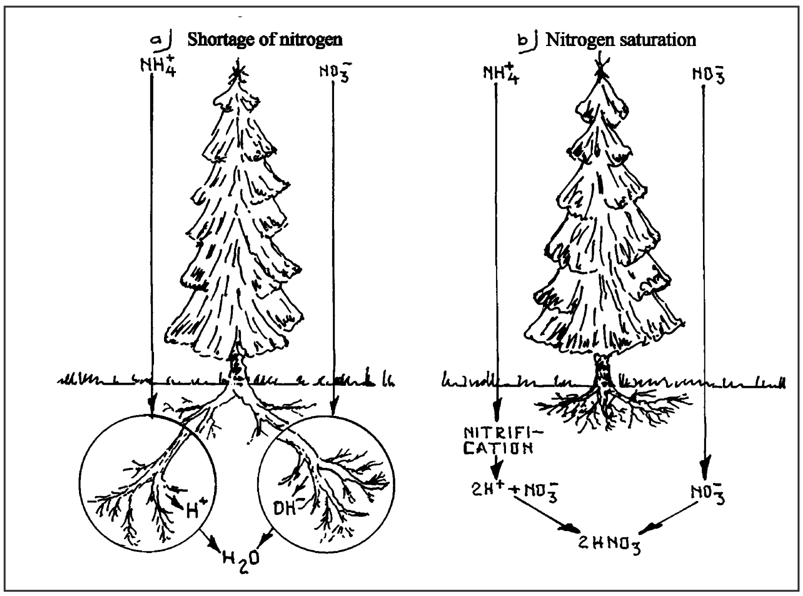


Figure 5.5. *When there is a shortage of nitrogen in the soil the plant assimilate nitrate in exchange for a hydroxyl ion that is secreted from the roots, while ammonia is assimilated in exchange with a hydrogen ion. If there is a surplus of nitrogen the nitrate leaches and ammonia is nitrified. During nitrification hydrogen ions are formed, and the soil and water becomes acidificated (KTH, 1996).*

6. Methodology

In this chapter the used methods are presented. Land use maps are an essential utility in order to analyse the collected data, and the operations used for land use mapping is: interpretation of aerial photos, sampling schemes for evaluation points, digitizing and finally accuracy assessment using the Kappa coefficient of agreement. Water samples were collected for laboratory analysis of total-N, nitrite/nitrate, and conductivity. Finally, a Digital Elevation Model (DEM) was made in order to isolate sub-drainage basins within the watersheds. The methodology used for further analysis of data is explained more accurate in the chapter “Results and discussions”.

6.1. Creation of land use maps

One component necessary to determine how different kinds of land use affect the nitrogen leakage is the need of updated and accurate land use maps. In this study land-use maps of the two watersheds of the rivers Graisupis and Vardas were made.

6.1.1. Interpretation of orthophotos

The investigation was based on interpretation of black and white aerial photos from 1995. These photos were orthometrically rectified in Lithuania and the result obtained was an image that has orthographic properties rather than those of the central perspective of the original aerial photo. These are called orthophotomaps and can be used for most purposes as maps, because they show correct planimetric position and preserve consistent scale throughout the image (Campbell, 1996). The images were of good quality and free of cloud cover.

Former land use maps at LWMI were created from the same orthophotos that were used for this study. When LIWM creates land use maps, they copy parts of the photos into several maps in A4-size, showing only enlarged parts of the watershed. These enlarged copies are then brought out in the field where land use is observed, and borders and distances are paced out. This method is very time consuming and therefore, as part of the aim, a new method including the use of GPS and aerial photo interpretation was introduced to the institute.

The orthophotos used had a scale of 1:10 000, and from these photos training sites were chosen and then visited in order to construct an appropriate classification system. The classes defined are presented in table 6.1.

Table 6.1 Land use classification system**.**

ID	Land use	Definition	Ground features	Image appearance
1	Agricultural land	All agricultural land that are ploughed within five years.	Ploughed farmland, farm roads	Fields frequently have straight or even sides. Sharp boundaries. Contour plowing.
2	Pasture	Areas without trees, bushes, meadows that are kept open by grazing animals.	Open grassland, farm roads, occasional isolated shrubs, trees.	Field frequently large. Irregular shape, indistinct boundaries. Homogenous surface. No tracks from machines
3	Deciduous forest	Forest that contain 100 per cent deciduous trees like birch, oak, alder etc.	Tree crowns	Tree crowns usually dominant features. Coarse texture.
4	Mixed forest	Forest containing both deciduous- and coniferous trees. Never more than 20 per cent coniferous trees in a mixed forest.	Tree crowns, spots with coniferous trees.	Tree crowns usually dominant features. Coarse texture. Darker than deciduous forest.
5	Settlement	Houses, gardens and orchards.	Individual homes, lawns, streets, trees.	Regular street pattern, rooftops visible, rectangular buildings arranged in clusters.
6	Roads	All roads	Broad roads, farm roads, streets.	Regular street pattern, boundaries sharp.
7	Wetlands	Swamps and marshes.	A flat area	Texture, homogenous surface.
8	River	The main river branches of Graisupis and Vardas, together with second order tributaries.	River branches.	Regular pattern with meandering branches.
9	Water	Small pond near settlement.	Small irrigation ponds.	Circular pattern with very homogenous surface.

The interpretation was dependant of our skill of determining the classes and the interpretation was sometimes aided by the knowledge of the staff of LWMI. The result of the interpretation was then recorded on a translucent film that registers to the image. This was done for both drainage areas. The interpretations were then copied and brought out in the field, when sampling for the accuracy assessments were performed.

6.1.2 Land use maps and accuracy – brief overview

Land use maps based on aerial photography require evaluation by field observations. Although the prediction method may have been based upon field data, its reliability as a method can only be ascertained by a post facto test using independently sampled field observations. This because there is a need to determine the accuracy or frequency of error to which the interpretation is prone (Hay, 1979). Thus, a map is useless without any knowledge of its accuracy. Accuracy defines correctness and it thereby measures the agreement between a standard assumed correct and a classified image of unknown quality. Accuracy consists of bias and precision and within statistical context high accuracy means that bias is low and that the variability of estimates is low (Campbell, 1996). Accuracy question can be answered with complete confidence if the study contains many samples. However, many samples involve field observations, which the prediction technique is presumably designed to avoid (Hay, 1979).

6.1.3 Accuracy, sampling schemes and GPS

In order to determine the location of evaluation points for the accuracy assessment a GPS receiver was used. Evaluations of the land use was carried out by road sampling in Graisupis and transect sampling in Vardas, figure 6.1. Road sampling is conducted by driving along the roads in an area, and in a certain interval a GPS point is measured. Transect sampling means walking along a randomly distributed transect in the area, either north–south or east-west, and at a certain interval stop and measure your position. The land use class that a position belonged to was decided out of a 25 m radius from the center of the spot. The location belonged to the category that it shared the largest part of.

The evaluation points were measured with a Garmin 12 XL navigator. This GPS receiver has 12 channels and the position is updated every second. All measurements were carried out during good conditions, and signal quality (SQ) was therefore satisfying. In 2-dimension navigation mode, the GPS uses at least three satellites with satisfying SQ to calculate a 2D position, for example latitude and longitude. The accuracy of the equipment is about 15 m in normal mode, but can vary between 0-100 m according to GARMIN (1997).

Graisupis

Road sampling was the chosen sampling scheme for Graisupis. All drivable roads in the watershed were followed and each 200 m the car stopped and a point was measured approximately 30 m from the road. The reason for choosing road sampling was that the farmers were not that keen on having strangers walking around on their properties. No one from LIWM had time to spend in the field at the time of sampling, and the farmers do not speak English at all, which made it difficult to explain the purpose of the study without staff from the institute. Forty-five sample points were collected with road sampling, and six of them were used as GCP (Ground Control Points) in the digitizing.

Vardas

In Vardas, guidance by staff from LIWM made it possible to walk around in the drainage area. This gave us the opportunity to carry out transect sampling, which was to prefer in this area because there were not that many roads. Transect sampling was the planned sampling scheme for both drainage areas before leaving for Lithuania, but it was, as mentioned, changed for Graisupis.

The five transects were randomly distributed in an east-west direction in the drainage area. A GPS position was measured every 100 m in order to get a representative view of the entire area because the area is very heterogeneous. A total of eighty-three points were collected in Vardas, and five of them were used as GCP´s.

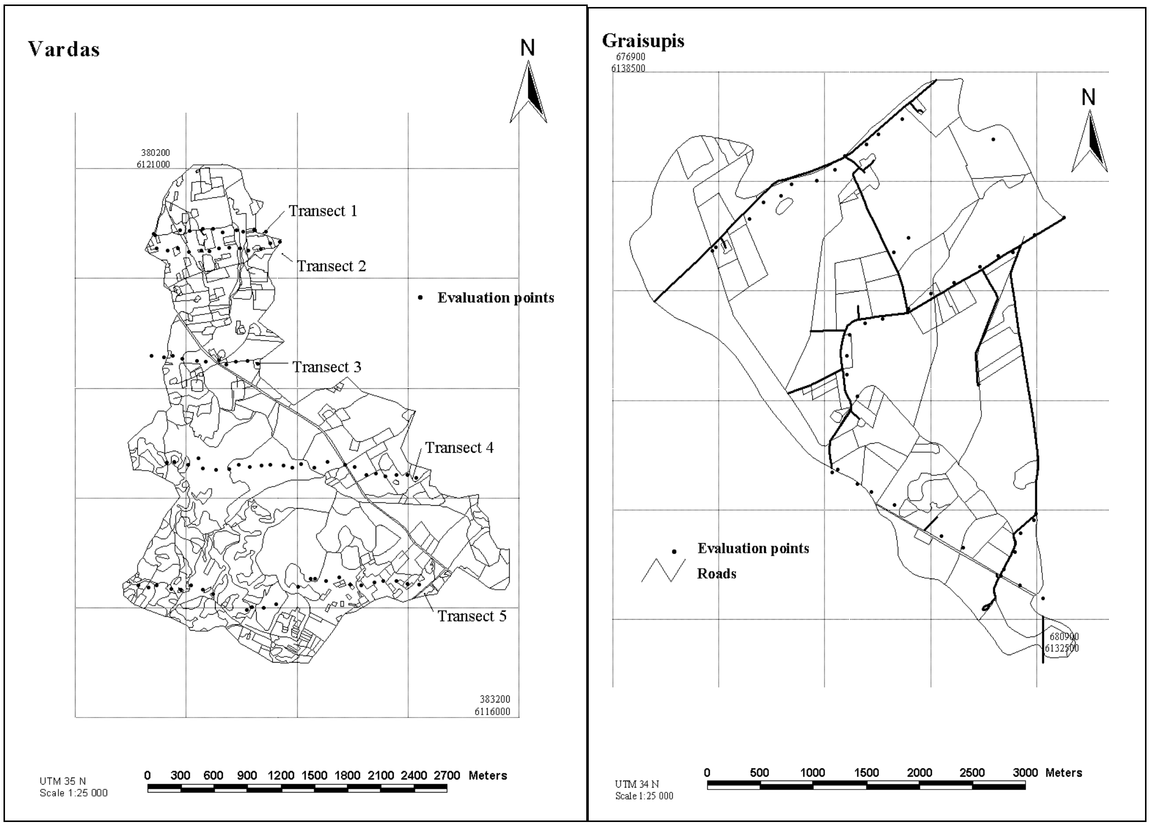


Figure 6.1. *Maps showing the transect sampling in Vardas and the road sampling in Graisupis.*

Map datum and reference system

The orthophotos used for the interpretation had WGS84 as map datum, but the reference system was an uncertainty. Most likely the reference system was UTM and this was thereby chosen (LIWM pers. com). The GPS was then programmed for WGS 84 and UTM when the samplings were carried out. UTM was also chosen because the positions are given in m and thereby no conversion from degrees to m is necessary. The UTM system divides the earth into 60 zones each 6 degrees of longitude wide. These zones define the reference point for UTM grid coordinates within the zone. UTM zones extend from latitude of 80° S to 84° N. The zones are numbered 1 through 60, starting at the international date line, longitude 180°, and proceeding east. Zone 1 extends from 180° W to 174° W and is centered on 177° W. Lithuania is situated between the 34:th and 35:th zone. Consequently, the watershed of Graisupis lies in zone 34 and the watershed of

Vardas, which lies more to the east, is in zone 35. UTM easting coordinates are referenced to the centerline of the zone known as the central meridian. UTM northing coordinates are measured relative to the equator (Internet 5).

6.1.4 Digitizing

In both catchments, fix points were measured in places that could easily be recognized in the orthophotos. These fix points was later used in the digitizing. In every location, five GPS coordinates were measured, i.e one coordinate in every minute for five minutes.

In order to digitise the produced maps, the program Carta Linx version 1.1 (ClarkLabs, 1998) was used. A coverage in Carta Linx consists of two files in which the first contains the spatial frame and the second contains its associated attribute data table. The reference system was set to UTM 34N for Graisupis and UTM 35N for Vardas and the reference unit was m. In order to register the digitizing tablet the reference points measured in the field with the GPS were used as control points. These reference points were applied straight from the GPS and therefore they had position errors. These locations/positions were used for the reason that the orthophotos was in an unknown reference system and reference points could not therefore been taken from the photos.

A mean of the raw GPS points were calculated with vector addition (Ardö, pers.com. and Pilesjö, 1992). This was made in order to obtain more accurate coordinates. Vector addition means that you measure the greatest distance in both X and Y from a reference point. Our reference points consist of a mean of five measurements. From this five measurements two extremes were excluded and a mean were calculated on the remaining three. These new coordinates were put in an ungenerate file together with an ID. This file was imported in IDRISI (Clarklabs, 1998) with Arcidris and converted to a vector file. A documentation file was created and then the file was converted to binary format. Then it was exported to ArcView as a point shapefile. This shapefile could then be imported in ArcView.

The entire land use maps were digitised as one coverage and in point mode. Then polygon locators were inserted in the areas that would represent polygons. These polygon locators were associated with a unique identifier and a category. The polygon locators contain information about each polygon and its ID has to be unique. Even the roads and streams got unique identifiers. The RMS (Root Mean Square) for the control points was 25 m for Graisupis and 14.5 m for Vardas. RMS explains the internal positional error between the measured GPS points (Clarklabs, 1998). Finally, a filter was designed to erase all dangling arcs. The polygons were digitised so that the roads or rivers separated them, and where no rivers and roads existed, the polygons shared a common arc. The main road in both Graisupis and Vardas was digitised as a polygon. The reason for doing this was that this road was wider than the roads leading to farms and villages. Thus, a single arc would not be representative as the main road.

Coverage contents are exported on a layer basis. However, one can only export the polygons, the nodes, or the arcs at each time. This means that it is necessary to carry out three export operations in order to obtain a complete coverage. The coverages were then exported as ArcView shapefiles and then modified in ArcView in order to be representable.

6.1.5 Accuracy assessment using Kappa

The kappa coefficient of agreement is frequently used to summarize the results of an accuracy assessment used to evaluate land use or land cover classification obtained by remote sensing. Kappa can vary between –1 and +1 and expresses in which proportion the map differs from a random. Thus, +1 means that the map is 100 per cent correct whilst 0 means that the mapping is just as good as a randomly spread set of evaluation points would give. By comparing the created land use maps with the expected land use, kappa was calculated (Stehman, 1996).

Kappa is obtained by $k=\dfrac{\sum_{i,i=1}^{n} p_{ii} - \sum_{i,i=1}^{n} q_{ii}}{1-\sum_{i,i=1}^{n} q_{ii}}$ where

k = kappa, coefficient of agreement
i = classindex
n = number of classes
p_{ij} = proportion of observed agreement
q_{ij} = proportion of expected agreement

To achieve the coefficient of agreement, Kappa, four confusion matrices were done. A confusion matrix is a cross tabulation between the map that is going to be assessed, and the reference data that it will be assessed and compared to.

6.2. Watersampling

Water samples were needed to find out total-N and nitrite/nitrate leakage from land to surface water. The sample values of conductivity and nitrite/nitrate are used in the regression analysis, and the total-N values together with nitrite/nitrate are used together with the land use maps and the DEMs in order to investigate the leakage from different land use classes.

According to Enell and Larsson (1985) you cannot randomly collect your samples. That is the reason for creating a sample scheme of your own regarding the aim of the analysis. The sampling sites were therefore manually selected according to the morphology of the watersheds. Samples were taken before and after every river junction, at the outlet, and in every beginning of a river branch, figure 6.2. The samples were also collected upstream the sample site in order to avoid turbulence and sedimentation caused by us. Some of the river branches were dried out and no samples were therefore collected in these places.

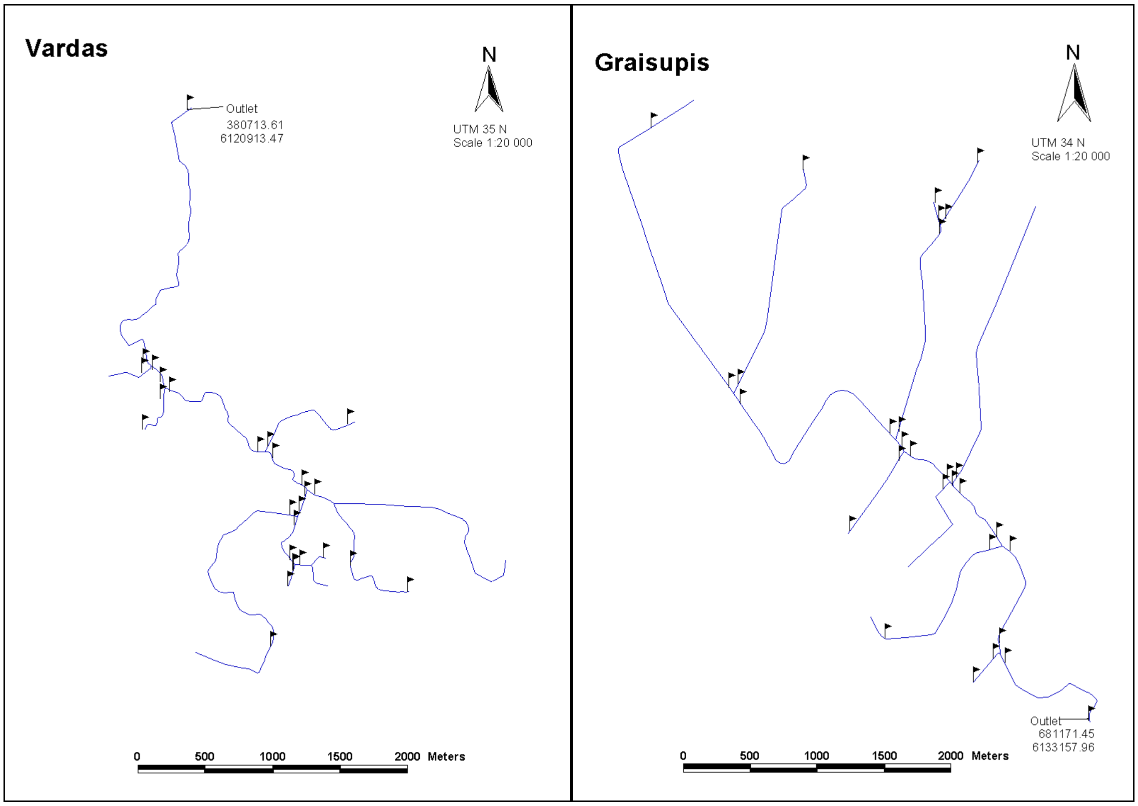


Figure 6.2 *Maps showing the sample sites of the collected watersamples for laboratory analysis of total-N and nitrite/nitrate.*

According to Enell and Larsson (1985) the sampling should be done in one day, which makes the study momentous. If the samples were not collected in one day, a sudden rainfall would change the chemical properties of the river water, which in turn would make comparisons within, and between, the watersheds impossible. After the samples had been collected, they were kept dark and cold until analyzed the day after. The laboratory in Kedainiai analyzed total-N, NO_3^-, NO_2^-, and conductivity, both dissolved and solved matters. The nitrogen was measured with the FIA star 5012-system from the Swedish firm TECATOR. Flow injection analysis AN 562 and AN 5621 measured the sum of the nitrite/nitrate in water, and the water was filtered before analysis. The total nitrogen in water was measured by flow injection analysis ASN 5623, and the analysis was performed after the sedimentation in the bottles. PH should have been measured as well, but due to language difficulties, the laboratory did not do that.

When measuring conductivity a portable conductivity gauge (Coductivity meter HI8733, Hanna Instruments) was used and calibrated to 18° C at the Department of Ecology in Lund. The calibration was also checked twice in Lithuania, where 0.1M KCL solutions were used. The solution should then show 11.67 ms/cm if the gauge was properly calibrated. The conductivity gauge was used for continuously measuring the conductivity along the river branches, at a distance of about every 50 m. When passing areas of homogenous land use on both sides of the river, conductivity was measured at closer intervals. The output value from the conductivity gauge was in mS/cm. Conductivity for the sample points were analyzed in laboratory as well. This was done in order to compare our own measured values with the values from the laboratory analysis. The total number of conductivity sample points collected in Graisupis was 88, but only 24 of them were used in the regression analysis, because they were to be compared with the nitrite/nitrate values. In Vardas a total of 66 conductivity samples were collected, and 25 of them was used in the regression analysis.

6.3 Creation of the DEM: S

Digital Elevation Models (DEM) is in this study used to compute the area of sub-drainage basins of a specific water sampling point. This enables the possibility to examine how specific land use classes within an isolated drainage basin affect the nitrogen leakage in a certain point.

In order to create DEMs for the watersheds, topographic data was collected from LIWM. This data did not fit the produced digital maps so they were changed to UTM 34N and UTM 35 N. This was carried out in ArcInfo with the help of command transform that changes one map into another with the help of tic points. The operation simply move one coverage to another position by shifting the x and y coordinate. The resulting map was then in UTM and could be used in Hutchinson ANUDEM-topogrid, which was the interpolation method used. This is a spline based interpolation process, which uses drainage enforcement. This procedure requires that all arcs are pointing downslope and that no braided streams or polygons exists in the network. The arcs were turned downslope by flipping the arcs in a module in ArcInfo. Topogrid generates a hydrologically correct grid of elevation from point, line and polygon coverages. The interpolation process has been designed to take advantage of the types of input data commonly available, and the known characteristics of elevation surfaces. Water is the primary erosive force determining the general shape of most landscapes. For this reason, most landscapes have many local maximums and few local minimums. Topogrid uses this knowledge and imposes constrains on the interpolation process that results in connected drainage structure and correct representation of ridges and streams (ESRI, 1997).

In the created DEMs, contour lines were used as input in the interpolation process and the grid resolutions were set to 5 m for Vardas and 10 m for Graisupis. The high resolution was chosen in order to locate the points in which the water samples were taken as accurate as possible. The reason for the differences in resolution was determined by the capacity of the computers.

The DEMs were used in ArcView in order to fill sinks, and calculate flow direction and flow accumulation. These operations are a necessity in order to obtain which parts of a DEM that drains to a certain point. The flow calculated is a one-directional flow, which is a very general way of describing flow direction. Nevertheless, it is at the same time a very easy way to obtain flow direction. The output of the flow direction request is an integer grid whose values range from 1 to 255. The values for each direction from the centre are, figure 6.3:

32	64	128
16	X	1
8	4	2

Figure 6.3. *A pixel is given one of the above values depending on its flow direction.*

If a cell is lower than its eight neighbours, that cell is given the value of its lowest neighbour and flow is defined towards this cell (ESRI, 1997).

An application written in Visual Basic 6.0 for one-directional (Eklöf, 1999) flow was used for the drainage basin analysis. The application uses the calculated flow direction layer in order to obtain the drainage basin of a pixel. The input to the application is the number of rows and columns in the grid used, and the row and column value for the wanted pixel. The layer with flow accumulation was imported to Idrisi where the points for watersampling were located, and from this location, the drainage basin was calculated. In order to find the points that gave the drainage area for the wanted pixel forced us to search along the vector data layer representing rivers. A pixel that is situated in the bottom of a valley and on the vector layer representing the river usually gets a very high pixel value. The chosen pixel was determined by its place according to the water sample point. That was about 20-25 m from every river junction. The layer with land use was imported into Idrisi and then a cross tabulation was performed in order to achieve the area for every single land use class in its specific sub-drainage area.

7. Results and discussions

In this chapter, the results and discussions of the specific aims are presented. For the last three of the four aims the methods of analysis are described as well.

7.1 Aim 1: Land use maps of river Graisupis and Vardas watersheds

The produced land use maps of river Graisupis and Vardas are used both for the third aim; which is the conductivity values and land use, and the fourth aim; which is the analysis of land use contra nitrogen leakage. The maps are presented in the scale 1:25 000.

7.1.1 Results

Graisupis and Vardas

Figure 7.1 and 7.2 shows the resulting land use map made for both drainage basins. The distribution of land use in the basins is presented in table 7.1.

Table 7.1. The percent distribution of land use within the watersheds of river Graisupis and Vardas.

Landuse	**Graisupis, km^2**	**Per cent**	**Vardas, km^2**	**Per cent**
Cropland	8.11	71.8	1.39	18.4
Pasture	0.32	2.8	3.95	52.3
Mixed forest	1.27	11.2	0.79	10.5
Deciduous forest	1.25	11.1	1.00	13.2
Settlement	0.32	2.8	0.23	3.0
Road	0.03	0.3	0.05	0.7
Wetland	-	-	0.14	1.9
Water (Pond)	-	-	0.00	0.1
Total	11.30	100%	7.55	100%

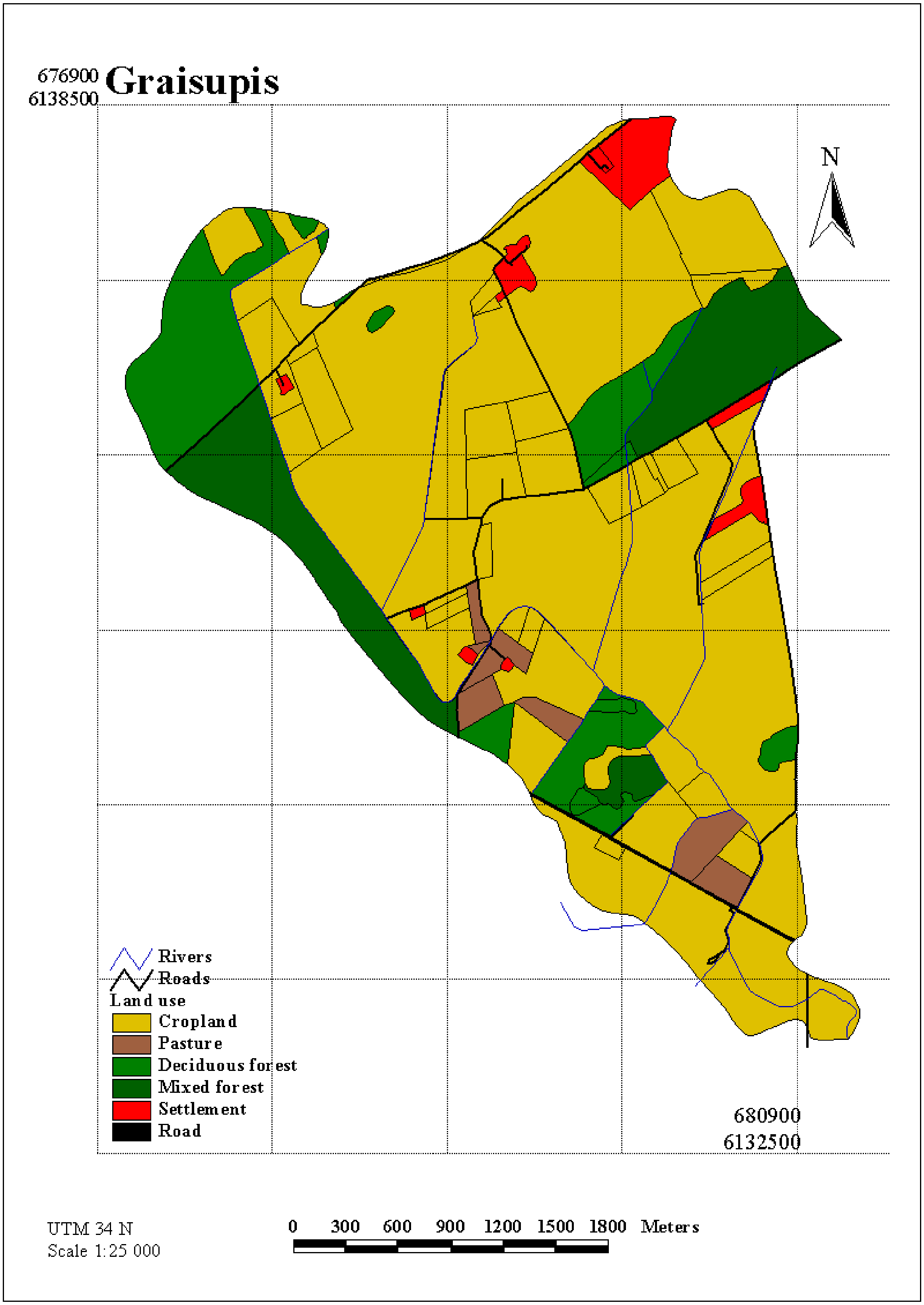


Figure 7.1. *Land use map of Graisupis watershed.*

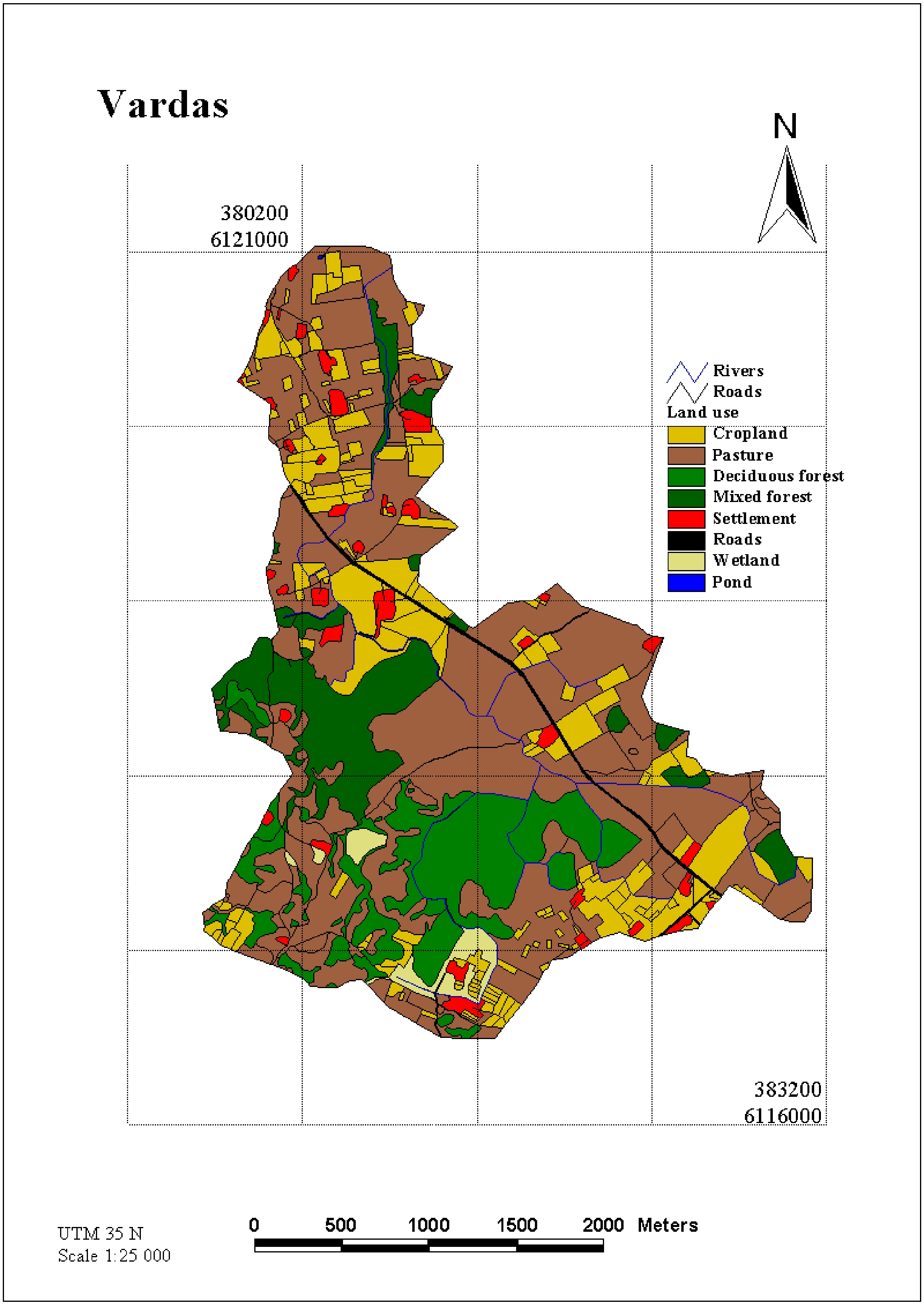


***Figure 7.**2. Land use map of Vardas watershed.*

The Kappa coefficient of agreement – results

The results of the accuracy assessment when using Kappa shows that the land use map of the watershed of river Graisupis has an accuracy of 0.67, and the watershed of river Vardas has 0.55. A value of +1 means that the map is completely correct, and the value 0 means that the map is not better than a haphazard distribution of accuracy points would give. The results show that the created land use maps are satisfying regarding to the intention they are used for in this study. The matrices used for the calculation of Kappa are presented in appendix III.

7.1.2. Discussion

The produced maps give an approximate view of the two watersheds and that was the intention. Thus, the maps were satisfying for the analysis according to the Kappa coefficient of agreement. The accuracy of the maps may be satisfying, however, the method and material used was not ideal. According to Hay (1979), a time interval between the time when the aerial photos were taken and the time of interpretation and field survey may result in error in the interpretation. This was the case with the photos used in this study. The photos were four years old and considering for example that the crop rotation is five years, one can imagine that the land use has changed. Another source of error was that the tic-points used when digitizing was based on GPS-measured locations, which means that internal errors occur. In this case, a GPS error of 14.5 m for Vardas and 25 m for Graisupis was obtained. Consequently the error increases due to the fact that a GPS in normal mode was used, which produce positioning errors between 0 - 100 m. Ideal would have been using new aerial photos and differential GPS. If LIWM adopt the method used in this study they are probably going to achieve better accuracy than what was presented in this study, because they are soon able to use D-GPS.

Digitizing the maps in CartaLinx (ClarkLabs, 1998) was not easy. Learning the entire package was necessary in order to carry out the digitizing. If redoing this operation, ArcInfo (ESRI) should be used, because that software is easier to handle concerning file formats and the structure of the produced map.

7.2 Aim 2: Regression analysis of nitrite/nitrate and conductivity

7.2.1 Methods

The aim was to examine if a relationship between conductivity and nitrite/nitrate could be established in both watersheds. A strong significant relationship between these two variables was found in the Genevad drainage basin in Halland, Sweden (Wickberg, 2000).

Before doing any statistical tests and analysis there is a need to check if the samples are normally distributed (Shaw and Wheeler, 1996). The Anderson – Darling normality test was used to examine the degree of normality in numbers. Considering the p-value from the Anderson-Darling normality test, the value should be lower than the significance value (0.05) in order to reject H_0. H_0 says that the data follow a normal distribution. When the p-value is less than 0.05 the distribution is said not to be normal (Minitab Inc., 1998 and Bärring, pers.com.).

When analyzing the conductivity values in *Graisupis*, measured with the portable conductivity meter, they did not show a normal distribution, table 7.2. Six conductivity values were ignored because the sample sites were situated next to straw- and manure stacks, which lead to abnormally high conductivity values. However, the analysed values for nitrite/nitrate showed a normal distribution. To make the samples of conductivity normally distributed a data transformation was made using the logarithms of the values (Shaw and Wheeler, 1996). The logarithms were used for both conductivity and nitrite/nitrate to be able to compare the samples in a proper way. The conductivity data then became normally distributed, but not the nitrite/nitrate data. Thus it was decided to use the original data, and not the transformed, in the regression analysis.

Neither the conductivity nor the nitrite/nitrate values for *Vardas* were normally distributed. When using the logarithms of conductivity the samples did not show a normal distribution, but nitrite/nitrate did, table 7.2. It was decided to use the transformed values in the regression plots for Vardas, because at least the values of nitrite/nitrate became normally distributed when transformed.

Table 7.2. The p-values of the Anderson-Darling normality test of the samples. A p-value lower than 0.05 at the significance level 95 per cent says that the samples are not normally distributed (Minitab Inc, 1998). G= Graisupis, V= Vardas.

Variable	P-value	N (sample size)	Normally distributed
Conductivity (G)	0.028	24	No
Nitrite/nitrate (G)	0.419	24	Yes
Conductivity (V)	0.000	25	No
Nitrite/nitrate (V)	0.874	25	Yes

When examining if a relationship existed between conductivity and nitrite/nitrate, regression analyses were made using the same variables as in the Genevad study (Wickberg, 2000). Regression analysis shows how one variable controls another (Shaw and Wheeler, 1996). This analysis does not require data to be normally distributed (Eklund and Bärring, pers. com.).

When doing a regression analysis there is a need to measure and determine the strength of the statistical relationship between the two variables. This is done through the method of correlation analysis. The correlation analysis shows that there is a complete absence of any statistical relationship if the value is 0.0 (Shaw and Wheeler, 1996). The correlation values were obtained by the use of Pearson´s correlation test in Minitab, as well as from the RSq-values showed in the regression plot. To examine if the variables correlate or not the critical values of Pearson's correlation coefficient were used (Shaw and Wheeler, 1996 and Minitab Inc., 1998).

7.2.2 Results

Graisupis

The regression plot for conductivity and nitrite/nitrate for Graisupis watershed shows a percent-explained variation (R-Sq) of 3.6 per cent, figure 7.3. The correlation of this regression is 0.190. Six extremely high values were ignored, because the samples were taken next to straw- and manure stacks, which of course makes them abnormally high due to the leakage of nutritive salts.

When looking at the critical values of the Pearson correlation coefficient the observed correlation is significant if it exceeds the tabled value of 0.404 when the sample size is 24 (Shaw and Wheeler, 1996). Obviously the correlation value in this regression (0.190) does not exceed the tabled value. Thus, there is no relationship between conductivity and nitrite/nitrate in river Graisupis.

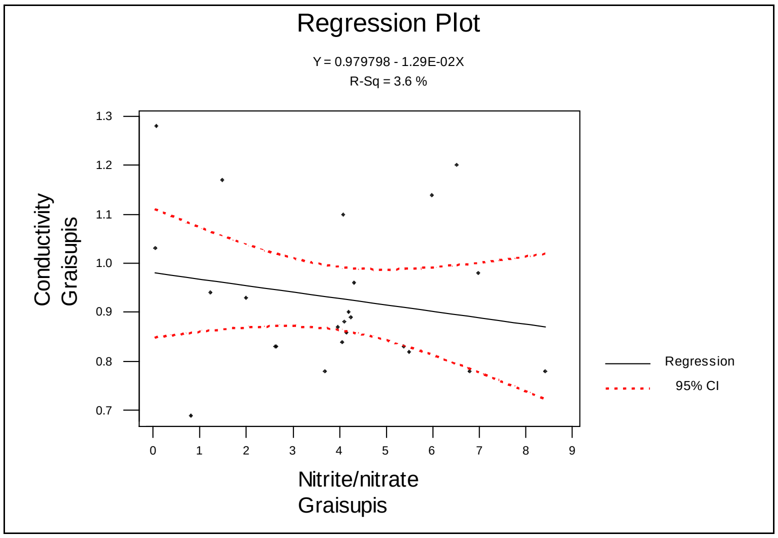


Figure 7.3 *Regression plot of conductivity and nitrite/nitrate from river Graisupis. The dotted line shows the confidence limits. If the confidence limits are narrow the estimate is reliable, and if they become wider the data is more circumspect (Shaw & Wheeler, 1996).*

Vardas

The regression plot between conductivity and nitrite/nitrate in Vardas has a percent explained variation (RSq) of 3.4 per cent, and a correlation of 0.184, figure 7.4. In this regression the Pearson correlation coefficient for 25 samples is 0.396, and when comparing with our correlation value (0.184) one can see that there is no correlation in this regression (Shaw and Wheeler, 1996). Thus, there is no statistical relationship between conductivity and nitrite/nitrate in river Vardas.

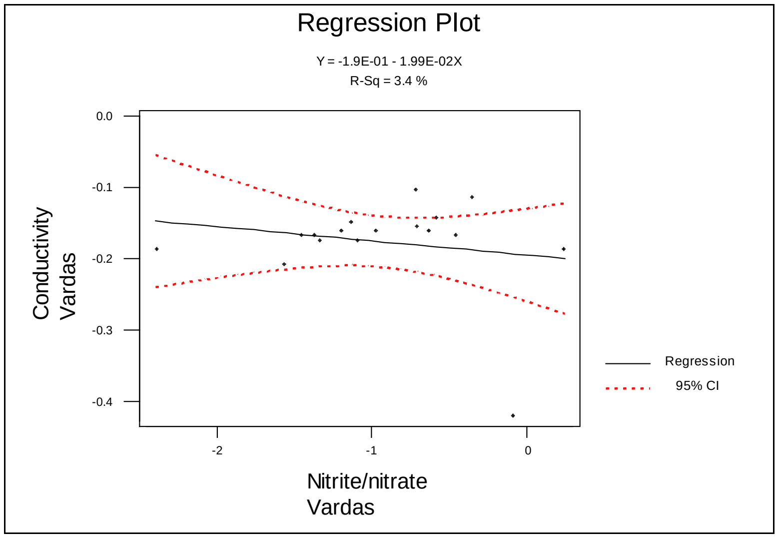


Figure 7.4. *Regression plot of conductivity and nitrite/nitrate in river Vardas. The dotted line shows the confidence limits, and also here it is rather wide.*

Comparison between Graisupis and Vardas - summary of results

There is no significant statistical relationship between conductivity and nitrite/nitrate in either of the rivers Graisupis or Vardas.

After the regressions are made one can examine the residual plots and other regression diagnostics to assess if residuals are random or normally distributed. Residuals are the difference between the observed values and predicted or fitted values, data minus fits (Minitab Inc., 1998). When observing the normal plot of residuals, the points in the plot should form a straight line if the data are normally distributed. The residual plots for the regression analysis for Graisupis shows a slight normal distribution, but the plots of Vardas has no normality imposed on them. Thus, the data should not be used in further analysis (Shaw and Wheeler, 1996).

7.2.3. Discussion

In one way it is natural that no relationship exists between conductivity and nitrite/nitrate, because the conductivity is most often affected by other major ions in water. Conductivity, expressed as the salinity of the water, is the sum of the ionic composition of the eight major cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and anions (CO_3^{2-}, SO_4^{2-}, Cl^{-}). Nitrate (NO_3^{-}-N) is also an ion, and in some places it may contribute to the conductivity if it has very high values. Most often nitrate concentrations are so low that it does not affect the conductivity (Leonardsson, pers. com. and Wetzel, 1986). Salinity, in turn, depends upon ionic influences of drainage and exchange from the surrounding land, like the composition of soil and rock, precipitation, and the evaporation-precipitation process. Calcium and bicarbonate are the dominating ions that affect conductivity in large regions of the temperate zone, in which also Lithuania is included (Wetzel, 1983). All over the country of Lithuania the soil is rich in calcium (LIWM, pers.com.). High calcium values are therefore the reason for the high conductivity values in both Graisupis and Vardas (Leonardsson, pers.com). In fact, our conductivity values are twice as high compared to the values of, for example, Sövdesjön in Scania, Sweden. The most important thing though, is that the values of conductivity are high but reasonable (Leonardsson, pers. com.).

In the Genevad drainage basin Wickberg (2000) found a strong relationship between conductivity and nitrate (correlation coefficient 0.91 - 0.93 at the 95% significance level). Wickberg (2000) discussed in his paper that it would be interesting to see if the relationship existed anywhere else than in the Genevad drainage basin, or if it was valid only there. However, this study shows that the relationship probably exist only in the Genevad drainage basin due to factors specific for that study area. These factors are; the absence of large retention areas (lakes and wetlands), the geochemical conditions in rock and soil, the absence of point sources, and the fact that the land use strictly follows the variation in soil type (Wickberg, 2000). The difference in geochemical conditions of rock and soil is probably the main factor that contributes to the differences between the Genevad drainage basin and the two watersheds in Lithuania. In Lithuania, as mentioned above, calcium plays a more important role for conductivity than nitrate does.

Sources of error
If there are few samples it is less apparent to have a symmetrical and normal distribution because irregularities from class to class are more likely to occur (Shaw & Wheeler, 1996). However, in the regression analysis, only 24 and 25 samples were used. Normally there should be at least 30 samples in order to perform a statistical test (Shaw and Wheeler, 1996). Another error could have been that the samples was not analysed the same day as they were collected. This means that the chemical composition could have changed.

7.3 Aim 3: Analysis of conductivity values in water from different land use classes

7.3.1 Methods

The aim of this analysis was to use the established relationship between nitrite/nitrate and conductivity in order to calculate the nitrate/nitrite concentrations by only measure conductivity at several different locations along the streams. The measured conductivity value was to be used in the regression equation in order to obtain the nitrite/nitrate concentration in a certain point. This would then be an easy, cheap and fast way to measure the nitrogen leakage from different kinds of land use.

There was no relationship between conductivity and nitrite/nitrate in either of the watersheds, so the regression equation could not be used to estimate the concentration of nitrite/nitrate. Despite this, it was interesting to investigate how and why the conductivity values where distributed in the way they were. For example, conductivity is higher in more nutritive waters, and it is a measure of the amount of nutritive salts that leaks to the water (Wetzel, 1983). Conductivity values can also be used to find out how acidified the water is, when higher conductivity values shows a higher degree of acidification. These two examples can tell how polluted the river water is due to the leakage of several different nutrients. When studying the distribution of conductivity values there might as well be explanations for not having a strong relationship with nitrite/nitrate.

In order to study the conductivity values several classes was created based on their homogeneity. A homogenous class means that there is the same land use at both sides of the river branch. Non-homogenous classes have different land use on the two sides of the river branch. It is important to mention that the land use on each side of the river is not only a narrow strip; it reaches at least 20 m from the river. The classes are:

Homogenous

1. Cropland without crops - Cropland without crops
2. Cropland with winter crops - Cropland with winter crops
3. Forest - Forest
4. Pasture - Pasture
5. Fallow - Fallow

Not homogenous

6. Cropland without crops - Pasture
7. Cropland without crops - Cropland with winter crops
8. Forest - Cropland without crops
9. Forest - Cropland with winter crops
10. Forest - Pasture
11. Cropland with winter crops - Pasture
12. Cropland without crops - Straw stack

As one can see (table 7.3) there are large differences in how many samples that were taken in each class. The samples were collected about every 50 m. When passing a homogenous class along the river, some extra samples where collected. There are also values missing in some classes, because every class was not represented in both watersheds. The study was momentous, and it was therefore not possible to collect more samples at another occasion, because the conductivity value may then have been different due to chemical changes of the water caused by precipitation etc.

Table 7.3. Average conductivity values from different land use classes. Within the parenthesis are the numbers of samples taken in each class. Conductivity values are measured in mS/cm.

Class	1	2	3	4	5	6
Graisupis	0.91 (13)	0.83 (1)	1.01 (8)	-	-	0.91 (3)
Vardas	0.67 (6)	-	0.70 (3)	0.69 (3)	0.63 (5)	0.65 (10)

Class	7	8	9	10	11	12
Graisupis	0.86 (32)	0.85 (11)	0.85 (7)	0.89 (2)	0.86 (3)	1.56 (5)
Vardas	-	0.73 (9)	-	0.70 (32)	-	-

7.3.2 Results

Graisupis

When examining the *homogenous* land use classes and their values one can see that for Graisupis the highest conductivity values are found in class 3 which is forest - forest (1.01). Next class in the ranking is class 1, cropland without crops - cropland without crops (0.91). The third class in the ranking of homogenous land use classes is number 2, crop land with winter crops - cropland with winter crops (0.83).

The value for class 12, cropland without crops - straw stack (1.56), is higher than all the other values, but it is not representative. The reason for this is that this value is very high because of the location of the sample point next to a manure and straw, which leak lots of nutrients and nutritive salts.

It is also interesting to examine the *not homogenous* class 6, cropland without crops – pasture (0.91), and class 10, forest - pasture (0.89). These classes have values almost as high as class 1 with cropland without crops on both sides.

Vardas

Also in Vardas one of the highest conductivity values is found in class 3, forest - forest (0.7) when looking at the *homogenous* land use classes. The second rank here is class 4, pasture – pasture (0.69). Class 1 with cropland without crops – cropland without crops has a value of 0.67. In Vardas there is also a class with fallow – fallow, which has the lowest conductivity values of all classes (0.63). It is strange that class 1, cropland without crop – cropland without crop, has such a low value in this area (0.67).

When looking at the *not homogenous* class 8, forest – cropland without crops, this class has the highest value of all in this watershed (0.73). Another high value is class 10, forest – pasture, that has a value of 0.70, which is as high as class 3.

Comparison between Graisupis and Vardas – summary of results

In both watersheds the homogenous class with forest on both sides of the river has high conductivity values. Another class that has high values is forest on one side and pasture on the other. In Vardas there are high values when there is pasture on both sides of the river. In conclusion; forest and pasture has a large effect on conductivity in both areas.

Graisupis has high values when there is cropland without crops on both sides. However Vardas does not have high values in this class. Vardas has instead high conductivity values when there are forest on one side and cropland without crops on the other, and Graisupis not.

The lowest values in Graisupis come from cropland with winter crops on both sides. In Vardas it is fallow on both sides of the river that shows the lowest values.

7.3.3 Discussion

The results from the water samples in both the rivers Graisupis and Vardas show that forests have the highest conductivity values. This is strange, because croplands usually have higher conductivity values than both forest and pasture. Cropland gets nutritive salts from fertilisers, and when ploughing, the nutritive salts circulate in the soil and are more easily transported and moved by the water (Andersson, 1986). In fact, these results show the opposite of what is normal compared with Sweden. In addition, the conductivity values are very high compared to normal values in Sweden (Leonardsson, pers. com.).

Forests

As mentioned above, conductivity is largely based upon the ions of which the soil and rock consists of. The soils chemical properties are closely related to the composition of parent rock, of which calcium is typical for Lithuania (Sileika *et al.*, 1998). Therefore the conductivity values here are most affected by the amount of calcium, which is also a cation. The results showed that the highest conductivity values came from forests. The humus layer in a forest soil, and the dead organic matter in the root zone, contains a large amount of cations. This storage of cations in a forest represents 50 years fallout from the atmosphere. When the amount of hydrogen ions in precipitation rise, when the pH value drop, the exchange of ions in the humus will change and finally at the end adjust to the changed composition in precipitation. Thus, when forest is exposed to acid rain, basic cations are released and exchanged with hydrogen ions. These released cations, which will not be assimilated by the roots, leave the root zone with the percolating water (Grip and Rodhe, 1994). In humid, well-drained regions, water selectively removes cations from weathering rocks and soils, and calcium is one of the most dominant exchangeable cations in neutral or alkaline soils (Wetzel, 1983). These percolated cations may explain the high conductivity values which are measured in the forests of the watersheds when the forests are affected by acid rain, together with the high amount of calcium in the soil.

Another explanation for high conductivity values in forest areas is an intense deforestation. When a forest is clear-cut the humus layer gets additional material like twigs and needles. This material is easily mineralised due to, among other things, the higher temperature in the ground in the clear-cut area when the forest is no longer protected from the sunshine. Through mineralisation the material is transformed into nutrients. Before any other vegetation settle down there are no roots that can use the released nutrients, and therefore they get lost to the groundwater (Grip and Rodhe, 1994). Clear cutting releases nitrates and other nutrients and salts to surface water flowing through forests, and if the concentration of these nutrients and salts are high, they may affect the conductivity (Fleischer *et al.*, 1991). There were no intensive forestry activities in anyone of the two watersheds, but in Graisupis there was a 1-2 ha clear-cut area in the northwestern part of the watershed. This area may affect the leakage of nutrients there. Mostly there were rather young trees in both watersheds. This can have three causes.

Between 1992-1996 the insect *Typographus* damaged all fir trees in Vardas, and they were later cut down. In the beginning of 1990s, due to changes in the economical situation and privatisation, some people made use of the unstable situation and cut trees in the forests, which was state property, for their own private needs. In addition, some years ago heavy storms caused quite many wind fallen trees (LIWM pers.com.). These three causes were the reason for the loss of older tress, and it probably affected the nutrient leakage from forests as well.

Pasture

When looking at the results from both watersheds, the surface water flowing through pasture has high conductivity values. The nitrogen leakage, and also the nutritive salts, from pasture should have low values. This depends on the fact that pastures never, or rarely, is ploughed. When it is not ploughed the nutrients are not circulated in the same way as in cropland, and therefore have lesser chance to be lost through leakage (Fleischer *et al*., 1991 and Leonardsson, pers.com.). Occasional high conductivity values may depend on adjacent forest areas.

Cropland

Graisupis has high conductivity values when there is cropland without crops on both sides of the river. This is normal because fields without crops cannot use the nutrients and nutritive salts in the soil. If winter wheat or winter rye is planted in autumn, they reduce the nitrogen leakage with 20-30 per cent, which is caused by crop uptake of nutrients and that water is lost through evapotranspiration rather than percolating down through the soil. The reason for Vardas having rather low values in this class can be explained by the lower storage of nutrients in the soil because the farmers do not use and have not used as much fertilisers as in Graisupis. In Vardas there are mostly small family farms with bad economy that can not afford to buy large amounts of fertilisers (LIWM, pers.com.). The above explanation also states why there are low conductivity values in Graisupis when there is arable land with winter crops on both sides

The lowest conductivity in Vardas was found with fallow on both sides of the river. According to Andersson (1986), fallow should not have any growing vegetation and the runoff should be twice as high as from fields that have vegetation all year around. However, in Vardas these fields were covered with grass vegetation, which reduced the leakage and consequently the conductivity.

General comments

In general, the conductivity is high in the waters of the two watersheds (Leonardsson, pers.com.). Data from LIWM, which are not allowed to be published, shows that apart from calcium, sulphate (S) is a dominating ion in stream water in Graisupis (unfortunately there is no data available for Vardas). As mentioned in the theory chapter, sulphate comes as acid rain (SO_4^{2-}) or dry particles (SO_4) from the atmosphere. These sulphates reach the watershed as wet- and dry deposition, not only in the forest canopy but also on the ground and on water surfaces. The high sulphate concentrations, confirmed by the chemical composition of precipitation, measured and analysed by LIWM (1999), probably cause high conductivity values in the watershed of Graisupis.

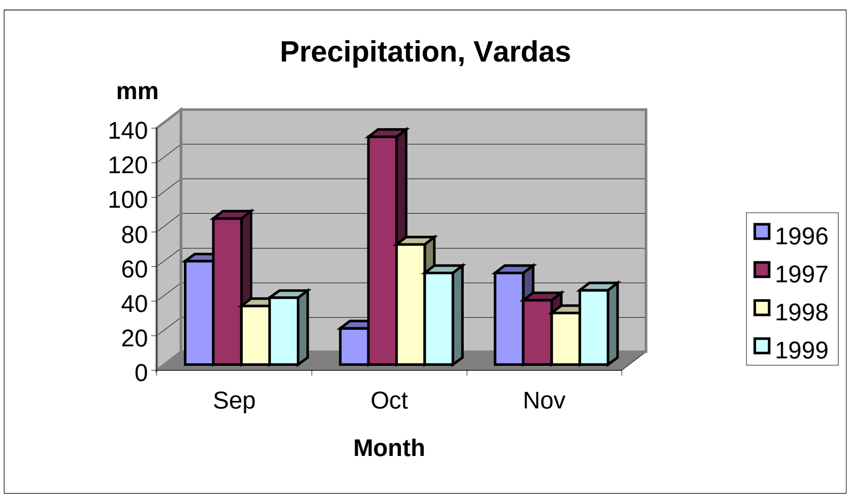
The reason for this is that sulphate is an anion (SO_4^{2-}), which also affects the salinity and therefore the conductivity. Sulphate is also a major constituent in acid rain, and it comes from the combustion of fossil fuels. There are lots of industries in countries neighbouring Lithuania, and also in Lithuania, that use fossil energy sources that may contribute to acid rain (Grip and Rodhe, 1994 and Wetzel, 1983). The acid rain releases the basic cations in the humus, as mentioned before, and thus the deposition of sulphate contributes to high conductivity values.

Oxidation of sulphides in the soil can also be a major source of sulphate for natural waters, usually in the form of dilute sulphuric acid (Wetzel, 1983). Subsurface drainage, e.g. through drainage pipes, considerably increases the aerobic zone in the soil and thus the amount of sulphuric acid produced. In aerobic conditions the sulphides are oxidised into sulphuric acid at a rate exceeding the soil buffering and neutralising capacity. Aluminium, iron and other metal cations are then dissolved during acidic conditions and leaches out of the soil profile. In addition, the acid sulphate topsoil also hinders plant nutrient uptake. This kind of sulphate rich soil is found in both Graisupis and Vardas (Joukainen, 1999).

The relationship between precipitation and conductivity

The precipitation data received from LIWM shows that in Graisupis watershed it rained little in September compared to the average rainfall during many years, figure 7.5. The amount of rain in October and November was rather normal compared to average precipitation. In Vardas it rained less in both September and October compared with the average, but normal in November.

During the time of the field study, three weeks in October – November, the waters of Graisupis and Vardas consisted of old groundwater due to the fact that it did not rain. This explains the high conductivity in the river water. The water discharge comes some time after the rain, or when the intensity of the rainfall has diminished. If it is a small stream it only takes a few hours. Hence, if it had been a rainfall during the time of the field study, a higher water discharge would have been noticed, and lower conductivity values as well.



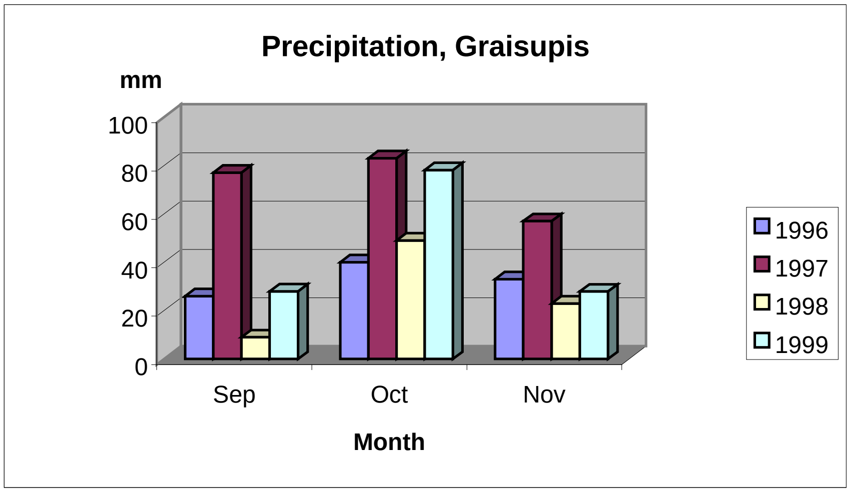


Figure 7.5. *Precipitation data for September, October and November measured in Dotnuva (near Graisupis) and Remeisiai (near Vardas) for the past four years (LIWM, pers. com.).*

Further down a river in a watershed the water constitutes of long-transported groundwater. Therefore the water in a stream has higher conductivity further downstream (Grip and Rodhe, 1994). This is true for Vardas but not for Graisupis. Graisupis probably has a more complex cycle concerning nutritive salts together with many point sources that affect the conductivity.

Sources of error

It is important to notice that there are very small differences in conductivity between land use classes within the two watersheds. These differences may be too small in order to make the conclusion that a certain land use class has a higher conductivity value than another. The class called forest that is used in this study is sometimes in fact only groves. These small groves may not represent the class forest in a representative way. Larger and more homogenous areas of forests are to prefer. Too few samples in a class may also affect the result negatively.

7.4 Aim 4: Nitrogen leakage from different kinds of land use in the watersheds of Graisupis and Vardas.

7.4.1 Methods

The DEM:s are used in this analysis in order to isolate sub-drainage basins within the two watersheds. In these small drainage basins the percent proportion of the different land use classes were calculated. Afterwards the correlation coefficients were obtained through regression analysis between the percentage share of land use classes and the total-N and nitrite/nitrate values in order to see how the land use affects the nitrogen leakage, appendix IV. This method of analysis is used in several studies, for example by Fleisher *et al* (1991) and Arheimer (1998).

In the analysis both the values of total-N and nitrite/nitrate were used. Total-N is the sum of dissolved inorganic nitrogen compounds and organic nitrogen in dead or living material (Statistics Sweden, 1996). In the waters of Graisupis and Vardas, the nitrite/nitrate values contribute to a very large extent to the total-N values (Leonardsson, pers.com.).

7.4.2 Results

Table 7.4 and 7.5 show the final result for the regression analysis of the sub drainage basins. Every drainage basin that did not contain a fraction of the specific land use class investigated was deleted from the analysis. This was done in order to compare only the specific land use class with its measured nitrogen value.

Graisupis

The results show that there is no correlation between total-N and nitrite/nitrate with the fraction of cropland in the sub drainage basins, table 7.4. Thus, it is impossible to say that the amount of nitrogen varies with the distribution of cropland.

There is no significant relationship between pasture and total-N and nitrite/nitrate, which indicates that the amount of nitrogen cannot be explained by the distribution of pasture.

Table 7.4. The coefficient of explanation (r^2) for the percentage share of land use and the amount of nitrogen in the streams in Graisupis. N, number of samples.

Land use	Fraction of N	R^2	N
Cropland	Tot-N	0.0987	30
	NO_3-N/NO_2-N	0.0327	30
Pasture	Tot-N	0.2470	12
	NO_3-N/NO_2-N	0.1849	12
Mixed forest	Tot-N	0.3356	20
	NO_3-N/NO_2-N	0.2585	20
Deciduous forest	Tot-N	0.2816	25
	NO_3-N/NO_2-N	0.3977	25

Both the classes of mixed forest and deciduous forest show a minor relationship between its percentage share of the drainage area and the amount of total-N and nitrite/nitrate in the river. The conclusion is that a larger fraction of forest gives higher amounts of nitrogen in river water.

Vardas

There is no correlation between the distribution of cropland and the values of total-N and nitrite/nitrate, table 7.5. Thus, it was concluded that the percentage share of cropland does not affect the amount of nitrogen in the river.

Pasture shows a no statistical relationship between the amount of nitrite/nitrate or total-N. Thus, the conclusion is that the distribution of pasture does not affect the amount of nitrogen.

The percentage share of mixed forest and deciduous forest has no correlation at all with the amount of nitrogen in the rivers.

Table 7.5. The coefficient of explanation (r^2) for the percentage share of land use and the amount of nitrogen in the streams in Vardas. N, number of samples.

Land use	**Fraction of N**	**R^2**	**N**
Cropland	Tot-N	0.1256	24
	NO_3-N/NO_2-N	0.0168	24
Pasture	Tot-N	0.1238	26
	NO_3-N/NO_2-N	0.1602	26
Mixed forest	Tot-N	0.1701	13
	NO_3-N/NO_2-N	0.1357	13
Deciduous forest	Tot-N	0.0815	22
	NO_3-N/NO_2-N	0.0009	22

Comparison between Graiuspis and Vardas – summary of results

There exist no correlation between neither the distribution of cropland and nitrogen nor the distribution of pasture and nitrogen in either of the two watersheds. This absence of correlation states that the amount of nitrogen does not vary with the distribution of arable land or pasture within the watersheds.

Concerning the fraction of forest, the percentage share of forests in Graisupis shows a minor relationship with nitrogen. Therefore you can say that a larger area of forest corresponds to a higher amount of nitrogen. However, this is not valid in Vardas.

7.4.3. Discussion

Cropland

The results show no correlation between the distribution of cropland and the amount of nitrogen in the rivers. Normally a strong correlation exists between a large distribution of cropland and high nitrogen leakage, because nitrogen concentrations are generally considered to be much higher in leakage from agricultural soils than from soils having another type of land use (Fleisher *et al*., 1991 and Arheimer, 1998). This depends on that agricultural soils are often rich in nutrients, tilled, drained, and fertilized regularly, and they periodically lack the vegetation cover and uptake, and this normally causes an increase in nutrient leakage (Arheimer and Lidén, 1998).

The values of the distribution of cropland and the amount of nitrogen do not even covariate. Explanations for not having this covariation could be leakage from point sources observed during the field study, like sewage water from farms, inappropriate manure handling on smaller farms, straw- and manure stacks along the river, and waste that is thrown at the riverside. These point sources create a fragmentation of a normally homogenous watershed of cropland, which makes it more difficult to achieve a correlation between distribution of cropland and the amount of nitrogen in the river. In addition, the use of winter crops, which are used mainly in Graisupis, affects the nitrogen leakage at a large extent. Field with these kind of crops reduces the leakage to the river by 20-30 per cent (Andersson, 1986). The main crops grown in Graisupis are winter wheat, sugarbeets, and grain cereals. In a study from Sweden (Tagesson and Wramneby, 1999) the results showed that fields with root vegetables, like sugarbeets, and cereals have the highest leakage of nitrogen. This is also confirmed from other studies (Andersson, 1986), and thus, most fields in Graisupis should have high leakage values, which is the case. In 1998 the total nitrogen losses from Graisupis was 30.8 tonnes. The loss from the demonstration farm was 84.3 kg ha^{-1} in 1996, and the amount of mineral fertilizers used was 65 kg ha^{-1}. The high leakage value, compared with the amount of fertilizers used, shows that there is a large amount of nitrogen in the soil. This nitrogen has been stored in the soil since the Soviet times, when large amounts of fertilisers were used. In 1998 the average rate of fertilizers used in the watershed was 103 kg ha^{-1}. Unfortunately no later measurements have been published. In 1999 the leakage situation was much better, only 16.4 tonnes from the entire watershed (Sileika *et al*., 1998 and LIWM, pers.com.).

Also in Vardas there is a low correlation between the distribution of cropland and the amount of nitrogen in the river. This is to some extent explained by the fact that there are only small areas of cropland scattered over the watershed, no large coherent fields, and that pasture is the main land use. These small areas of cropland do not represent the category in a proper way. Another explanation for low correlation can be that along several river branches there are natural, narrow strips of trees. These strips serve as buffer zones that effectively assimilate the nitrogen that leaks from the croplands (Gaigalis *et al*., 1999). Further causes for low correlation can be that in Vardas the growing of grass ley, which is one of the dominant crops, leads to a decrease of the nitrogen leakage. Grass ley has a long growing period and also a deep and large root system that more effectively can use the nitrogen in soils (Andersson, 1986). The farmers in Vardas do not use a large amount of fertilisers (LIWM, pers.com.), and thus, there is not a high surplus of nitrogen in the soil that can leak to the river. The amount of nitrogen fertilisers used on the farms in 1996 was 6.2 kg ha^{-1}, compared to Graisupis that had 65 kg ha^{-1} the same year. Unfortunately there are no values for the loss of nitrogen through leakage that year. In 1998 the total nitrogen losses from Vardas watershed was 16.4 tonnes, and in 1999 the losses decreased to 4.9 tonnes (Sileika *et al*., 1998).

The soil texture and soil type also affects the nutrient leakage. In Graisupis the soil consists of sandy loam and loam, which makes the area ideal for crop production. This fine-textured soil should reduce the leakage, but due to the high amount of fertilisers used, and the large storage of nutrients in the soil, the leakage is large despite of the soil type. Vardas has sandy loam, moraine sandy loam, sand and peat in the watershed. These soil types should increase the leakage, but instead the minimal use of fertilisers gives lower losses. Vardas can have more water quality problems in the future if agricultural production is developed as intensively as in Lithuanian Middle Plain, where Graisupis is situated. The sandy soils in the hilly region cannot use the fertilisers in an effective way, and thus more nutrients will be lost through leakage (Sileika, 1999).

During Soviet times most of the arable land in Lithuania was pipe drained. Today LIWM has started an investigation to register where these pipes are located in the watersheds. The drainage pipes that were discovered were in some places dried out during the period of the field study. During wet periods, when water percolates through the soil profile of arable lands, there can be a considerable leakage of mainly nitrate through the pipes and groundwater is not formed. In many agricultural areas, the surface water receives the fertilizer surplus directly via the drainage pipes (Andersson, 1986 and Grip & Rodhe, 1994). LIWM has made an investigation about the nitrogen leakage from drainage pipes in Graisupis and Vardas, and the results show that there are high leakage values (Askinis *et al.*, 1999). These pipes could be a point source, affecting the correlation between the distribution of cropland and the amount of nitrogen present during wet periods.

In the literature similar lack of significant agricultural influence on nitrogen leakage has been reported also in other regions (e.g. Beck *et al.*, 1985; Harper and Stewart, 1987 – in Arheimer and Lidén, 1998).

Pasture

The distribution of pasture cannot explain the amount of nitrogen in the rivers. It is notable though, that the nitrogen values from pasture are as high as the values from cropland. Most often in the literature studies do not separate the classes cropland and pasture (i.e. Arheimer and Brandt, 1999), thus it is difficult to compare the results in this study with others. However, some explanations for these high nitrogen values can be found. The major part of ammonia (NH_3) emissions from agriculture comes from the handling of manure and urine. If the manure is not stored in a correct way, ammonia can leave as gas emissions or it can percolate together with rainwater through the soil. Thus, most often manure is a point source of ammonia from farms. To ensure that manure is not produced in excess, it is important that there is a balance between the number of animals kept, and the area of land available for spreading manure (Jakobsson, 1999). In the watersheds of Graisupis and Vardas only the two demonstration farms have proper manure handling (Sileika *et al.,* 1998). This may explain high leakage of ammonia (NH_3) to the groundwater, and at the end high values of total-N in surface water of Vardas.

Pasture has probably been used as cropland at regular intervals, especially during the Soviet regime. The large storage of nutrients in the soil can be an explanation for the high values of nitrogen leaking from pasture.

Forests

In Graisupis forest areas gives a high amount of nitrogen. However, that is not the case in Vardas. Nitrogen is generally considered as the most limiting nutrient in terrestrial ecosystems in temperate regions, and it is rapidly assimilated by the vegetation, which means that nitrogen losses are usually low (Löfgren, 1991). However, an elevated nitrate leaching from forests has been noticed recently. Geographical differences in nitrogen export from forested catchments may reflect atmospheric deposition patterns and it may also reflect, for example, forest activities (Arheimer *et al.*, 1996).

A large atmospheric nitrogen deposition in forests during non-growing seasons might result in a high leakage of nitrate, which can rather easily flush through the soil system when the canopy does not assimilate the deposited nitrogen. The study in Lithuania was conducted in October - November, and the trees did not have any leaves left. Nitrogen deposition is also greatly influenced by the amount of precipitation (Löfgren, 1991). Atmospheric nitrogen is of course also deposited on water surfaces and land. If it is deposited on water surfaces and saturated discharge areas it will contribute more or less instantly to the nitrogen loading during flow events (Löfgren, 1991).

Negative effects attributable to air pollution in forests in Lithuania are observed around large industrial pollution sources (Armolaitis, 1998). The reason for high nitrogen values from forests in Graisupis, but not in Vardas, depends on that Graisupis is located in a more industrialized region of Lithuania, and atmospheric deposition is probably higher there than in Vardas.

A small area in Graisupis, 1 - 2 ha, was exposed to clear-cutting, and may partly explain the correlation between the distribution of forest and the amount of nitrogen in the watershed.

How the water discharge affects the nitrogen leakage

As several studies show, there is a strong relationship between water discharge and the transport of nitrogen from all terrestrial systems (i.e. Fleischer *et al.*, 1991, Arheimer, 1998). When analysing the values of water discharge in autumn 1999, they are extremely low, table 7.6. In Graisupis average water discharge of October – November 1999 is 7.2 l s^{-1} when compared to the average water discharge of October – November at Graisupis monitoring station during 1996 – 1999, which was 38.95 l s^{-1}. In Vardas average for the same months in 1999 was 1.1 l s^{-1}, and average water discharge of these months at Vardas monitoring station during 1996 – 1999 was 22.15 l s^{-1} (LIWM, pers.com.). This indicates that the river flow during the study period was extremely low. This is explained by low amounts of precipitation during the autumn. The normal amount of precipitation was reached in December, and the response of that is shown by the water discharge in table 7.6. A conclusion is that if the water discharge had been higher, the values of nitrogen in river water should have been even higher than during this study period.

Table 7.6. Water discharge (l s^{-1}) measured at the monitoring posts at the river outlets, in autumn 1999 (LIWM, pers.com.).

	October	November	December	Average Oct-Nov 1996-99
Graisupis	6.3 l s^{-1}	8.0 l s^{-1}	140 l s^{-1}	39.0 l s^{-1}
Vardas	0.5 l s^{-1}	1.7 l s^{-1}	37.9 l s^{-1}	22.2 l s^{-1}

General comments

When analysing the nitrogen values along the rivers, and the second order tributaries, they show that in Vardas there is effective nitrogen retention. Upstream in Vardas the nitrogen values are between 0.9 – 2.5 mg l^{-1}, and at the monitoring post the value is reduced to 0.3 mg l^{-1}. The retention is not that obvious in Graisupis, where the nitrogen concentration upstream (2.03–6.53 mg l^{-1}) can just as well be as high as at the river outlet (5.6 mg l^{-1}). The difference between the watersheds is probably caused by the many point sources in Graisupis, as discussed above.

A pH level between 4 - 8 favor denitrification, and in both Graisupis and Vardas the pH-value is between 7.17 - 7.87 in river water (LIWM, pers.com.). This means that conditions for denitrification can be favorable during the summer season in these areas. Denitrification is low at temperatures below 0°C, which leads to a higher nitrate leakage during winter. The air temperature during the time of the field study was 5-7°C, which indicates that denitrification could take place. The straightening of rivers results in faster transport of nitrogen through the system, especially in Graisupis. This prevents denitrification when the nitrogen cannot sediment because of the high water discharge. During the time of the field study, when the water discharge was extremely low, sedimentation may probably occur. The biological uptake of nitrogen is also low during winter, when no nitrogen is reduced from the water phase by plants. Thus, nitrogen retention through assimilation could not take place, unless the fields were covered with winter crops.

Acidification primarily affects the composition and availability of organic matter, which may result in a decreased denitrification activity (Leonardsson, 1994). Acidification of soils and water from atmospheric deposition decrease denitrification. The acidified soils in both watersheds may contribute to less denitrification in the areas.

Sources of error

It was not possible to evaluate the DEMs because the Russian military maps available did not show the elevation of the contour lines. Thus, we had to rely on the formerly created GIS maps of elevation that LIWM had. One large source of error was that the areas of the isolated sub-drainage areas in the DEMs continue outside the large watershed. This affects the area distribution of land use-classes, and thus gives somewhat false results regarding to the nitrogen leakage from different classes within the sub-drainage area. This problem could not be avoided due to the fact that the extent of the watersheds already was determined by the LIWM. The error could have its origin both in the original maps, and in the interpretation and digitizing of the contour lines of the maps as well as in the analysis made back in Sweden.

Unfortunately, during the field study the rivers contained only groundwater. It had not rained for a long time, and the water discharge was extremely low. Thus, the river water consisted of old groundwater that most probably not represents the leakage of nitrogen in a proper way, because nitrogen is leaking with the percolating rain through the soil during rainfall events and high water discharge.

8. Preventive measures in the future

This chapter presents a discussion concerning preventive measures that needs to be taken in order to reduce nitrogen leakage in the future.

8.1 Preventive measures leading to reduced nitrogen leakage from terrestrial systems in the future

In order to prevent the nutrient leakage to surface waters, and in the end to the Baltic sea, there is a need for preventive measures, and measures that reduce the existing high amount of nitrogen in soils from reaching the surface water and seas.

Wetlands have been suggested for the reduction of non-point source pollution of nitrogen. Research has shown that wetlands reduce the nitrogen emissions to the sea, and also have positive effects on flora and fauna. It is also a more cost-effective establishment compared to other nitrogen-limiting measurements. The mechanisms that contribute to the nitrogen retention in wetlands are; sedimentation, plant assimilation of nutrients, and denitrification. Denitrification is the most important process that effectively hinders nitrogen to reach the sea. The highest nitrogen retention is attained in ponds, wastewater ponds, reed swamps, root-zone wetlands, artificial submerged macrophyte treatment systems, and infiltration wetlands. The nitrogen load can be reduced by 1500 kg N ha^{-1} $year^{-1}$ and more, by using these measurements. In wetlands, it is necessary to create long residence times for water and nutrients, e.g. at least 3-5 days in ponds (Leonardsson, 1994).

The safest way to reduce large nitrogen losses from forested ecosystems, and to reduce the wet- and dry deposition of nitrogen on land and surface water, is to reduce the atmospheric deposition of nitrogen and other harmful compounds (Löfgren, 1991). These pollutants are the product of combustion of different fuels, and consequently the usage of organic fuels should be reduced. To achieve this, implementation of international obligations and international conventions and agreements on local and global problems related to the changes of climate, are necessary (Zukauskas *et al.*, 1999).

Agricultural fields bordering a river have a strong effect on the nutrients leaking to the river, since the nutrients reach the river directly. If green corridors - buffer strips - are planted along the river, i.e. permanent perennial vegetation, they serve as natural purification sites. Groundwater from highly polluted agricultural fields then flow through the buffer zone, and parts of the nutrient load are assimilated by the forest (Gaigalis *et al.*, 1999). For the strips to work out well it is important that drainage pipes are removed and that the buffer strips are at least 10 m on each side of the river. The strips can also contribute to other positive effects, like increasing the habitats for birds and other animals (Leonardsson, 1994).

Agricultural production in the former Soviet Union was neither sustainable nor effective. The amounts of energy, fertilisers and pesticides used were high, and harvests low. Agriculture is the most important factor affecting the nutrient leakage to surface waters, consequently measures leading to reduce the leakage are of great concern. To lower the loss of nutrients to the environment, and to facilitate an acceptable economy for farmers, the use of European machinery to suit biological demands for crop production can in the former Soviet states increase the agricultural production. To obtain these goals environmental legislation, education, demonstration, advisory service and information suiting all levels of farming is needed (Carlson *et al*., 1999). There is a need to work out a Code of Good Agricultural Practice (GAP) with improvements of land cultivation, fertilisation, manure handling technology, implementation of sustainable crop rotations and calculation of nutrient balance. This should be done together with monitoring, information and demonstration activities on farms and watersheds, which will hopefully contribute to improve the water quality in Lithuania (Sileika, 1999).

Solutions of the problems discussed in this paper are of great concern when the future of freshwater and coastal waters is being considered.

9. Conclusions

These conclusions can be drawn from the study:

Aim 1
-The created land use maps showed satisfying results concerning accuracy, and the strategy used was suggested to LIWM. However, updated material and a DGPS are necessary in order to obtain an even better accuracy.

Aim 2
- There was no significant relationship found between conductivity and nitrite/nitrate in either of the river waters of Graisupis or Vardas. The conductivity is consequently not affected by the amount of nitrite/nitrate present. Instead the conductivity is probably affected by the high amount of calcium in the soil, which is typical for Lithuania. The fact that Wickberg (2000) found a strong relationship between conductivity and nitrate depends on factors specific for the area of the Genevad drainage basin, Sweden. Thus, geochemical conditions in soil and rock are probably the main factor that contributes to the difference between the drainage basins examined in Lithuania and the Genevad drainage basin.

Aim 3
- It was not possible to predict the nitrite/nitrate leakage using the collected conductivity values and the regression equation, because there was no statistical relationship between conductivity and the amount of nitrite/nitrate present. Instead analysis of conductivity values and land use was made. The results show that river water flowing through forests has the highest conductivity values. This probably depends on the fact that the forests are exposed to acid rain. The humus layer in forests adjusts to this high amount of hydrogen ions from precipitation, and exchanges the basic cations with them. These released cations then leave the root zone with the percolating water. The high conductivity values are of course affected by calcium as well, which is the most dominant exchangeable cation. There have been some forest activities in the watersheds that may have affected the nutrient leakage as well. The results also indicate that water flowing through pasture has high conductivity values. This is to some extent explained by that there are forests on the opposite side of the river. Arable land without crops has high values, which is normal when the absence of winter crops explains why the nutrients are not assimilated, and therefore percolates through the soil to the groundwater. This explains why arable land with winter crops has low values.

Aim 4
- The fourth aim was to show how different kinds of land use affect the nitrogen leakage. No correlations were established between the distribution of cropland and pasture and the amount of nitrogen in the rivers in either of the two watersheds. Explanations for the non-existing relation between cropland and nitrogen in Grasisupis can be leakage from point sources, and the use of winter crops. In Vardas the small areas of cropland are scattered over the watershed, and along many river branches there are natural buffer strips with trees. This, and the fact that the farmers use very small amounts of fertilisers, explains the

non-existing correlation between cropland and nitrogen there. Pipe drainage is also common in both areas. These pipes contribute as a point source of nitrogen leakage.

In neither of the two watersheds the distribution of pasture does not affect the amount of nitrogen. It is also worth mentioning that the values of nitrogen are as high as the values from cropland. Probable reasons for the high values are that small farms have no proper manure handling, and that there is a large storage of nutrients in the soil.

A forest area has a minor relationship with high amounts of nitrogen. In the case of Graisupis this is probably explained by high atmospheric deposition, as the watershed lies in an industrialised region of Lithuaina.

Overall aim

The overall aim of this study was to develop and evaluate a fast, easy and cheap methodology to examine in what extent different kinds of land use affect stream water. This could unfortunately not be achieved when no statistical relationship between nitrite/nitrate and conductivity was established. Leakage concentrations in calculations of riverine transport of nitrogen are often based exclusively on land use, like in this study (e.g. Frink, 1991; Tippett *et al*., 1993; Wright, 1994 – in Arheimer and Lidén 1998). However, Arheimer and Lidén (1998) noticed that in order to estimate nitrogen losses, the influence of several other catchment characteristics on the terrestrial leakage must be considered. They explain this with the influence of other different catchment processes that varies spatially and temporally, because they may be more or less favoured by conditions in basins; like physiography, management or hydrology. Several authors have emphasised the importance of linking combinations of watershed characteristics to stream-water quality, since this enables further understanding of simultaneous influences from several different processes. Arheimer and Lidén (1998) point out that simple leakage coefficients based only on land use show large differences and have limited spatial representativity. In other words, the complex system of the nitrogen cycle can not only be analysed in concern to land use.

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Used software:

Esri, ArcInfo 7.5.2
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12. Appendices

Appendix I

These original sample values are used in the regression analysis (aim 2), and the analysis of leakage from different kinds of land use in minor drainage basins (aim 4). The four samples in a row presents all the values collected at one sample point.

Graisupis

Conductivity 18°C (mS/cm)	Conductivity in laboratory 18°C (mS/cm)	Nitrite, NO_2^- Nitrate, NO_3^-	Total-N
0.82	0.84	5.49	5.79
1.03	1.02	0.033	0.77
	0.99	0.044	1.17
0.83	0.84	5.38	6.08
0.78	0.8	6.79	6.88
0.78	0.78	8.42	8.61
	0.79	10.76	10.88
	0.87	3.6	4.04
0.87	0.87	3.95	4.2
0.84	0.87	4.04	4.47
0.94	0.92	1.22	1.92
1.28	1.36	0.042	0.82
0.88	0.87	4.09	4.59
0.9	0.89	4.2	4.55
0.93	1.08	1.99	3.17
0.89	0.9	4.24	4.6
0.86	0.88	4.15	4.36
0.83	0.84	2.64	2.96
0.83	0.84	2.61	2.85
1.17	1.17	1.46	2.03
0.78	0.81	3.68	4.07
1.97	4.85	4.45	14.7
1.14	1.14	5.99	6.53
1.2	1.15	6.51	6.85
1.1	1.12	4.07	4.56
0.98	0.99	6.98	7.5
0.96	0.96	4.3	4.86
	0.84	5.23	5.6
0.69	0.7	0.8	1.78
	1.14	5.6	5.91

Vardas

Conductivity 18°C (mS/cm)	Conductivity In laboratory 18°C (mS/cm)	Nitrite, NO_2^- Nitrate, NO_3^-	Total-N
0.7	0.69	0	0.338
0.68	0.68	0.042	0.508
0.64	0.91	0	0.417
0.68	0.78	0.035	0.511
0.67	0.67	0.046	0.465
0.6	0.6	0	0.151
0.69	1.46	0.063	0.188
0.71	0.67	0.073	0.613
0.67	0.67	0.08	0.615
0.71	0.72	0	0.32
0.62	0.56	0	0.535
0.69	0.69	0.233	1.075
0.69	0.68	0.105	1.165
0.7	0.69	0.195	1.4
0.72	0.7	0.26	1.453
0.79	0.68	0.193	0.988
0.65	0.62	0.004	1.92
0.62	0.63	0.027	2.092
0.65	0.67	1.753	2.563
0.63	0.62	0	1.055
0.38	0.37	0.812	2.463
0.77	0.77	0.442	1.112
0.78	0.78	0	0.464
0.68	0.71	0.35	1.004
0.69	0.67	0	0.5

Appendix II

Sample values of conductivity measured with the portable conductivity gauge. The sample values are used in the analysis of conductivity values from different land use classes (aim 3).

Vardas Conductivity 18°C (mS/cm)		Graisupis Conductivity 18°C (mS/cm)		
0.7	0.69	0.81	0.85	1.58
0.69	0.68	0.75	0.86	0.8
0.7	0.67	0.75	0.85	0.8
0.7	0.67	0.75	0.87	0.78
0.7	0.71	0.78	0.84	1.84
0.7	0.69	0.81	0.94	1.97
0.7	0.62	0.79	1.28	1.03
0.7	0.69	0.78	0.88	1.07
0.7	0.69	0.79	0.9	1.13
0.71	0.69	0.84	0.93	1.14
0.72	0.7	0.82	0.69	1.2
0.72	0.72	0.79	0.62	1.1
0.73	0.79	0.84	0.84	0.65
0.72	0.66	0.83	0.83	0.97
0.74	0.65	0.82	0.84	0.98
0.73	0.64	1.03	0.89	1.04
0.69	0.65	1.02	0.87	1.04
0.69	0.62	1.04	0.86	1.1
0.69	0.67	1.08	0.87	1.01
0.68	0.65	0.95	0.87	0.96
0.64	0.63	0.85	0.86	0.69
0.68	0.74	0.83	0.89	
0.69	0.38	0.83	0.88	
0.67	0.77	0.83	0.85	
0.6	0.78	0.82	0.84	
0.62	0.79	0.83	0.83	
0.56	0.8	0.81	0.83	
0.49	0.78	0.78	0.83	
0.69	0.74	0.78	0.84	
0.71	0.72	0.77	1.17	
0.71	0.68	0.75	1.15	
0.69	0.69	0.76	1.11	
0.72		0.76	1.51	

Appendix III

The matrices for the Kappa coefficient of agreement regarding the land use map of the watershed of river Graisupis. The correct mapped sample points are presented diagonally.

A	Cropland	Pasture	Deciduous forest	Mixed forest	Total
Cropland	**25**	0	0	1	26
Pasture	1	**0**	0	0	1
Deciduous forest	1	0	**1**	2	4
Mixed forest	0	0	0	**5**	5
Total	27	0	1	8	**36**

B	Cropland	Pasture	Deciduous forest	Mixed forest	Total
Cropland	**702**	0	26	208	936
Pasture	27	**0**	1	8	36
Deciduous forest	108	0	**4**	32	144
Mixed forest	135	0	5	**40**	180
Total	972	0	36	288	**1296**

C	Cropland	Pasture	Deciduous forest	Mixed forest	Total
Cropland	**0.694444**	0	0	0.027778	0.722222
Pasture	0.027778	**0**	0	0	0.027778
Deciduous forest	0.027778	0	**0.027778**	0.055556	0.111111
Mixed forest	0	0	0	**0.138889**	0.138889
Total	0.75	0	0.027778	0.222222	**1**

D	Cropland	Pasture	Deciduous forest	Mixed forest	Total
Cropland	**0.541667**	0	0.020062	0.160494	0.722222
Pasture	0.020833	**0**	0.000772	0.006173	0.027778
Deciduous forest	0.083333	0	**0.003086**	0.024691	0.111111
Mixed forest	0.104167	0	0.003858	**0.030864**	0.138889
Total	0.75	0	0.027778	0.222222	**1**

Correct	0.861111
Expected	0.575617
Kappa	**0.672727**

The matrices of the Kappa coefficient of agreement regarding the land use map of the watershed of river Vardas.

A	Cropland	Pasture	Deciduous forest	Mixed forest	Total
Cropland	**11**	7	1	0	19
Pasture	2	**32**	0	1	35
Deciduous forest	3	5	**2**	0	10
Mixed forest	0	0	0	**8**	8
Total	16	44	3	9	**72**

B	Cropland	Pasture	Deciduous forest	Mixed forest	Total
Cropland	**304**	836	57	171	1368
Pasture	560	**1540**	105	315	2520
Deciduous forest	160	440	**30**	90	720
Mixed forest	128	352	24	**72**	576
Total	1152	3168	216	648	**5184**

C	Cropland	Pasture	Deciduous forest	Mixed forest	Total
Cropland	**0.152778**	0.097222	0.013889	0	0.263889
Pasture	0.027778	**0.444444**	0	0.013889	0.486111
Deciduous forest	0.041667	0.069444	**0.027778**	0	0.138889
Mixed forest	0	0	0	**0.111111**	0.111111
Total	0.222222	0.611111	0.041667	0.125	**1**

D	Cropland	Pasture	Deciduous forest	Mixed forest	Total
Cropland	**0.058642**	0.161265	0.010995	0.032986	0.263889
Pasture	0.108025	**0.297068**	0.020255	0.060764	0.486111
Deciduous forest	0.030864	0.084877	**0.005787**	0.017361	0.138889
Mixed forest	0.024691	0.067901	0.00463	**0.013889**	0.111111
Total	0.222222	0.611111	0.041667	0.125	**1**

Correct	0.736111
Expected	0.375386
Kappa	0.577517