DANMARKS OG GRØNLANDS GEOLOGISKE UNDERSØGELSE RAPPORT 2006/85

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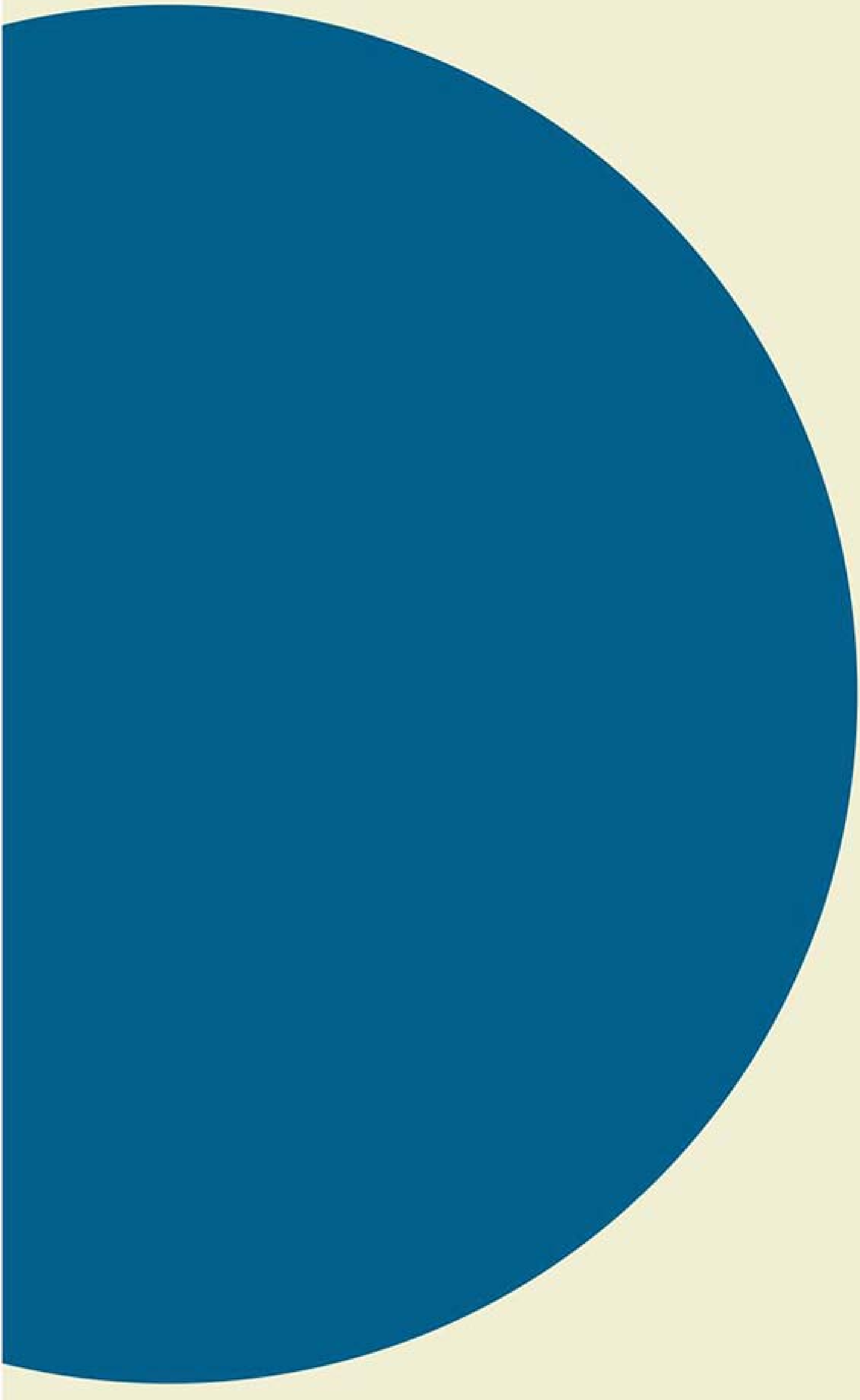

GEOLOGICAL SURVEY OF DENMARK AND GREENLAND
MINISTRY OF THE ENVIRONMENT

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Agricultural influence on Groundwater in Latvia

Miljøbistand Øst - DANCEE

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GEUS

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Contents

EXECUTIVE SUMMARY

Several progress reports describing the activities within this project, *Agricultural Influence on Groundwater in Latvia,* have been prepared during the last three years. Information about progress for the various tasks and presentation of the preliminary results and conclusions is included in these reports.

In this final report all the essential results and conclusions covering the whole project period are presented in order to make references to the earlier reports redundant.

Results and conclusions included in this report are based on a large amount of information collected within a relatively short time period using unified methodologies of sampling and analyses and providing the best possible data quality assurance.

A total of 799 water samples were analysed. These were collected in the following way: 350 from shallow wells drilled for sampling, 169 from existing shallow monitoring and water supply wells, 210 from springs and finally 70 from drain outlets. All samples were analysed for major ions, nitrogen compounds and for a large number of minor and trace elements. Besides, all groundwater samples were screened for pesticides and 111 subsequently selected for pesticide verification.

The main outputs from this project can be summarised under three headings:

- Investigation of the level of contamination of the upper groundwater and an estimation of the risk of contamination of deeper water supply aquifers,
- Estimation of background and threshold values for trace elements in the upper groundwater,
- Input to the Latvian groundwater monitoring programme and preparation of a national guidelines dealing with groundwater assessment, particularly in relation to the requirements of the Water Framework Directive, the Nitrate Directive and the draft Groundwater Directive.

Investigation of the level of contamination of the upper groundwater and an estimation of the risk of contamination of deeper water supply aquifers

The level of impact on the upper aquifers by nitrogen compounds, pesticides and other substances was investigated. Before this project the degree of diffuse contamination of the groundwater was poorly known due to the low density of groundwater monitoring points, combined with only old groundwater quality data obtained during geological mapping (geological mapping in Latvia stopped in the beginning of the 1990s)

The selection of sampling locations was to some degree influenced by the expected pressure (diffuse or point source) on groundwater as areas with higher load were typically selected for sampling.

In spite of this site selection method biased towards expected higher concentrations of nitrate and pesticides, the general status of the upper groundwater is not alarming. In 360 of 799 samples concentration of N-compounds exceeding typical background value of 2 mg/l expressed as total nitrogen was found, while the maximum acceptable concentration (MAC) for nitrates of 50 mg/l was exceeded in 60 samples.

Practically all groundwater samples were screened for pesticides and the majority of the positive samples was analysed by more robust methods. Pesticides in concentrations exceeding detection limits were found at 65 of 111 locations while the MAC for groundwater was exceeded at 34 locations. Before this project, data about pesticides in Latvian groundwater were totally absent.

As new data on groundwater age obtained in frame of this project show, the travel time from the surface to deeper aquifers typically is more than 50 years. This may explain the absence of pesticides and N-compounds above background concentration in the traditional monitoring wells, surveying deeper and thus typically older groundwater. This of course does not mean that the situation can not deteriorate in the future.

The results obtained within this project show that N-contamination occurs in the upper aquifers and in mobile parts of groundwater flow, captured by springs. At present it is not quite clear what will happen to this contamination on its way to deeper, water supply relevant aquifers. There are strong indications that the deeper aquifers are equipped with efficient protection mechanisms (as reduction) which prevent N-contamination. However, there is a need to collect more information in order to elucidate this.

Estimation of background and threshold values for trace elements

A total of 799 samples were analysed by the ICP-MS method, providing concentrations of 66 minor and trace elements, and 785 of these analyses were evaluated to provide reliable data. The experience obtained through analyses of a large number of samples by the ICP-MS method allows us to group the various elements into different classes depending on the reliability of the determination within the concentration intervals typical for Latvian groundwater.

This is the first wide application of the ICP-MS method for investigation of groundwater in Latvia, and it fills in missing data on concentrations of several minor and trace elements. These data are necessary for the development of Latvian requirements and methodological recommendations for the investigation of groundwater contamination around point-pollution sources, and for investigation of groundwater reserves for water supply.

Based on the large amount of information collected during this project, a set of background as well as threshold values for minor and trace elements in typical Latvian aquifers have been defined, as required in the draft Groundwater Directive.

Groundwater monitoring programme and EU directives

Latvia is obliged to prepare several documents required by various EU directives. The information necessary for this purpose can only partially be provided by the existing groundwater monitoring programme which is mainly based on monitoring wells screened in deeper aquifers utilised for drinking water supply. Monitoring of the upper and youngest groundwater does not exist at a regional scale.

The future groundwater monitoring programme in Latvia will rely heavily on the information collected within this project and the large number of chemical analyses performed will be useful in the context of Latvian obligations in relation to the Water Framework Directive, Groundwater Directive and Nitrate Directive of the EU.

Recommendations to improve the Regional Groundwater Monitoring system were prepared, including a rational list of pesticides and heavy metals to be monitored, where to establish additional monitoring stations in areas with the most vulnerable groundwater, and finally a list of relevant and representative springs suitable for the Regional Groundwater Monitoring Network. Information on the quality of spring water seems to give an important input to the characterisation of young groundwater in Latvia. Of particular concern is the surprisingly large number of cases where nitrate concentrations in spring water are higher than the MAC for drinking water.

In total, the project outputs are much wider than the investigation of the agricultural contamination of groundwater.

DANSK RESUMÉ

I denne rapport opsummeres resultaterne fra det DANCEE støttede projekt “ *Agricultural Influence on Groundwater in Latvia”,* gennemført i perioden 2002 til 2006. Rapporten samler i al væsentlighed projektaktiviteter, resultater og konklusioner, således at det ikke er nødvendigt at gennemlæse halvårlige og årlige projektafrapporteringer for at få et overblik.

Resultater og konklusioner er baseret på en stor mængde data indsamlet over forholdsvis kort tid. Data er indsamlet under hensyntagen til standardiserede metoder for prøveudtagning og analyse. Desuden er usikkerheden søgt minimeret bedst muligt.

I alt er 799 vandprøver blevet analyseret: 350 fra nye, terrænnære boringer etableret som en del af projektet, 169 fra eksisterende overvågnings- eller indvindingsboringer; 210 fra naturlige kilder og endelige 70 fra dræn. Alle vandprøver er analyseret for hovedkomponenter, kvælstofforbindelser og for et stort antal sporelementer. Desuden er alle grundvandsprøver screenet for pesticider og 111 er efterfølgende udvalgt til en egentlig kvantificering af eventuelt pesticidindhold.

Hovedresultaterne kan opsummeres under 3 overskrifter:

- Undersøgelse af hvorvidt det øvre grundvand er påvirket af forurening og en vurdering af risikoen for forurening af dybereliggende grundvandsmagasiner egnede til drikkevandsforsyning
- Vurdering af baggrunds- og tærskelværdier for sporelementer i det øvre grundvand
- Optimering af det lettiske grundvandsovervågningsprogram samt udarbejdelse af en national vejledning om vurdering af grundvandsressourcen, især i forhold til kravene i Vandrammedirektivet, Nitratdirektivet og Grundvandsdirektivet.

Undersøgelse af hvorvidt det øvre grundvand er påvirket af forurening og en vurdering af risikoen for forurening af dybereliggende grundvandsmagasiner egnede til drikkevandsforsyning

Det er blevet vurderet, i hvor høj grad det øvre, terrænnære grundvand er påvirket af kvælstofforbindelser, pesticider mv. Tidligere var der kun begrænset viden om den diffuse forurening af grundvandet, da det eksisterende grundvandsovervågningsnet dels havde begrænset udbredelse og dels kun indebar analyser for et begrænset antal parametre. Desuden var data af ældre dato, idet de typisk var indsamlet i forbindelse med den geologiske kortlægning i Letland, der blev stoppet i starten af 1990´erne.

Udvælgelsen af prøveudtagningssteder har i nogen grad været præget af, at der er udvalgt lokaliteter, hvor der forventedes at være en påvirkning af grundvandet, enten i form af punktkilder eller diffuse kilder. Dermed kan resultaterne være skævvredne, idet der kan være konstateret et højere forureningsniveau i grundvandet end tilfældet er gennemsnitligt set. Alligevel viser projektresultaterne, at det øvre grundvand generelt ikke er voldsomt påvirket af overfladeaktiviteter som landbrug. I 360 af de 799 vandprøver oversteg indholdet af kvælstofforbindelser en baggrundsværdi fastsat til 2 mg/l total N, mens grænseværdien for nitrat i drikkevand på 50 mg/l NO_2 pr. l kun blev overskredet i 60 vandprøver.

Før iværksættelsen af dette projekt var der stort set intet kendskab til forekomsten af pesticider i grundvand i Letland. Derfor blev næsten alle grundvandsprøve screenet for pesticider og hovedparten af prøver med positivt screeningsresultat blev analyseret med en mere robust metode for at kvantificere indholdet. I 65 af 111 prøver (lokaliteter) blev der konstateret pesticider over detektionsgrænsen, mens grænseværdien for drikkevand (0,1 µg/l) blev overskredet i 34 (lokaliteter) prøver.

Grundvandets alder er blevet bestemt gennem et mindre antal CFC-analyser. Den gennemsnitlige alder på grundvandet er omkring 50 år, hvilket kan forklare de forholdsvis få fund af pesticider og kvælstofforbindelser i de eksisterende overvågningsboringer, der typisk overvåger dybere og dermed ældre grundvand. Dette kan betyde, at situationen kan forværres i fremtiden, afhængig af nedbrydningskapacitet mv.

Projektresultaterne viser, at landbrugspåvirkning i form af kvælstofforbindelser forekommer i de øvre grundvandsmagasiner, fortrinsvis i dele af disse præget af hastigt strømmende grundvand, der springer som kilder. Det er ikke nærmere belyst, om påvirkningen er på vej mod dybere magasiner, relevante i drikkevandsforsyningssammenhæng, men der er stærke indikationen på, at disse dybereliggende magasiner er velbeskyttede, idet grundvandet bliver udsat for effektiv kvælstof-reduktion på dets vej nedad. Der er dog behov for mere viden på dette område.

Vurdering af baggrunds- og tærskelværdier for sporelementer i det øvre grundvand

I alt er 799 vandprøver blevet analyseret (ICP-MS) for 66 sporelementer. Enkelte analyser måtte udelukkes pga. usikkerheder, men 785 prøver er vurderet troværdige. Dette data sæt tillader en gruppering af grundvandet baseret på indhold af hovedbestanddele og sporelementer i koncentrationsintervaller typiske for lettisk grundvand.

Det er første gang, ICP-MS analysemetoden er blevet anvendt til indsamling af et dækkende datasæt i Letland. Herved er nye data og ny viden om koncentration af flere sporelementer fremskaffet. Disse data er nødvendige for at udvikle lettiske vejledninger til brug for undersøgelse af grundvandforureninger omkring punktkilder og til undersøgelser og kortlægning af grundvandsressourcer til vandforsyning.

På baggrund af dataindsamlingen i dette projekt har det været muligt at fastsætte et sæt baggrundsværdier for sporelementer i typiske grundvandmagasiner i Letland og hermed imødekomme kravene i det europæiske Grundvandsdirektiv.

Grundvandovervågningsprogram og EU direktiver

Som de øvrige EU-lande er Letland forpligtiget til at udarbejde diverse vejledninger i henhold til forskellige EU direktiver. Med hensyn til grundvandet er det eksisterende overvågningsnet kun delvist i dækkende, da det fortrinsvist overvåger det dybereliggende grundvand, der anvendes til drikkevandsformål. Før dette projekt blev det øvre og yngste grundvand ikke overvåget på regional skala.

Det fremtidige grundvandsovervågningsnet i Letland vil i høj grad blive baseret på data og viden indsamlet i dette projekt. Yderligere vil datasættet i høj grad være nyttigt i forbindelse med Letlands forpligtigelser i henhold EU-lovgivning som Vandrammedirektivet, Grundvandsdirektivet og Nitratdirektivet

Der er blevet udarbejdet en række anbefalinger til forbedringer og udbygning af det lettiske regionale grundvandsovervågningsprogram, herunder en liste af relevante pesticider og tungmetaller, der bør overvåges; hvor der bør etableres yderligere overvågningsstationer i områder med følsomt grundvand; og endelig en liste over relevante og repræsentative kilder, der kan indgå i det regionale grundvandsovervågningsnet. Viden om kvaliteten af kildevand giver tilsyneladende et væsentligt input til karakteriseringen af det unge grundvand i Letland. Især er det bemærkelsesværdigt at der i flere tilfælde er konstateret nitrat i koncentrationer over grænseværdien for drikkevand i et stort antal kildevandsprøver.

Samlet set har projektet beskæftiget sig med og givet resultater, der rækker langt udover undersøgelsen af landbrugets påvirkning af det øvre grundvand.

1. Project activities

The activities within this project included collection of existing data on agricultural influence on groundwater and collection of new data to fill in different “white spots”. For the planning of a rational groundwater sampling and analysis programme various data were assessed. The project should lead to the following:

- A list of possible contaminants originating from agriculture and a necessary spectrum of parameters analysed,
- A delineation of main areas potentially influenced by agriculture, and a rational groundwater sampling network;
- An assessment of the possible depth of groundwater contamination and a rational depth of groundwater sampling.

1.1 Groundwater contamination due to agriculture

The most abundant and known agricultural contaminant is nitrogen and many studies show that agricultural practices have resulted in nitrate contamination of groundwater. This is caused by the high content of nitrogen in widely applied fertilisers like urea, ammonia, ammonium nitrate and animal manure. Further, the high mobility of nitrogen in the aquatic environment, mainly in form of nitrate, enhances the problem.

However, fertilisers and agricultural additives contain a wide spectrum of elements. In addition to the well known primary macronutrients - nitrogen, phosphorus and potassium, the micronutrients – boron, copper, iron, chloride, manganese, molybdenum and zinc - are often applied to accelerate plant growth. Moreover, the fertilisers contain a lot of accompanying and trace elements such as sulphate, fluoride, strontium, selenium, chromium, lead, nickel, cadmium, vanadium, thallium, radium, uranium and other rare earth metals.

Calcium, magnesium, strontium and bicarbonate often derive from dolomite commonly applied to neutralize acid soils. Several pesticides contain barium, arsenic, antimony, cooper, bromine etc. Besides, many organic substances, especially the fatty acids, originate from organic fertilisers.

Additionally the indirect effects of agricultural activities should be taken into account. A flux of nitrates and other electron acceptors intensify the oxidation of sulphide minerals and organic carbon, the weathering rate of sediments change the ion-exchange equilibrium, which may alter the concentrations of several toxic elements in groundwater like arsenic, zinc, nickel, copper, cadmium (Böhlke 2002). Further, a high rate of agricultural phosphate loading might release arsenate from soils.

The nitrification of reduced nitrogen from fertilisers and manures in soils can result in mobilization of calcium, magnesium and bicarbonates from the carbonate minerals naturally occurring in soils and sediments. In addition to nitrogen fertilisers and manure, nitrogen is released in groundwater from pre-existing soil matter or crop residues (nitrogen “mineralization”). Atmospheric nitrogen deposition and fixation of atmospheric nitrogen by several crops is another potential source of nitrogen in agriculture.

Treating of soils by manure and a high livestock density may contaminate groundwater by pathogenic micro-organisms. In this case, however, high concentrations of chloride and ammonium in the groundwater would be expected, as these are more mobile than pathogens in the subsurface environment and thus are core indicators. Therefore the pathogens were not investigated within this project.

It may be concluded that a wide spectrum of elements and substances should be analysed for identification of all possible changes in groundwater chemistry caused by agriculture.

1.2 Analysis of Latvian data of agricultural load and groundwater quality

Agricultural loads - nutrients:

Several maps (with complementary overviews) showing agricultural pressure were prepared by Dr. V. Jansons at the Latvian University of Agriculture in frame of this project in 2004. All these maps were prepared on the level of parishes or regions depending on the availability of statistical data.

The map of Agricultural Land (Figure 1) shows the percentage of respective land uses within the parishes. At present the acreage of arable crops in Latvia has decreased and the grassland or even abandoned land has increased drastically. The sown area ranged from 0.91 to 1.00 million ha during 1995-1999, which is 2.5 times lower compared to 1980s.

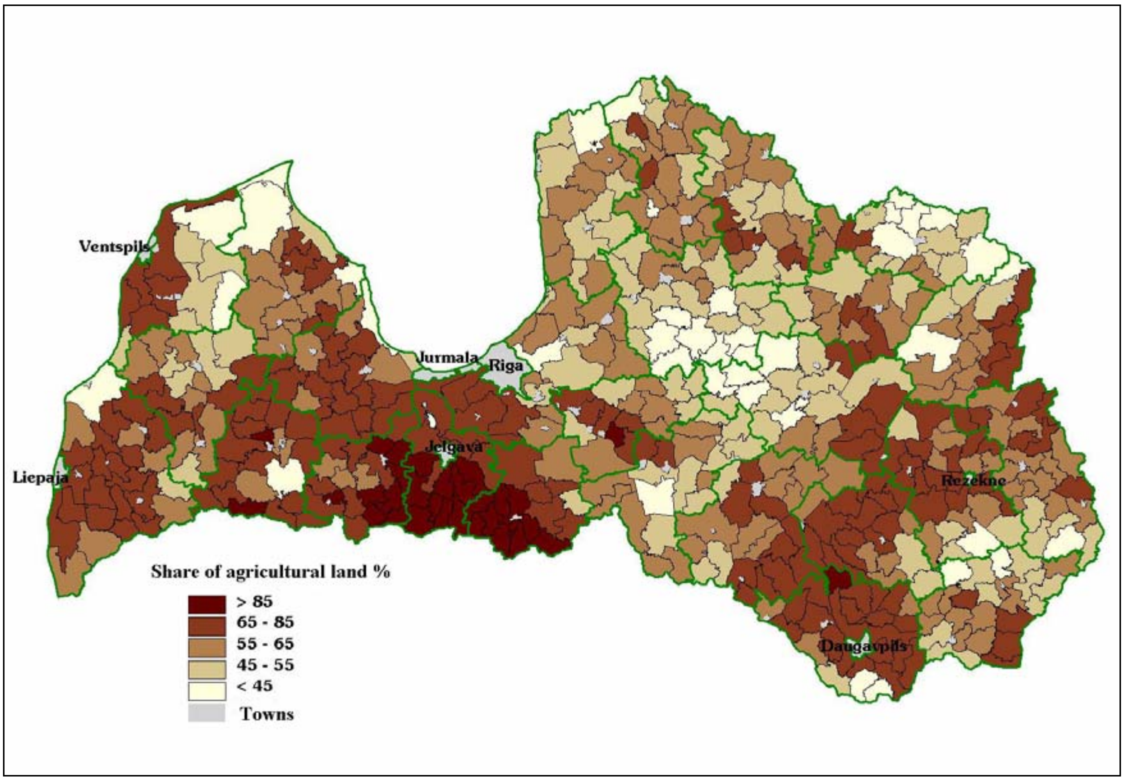

Figure 1. *Agricultural land*

Arable Land (Figure 2) ranges from 0-10 % of the total land area in many parts of Latvia to 50-80 % in the central part of the country. The results of the Agricultural Run-off Monitoring Research Programme (1994-2003) supported the general conclusion that the concentrations of nutrients in leakage strongly correlate to the percentage of agricultural land area in the studied river basins. The highest losses were observed in catchments where arable land constitutes 80-90% of the land use in the central part of Latvia.

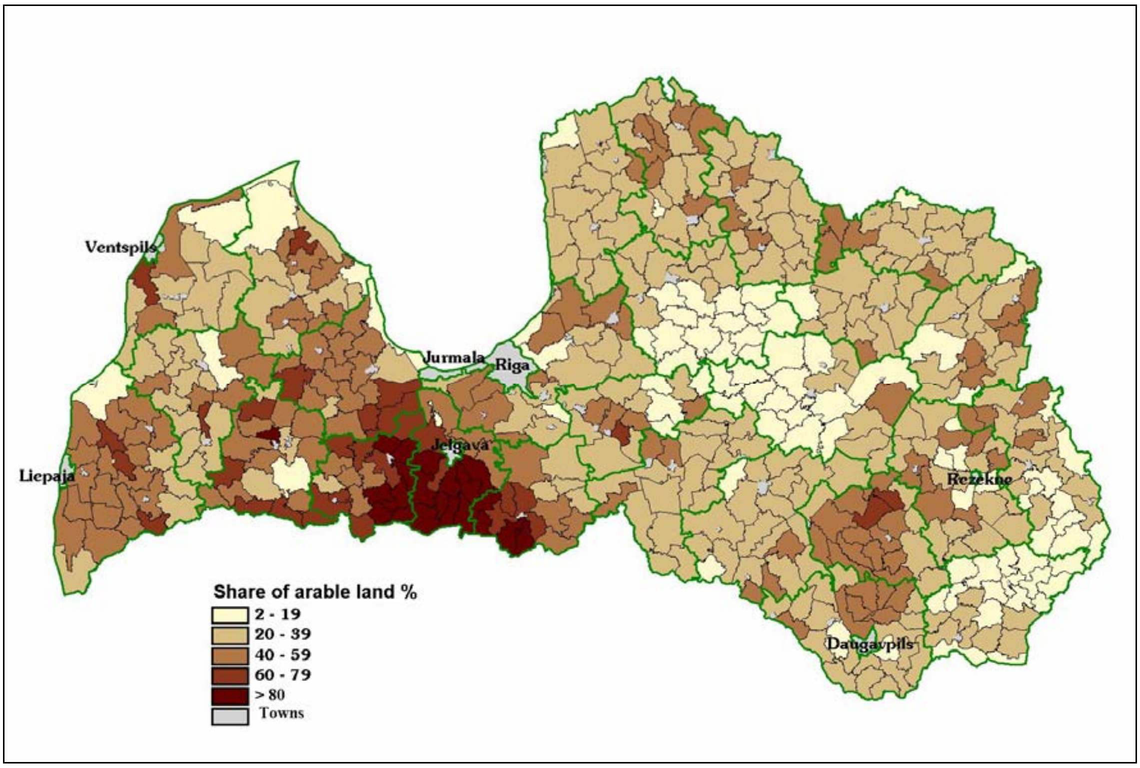

Figure 2. *Arable land*

The map of Animal Husbandry (Figure 3) shows the animal density in municipalities, which vary from <0.1 to > 1.4 livestock units per ha of agricultural land.

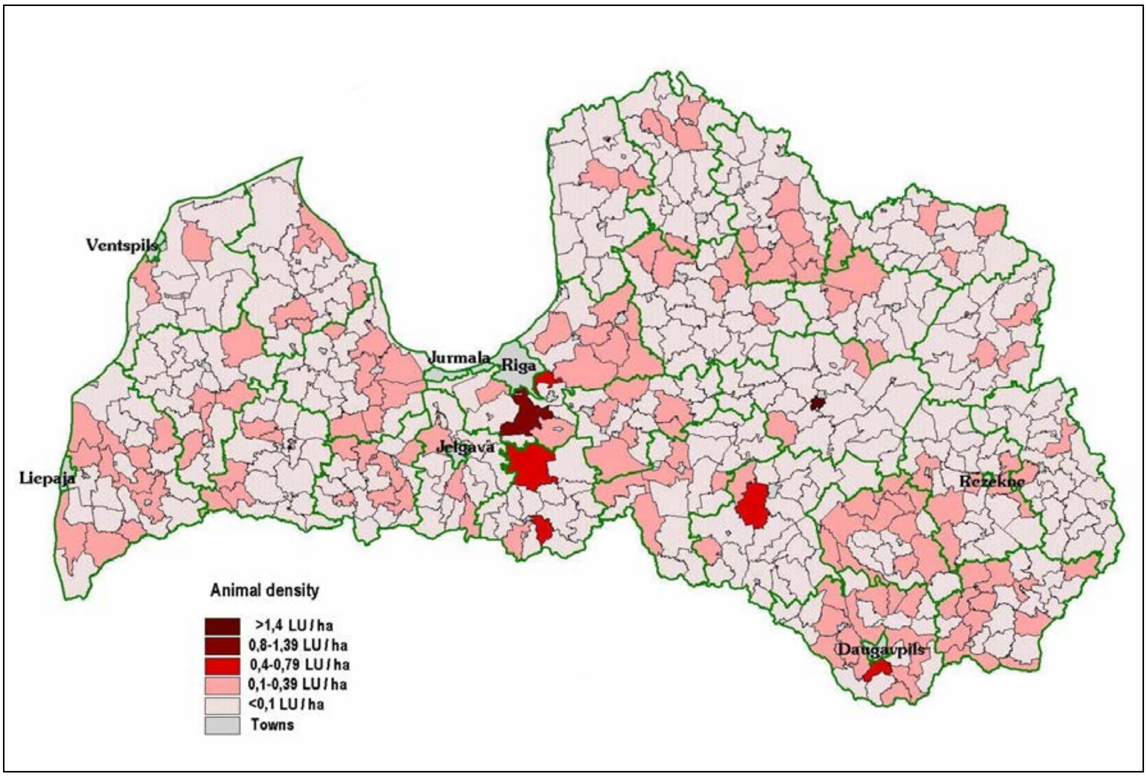

Figure 3. *Animal husbandry*

The reconstruction of land ownership towards smaller individual private farms as well as economical problems for the new farmers has during the 2 last decades reduced the diffuse pollution. In many cases the former large animal farms, despite a drastic decrease of production, had to decrease the available agricultural land even more, leaving too little area necessary for manure application. The resulting increase of animal density at these large farms could extend the negative impact of these farms as sources of pollution in the formerly heavy polluted areas. Monitoring data has shown that the former Soviet type large animal farms with poor manure storage facilities and high animal density may be considered as agricultural point sources and thus must be the main target today to minimize negative environmental impacts of agriculture in Latvia.

The maps of Fertiliser Application show the share of agricultural lands treated with mineral fertilisers and manure (Figures. 4 and 5). There is no accurate national statistical data on farm and municipal level of fertiliser application. Therefore, the map was prepared based on the results of the 2001 Agricultural Census.

Fertiliser application in agriculture must always be expected to contribute to nutrient loading in natural waters as a diffuse source. On the other hand shortage of nutrient may limit primary production of plants. Accumulation of N and P and risk of nutrient run-off will occur, when the yearly addition of fertiliser nutrients exceeds the amount that can be removed with the crops at harvest. Generally the average nutrient application rate with fertilisers is low in Latvia (33-59 kg NPK ha^{-1} during 1997-2002) and does not cover output of nutrients with the yield. However, there is a large diversity in application rates in both farm and regional level e.g. nitrogen fertiliser application reached 220 kg ha^{-1} in DobeleAgra farm (Dobele region) in 2003.

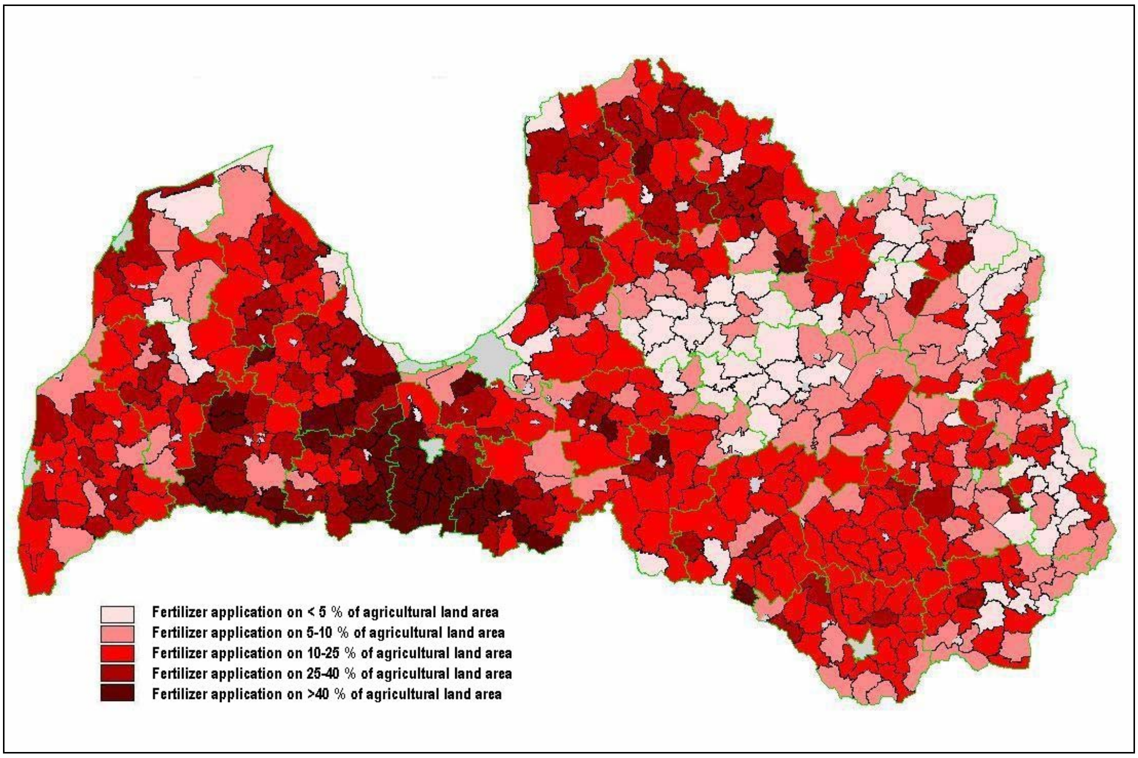

Figure 4. *Application of mineral fertilisers*

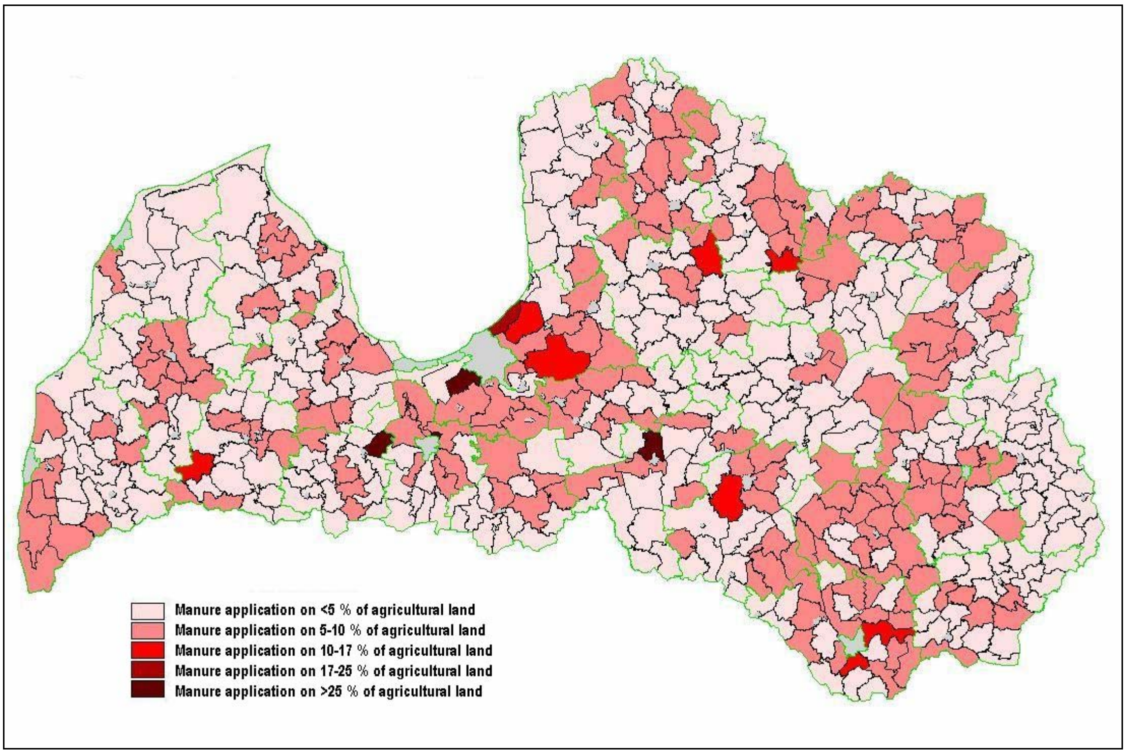

Figure 5. *Application of manure*

Agricultural loads – plant protection products:

The map of Application of Plant Protection Products shows the percentage of agricultural lands treated with plant protection products (Figure 6). There is no national statistical data on farm or even municipal level about application of plant protection products (PPP). Therefore, the evaluation of the pesticide load on *groundwater* quality were based on the results of 2002 data only, where treated land area (ha and %) and used amount of PPP (t) were available on level of regional agricultural boards (7 regions). Only plant protection products which are included in the register of plant protection products allowed to be imported, marketed and used in Latvia, are taken into account.

For evaluation of application technology and the effect of legislative measures, an inventory of existing problems and monitoring has not yet been performed. Pesticide use was 1.0 kg active ingredients (a.i.) per ha in 1980 and until 1990 up to 1.2 kg a.i. per ha. After 1990 a dramatic decline in the use of pesticides started, so that the use in 1999 was only 0.19 kg per a.i. per ha. This has been increased in 2002 to 0.42 kg a.i. per ha. More than half (467,932 ha) of the total sown area (877,700 ha) was treated with PPP in 2002 but the spatial variation of PPP use is very high.

All the above maps demonstrate that the highest agricultural pressure is in the central and south-western part of Latvia. Due to dramatic political and economical changes in the beginning of the 1990s the amount of arable crops, the application of mineral fertilisers, the number of livestock and other parameters related to agricultural load were decreased by a factor 3 – 10 (Stålnacke P. et al 2003). However, the distribution of agricultural lands within Latvian did not change significantly, thus the maximum groundwater contamination due to superposition of old and recent fluxes of contaminants is most expectable in Central and South-western Latvia.

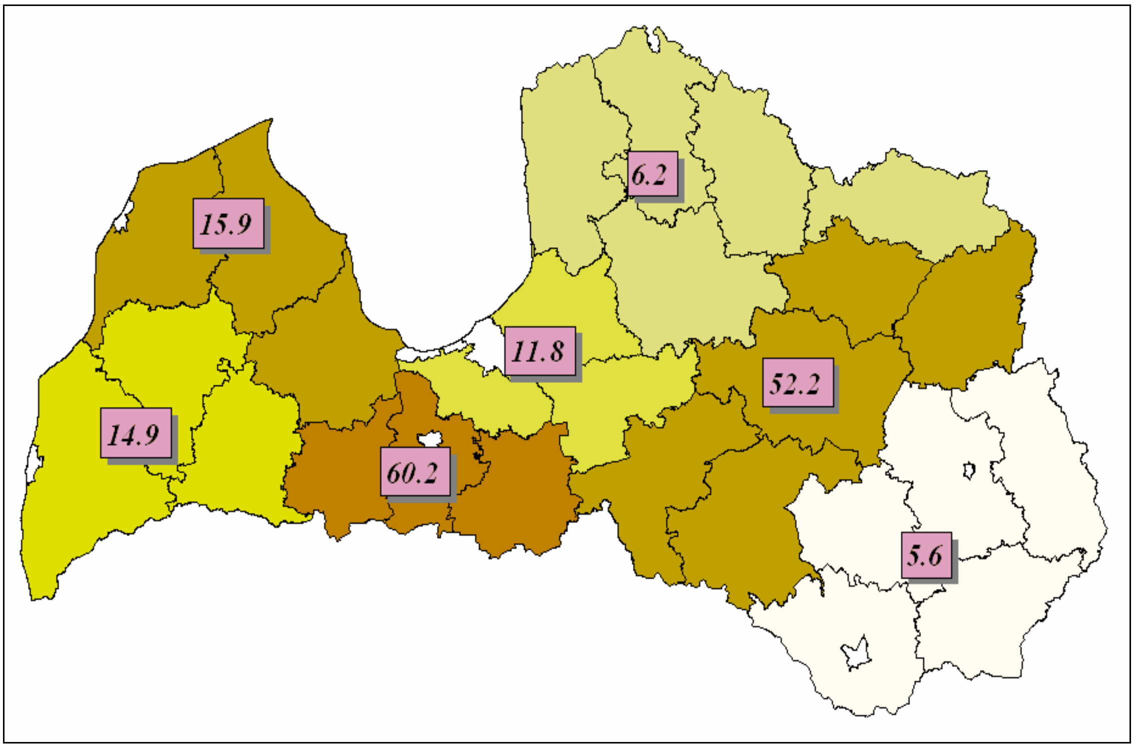

Figure 6. *Application of plant protection products*

During the 1980 - 1990s up to 200 pesticides and growth regulators (as active substances) were used in Latvia. Of these 55 were sold in amounts exceeding one ton per year. Since 1990 the application of pesticides has decreased 8 times (Figure 7). Simultaneously the persistent organichlorine pesticides[1] were step by step replaced by unstable and/or poorly leaching pesticides like pyretroids, amino acid derivatives and dinitroanilines (see Annex 1).

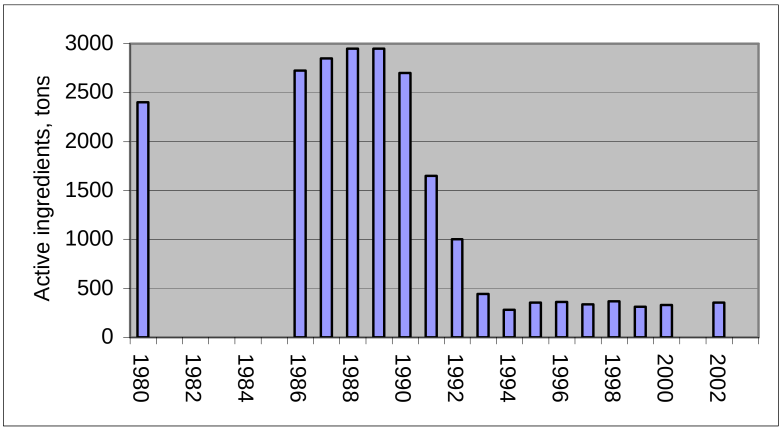

Figure 7. *Annual application of pesticides in Latvia*

Based on the above it may be concluded that the most expectable pesticides in Latvian groundwater are the earlier applied stable and mobile substances, used in the Soviet time, as well as recently applied mobile pesticides.

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[1] The majority of poorly degradable organochlorine pesticides like chlordane, dieldrin and HCH were restricted in 2000, as well as DDT in 1966, aldrin in 1972 and heptachlor in 1986.

The most widely applied pesticides are listed in Annex 1. This annex also describes mobility rating of pesticides which indicate the possibility for a particular substance to reach the groundwater. The rating varies from extremely low to very high. This evaluation taken from the US EPA Database on Pesticide Properties[2] is based on the half-life and sorption capacity of pesticides in soils. The last column in Annex 1 lists an evaluation of relative probability of pesticide occurrence in Latvian groundwater, based on first-order reactions combining the application rate and mobility of pesticides with the time typically necessary for infiltration from the surface down to the groundwater table[3]. This assessment was necessary because it is impossible to determine all pesticides historically applied in Latvia by analysing groundwater samples due to the high costs of analyses and the large volume of required sampling.

As an additional criterion for the determination of the priority pesticides, data on their distribution in different Latvian environment components and in Lithuanian groundwater have also been used.

During the 1980s the State Company “Raziba” collected large amounts of data on pesticides in Latvian soils and drainage waters. Often TCA, 2,4-D, simazine, atrazine and lindane were found in drainage water while in soil samples typically simazine, prometryn, metribuzin, trifluralin, TCA and 2,4-D reached the highest concentrations (personal communication, with V. Dane from Centre of Agrochemical Researchers (former “Raziba”))

Data on pesticides in Latvian groundwater is scarce. Only DDT, HCH, 2,4-D and organophosphorus pesticides were analysed in 92 groundwater samples taken in the 1970s within the Basic Groundwater Monitoring Network and only in one of these samples traces of 2,4-D was detected. In 1994 20 samples collected within the Basic Groundwater Monitoring Network were analysed, and the content of DDT and HCH and their metabolites was below detection limit.

Data on pesticide concentration in Lithuanian groundwater collected in 1998-1999 are very relevant as there are many similarities between Latvia and Lithuania when it comes to the history of land use.

26 groundwater samples from the Basic Groundwater Monitoring Network in Lithuania were analysed for 11 organochlorine pesticides, 7 triazine pesticides, 2,4-D, MCPA and TCA, but only one pesticide (2,4-D) was found in four wells (personal communication with Dr. K. Kadunas, Geological Survey of Lithuania). Three of these wells are screened in the water table aquifer[4]; the fourth well in a moderately deep karstic aquifer. Additionally, triazines (atrazine, simazine, prometryn and propazine) and MCPA were found in shallow wells around the 3 biggest pesticide storehouses. In spite of high concentrations of organochlorine pesticides in the soil, only lindane was found in one well with very low concentration.

Based on the above mentioned criteria and information, it was possible to determine the following pesticides that obviously should be analysed in this project in Latvia:

- chlorophenoxy acids: MCPA, MCPB, 2,4-D;
- triazines: simazine, prometryn, propazine;

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[2] National Protection Information Center, Oregon State University: http://npic.orst.edu/ppdmove.htm

[3] For the hydrogeological conditions in central Latvia where the application rate of pesticides is the highest.

[4] In this report the term “water table aquifer” describes the uppermost shallow groundwater aquifer with a free water table. Water table aquifers contains significant amount of groundwater compared to “drift aquifers” (alternating sandy and till layers) that are very local and may not contain significant amount of groundwater.

- organochlorine pesticides: lindane;
- TCA (trichloroacetic acid).

Several groundwater sampling campaigns around former pesticide storehouses were planned in frame of this project for the identification of priority pesticides potentially leaching to Latvian groundwater since the Soviet time. To select the best locations for sampling, a map of former pesticide storehouses was prepared based on the data provided by the Share Holding Company "BAO". This company collected dangerous chemicals, including restricted pesticides, from the whole country during the 1990s. In this period the pesticides were collected from 680 former storehouses and stored in 2 depots: Gardene and Knavas. The main part was stored in the Gardene depot and the list of pesticides for which the stored amount exceeds 3 tons is given in Annex 2. This list characterises the spectrum of pesticides used in the past in Latvia.

The groundwater contamination by pesticides has earlier only been investigated at 9 former pesticide storehouses. Moreover, the analyses were carried out for a limited number of pesticides and the sensitivity of the applied analytical methods was insufficient.

Five of former storehouses where more than 10 tons of pesticides were collected – Vilani, Dukuli, Jelgava, Iecava and Ziras - have been selected for drilling and sampling within this project. These are located within the areas where sandy deposits are distributed in the upper part of Quaternary section, i.e. where the shallow groundwater is highly vulnerable and where sampling is simple.

Geochemical mapping:

From 1997 until 2002 the State Geological Survey of Latvia (SGSL) conducted a geochemical mapping of Latvia at scale 1:500,000. A lot of geochemical anomalies were found, including anomalies characterised by high concentrations of Mg, Ca, Sr, P and Ba, which were interpreted as agrochemical anomalies interesting for the groundwater sampling within this project.

The groundwater samples were taken at several selected locations, where subsoil consists of sand or sandy-gravel deposits.

To define the possible depth of groundwater contamination caused by agriculture a map of nitrogen concentration in water supply wells were prepared based on the SGSL database "Wells".

The reason for selecting total inorganic nitrogen (sum of ammonium, nitrate and nitrite nitrogen) was inadequate storage capacity and the transformation of ammonium into nitrite and nitrate in water samples during storage.

Figure 9 shows the distribution of concentrations of inorganic nitrogen related to the depth of the aquifer. Three depth intervals are selected, each covering around 33% of the total number of water supply wells: down to 50m, 50-100m and more than 100m. From the figure it is clear that the natural background concentration of inorganic nitrogen is 0.1 – 0.3 mg/l, and that an increased nitrogen concentrations possibly related to the land use are observed as deep as down to 50m

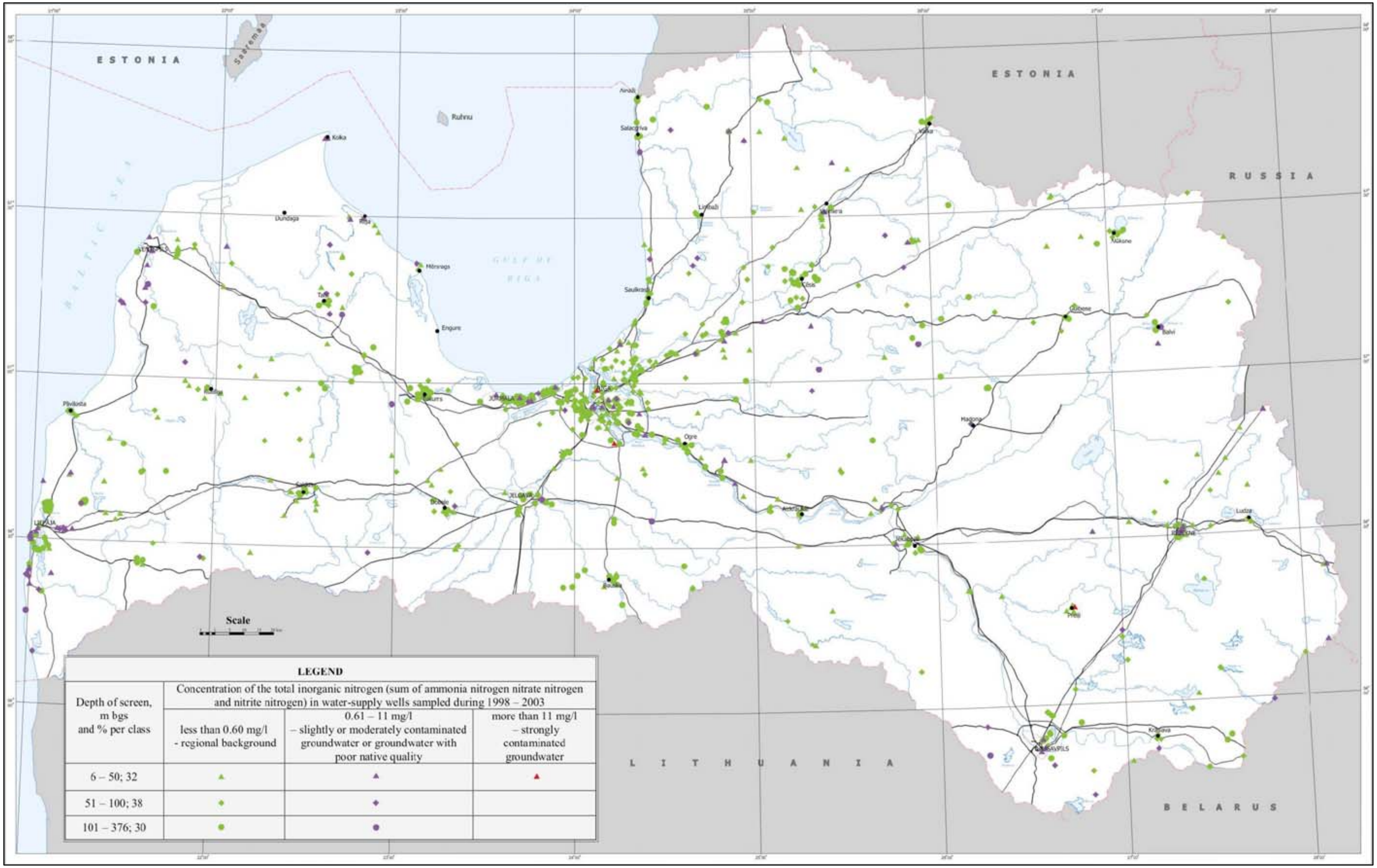

Figure 8. *Inorganic nitrogen in water supply wells*

Figure 9 shows the distribution of concentrations of inorganic nitrogen related to the depth of the aquifer. Three depth intervals are selected, each covering around 33% of the total number of water supply wells: down to 50m, 50-100m and more than 100m. From the figure it is clear that the natural background concentration of inorganic nitrogen is 0.1 – 0.3 mg/l, and that an increased nitrogen concentrations possibly related to the land use are observed as deep as down to 50m.

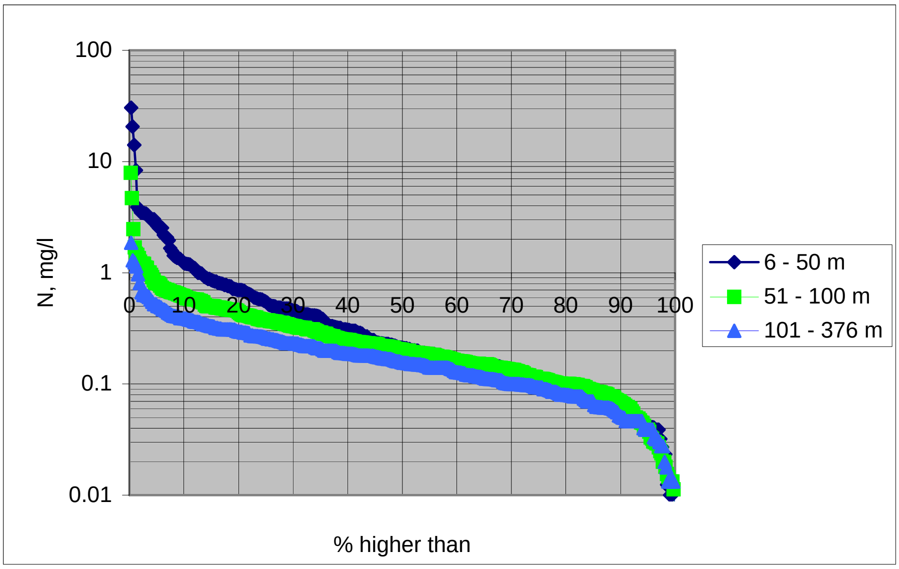

Figure 9. *Inorganic nitrogen in water supply wells as a function of screen depth*

Water table aquifer map:

The basic knowledge on Latvian geology and groundwater was analysed in frame of this project to select the optimal locations of groundwater sampling, and a water table aquifer map was prepared (Figure 10).

The water table aquifer map shows the distribution of water-saturated Quaternary sands on the surface. Such locations are preferred for simple groundwater sampling and at the same time characterised by having the highest risk of being contaminated by shallow groundwater.

Three data sets were used for preparation of the map:

- Geological data on 8,573 representative[5] boreholes loaded until 2003 into the SGSL database “Wells”,
- Description of sub-soils in 2,572 points of geochemical sampling from the SGSL database “Soils”,
- A geological map of Quaternary deposits in scale 1:500,000 prepared Staume,1981).

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[5] Mapping and investigative boreholes plus water supply wells with logging.

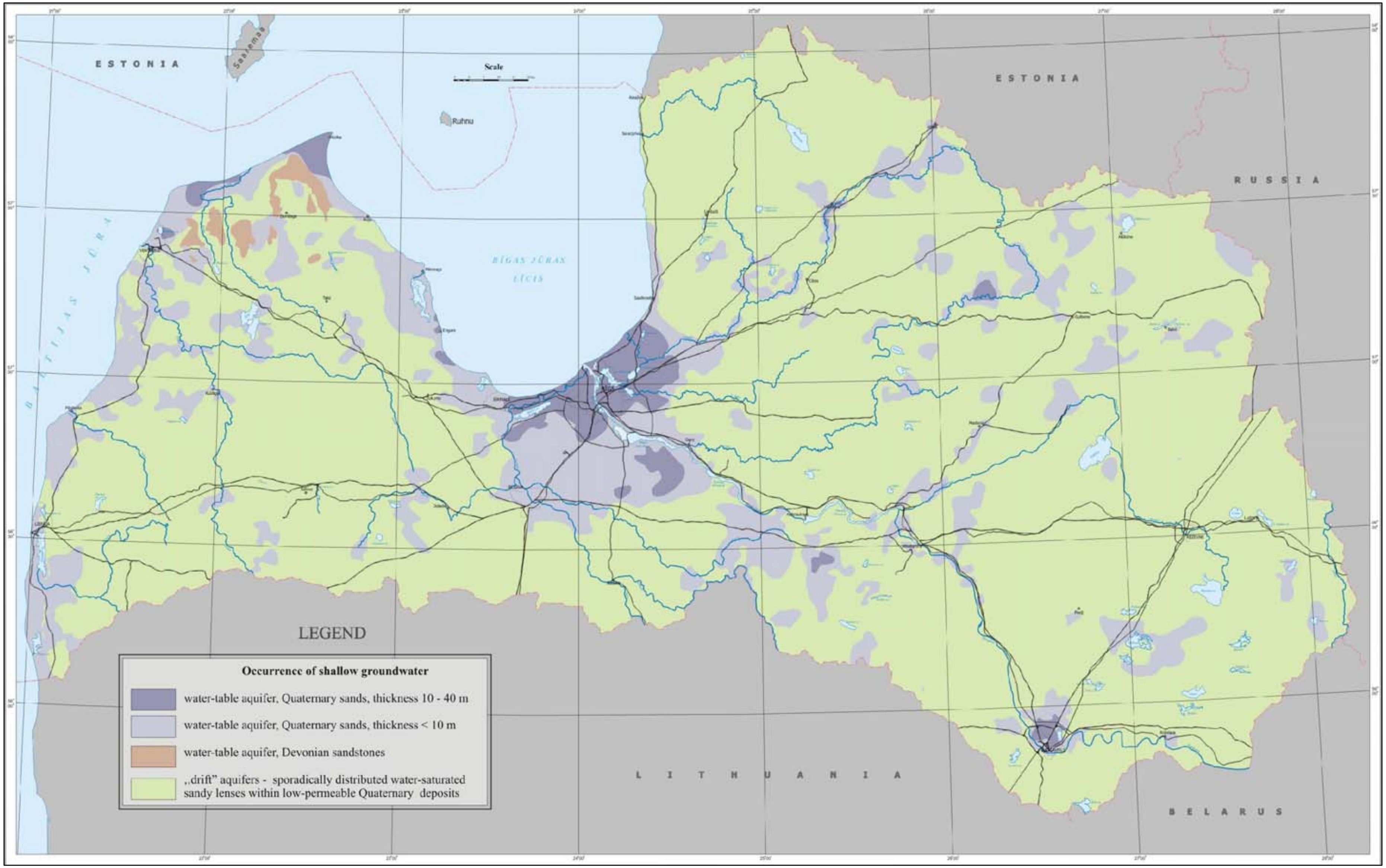

Figure 10. *Water table aquifer map*

Only areas where thickness of the water-saturated sands exceeds 1m are presented on the map as thinner layers are unfavourable for groundwater sampling. Such areas may occur in the Baltic Ice Lake in terms of glaciolacustrine and glaciofluvial deposits. Note that narrow zones of alluvial sands are not shown in the map. The saturated thickness reaches 10 - 40m in few locations only.

A preliminary map prepared in 2003 was updated in 2005, based on the drilling data obtained in frame of this project, and on borehole data added to the database “Wells” during 2003 - 2005.

1.3 Groundwater sampling

In total 799 water samples have been collected within this project:

- 350 samples from shallow wells drilled within the frame of this project,
- 169 samples from already existing shallow monitoring and water supply wells,
- 210 samples from springs,
- 70 samples from drainage outlets.

The locations where sampling was carried out are shown at Figure 11.

As the investigation focused on diffuse contamination of groundwater, shallow and moderately deep aquifers down to 50m have been sampled. The depth of 50m has been preliminary recognised as the bottom of the zone of diffuse contamination based both on distribution of nitrogen in Latvian water supply wells (chapter 1.2) and on data from other countries with similar conditions. For instance, the Danish monitoring network demonstrates concentrations of nitrate and pesticides above MAC until the depth 50m (Stockmarr, 2005).

Just 20 samples were taken from deeper wells to determine background concentrations of minor and trace elements in Latvian groundwater. The majority of samples were taken from the water table aquifers and drift aquifers down to the depth of 10m, where the groundwater is most influenced by land use (Figure 12).

Note that a large number of samples were collected from natural springs. The number is much larger than planned because of uncertainties in the sources of water and contributing land use area. However, the first results exhibited a surprisingly high difference of contamination in springs and wells, which confirm the presence of two different groundwater flows (rapid and slow) within same aquifers (see chapter 3.4). Therefore, for a better understanding of the distribution of diffuse contamination in Latvian groundwater, more samples from springs were collected.

70 water samples were collected from shallow drainage outlets. The sampling of drainage outlets has been carried out only within the agricultural areas in order to clarify a primary spectrum of agricultural contaminants.

The groundwater sampling was concentrated in the central and south-western part of Latvia, characterising by the highest agricultural load (Figure 11). 156 samples were collected at 15 agricultural run-off monitoring stations selected by the Latvian University of Agriculture as the most representative areas of land use.

In the sampling programme, major attention was put into investigating regional diffuse groundwater contamination, while only 36 samples were collected at point-pollution locations (mainly around former agrochemical storehouses). The main idea of this sampling was to determine the spectrum of stable pesticides leached to the groundwater since the Soviet time.

The majority of groundwater samples were collected from shallow temporary wells drilled by a small rig Sedidrill 80, purchased for this purpose. Groundwater samples were taken after continuous pumping from the wells by a submersible pump until stabilisation of pH and specific conductance (EC). These field parameters were measured in all 799 samples.

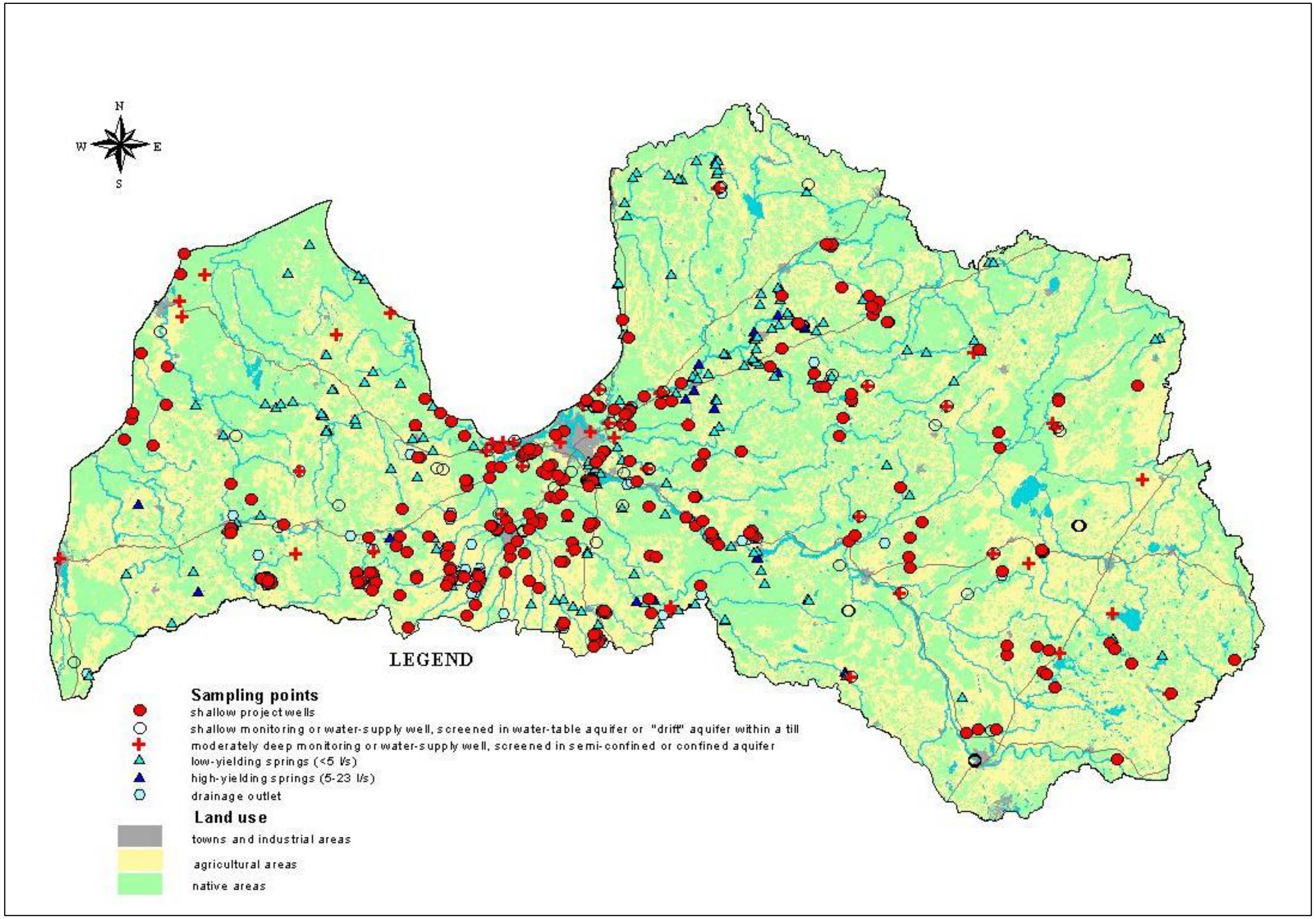

Figure 11. *Groundwater sampling points*

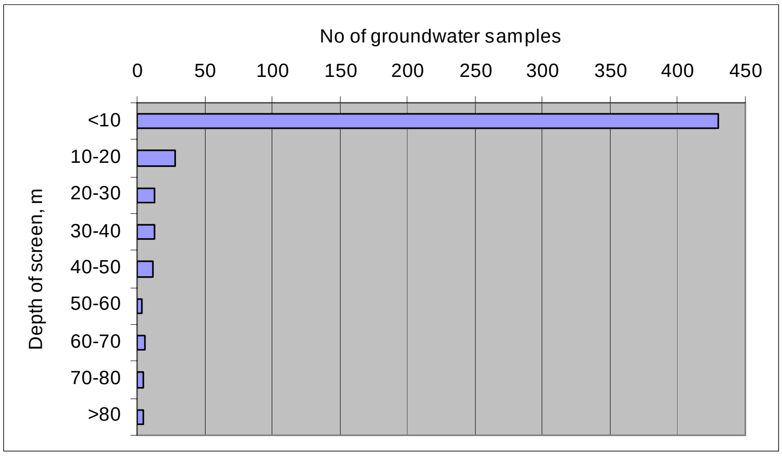

Figure 12. *Distribution of groundwater samples compared to depth*

Eh (Red-Ox potential) and dissolved oxygen were measured in 160 wells with good water inflow, where it was possible to provide a continuous groundwater flow through a closed chamber to prevent contact with the atmosphere. Wells with moderate inflow were pumped several times before they ran dry and the groundwater samples were taken during the last pumping. The groundwater samples from wells with very poor inflow (screened in clayey deposits) were pumped and sampled next day after inflow of fresh groundwater.

Groundwater samples were stored in cooling boxes and delivered at the laboratory no later than 3 days after sampling. The pesticide samples were stored in hermetic dark glass bottles and delivered at the laboratory no later than the day after sampling. Samples for ICP-MS analysis were passed through a 0.45 µm filters into acid-rinsed polyethylene bottles and acidified by ultra-pure nitric acid to stabilise metals. These samples were stored up to 1 – 2 months before sent to a Canadian laboratory. The experiments conducted within this project confirm that the storage of stabilised samples within few months does not influence the concentrations of heavy metals (see chapter 1.5).

Within this project a data set on the age of Latvian groundwater (residence time or the time elapsed since recharge) were obtained for the first time ever. 27 groundwater samples for determination of CFCs (chlorofluorocarbons) were taken and analysed at the CFC-laboratory at the Geological Survey of Denmark and Greenland (GEUS) following the method described by Busenberg & Plummer (1992).

CFC-12, CFC-11 and CFC-113 are broadly used indicators in groundwater dating (IAEA 2006; Plummer & Busenberg 1999). Concentrations of CFCs have been increased in the atmosphere at known rates since they began to be used industrially. Recharging rainfall contains CFCs dissolved in proportion to the atmospheric concentrations at the time precipitation. Groundwater age may be determined with an accuracy of 2 years, based on the concentrations of CFCs. As CFCs have been widely produced since the 1940s, the method is suitable for dating of young groundwater with ages up to 60 years.

Groundwater samples for CFCs analyses were sealed on site by flame in glass ampoules, and to avoid any contact with the atmosphere the sampling equipment was flushed with pure argon while sampling. A special field training courses were performed by a GEUS expert[6] to insure adequate CFC sampling.

As the groundwater samples were taken from monitoring wells screened in typical hydrogeological conditions, the obtained results must describe typical residence times of Latvian groundwater. However, no dating of spring water was done, which would be helpful to clarify the observed strong difference of the level of contamination in wells and springs (see chapter 3.4). This arises from the fact that the most interesting Latvian springs arise from caves in sandstones that are not fully filled by water (an “air cap” is present in the upper part of the cave)[7]. Thus it will unfortunately not be possible to prevent a mixture with air in these spring water samples, making CFC-dating impossible.

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[6] Troels Laier.

[7] During the project it was tried to take CFCs samples from two springs after establishing a dam in front of the caves to increase the water level in the cave, and putting a small submersible pump as deep as possible into the cave. In both cases, however, an anomaly high content of oxygen was found in the pumped water, indicating the presence of excess air. As even small contamination of sample by modern air results in high uncertainty in groundwater dating (too young age), it made no sense sending these samples to the laboratory at GEUS.

1.4 Chemical analysis of groundwater samples

Chemical analyses of project samples in the laboratories included:

- Traditional parameters (major ions, nitrogen compounds, COD), fluoride and phosphorus - totally 799 samples;
- Around 50 minor and trace elements by ICP-MS - totally 799 samples;
- Pesticide screening by immunoassay test kits - totally 799 samples;
- Pesticide verification by GC/LC – MS - 111 samples;
- CFCs - 27 samples.

The traditional groundwater quality parameters – all major ions[8], nitrogen and phosphorus compounds, and a total content of organic matter by COD-Mn[9] were analysed in a Latvian laboratory "LAANE" using the standard techniques of automated colorimetry.

However, a wide spectrum of additional trace elements should be determined in the groundwater (see chapter 1.1). As the background concentrations of several trace elements potentially influenced by agriculture are very low (micrograms and parts of micrograms per litre), sensitive analytical methods had to be applied to detect diffuse contamination of the groundwater.

The detection limits and prices of different analytical methods and capabilities of Latvian and foreign laboratories were taken into account and it was concluded that the best technique was the ICP-MS (inductively coupled plasma – mass spectrometry) method. The analyses were performed by a Canadian laboratory (ACME) characterised by good sensitivity of analyses and cost-effectiveness for large sample loads[10]. However, the sensitivity of ICP-MS method is insufficient for fluoride and mercury. Therefore fluoride has been measured by ion-selective electrode in a Latvian laboratory. Additional determination of mercury has been considered as irrational, because:

Pesticides containing mercury have not been used in Latvia for a very long time;

Still, the ICP-MS analysis is sensitive enough to discover mercury concentrations exceeding the MAC for drinking water (0.1µ/l);

A representative sampling for determination of near-background concentration of mercury (few ηg per litre) is impossible for large sample loads[11];

Detecting the whole spectrum of pesticides in each sample was impossible due to the very large number of historically applied pesticides and the costs of analyses. Moreover, at least 1.0 l for each pesticides group is required in Latvian laboratories, and several groups of pesticides were to be analysed. This posed a serious problem due to the limited volume of field refrigerators. The samples could not be sent to foreign laboratories requiring a lesser volume of sample due to quick degradation of pesticides.

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[8] Calcium, magnesium, sodium, potassium, chloride, sulphate and bicarbonate (alkalinity).

[9] Permanganate index.

[10] The prices in alternative European laboratories applying the ICP-MS and the Latvian laboratories applying the atomic absorption spectrometry are 5 – 7 much higher.

[11] Complicated requirements for preparation of sampling bottles and for sample storage, and a limited time of sample storage did not allow the use of foreign laboratories. The Latvian laboratories are at present not able to determine the near-background concentrations of mercury.

Therefore a step-by-step strategy was chosen for the determination of pesticides:

1. First an immunoassay screening of triazines and chlorophenoxy acids in all 799 samples very carried out. These two groups have the highest priority considering Latvian groundwater, and the appropriate sufficiently sensitive (0.01-0.1 ppb) screening tests are commercially available. Immunoassay methods are based on use of specific antibodies combined with their target analytes. Among the most important advantages of immunoassay method are rapidity, sensitivity for both pesticides and their metabolites, and a small sample volume (few millilitres). The main disadvantage of the method is unpredictable interference with other species occurring in groundwater. Therefore the immunoassay method is useful only for preliminary screening of pesticides and not for quantification of the concentrations of pesticides;
2. Secondly a screening by GC (gas chromatography) or LC (liquid chromatography) for a wide spectrum of pesticides of selected samples was performed, i.e.:
    - Selected repeated samples from wells and springs with a positive results of immunoassay screening,
    - Selected samples with other signs of agricultural contamination,
    - All samples collected around former pesticide storehouses.
    - Finally a MS (mass-spectrometric) quantification of few pesticides found during the second screening.

The GC / LC – MS analyses were performed by a Latvian laboratory at the State Food and Veterinary Service.

CFCs concentrations were determined at GEUS´ laboratory using gas chromatograph equipped with an ECD detector. The interpretation of the results from the CFC sampling was done at GEUS. The more stable CFC-12 was used as a main indicator of groundwater age, as CFC-11 and CFC-113 may be influenced by microbial degradation in anoxic aquifers. Additionally, a little correction of CFC-12 results was done by elevation of detection limit, because the trace concentrations of CFC-12 measured in several samples may be related to leakage from the sampling equipment or from the well itself.

1.5 Data quality assurance

The analytical concentrations of a few key species were controlled by independent analytical methods: the permanganate index (COD-Mn) by the ultra-violet absorption at the wavelength 254 nm, the individual nitrogen forms by the total nitrogen.

The traditional charge balance (ionic balance) was calculated in all the samples. If the charge balance error was greater than 10%, repeated analyses were performed until the appropriable charge balance was obtained. The final verified charge balances are perfect (less than 1.5%) in 50% of the samples, and only in 10% of the samples the charge balance varies from 5 to 10%.

Because this was the first wide application of ICP-MS on Latvian groundwater, extra effort was put into validating the ICP-MS data of the Canadian laboratory ACME by performing frequent doublet and standard analyses and by investigating the influence of various factors on the analytical results, i.e.:

- Calculation of percentage of non-detects (the concentrations of given element below detection limit);
- Analyses of 78 duplicate samples and repeated analyses of 7 anomalous samples to estimate the reproducibility and the limit of quantification;
- Analyses of 25 standards to measure the bias;
- Analysis of 19 blank samples to control the purity of nitric acid used for conservation of samples and to determine the influence of the leaching of the microelements from the sampling bottles on the analytical concentrations. The blank samples consisted on Millipore water with a different admixture of ultra-pure nitric acid (0, 0.5 and 5 ml of HNO_3 per 50 ml of Millipore water);
- Analyses of 2 duplicate samples with a storage period of 19, 139 and 305 days to evaluate the influence of sample storage on the analytical concentrations;
- Evaluation of the real quantification limit of the method taking into account all possible factors influencing the analytical concentrations of a given element.

The results of determination of 17 elements (Ag, Au, Bi, Ga, In, Ir, Os, Pd, Pt, Re, Rh, Ru, Sc, Ta, Te, Ti and Tl) were not analysed in the report and were not included in the database. This is due to the very poor sensitivity of the method regarding the typical concentrations of these elements in groundwater: the number of non-detects exceeds 90%.

The results of the evaluation of reliability of ICP-MS data of the remaining microelements and trace elements are given in the Table 1 and can be summarised as follows:

The storage of acidified groundwater samples up to 305 days does not essentially influence the concentrations of any element - the changes of concentrations of all elements were within the analytical error (less than 15%);

The bias of determination of the majority of elements is appropriable - from few to 30 percents. The accuracy of analyses of Cr, Hg, Ni and Sn is lower – the analytical bias exceeds 50%. The results of analyses of mercury and tin characterised by the highest bias (80 and 160%) were assessed as too inaccurate and were deleted from the database;

As expected the reproducibility of analyses increases with increasing concentration of elements. A limit of quantification given in the table was defined as a minimum concentration of given element analysed by ICP-MS with reproducibility better than 20%. The data on beryllium was removed from the database because of very poor reproducibility – 110%;

Table 1. *Validity of ICP-MS data provided by ACME*

Element	Declared Detection Limit, µg/l	No. of samples with concentration below Detection Limit, %	Bias within usual concentrations, %	Reproducibility within usual concentrations, %	Influence of leaching from the sampling bottles[12], %	Defined Quantification Limit, µg/l	No. of samples below Quantification Limit, %
Al	1	<10	25	13	<10	5	30
As	0.5	50	10	10	<10	0.5	50
B	20	55	17	5	<10	20	55
Ba	0.05	<10	10	3	<10	<<10	<10
Be	0.05	85	n.d.	110	<10		
Br	5	<10	10	7	<10	5	<10
Cd	0.05	50	<10	34	<10	0.3	85
Co	0.02	13	<10	12	<10	0.1	45
Cr	0.5	<10	65	10	50	4	90
Cs	0.01	75	n.d.	24	<10	0.05	>90
Cu	0.1	<10	25	12	25	2	85
Fe	10	<10	20	13	<10	100	20
Ge	0.05	80	n.d.	35	<10	0.15	>90
Hf	0.02	85	n.d.	21	<10	0.05	>90
Hg	0.1	60	80	28	85		
Li	0.1	<10	<10	12	<10	1	<10
Mn	0.05	<10	10	5	<10	1	<10
Mo	0.1	<10	<10	9	60	2	90
Nb	0.01	40	n.d.	12	<10	0.1	>90
Ni	0.2	30	55	43	70	3	90
Pb	0.1	14	40	26	65	0.5	85
Rb	0.01	<10	n.d.	5	<10	0.1	<10
REE	0.01	<10	<10	10	<10	0.1	30
Sb	0.05	60	50	17	<10	0.1	80
Se	0.5	70	20	22	<10	1	>90
Si	1	<10	n.d.	6	<10	2	<10
Sn	0.05	45	160	32	30		
Sr	0.01	<10	<10	4	<10	<<10	<10
Th	0.05	80	n.d.	18	<10	0.2	>90
U	0.02	<10	n.d.	5	<10	0.1	25
V	0.2	30	30	8	<10	0.5	60
W	0.02	25	n.d.	35	80		
Zn	0.5	<10	<10	7	<10	5	40
Zr	0.02	<10	30	14	<10	0.2	60

In spite of the pre-cleaning procedure of the polyethylene sampling bottles by nitric acid an analysis of blank samples confirmed that leaching from the sampling bottles took place, which may result in elevated apparent concentrations of many elements like Al, Ba, Br, Cd, Fe, Li,

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[12] Percentage of groundwater samples with analytical concentrations of a given elements below the concentrations in blank samples or below the concentrations produced due to leaching from the sampling bottles.

Mn, Nb, Rb, Si, Sr, Zn, Zr, REE[13] etc. The concentrations in blank samples were compared with the frequency curves of analytical concentrations of given elements in groundwater. This data analysis led to the conclusion that leaching from the bottles is unessential for the majority of elements which concentrations in more than 90% of the groundwater samples are higher than the concentrations that can be caused by leaching. However, the leaching effect should be taken into account regarding the analytical concentrations of Cr, Cu, Hg, Mo, Ni, Pb, Sn and W. The analytical concentrations of Cr, Cu, Mo, Ni and Pb were corrected and the respective quantification limits were elevated. The data of Hg and Sn were removed from the database due to high bias and strong influence from the leaching; additionally the data of W was deleted due to the too high leaching effect.

The last column of the table represents the real sensitivity of ICP-MS of the laboratory ACME and summarises the reliability of the method for the background and heightened concentrations of elements in groundwater:

- ICP-MS provides reliable data *within whole ranges of concentrations* for 7 minor elements (Al, Ba, Br, Fe, Mn, Si and Sr) and 7 trace elements (As, Co, Li, Rb, U, Zn, and Y) and several rare earth elements (Ce, La etc). As rare earth elements and yttrium show a very close migration pattern, the sum of concentrations of these elements marked as REE is used for consecutive data processing;
- ICP-MS provides reliable data *regarding elevated concentrations* of 2 minor elements (B, P) and 9 trace elements (Cd, Cr, Cu, Mo, Ni, Pb, Sb, V and Zr);

ICP-MS provides reliable data *regarding only very high concentrations* of 6 trace elements (Cs, Ge, Hf, Nb, Se and Th).

Only the results of analyses of the above mentioned reliable elements are presented in the database, and the data processing is concentrated on the mentioned reliable elements.

Note that inadequate filtration of samples before acidification results in drastically increased concentrations of almost all elements up to thousands percents, especially Cs, Al, Be, Cd, Pb and Zn. Only boron, bromine and strontium do not increase in acidified samples with presence of suspended matter. Based on this, 6 water samples were identified to be inadequate filtered due to damaged filters; the respective results of analyses from these samples were deleted from the database.

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[13] RRE= rare earth elements and ytrium

1.6 Data storage and processing

The information obtained within this project is stored in six annexes that where relevant are interlinked by sample numbers and well numbers:

Annex 1: "The most typical pesticides characterised by the highest expected relative probability of their occurrence in Latvian groundwater"

Useful background information on the pesticides most relevant in this context is listed in this annex. Based on the application rate of pesticides and their mobility an evaluation of the relative probability of pesticide occurrence in Latvian groundwater was carried out (see chapter 1.2).

Annex 2:" List of pesticides collected in the 1990s at the former agrochemical storehouse "Gardene" "

This list includes pesticides collected in Latvia during the 1990s in amounts exceeding 3 tons and thus must characterises the spectrum of pesticides used in the past in Latvia.

Annex 3: "CFCs Analyses"

The result of 2 sampling campaigns (June 2005 and July 2005) for groundwater age determination of 27 samples carried out by GEUS and SGSL.

Annex 4: "High-yielding Latvian springs found and sampled within this project"

A number of springs has been selected and sampled in frame of this project. Based on project results the most representative high-yielding springs were selected to enter and improve the groundwater monitoring programme. The springs mentioned in Annex 3 were already in 2004-2005 included in the Basic Groundwater Monitoring Network for better control of the modern diffuse contamination (chapter 3.4 and 5.1)

Annex 5: "Groundwater Chemistry"

Annex 5 is the main database, stored in an excel table at the enclosed CD, and contains;

- Various types of information on sampling sites: sample no., GPS co-ordinates, land use, aquifer type and index, aquifer deposits etc,
- Information about sampling / drilling: well casing material, sampling method and date, a depth of water table or spring rate.
- In-situ measured parameters of groundwater quality (EC, pH, Eh, oxygen),
- Results of reliable chemical analyses of the collected samples (91 parameters) and quality control data (calculated charge balance and EC balance),
- Sample no. for determination of pesticides providing the link to the database containing the results of GC / LC – MS analyses of pesticides (50 parameters).

The groundwater chemistry data were processed by traditional statistical methods such as frequency analysis, rank correlation and factor analysis, see chapter 2.2.

Annex 6: “Site pictures”

The annex contains pictures in jpg format for a number of the sites where the drilling and sampling has been carried out. The linking between sites and pictures can be found in annex 5. Annex 6 is also available at the enclosed CD.

1.7 Establishment of observation wells at agrochemical run-off monitoring stations

By request of the Latvian University of Agriculture and by agreement with DANCEE, 10 observation wells were established in frame of this project at three selected agricultural run-off monitoring stations. This was necessary to fulfil the objectives of the European Nitrate Directive: while the surface and drainage water have been monitored at agricultural run-off monitoring stations since 1993, the contamination of groundwater has not been controlled due to the absence of observation wells.

The Latvian University of Agriculture defined three agricultural run-off stations as having the highest priorities for establishing new groundwater monitoring networks: Jaunberze, Mellupite and Skriveri. The main criteria for selecting these stations were agricultural load, contamination of surface and drainage water and possible changes in land use in the future. Based on geological data and data on groundwater contamination collected within this project, some corrections were made and the groundwater observation wells were established at agrochemical run-off monitoring stations at Jaunberze, Mellupite and Vecauce.

Totally 10 monitoring wells were established:

- 4 at Jaunberze,
- 3 at Mellupite,
- 3 at Vecauce.

Nine wells were screened in the uppermost drift aquifer in depths down to 10 m. One well was screened in a pre-Quaternary dolomite aquifer in the depth 15 – 22m downstream groundwater flow from Jaunberze, in order to control the potential contamination of this main aquifer (contamination of main deep aquifers at Mellupite and Vecauce is less expectable because of the large thickness of the confining till layer).

2. Natural quality of shallow groundwater

2.1 Distribution of elements in shallow groundwater

As mentioned in the previous chapter, a large number of minor and trace element have been analysed in this project. Mean concentration of these elements in shallow Latvian groundwater are given in Table 2

Table 2. *Mean concentrations of elements in shallow Latvian groundwater*

Major elements (>1 mg/l)	Mean, mg/l	Minor elements (10-1000 µg/l)	Mean, µg/l	Trace elements (0.1-10 µg/l),	Mean, µg/l	Ultra-trace elements (<0.1 µg/l)	Mean, µg/l
C / HCO_3	60	Al	10	As	0.5	Ce	0.07
$C_{org.}$	1.5	B	20	Co	0.1	Dy	0.01
Ca	80	Ba	80	Li	3	Gd	0.01
Cl	10	Br	30	Rb	1	La	0.05
K	2	F	250	U	0.4	Nd	0.05
Mg	20	Fe	600	V	0.3	Pr	0.01
Na	8	N / NH_4	150	Zn	5	Y	0.07
S / SO_4	7	N / NO_3	400	Cr	<3	Ag	<0.05
Si	4.5	Mn	50	Cu	<1	Au	<0.05
		P	20	Mo	<1	Be	<0.05
		Sr	100	N / NO_2	<3	Bi	<0.05
				Ni	<2	Cd	<0.1
				Pb	<0.3	Cs	<0.01
				Sc	<1	Er	<0.01
				Se	<0.5	Eu	<0.01
				Ti	<10	Ga	<0.05
						Ge	<0.05
						Hf	<0.02
						Hg	<0.1
						Ho	<0.01
						In	<0.01
						Ir	<0.05
						Lu	<0.01
						Nb	<0.01
						Os	<0.05
						Pd	<0.2
						Pt	<0.01
						Re	<0.01
						Rh	<0.01
						Ru	<0.05
						Sb	<0.05
						Sm	<0.02
						Sn	<0.1
						Ta	<0.02
						Tb	<0.01
						Te	<0.05
						Th	<0.05
						Tl	<0.01
						Tm	<0.01
						Yb	<0.01
						W	<0.1
						Zr	<0.2

In order to make the data collected during this project more representative for the entire shallow groundwater, the data were grouped in four data clusters: data from water table aquifers, from drift aquifers (alternating sandy and till layers), from confined aquifers and from springs. The mean concentrations of elements for the entire shallow groundwater were calculated as weighted average values, taking into account the distribution of each groundwater type.

The mean values of 43 trace and ultra-trace elements were not determined due to insufficient sensitivity of the analytical methods or due to cross-contamination from sampling bottles (see chapter 1.5). These elements are classified as trace or ultra-trace elements by various other studies (Aastrup et al 1995, BGS 2003, Frengstad et al 2000, Krainov & Shvetc 1987, Shvartsev 1998, Vissers 2005). It should be noted that the concentrations of the various elements significantly differ within the data set (Figure 13). The variance of the concentrations of elements was calculated as:

Var (%) = (C99% - CMe)*2/CMe*100, where:

C99% = 99-percentile of concentration of the given element,

CMe = median concentration of the given element.

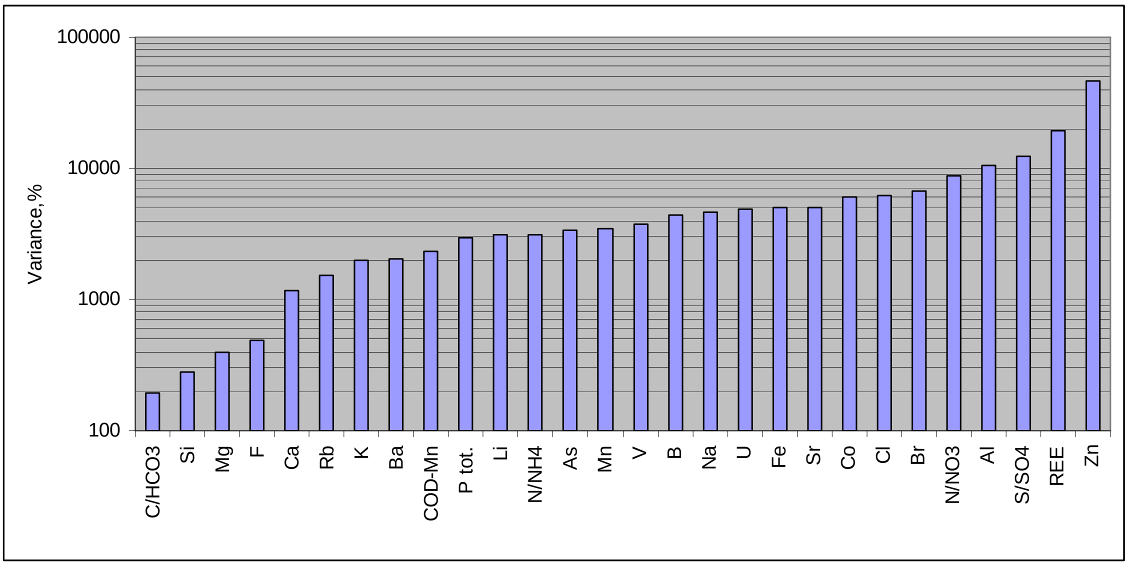

Figure 13. *Variance of concentration of elements in shallow groundwate*

The concentrations of bicarbonate, silica, magnesium and fluoride are rather similar for different aquifers while the concentrations of zinc, aluminium, REE[14], sulphates, aluminium and nitrates vary by more than four orders of magnitude. These differences are caused by several geochemical reactions which alter the distribution of elements, for example:

- Low variance of bicarbonate and silica due to the limit of solubility;
- High variance of aluminium and REE due to strong pH-dependence of these elements;
- High variance of nitrates due to competitive contamination and denitrification processes;

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[14] As mentioned in chapter 1.6 the concentrations of rare earth elements and yttrium, showing a very closed migration pattern, are summed up.

- High variance of sulphates due to opposite processes of dissolution of gypsum and sulphate-reduction.

It should be noted that the extremely high variance of zinc could be caused by cross-contamination of samples from the well-screen material, which contains zinc. The highest concentrations of zinc were found in drift aquifers characterising by a very poor permeability. The groundwater samples collected from drift aquifers had the longest contact with the well casing, because they were taken next day after drilling of the borehole[15].

The distribution curves (cumulative frequency plots) of 28 well investigated elements are given on Figures 14 and 15. Examples of spatial distribution of four minor and trace elements (arsenic, uranium manganese and zinc) are presented on Figure 16.

As often, the distribution of geochemical data is neither normal nor lognormal (BGS, 2003). Nevertheless, the linearity of the middle part of the logarithmic frequency curves indicates approximation to a log-normal distribution of the majority of elements. The skewness of the nitrate-plot reflect the concurrent processes of contamination and denitrification, while the skewness of the manganese-plot reflect the heterogeneity of the data set – water table aquifers with a high native content of organic matter have an increased concentration of manganese.

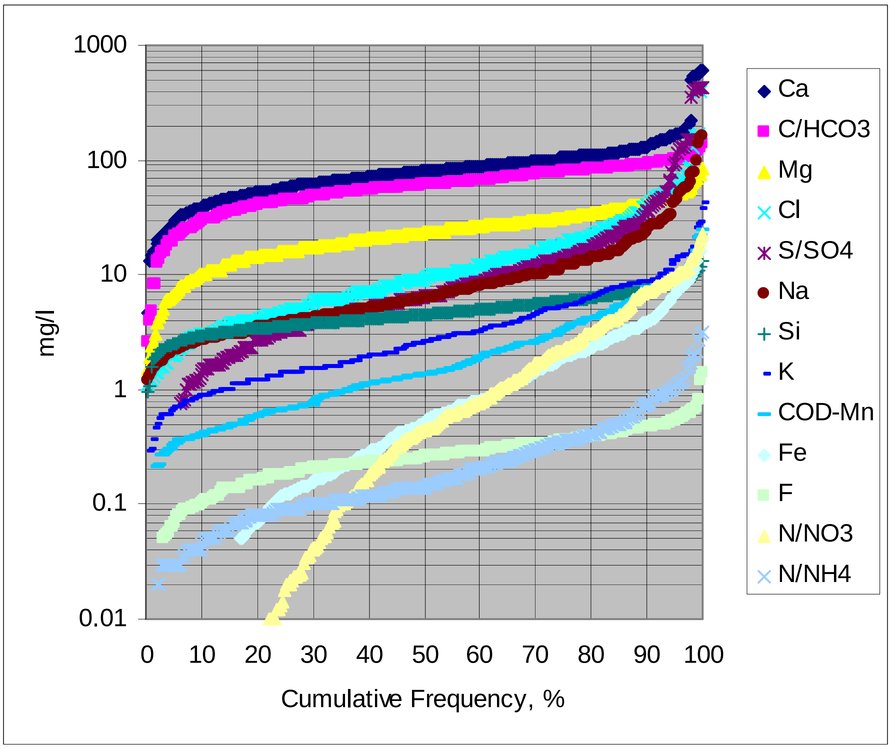

Figure 14. *Distribution of major elements and substances in shallow groundwater*

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[15] After refilling of the well by fresh groundwater.

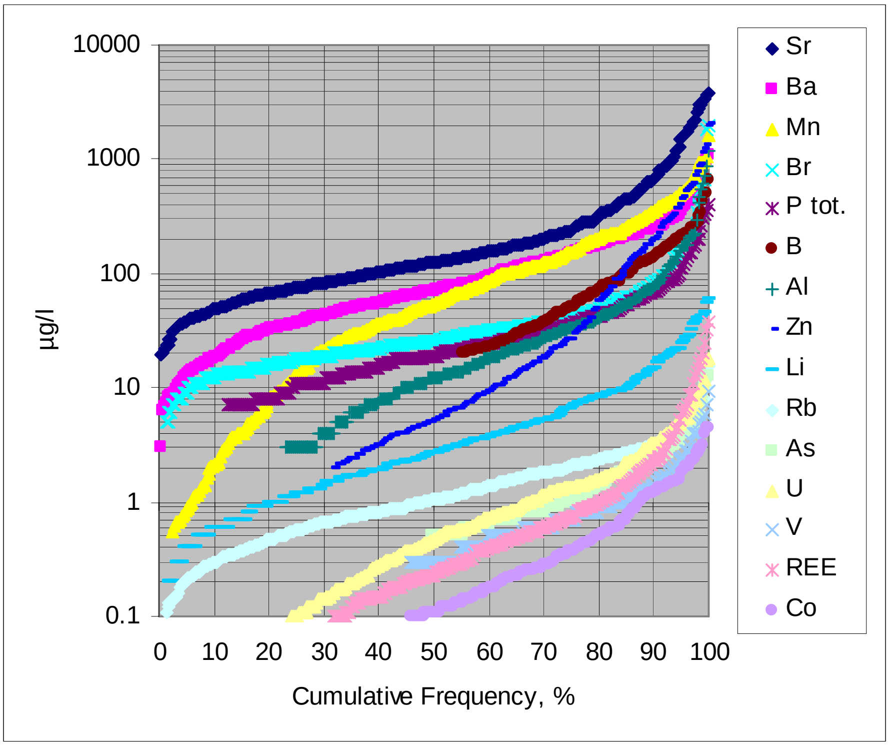

Figure 15. *Distribution of minor and trace elements in shallow groundwater*

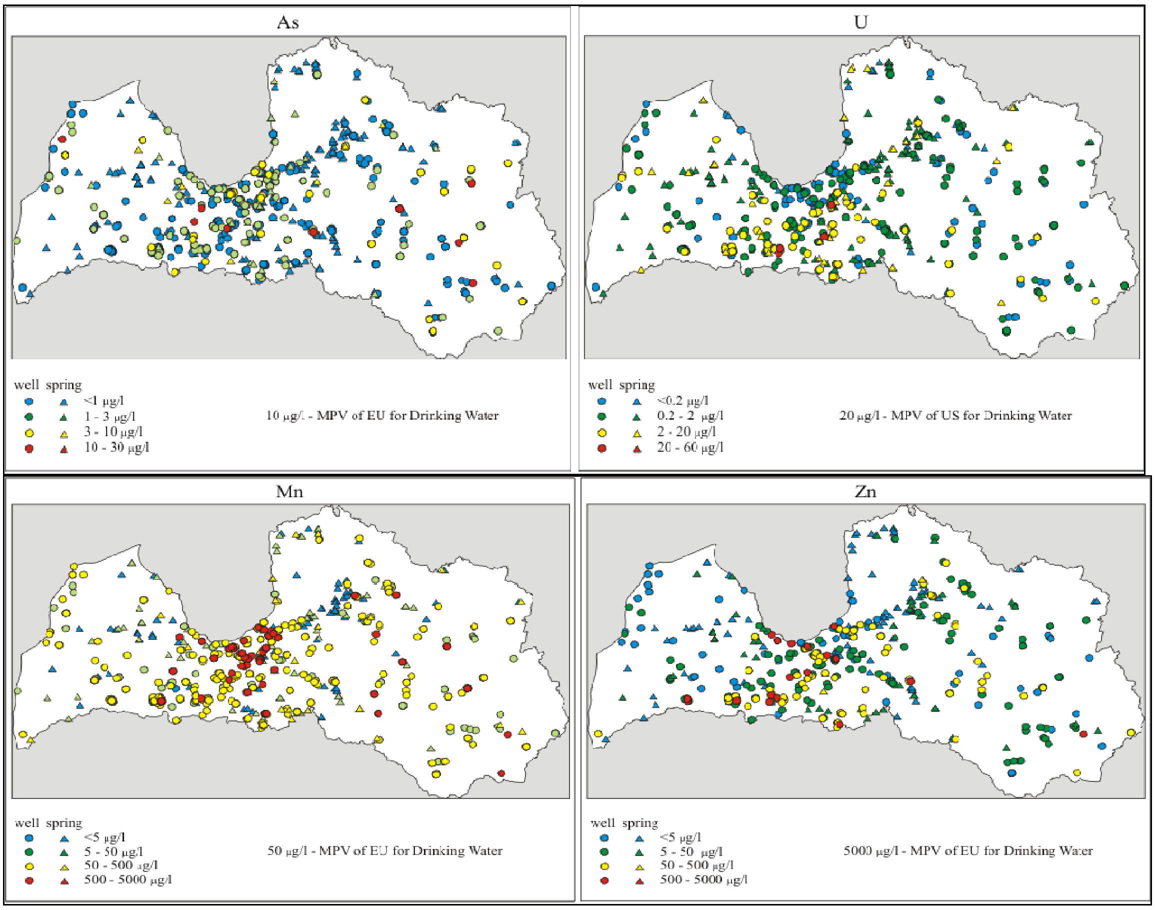

Figure 16. *Spatial distribution of arsenic, uranium, manganese and zinc in shallow groundwater*

2.2 Factors influencing groundwater quality and behaviour of elements

The chemical composition of groundwater depends on several factors like chemical composition of precipitation and water-bearing sediments (firstly presence of well-soluble minerals and organic matter); residence time of groundwater or the time of groundwater-sediments interaction; confinement degree of the aquifer, defining the aerobic or anoxic conditions; water exchange between aquifers forming the mixed groundwater types; anthropogenic input etc.

The groundwater chemistry data were processed by traditional statistical methods such as frequency analysis, rank correlation and factor analysis. A non-parametric technique (cumulative frequency plots, median and quartile values, Kruskal – Wallis median tests, correlation by Spearmen) was applied because the results are more resistant to outliers and poly-modal distributions.

Factor analysis - principal component analysis with consecutive Varimax rotation, which can simultaneously analyse a large number of the groundwater quality variables, was performed to explore the hydrogeochemical processes.

The factor analysis is the multivariate statistical method applied in various sciences from psychology to geology to identify processes affecting the distribution of the variables – the concentrations of elements in groundwater in our case. Factor analysis reduces a large data set to a few independent composite variables (factors) that explain much of the variance of the original data. Component loadings show the degree of correlation between the original variables and factors. Variables that are highly correlated with a factor are considered to represent a particular process influencing the data. Factor scores show the influence of a factor on individual samples (Davis 1970).

For identification of “universal” and stable factors a reiterated factor analysis was run for different data sets, which includes different combinations of variables and cases (samples). A preliminary cleaning of the data set included removal of strong outliers, of variables with a poor reproducibility, and the rather large percentage of non-detections according to the recommendations of Farnham I. et al. 2002[16], as it is important that the variables included in the factor analysis are good descriptors of the groundwater systems and not simply describing noise. The observations below detection limit (DL) were substituted with DL/2.

By this factor analysis of different data sets, depending on selected variables and cases[17], 8 to 15 factors with Eigen values higher than 1.0 have been identified, which formally can be assessed as statistically significant factors. Table 3 represents the most reliable results of factor analyses after removal of elements with a poor reproducibility and high bias, elements with non-detects exceeding 25% as well as strong outliers.

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[16] These authors estimated that the performance of multivariate analysis deteriorates quickly when the variation between duplicates exceeds 30% of the total variance over all measurements, or when non-detects exceed 30% of the observations.

[17] For an identification of “universal” and stable factors, repeated factor analyses of the project data were made for different data sets, which include different combinations of variables and cases (samples).

The first six factors with Eigen values higher than 2.0, explaining 58% of the total variance of the data set, are presented in the Table 3. 58% of the total variance may be regarded as a rather high figure due to the large number of variables and statistically significant factors.

Table 3. *Statistically significant loadings at p < 0.001 from principal components analysis after Varimax rotation*

Groundwater quality variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
pH			-0.59			-0.25
HCO_3			-0.32		0.64	0.44
SO_4	0.93					
Cl		0.95				
Ca	0.87				0.22	
Mg	0.41	0.28	-0.27		0.59	0.22
Na		0.90		0.14		
K				0.83	0.20	
NH_4		0.18		0.45	-0.16	0.32
$NO_3 + NO_2$			-0.15	0.24	0.57	-0.26
COD-Mn			0.61	0.36		0.14
Al			0.77			
Ba	-0.13		-0.22			0.55
Br		0.83				
Co			0.29	0.14	0.45	0.27
Cu			0.19		0.29	
F	0.73					0.27
Fe			0.16	0.41		0.55
Li	0.86					
Mn			0.14	0.32	0.16	0.41
P			0.20	0.41		
Rb			0.17	0.83		
Si	0.29		0.21			0.64
Sr	0.89					
U				-0.15	0.69	
Zn			0.18		0.20	0.21
REE			0.76	0.13		
Explained variance, %	15	10	9	9	8	8

Factor *1* is grouping the positive loading of sulphates, calcium, magnesium, fluoride, lithium, strontium and can be interpreted as a factor of dissolution carbonate rocks with gypsum, or a factor of influx of saline sulphate groundwater from deeper aquifers. This factor confirms the well-known fact that heightened concentrations of fluoride and strontium usually occur in saline sulphate groundwater[18]. Note that the distribution of accompanying lithium has not been investigated earlier in Latvian groundwater.

Factor 2 reflects an upward injection from greater depth of chloride sodium saline groundwater characterised by an increased content of bromide.

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[18] As even the highest concentrations of fluoride in the data set do not exceed 1.5 mg/l they are not controlled by solubility of calcium chloride.

Selenium and boron were not included in the data set for factor analysis due to the large number of non-detects in fresh groundwater. However, a simple statistical analysis (Kruskal – Wallis median test) indicates an increase of selenium in chloride saline groundwater and an increase of boron in both chloride and sulphate saline groundwater.

In ***Factor 3*** organic matter measured by permanganate index, aluminium, REE, cobalt and several other metals are inversely related to pH. The scores of this factor are highest in slightly acid groundwater, occurring in water table aquifers of organic rich Holocene deposits. This factor can be explained by dissolution of carbonate cement and hydrolysis of aluminium silicate minerals by infiltrating water containing carbon dioxide and organic acids, as well as by the well-known dependence of trace metals on acidity and dissolved organic matter in the solution.

A correlation analysis of the data indicates that a decrease in acidity is accompanied by a decrease of concentrations of aluminium, cobalt, iron, manganese, rubidium, zinc and REE (Figure 17).

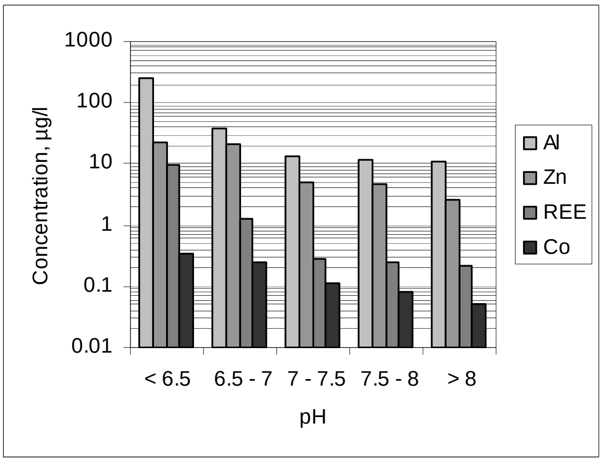

Figure 17. Median concentrations of selected pH-dependent elements (n = 502). Respective coefficient of rank correlation with pH are -0.19, -0.22, -0.23, -0.30, -0.21, -0.22 and -0.32. There are no elements with a positive correlation to acidity.

Similar pH dependences of elements were reported by several studies (Aastrup at el. 1995, Frengstad at el. 2000, Krainov at el. 1987 etc.). Most metals occur in solution as cations and generally become insoluble as pH increases due to both precipitation and absorption on soil particles. However, forming of well-soluble chelates (complexes of metals with organic matter) prevents the precipitation and absorption of metals even in strongly alkaline solutions. Therefore the concentration of such metals is directly related to dissolved organic matter and inversely related to pH, which are the most important factors controlling the concentration of heavy metals.

Factor 4 has the highest scores in the vicinity of former agrochemical storehouses and pig farms. This factor, responding an increase of potassium, ammonia, nitrates, phosphorus, organic matter and other elements, indicates point-pollution.

Factor 5 groups the positive loadings of bicarbonates, magnesium, nitrates, uranium, cobalt and copper. An increase of concentrations of these elements is observed in water table aquifers beneath agricultural areas - this factor reflects the diffuse contamination of groundwater. All these compounds occur in agricultural additives as organic and inorganic fertilisers and dolomites used for neutralisation of soil acids. Additional quantities of some metals may be released from deposits due to oxidation reactions caused by a continuous flux of nitrates present in infiltrating water (Böhlke, 2002). Perhaps the aeration of groundwater, caused by artificial drainage and irrigation, plays some role in the increase of uranium, as uranium tends to be mobile under oxidising conditions.

The interpretation of ***Factor 6*** is more difficult. Note (table 3) the inverse relation of iron and ammonium to nitrates and the highest scores of this factor in anoxic aquifers with no nitrates and low Eh. Thus, this factor can be interpreted as an indicator of denitrification and nitrate reduction combined with other geochemical processes sensitive to the Red-Ox, and of confining conditions of an aquifer.

Because of the absence of Eh measurements in the majority of the samples[19] this parameter has not been included in the data set for the factor analysis. The influence of Red-Ox potential on the behaviour of various elements has been determined by a simple correlation analysis. Nitrate, uranium and cobalt have a statistically significant positive rank correlation with Eh (r= +0.59, +0.48 and +0.45 respectively) and are shown to be mobile under oxidising conditions, while ammonium, iron and arsenic exhibits the opposite trend (r = -0.31, -0.26 and -0.25 respectively), see Figure 18. The forming of insoluble sulphides is one of the possible processes responsible for the decrease of the concentrations of several metals under strongly reduced conditions.

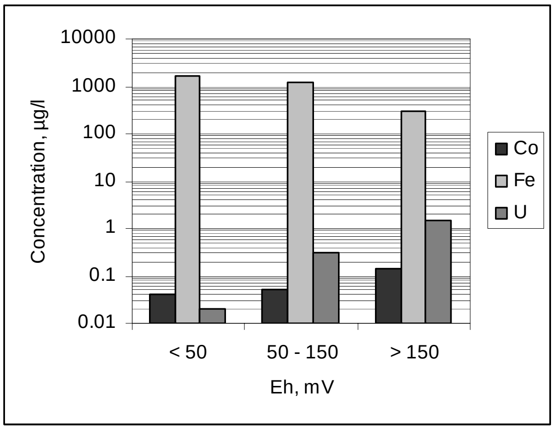

Figure 18. *Median concentrations of selected Eh-dependent elements (n = 102 after removal of strongly contaminated and organic rich groundwater samples)*

In contrast to the majority of minor and trace metals - which concentrations are limited by precipitation and absorption and can exceed the MAC only in shallow organic rich, acid and aerobic groundwater - arsenic and nitrogen are mobile over a wide range of Red-Ox and pH conditions. High concentrations of these elements may occur under alkaline and reducing conditions typical in the main Latvian aquifers.

The highest concentrations of arsenic (up to 20 µg/l) were observed in strongly anaerobic confined aquifers of methanogenic stage, characterised by a negative Red-Ox potential, by oxygen and nitrate contents below detection limit and by sulphate contents less than 1 - 2 mg/l.

Red-Ox and pH are the most important factors controlling nitrogen: nitrate is dominant under aerobic and alkaline conditions, while ammonium becomes dominant under reducing and acid conditions (Figure 19). Therefore the high concentrations of nitrates may occur only in shallow secondary Latvian aquifers. In major confined Latvian aquifers nitrate be-

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[19] Eh was not measured in springs and low-yielding boreholes, where it is very difficult to prevent an addition of excess air in the samples.

comes geochemical unstable, and the agricultural contamination can be reflected in increased concentrations of ammonium (natural ammonium plus the remaining after denitrification of the anthropogenic nitrogen).

Note that the conducted factor analysis did not reveal any influence from lithology of water-bearing sediments on groundwater quality, except the presence of well-soluble gypsum (Factor 1). The Kruskal – Wallis median test also confirms that the differences in concentrations of all ions and elements in confined aquifers of Devonian dolomites, limestones, sandstones or Pleistocene sands are statistically insignificant. This rather disappointing conclusion is clarified by the fact that silicate aquifers contain carbonate minerals as cement around sand grains, as well as by a the major control of the groundwater chemistry by a range of hydrochemical processes such as mixing, Red-Ox reactions and ion-exchange reactions, which hide the lithological signatures (Edmunds, 2003; BGS, 2003).

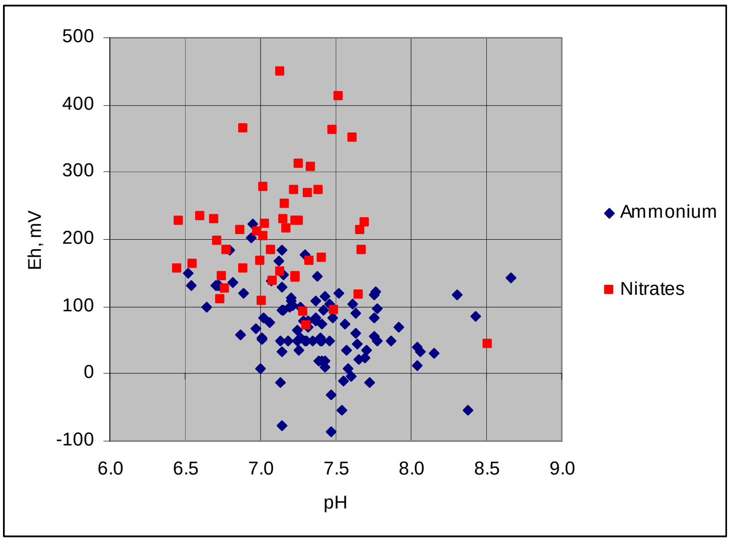

Figure 19. *Nitrogen in groundwater depending on pH-Eh*

2.3 The role of groundwater residence time

The groundwater residence time or the time of interaction of groundwater with sediments is assessed in many papers as one of the most essential factors influencing the groundwater chemistry.

27 groundwater samples were taken from monitoring wells to obtain the first data on residence time of Latvian groundwater ever, estimated by the CFC-dating method (Chapter 1.4, Annex 3). No CFCs were detected in 17 of the 27 wells, meaning that the groundwater is more than 55 -60 years old. The youngest groundwater was found in the depth of 5m in aquifers of sand-gravel deposits and dolomites at the monitoring stations Griva and Stirniene, 10 and 20 years respectively. Note that groundwater residence time in the same depth in sand-gravel drift aquifer at monitoring station Skrunda reached 35 years.

In spite of the very limited number of CFCs samples, taking into account that the most typical hydrogeological conditions were covered in the sampling, it may be concluded that Latvian groundwater seems to be twice as old as Danish groundwater from the same depth. The typical age of Danish groundwater is 15 – 25 years in depths of 20m and 30 – 40 years in the depths of 50m (Laier 2002). The respective values for the Latvian groundwater are 30 – 40 years and more than 55 - 60 years (see Figure 20).

Figure 20. *CFC residence time of Latvian groundwater depending on depth; CFCs – free samples with groundwater residence time above 55 years are marked by empty circles. N = 27*

The observed difference may reflect both the lower abstraction rate of Latvian groundwater and a higher extent of rapid preferential flow in fractured Latvian aquifers: the youngest groundwater pass through the narrow high-permeable zones around the broad zones of “stagnant” groundwater, where the monitoring wells are installed and CFCs samples were taken.

The number of groundwater age data is too small for a direct determination of related signatures of groundwater chemistry. Tracing evolution of groundwater chemistry along flow paths is also impossible due to the complexity of the groundwater flow and the limited data on deep groundwater[20]. Thus the influence of groundwater residence time on groundwater

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[20] This project focused on investigation of shallow groundwater most sensitive to the land use.

chemistry was evaluated indirectly, by assuming that all groundwater is a mixture of younger and older components and that the percentage of modern water decreases in sequence springs – wells in unconfined aquifers – wells in confined aquifers. The respective median concentrations of elements, calculated after removing data from contaminated groundwater and groundwater with chloride or sulphate exceeding 70 mg/l and permanganate index exceeding 4 mg/l[21], are given in Table 4.

Table 4. *Median concentrations of selected elements and substances in different groundwater types*

Parameters		Springs (n=124)	Shallow wells in unconfined aquifers (n=153)	Shallow wells in confined aquifers (n=49)
HCO_3	mg/l	290	260	330
SO_4		16	15	6
Cl		8	7	4
Ca		70	66	65
Mg		19	17	24
Na		5	4	8
K		2	1	4
N/NH_4		0.1	0.1	0.2
N/NO_3		1.0	0.4	<0.01
F		0.28	0.24	0.22
Fe		0.1	0.3	1.5
Si		4.3	4.3	4.7
Ba	µg/l	61	49	220
Li		1.9	1.3	5.5
Mn		4	80	38
Rb		0.6	0.7	1.2
Sr		75	76	290

Note that this approach does not allow us to distinguish the role of the groundwater residence time from the role of the confinement degree of the aquifer, which defines the Red-Ox conditions of an aquifer. The most conspicuous differences in the above mentioned sequence are observed with respect to Red-Ox sensitive iron and nitrate; these regularities certainly are related to the confining conditions of the aquifer, rather than to the groundwater residence time.

However, the much higher concentrations of barium, lithium and strontium in confined aquifers compared to springs and unconfined aquifers may be explained only by the residence time, i.e. by the time of the groundwater-sediments interaction. These metals are pH and Eh insensitive; the selected data sets do not differ by pH and basic chemistry. Therefore it may be concluded that the residence time of groundwater is responsible for accumulation of barium, lithium and strontium.

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[21] The high content of organic matter and the admixture of saline water influence the concentrations of several elements and hide the influence of the residence time (see previous chapter).

2.4 Background concentrations of elements

Knowledge of the background quality of groundwater is an essential prerequisite for the identification of contamination and for imposing regulatory limits. Background values are defined here as the lower quartile, median and upper quartile concentrations of a given element or substance in groundwater, derived mainly from natural geological, biological and atmospheric sources, with very low anthropogenic alterations. Background values are calculated from a "cleaned" data set from which the samples of essentially contaminated groundwater were removed. i.e.:

- Samples collected from unconfined aquifers around point-pollution sources, within urbanised areas and areas of intensive agriculture;
- Samples with nitrate or ammonium nitrogen above 5 mg/l, and samples with COD-Mn above 30 mg/l[22], independent on recent land use:
- Samples with chlorides exceeding 70 mg/l, collected within areas where increased natural concentrations of chlorides are less expectable[23].

The median, lower quartile and upper quartile concentrations of elements in shallow Latvian groundwater for 6 groundwater types characterised by main hydrogeochemical processes to different extent are given in Table 5. The six groundwater types distinguished are:

- Wells in water table aquifers with low to moderate content of organic matter (COD-Mn < 4 mg O_2/l),
- Wells in water table aquifers with high content of organic matter (COD-Mn > 4 mg O_2/l),
- Wells in drift aquifers (alternating sandy and till layer),
- Wells in shallow confined or semi-confined aquifers,
- Groundwater with increased content of chlorides or sulphates (more than 70 mg/l),
- Springs.

The main differences between the selected groundwater types are as follows:

- organic rich groundwater with increased concentrations of ammonia, iron, silica, phosphorus, aluminium, manganese, lead, vanadium, REE and zirconium and lowered pH value;
- groundwater rich in chlorides and sulphates with an increased concentrations of calcium, magnesium, sodium, potassium, fluoride, boron, bromide, lithium, selenium and strontium;
- confined aquifers (compared to unconfined aquifers) with increased concentrations of arsenic, barium, boron, lithium and strontium and lowered concentrations of aluminium, manganese, nitrate, sulphate, REE, uranium, zinc and zirconium;
- Springs (compared to wells) with increased concentrations of nitrate and uranium and lowered concentrations of iron and manganese.

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[22] Such too high concentrations of nitrogen and organic matter can not be explained by natural reasons and are perhaps caused by historical land use.

[23] Outside areas of possible intrusion by deep saline groundwater or marine water.

Table 5. *Background concentrations of elements in different groundwater types*

Parameters		**Wells in water table aquifers with low to moderate content of organic matter, n = 110**			**Wells in water table aquifers with high content of organic matter, n = 64**			**Wells in drift aquifers, n = 53**		
		LQ	**Me**	**UQ**	**LQ**	**Me**	**UQ**	**LQ**	**Me**	**UQ**
pH		7.1	7.4	7.7	6.7	7.1	7.4	7.1	7.3	7.6
EC	µS/cm	270	380	490	280	370	500	360	520	640
HCO_3	mg/l	170	230	320	130	230	340	230	340	450
SO_4		9	15	24	10	16	30	8	15	30
Cl		4	6	11	5	8	13	5	8	12
Ca		45	63	82	38	62	86	55	80	100
Mg		9	15	22	8	13	19	15	21	32
Na		2.2	3.2	5.9	2.5	3.7	5.1	3.6	5.3	8.4
K		0.7	1.3	1.9	1.0	1.5	2.8	1.3	2.0	3.5
$N_{tot.}$		0.4	0.7	1.4	0.6	1.1	1.7	0.6	1.0	2.0
N/NH_4		0.07	0.11	0.15	0.14	0.28	0.65	0.11	0.21	0.45
N/NO_3		0.1	0.4	0.8	0.05	0.4	0.7	0.1	0.4	0.9
F		0.13	0.22	0.28	0.11	0.19	0.24	0.19	0.26	0.32
Fe		0.1	0.2	0.9	0.8	2.2	3.6	0.2	0.9	3.0
Si		3.3	4.0	5.4	4.3	6.0	7.8	3.4	4.6	6.2
COD-Mn		0.6	1.3	2.5	5.6	8.1	11.0	0.7	1.3	4.0
$P_{tot.}$	µg/l	11	20	32	22	45	110	<10	19	29
P/PO_4		7	11	21	11	29	97	7	9	19
Al		8	22	60	27	70	210	<3	16	35
As		<0.5	0.5	0.9	<0.5	0.7	1.4	<0.5	<0.5	0.8
B		<20	<20	<20	<20	<20	<20	<20	<20	26
Ba		21	37	81	35	52	87	45	80	140
Br		15	20	30	17	26	35	18	24	33
Cd		<0.1	0.1	0.3	<0.1	0.1	0.3	<0.1	0.1	0.3
Co		0.08	0.18	0.39	0.13	0.23	0.43	0.2	0.3	1.3
Cr		<3	<3	<3	<3	<3	<3	<3	<3	3.6
Cu		<1	<1	1.4	<1	<1	2.4	<1	<1	2.1
Li		0.4	1.0	2.0	0.6	1.0	2.2	1.5	2.4	5.0
Mn		22	74	180	110	220	410	50	110	220
Mo		<1	<1	<1	<1	<1	<1	<1	<1	1.1
Ni		<2	<2	<2	<2	<2	<2	<2	<2	4
Pb		<0.3	<0.3	0.3	<0.3	<0.3	0.7	<0.3	<0.3	0.5
Rb		0.4	0.7	1.1	0.6	1.3	3.4	0.5	1.0	1.6
Sb		<0.05	<0.05	0.10	<0.05	0.06	0.13	<0.05	0.09	0.20
Se		<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Sr		50	70	100	55	80	110	70	110	150
U		0.2	0.4	1.4	0.1	0.2	0.7	0.2	0.6	1.3
V		<0.3	0.3	0.6	0.7	1.9	3.5	<0.3	<0.3	0.5
Y+REE		0.2	0.5	1.1	1.1	3.8	13.0	<0.05	0.3	1.0
Zn		6	20	100	6	21	95	7	15	140
Zr		0.06	0.15	0.30	0.51	1.1	2.3	<0.05	0.13	0.37

Parameters		**Wells in shallow confined and semi-confined aquifers, n = 57**			**Groundwater with an increased content of chlorides or sulphates, n = 43**			**Springs, n = 121**		
		LQ	**Me**	**UQ**	**LQ**	**Me**	**UQ**	**LQ**	**Me**	**UQ**
pH		7.3	7.4	7.7	7.1	7.4	7.6	7.3	7.4	7.6
EC	µS/cm	380	460	540	930	1000	1900	340	440	540
HCO_3	mg/l	230	320	400	200	250	310	210	280	360
SO_4		1	6	13	48	160	860	10	16	23
Cl		2	4	7	12	130	410	5	8	13
Ca		48	65	80	75	140	270	54	70	86
Mg		16	23	28	25	37	55	13	18	26
Na		5	7	13	12	78	160	3.1	4.3	5.9
K		2.0	3.1	5.3	4.8	7.8	14.0	1.0	1.5	2.3
$N_{tot.}$		0.2	0.3	0.6	0.2	0.4	0.8	0.5	0.9	2.8
N/NH_4		0.11	0.24	0.41	0.09	0.13	0.32	0.08	0.11	0.15
N/NO_3		<0.01	<0.01	<0.01	<0.01	0.01	0.1	0.3	0.7	2.1
F		0.18	0.22	0.28	0.40	0.50	0.80	0.22	0.28	0.34
Fe		0.8	1.8	2.8	0.3	0.6	1.2	<0.1	0.1	0.2
Si		3.9	4.9	6.0	2.0	3.2	4.5	3.7	4.3	5.4
COD-Mn		0.7	1.2	2.5	1.0	2.3	4.5	0.4	0.8	1.8
$P_{tot.}$	µg/l	11	23	35	<10	14	22	<10	12	24
P/PO_4		8	15	28	8	13	19	7	9	18
Al		<3	3	11	<3	8	16	<3	8	33
As		<0.5	0.8	1.9	0.6	1.2	2.0	<0.5	<0.5	0.5
B		24	60	120	92	180	380	<20	<20	<20
Ba		120	200	270	21	33	84	34	60	130
Br		14	19	28	50	550	1900	15	20	28
Cd		<0.1	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	0.1	0.2
Co		<0.04	0.04	0.10	<0.04	0.07	0.26	<0.04	0.05	0.10
Cr		<3	<3	<3	<3	<3	<3	<3	<3	<3
Cu		<1	<1	<1	<1	1.9	5.2	<1	<1	1.0
Li		3.1	4.9	7.9	9.3	28.0	48.0	1.0	1.8	3.0
Mn		23	47	81	32	59	120	1	4	30
Mo		<1	<1	1.2	<1	<1	<1	<1	<1	<1
Ni		<2	<2	<2	<2	<2	<2	<2	<2	<2
Pb		<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Rb		0.8	1.2	1.9	1.3	2.2	3.4	0.3	0.6	1.0
Sb		<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Se		<0.5	<0.5	<0.5	0.7	1.9	2.8	<0.5	<0.5	<0.5
Sr		140	230	390	170	970	2400	50	75	110
U		<0.04	<0.04	0.2	0.05	0.1	1.0	0.3	0.7	1.4
V		<0.3	<0.3	<0.3	<0.3	0.3	1.0	<0.3	0.3	0.7
Y+REE		<0.05	0.1	0.2	<0.05	0.1	0.3	0.1	0.2	0.5
Zn		<2	<2	2	<2	<2	3	<2	3	6
Zr		<0.05	0.06	0.11	<0.05	0.05	0.15	<0.05	0.06	0.14

LQ – lower quartile, Me – median value, UP – upper quartile

The reasons for these differences are explained in chapters 2.2 and 2.3. These features of groundwater chemistry are taken into account for determination of the maximum background values, which allows the distinguishing of unpolluted from polluted groundwater.

Table 6. *Upper background values (UBV) of the minor and trace elements in shallow groundwater, mg/l*

Parameters	**UBV for a majority of shallow groundwater**	**Raised UBV for shallow organic rich groundwater**	**Raised UBV for shallow sulphate or chloride rich groundwater**	**Raised UBV for strongly anaerobic groundwater of methanogenic stage**	**Maximum Admissible Value for Drinking Water[24]**
K	10	25	25		
$N_{tot.}$	4	6			
N/NH_4	1	5			0.39
N/NO_3	3				11
F	0.5		2		1.5
Fe	6	20			0.2
$P_{tot.}$	0.1	0.5			
Al	0.2	3			0.2
As	0.01	0.02		0.02	0.01
B	0.15		1.5		1.0
Ba	0.5				
Br	0.1		5		
Cd	0.001				0.005
Co	0.002				
Cr	0.01				0.05
Cu	0.01				2.0
Li	0.01		0.15		
Mn	0.5	1			0.05
Mo	0.005				
Ni	0.01				0.02
Pb	0.001	0.01			0.01
Rb	0.005	0.02			
Sb	0.0005				0.005
Se	0.001		0.01		0.01
Si	10	15			
Sr	0.5		10		
U	0.005				
V	0.002	0.02			
REE	0.005	0.05			
Zn	0.5				
Zr	0.001	0.01			

The upper background values given in the Table 6 were estimated as 97.7 percentile values of the concentrations derived from the data sets, which include groundwater samples taken within native and slightly influenced areas, according to the recommendations of BGS (2003). Note that they are the *regional* maximum background values rather than the *natural* maximum background values, as all shallow groundwater can not be completely

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[24] According to the Drinking Water Directive.

pristine without any human impact. For instance, airborne nitrogen emitted by industry and combusted fuels inevitable impact the background of nitrates within the entire country even beneath the undeveloped and forested areas.

Table 6 identifies natural substances that cause problems for water supply:

- The upper background values (UBV) of ammonia, iron and manganese in shallow groundwater exceed the Maximum Admissible Concentrations for Drinking Water (MAC),
- The UBV of aluminium and arsenic are equal to MAC, thus the aluminium and arsenic may exceed the MAC due to natural outliers (geochemical anomalies),
- The UBV of lead in organic rich groundwater and the UBV of fluoride, boron and selenium in sulphate or chloride rich groundwater exceed or are equal to MAC.

The upper background values are taken into account for determination of the threshold values according the requirements of the Groundwater Directive[25], and for preparation of the recommendations for prospecting of the groundwater reserves (see chapters 5.2 and 5.3).

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[25] Expected to be adopted end 2006.

2.5 Comparison of natural quality of shallow groundwater in Latvia and Denmark

There are many similarities between Latvia and Denmark as far as climatic and geological conditions are concerned: the moderate and humid climate defines a similar net recharge of groundwater, both countries were covered by ice during several Quaternary glaciations and the glaciogenic deposits dominate the upper section of the geology etc. However, there are large differences with respect to groundwater discharge: while the majority of natural groundwater discharge remains in rivers and springs in Latvia, an essential part of the groundwater is captured by a dense network of abstraction wells in Denmark or flow directly to the sea. There are additional differences like broader distribution of marine deposits in Denmark than in Latvia, which may influence the natural chemical composition of groundwater.

The groundwater quality data obtained within this project was compared with the 1998-2003 data from the Danish groundwater monitoring network (GEUS 2004). As this project focused on shallow groundwater, only Danish monitoring wells screened in the depth until 50m were taken into account. As the different analytical programmes and methods were applied in Latvia and Denmark, only twelve well comparable minor elements are presented in the Table 7.

Table 7. *Background concentrations of selected minor elements in shallow groundwater of Latvia and Denmark, µg/l. LQ – lower quartile, Me – median value, UP – upper quartile*

Parameters	**Shallow groundwater Latvia (477 wells and springs)**			**Shallow groundwater Denmark (723 monitoring screens)**		
	LQ	**Me**	**UQ**	**LQ**	**Me**	**UQ**
F	180	250	370	100	170	270
Fe	100	600	2000	<50	600	2000
$P_{tot.}$	10	20	30	20	50	100
Al	3	10	30	<1	2	7
As	<0.5	0.5	1.0	0.2	0.7	2.0
B	<20	20	50	10	25	45
Ba	30	80	150	30	60	110
Br	20	30	40	70	100	130
Li	1	3	7	3	5	9
Mn	10	50	150	10	100	230
Sr	70	130	250	180	300	600
Zn	<2	5	30	1	3	9

Compared to shallow Danish groundwater, shallow Latvian groundwater is characterised by higher background concentrations of aluminium and fluoride and lower concentrations of bromide, lithium, manganese, phosphorus and strontium. A majority of the observed variations reflect the differences of the basic groundwater chemistry: the median values of the chloride, sulphate and permanganate index of the Danish data set (30, 45 and 3.1 mg/l respectively) are significantly higher than the corresponding values for the Latvian data set (10, 20 and 1.4 mg/l). Note than in both countries strontium and lithium have a positive correlation with sulphate; bromides with chloride, manganese and phosphorus with organic matter. Some of the differences between background concentrations of minor elements in

Latvia and Denmark may, however, be related to differences in the applied analytical techniques.

The anoxic and neutral conditions in the main Latvian aquifers are unfavourable for migration of the majority of heavy metals, which show concentrations much lower than MAC. Exceptions are manganese and arsenic, which are good migrants in reducing environment; the concentrations of these elements exceed MAC (50 and 10 µg/l, respectively) in 22% (Mn) and 1% (As) of the samples. Boron and selenium exceed the MAC (300 and 10 µg/l, respectively) only in saline groundwater, where the concentrations of sulphates or chlorides are significantly higher than MAC. In general, heavy metals in Latvian groundwater are a smaller problem for water supply than in Denmark, where manganese and arsenic exceed MAC in 63% (Mn) and 9% (As) of the monitoring screens. However, these compounds are to a great extent retained in natural sand filters at water supply plants (e.g. about 50% of the arsenic and most of the manganese).

Unlike Denmark, where nickel in some areas occur in concentrations above MAC (20 µg/l), caused by oxidation of sulphide minerals, high nickel concentrations is not observed in Latvia, where groundwater levels are lowered only in some deep intensively exploited aquifers rather than in shallow aquifers. In some areas of Denmark nickel is a problem due to a high Ni content in frequently occurring pyrite in Cretaceous chalk (where abstraction has been too heavy, lowering the groundwater table and thus causing oxidisation of the sediment).

3. Influence of agricultural land use on groundwater quality

3.1 Indicators of agricultural influence

Agricultural land use increases the concentrations of many elements and substances in groundwater (Tables 8 and 9). It was not surprising that total nitrogen and nitrate are the best indicators of agricultural influence on groundwater. The median concentration of nitrate nitrogen in shallow unconfined aquifers beneath areas of intensive agriculture is 12 - 15 times higher than the concentration beneath forests and undeveloped lands (Table 8).

The agricultural influence on groundwater does not confine itself to an increase of nitrates. There is a rather long list of elements and substances, which concentrations in shallow unconfined aquifers statistically increase in the sequence: forests – areas of extensive agriculture – areas of intensive agriculture. This list includes all major ions, Ba, Br, F, Li, Rb, Sr, U and Zn (Table 8). A majority of these elements have statistically significant positive loadings on Factor 5, which was earlier identified in chapter 2.2 as a factor of agricultural diffuse contamination.

Of the elements mentioned above (Table 8) uranium shows the strongest correlation with land use and nitrate (r = 0.49), and can be identified as the second priority indicator of agricultural influence after nitrate (Figure 21).

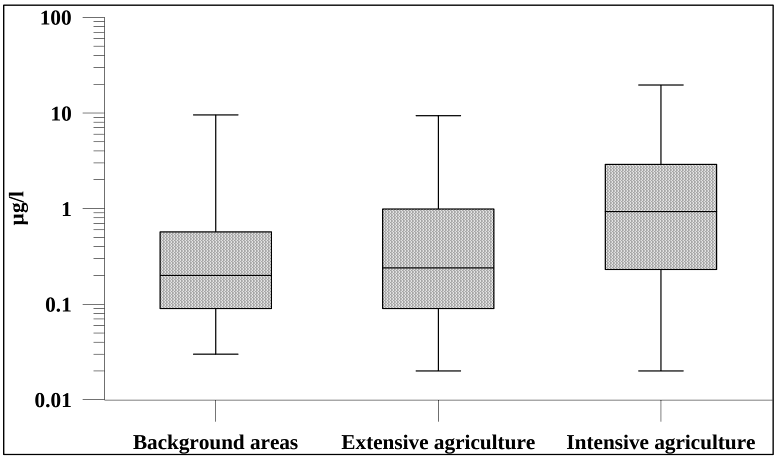

Figure 21. *Median, upper and lower quartile concentrations of uranium in shallow water table aquifers depending on land use (n = 228)*

Probably a complementary amount of uranium in groundwater is derived from the natural sediments as a result of the ‘disturbance of the water – sediments interactions: drainage and ploughing increasing the aeration of groundwater, while the uranium is more mobile under oxidising conditions (see chapter 2.2). Besides, some amount of uranium in groundwater originates from various mineral and organic fertilisers like super-phosphate, farmyard manure, which contain high amount of several heavy metals, including uranium (Eriksson 2001). A presence of external flux of uranium within the agricultural lands is confirmed by the fact that drainage water from agricultural lands has higher concentrations of both nitrogen and uranium if compared to groundwater (Table 10).

Table 8. *Median concentrations of selected elements and substances in shallow unconfined aquifers depending on land use and aquifer type*

Parameters		Water table aquifers				Shallow drift aquifers		
		Forestry areas (n=60)	**Areas of extensive agriculture (n=168)**	**Areas of intensive agriculture (n=44)**	**Urban areas (gardens) (n=16)**	**Forestry areas (n=10)**	**Areas of extensive agriculture (n=53)**	**Areas of intensive agriculture (n=51)**
HCO_3	mg/l	190	270	300	320	160	380	430
SO_4		12	23	34	35	22	18	33
Cl		6	9	12	19	7	10	20
Ca		52	81	83	89	43	90	110
Mg		11	18	25	26	12	27	33
Na		3	5	6	13	4	7	9
K		1	2	6	3	2	2	4
$N_{tot.}$		0.5	1.2	6.2	2.7	0.8	1.2	6.8
N/NH_4		0.1	0.2	0.1	0.9	0.2	0.2	0.2
N/NO_3		0.3	0.4	5.4	0.8	0.3	0.5	4.7
$P_{tot.}$		0.03	0.03	0.03	0.09	0.02	0.02	0.02
P/PO_4		0.02	0.02	0.03	0.05	0.01	0.01	0.02
F		0.18	0.24	0.25	0.30	0.22	0.27	0.33
Fe		0.7	1.0	0.2	2.4	0.8	0.7	0.5
Si		4.7	4.7	3.5	4.7	4.5	4.8	5.3
Al	µg/l	43	36	13	35	26	14	21
As		0.5	0.6	<0.5	0.9	0.7	<0.5	0.5
Ba		34	64	78	79	62	82	86
Br		19	27	35	44	24	31	34
Co		0.1	0.2	0.3	0.2	0.9	0.5	0.7
Li		0.7	1.3	1.4	1.6	1.5	3.5	7.6
Mn		74	210	200	220	100	150	130
Rb		0.8	1.0	1.5	1.1	1.0	1.1	1.4
Sr		63	91	140	150	73	130	170
U		0.2	0.3	1.3	<0.1	0.5	0.8	1.7
V		0.4	0.8	0.4	0.9	0.6	0.2	0.5
REE		1.0	1.1	0.5	1.5	0.3	0.3	0.4
Zn		17	27	36	57	14	25	66
$Pest_{tot.}$		<0.05	<0.05	0.11	0.06	<0.05	<0.05	0.07
COD_{Mn}	mg/l	1.4	3.7	1.9	4.5	1.6	1.7	1.5

Table 9. *Median concentrations of selected elements and substances in springs depending on land use*

Parameters		Forestry areas (n=80)	Agricultural areas (n=85)	Urbanised areas (n=45)
HCO_3	mg/l	260	340	350
SO_4		15	20	30
Cl		7	11	20
Ca		63	86	93
Mg		16	24	27
Na		4	6	10
K		1	2	5
$N_{tot.}$		0.9	3.0	8.3
N/NH_4		0.1	0.1	0.1
N/NO_3		0.7	2.4	7.3
$P_{tot.}$		0.01	0.02	0.03
P/PO_4		0.01	0.01	0.03
F		0.26	0.33	0.29
Fe		0.1	0.1	0.1
Si		4.2	4.5	4.3
Al	µg/l	9	11	19
As		<0.5	<0.5	<0.5
Ba		50	64	63
Br		20	27	36
Co		<0.1	<0.1	0.1
Li		1.6	2.1	1.6
Mn		4	5	4
Rb		0.7	0.7	1.1
Sr		64	91	120
U		0.5	0.8	1.0
V		0.4	0.3	0.7
REE		0.2	0.2	0.2
Zn		3	4	3
$Pest_{tot.}$		<0.05	<0.05	0.09
COD_{Mn}	mg/l	0.7	1.0	1.1

Note that organic matter and phosphorus in groundwater – the common ingredients of fertilisers – does not show correlation with land use. This conclusion is based on independent analyses of total phosphorus and orthophosphates, and permanganate index and ultra-violet absorption. Hereby our data confirm the opinion in many studies that the plants and soil micro-organisms effectively degrade the organic matter and assimilate the phosphorus, and that phosphate is sorbed strongly onto solid phases including iron and aluminium oxides in soils (Rodvang & Simpkins, 2001).

Table 10. *Median concentrations of selected elements and substances in shallow wells, springs and drainage outlets within agricultural areas*

Parameters		Drainage outlets (n=70)	Springs (n=85)	Shallow wells, unconfined aquifers (n=316)	Shallow wells, confined aquifers (n=52)
HCO_3	mg/l	420	340	320	330
SO_4		24	20	25	9
Cl		15	11	11	4
Ca		110	86	87	79
Mg		30	24	24	25
Na		6	6	6	9
K		2	2	2	4
$N_{tot.}$		5.9	3.0	1.6	0.4
N/NH_4		0.1	0.1	0.2	0.2
N/NO_3		5.2	2.4	0.7	<0.01
$P_{tot.}$		0.02	0.02	0.02	0.02
P/PO_4		0.01	0.01	0.02	0.01
F		0.25	0.33	0.25	0.25
Fe		0.3	0.1	0.7	2.0
Si		4.8	4.5	4.6	4.9
Al	µg/l	11	11	24	3
As		0.5	<0.5	0.5	0.8
Ba		77	64	77	160
Br		26	27	31	23
Co		0.2	<0.1	0.3	<0.1
Li		3.3	2.1	2.0	5.8
Mn		19	5	180	38
Rb		0.4	0.7	1.1	1.3
Sr		170	91	120	300
U		3.1	0.8	0.8	<0.1
V		0.4	0.3	0.5	<0.2
REE		0.3	0.2	0.7	<0.1
Zn		5	4	33	<2
$Pest_{tot.}$		0.08	<0.05	<0.05	<0.05
COD_{Mn}	mg/l	2.1	0.9	2.6	1.3

3.2 Lateral extent of agricultural contamination

The groundwater quality in shallow unconfined aquifers shows a very spotted pattern, because of discontinuity and heterogeneity both in the properties of the Quaternary deposits and in the agricultural loading. As a result the concentration of nitrates and other pollutants even in neighbouring wells within same aquifer may differ quite significantly (see chapter 4.3).

The density of recent reliable information usually is insufficient for preparation of a conditional water quality map for shallow unconfined aquifers. In fact only the data of this project can be used for this purpose, because geochemistry data obtained during the geological mapping of Latvia is too old, while all the recent monitoring observations are concentrated around specific point-pollution sources and does not characterise the regional quality and widespread diffuse contamination of groundwater.

Taking into account the all above mentioned, the groundwater quality on the prepared map of shallow aquifers is represented by point labels Figure 22). The prepared map confirms the strong variability of the groundwater contamination within the Latvian territory. While the seriously contaminated groundwater are concentrated in the southern part of central Latvia characterised by the highest agricultural load (Jelgava, Dobele, Bauska and Riga districts), many groundwater samples collected within the mentioned territories are without signs of contamination (Figure 23). That means that agricultural loading is reflected in groundwater quality only statistically (Figure 24).

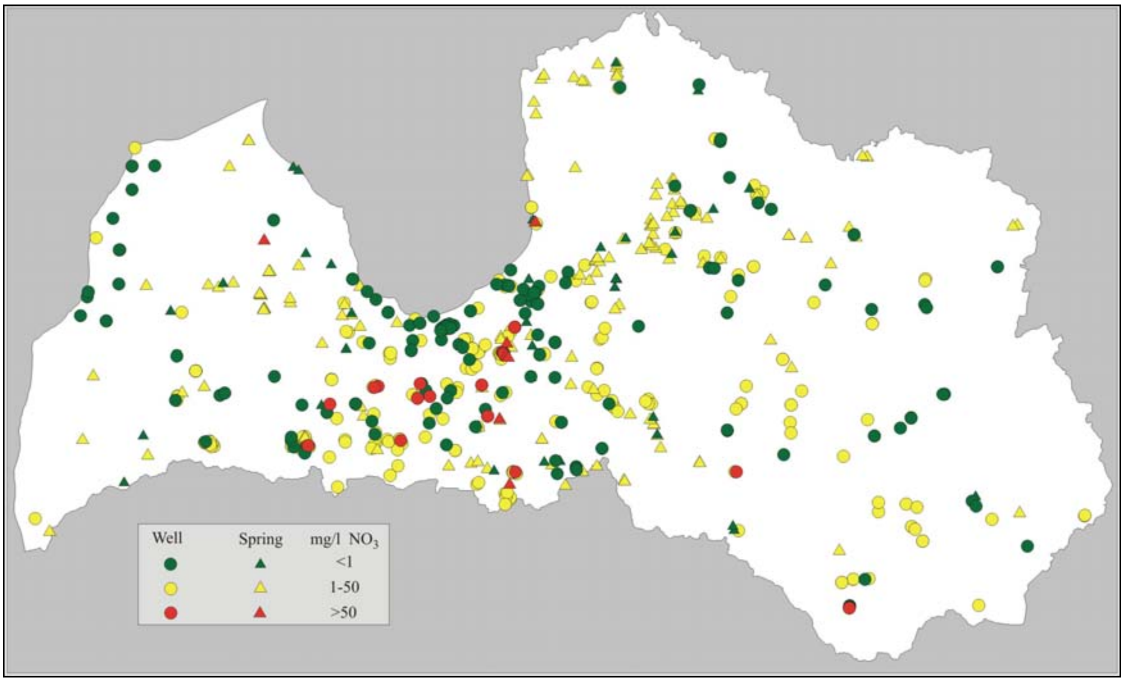

Figure 22. *Spatial distribution of nitrate in shallow wells and springs*

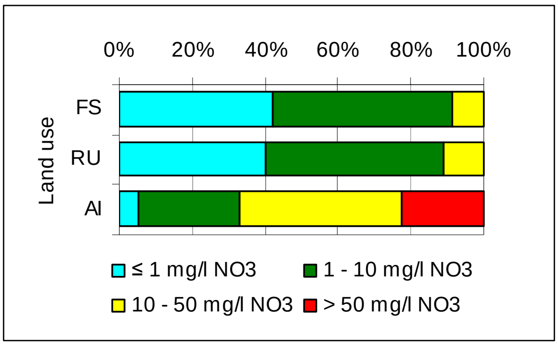

Figure 24. *Distribution of nitrate in shallow wells screened in unconfined aquifers grouped by land use. FS – forestry areas, n = 70; RU – rural areas with extensive agriculture (grasslands, sporadic small farms, undeveloped or abandoned lands), n = 221; AI – areas of intensive agriculture (permanently arable lands, intensive pasturing), n = 95*

Based on the distribution of nitrates within native territories and areas of extensive agriculture it may be concluded that extensive agriculture practically does not influence the groundwater quality (Figure 24). Even within territories of intensive agriculture the concentrations of nitrates above MAC (50 mg/l NO_3) occur only sporadically in 22 percents of the shallow wells. Taking into account that areas of intensive agriculture cover 10 – 15 % of the Latvian territory, it may be assumed that the shallow groundwater is seriously contaminated by agriculture within only 3% of the entire Latvian territory.

3.3 Groundwater vulnerability and the risk of contamination of main water supply aquifers

Understanding the complex concept of groundwater vulnerability requires the knowledge of many individual parameters including soil properties, thickness and lithology of the unsaturated zone, interaction of surface water and groundwater, groundwater pressure and geochemical conditions etc.

There are several soil maps of different scale in Latvia, including the 1: 200 000 digital map, prepared by the Latvian University of Agriculture. The sod-podzol soils, sod-podzol gleyey soils, typical podzols, sod-podzol carbonatic soils, boggy hydromorphic soils and artificial sub-hydromorphic soils are dominant in Latvia. Unfortunately, the existing Latvian soil maps can not be used for practical assessment of the groundwater vulnerability, because the common agro-technical typology of soils applied on the soil maps does not consider the contents of clay, organic matter and moisture in soil, which are the main factors influencing the capacity of the soil for contaminant degradation and sorption.

Assessments of groundwater vulnerability are often undertaken by calculating the travel time of contaminants from land surface to the groundwater table, on the basis of the thickness and lithology of the unsaturated zone. However, this criterion is not universal:

High groundwater table reduces the travel time of contaminants including pesticides and heavy metals to the groundwater, but on the other hand a high groundwater table promotes de-nitrification. Several studies have demonstrated significant denitrification in the soil surface horizon under anaerobic soil conditions. To meet these conditions, the groundwater table must remain close to the earth surface. Several studies indicate that nitrate concentrations in shallow groundwater can be positively correlated with the thickness of the unsaturated zone (Böhlke 2002, Starr 1993, Clement 2003 etc.). Moreover, the data collected in this project does not demonstrate a statistically significant dependence of concentrations of nitrates and other pollutants in the groundwater beneath the agricultural lands from the depth of the groundwater table (Figure 25). The apparently lower concentrations of nitrates within territories with groundwater tables higher than 1m are not obviously related to the denitrification - it may be caused by the lower agricultural loading within wetlands, because the permanently utilised arable lands usually are well-drained,

Traditional hydrogeology assumes that clayey sections of the unsaturated zone delay the downward travel of contaminants compared to sandy sections. However, the main part of Latvia is covered by clayey till rather than by homogenous clay. Several studies carried out in Denmark and other countries during the last decades have demonstrated the phenomena of preferential flow (e.g. Jørgensen et al, 2002). Preferential flow through root channels, macropores and fractures occurring in weathered till lead to direct rapid transmission of agricultural additives to the groundwater table (The Groundwater Group 2000, Rodvang 2001 etc.). Latvian data collected within this project does, however, not reveal differences in concentrations of pollutants in superficial sandy water table aquifers and drift aquifers of till beneath the agricultural areas (Table 8).

An assessment of vulnerability of deep water supply aquifers is more practicable compared to vulnerability assessment of shallow water table aquifers. The vulnerability of deep confined aquifers depends mainly on downward hydraulic gradient and lithology (permeability) of aquifer covering deposits, as well as on the geochemical conditions of aquifers.

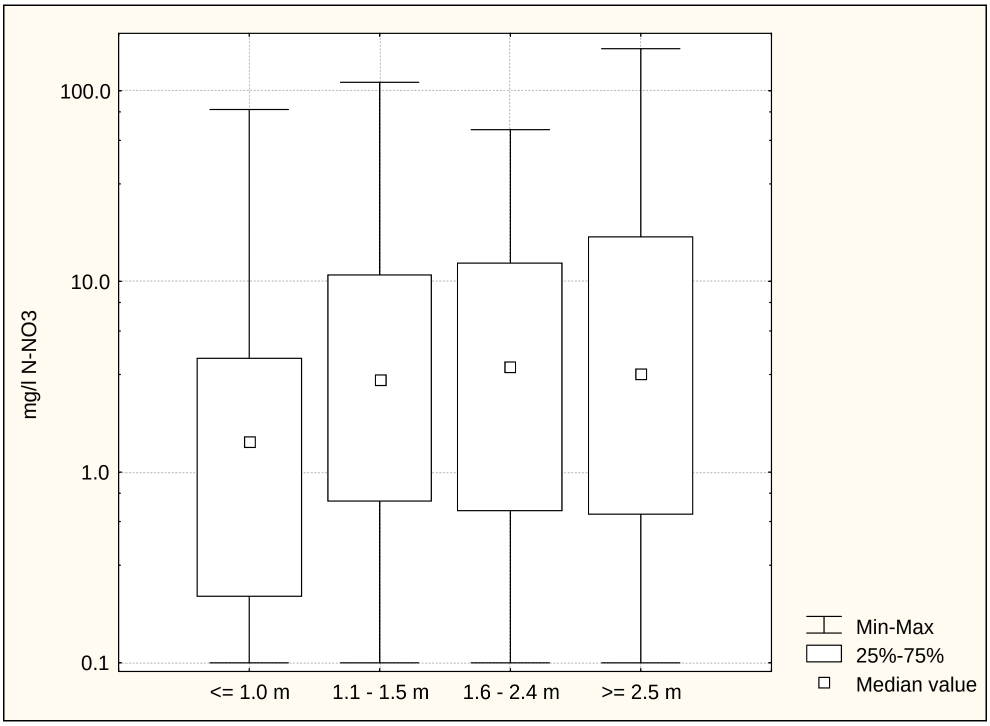

Figure 25. *Distribution of nitrates in shallow wells screened in unconfined aquifers compared to the depth of the groundwater table*

Eh potential strongly influence the behaviour of nitrogen compounds and heavy metals. Anoxic conditions are unfavourable for migration of the majority of contaminants (chapter 2.2). For nitrates, denitrification is the most important natural remediation reaction occurring in anoxic aquifers with almost no oxygen, confirmed by the data collected in this project (Figure 26). A direct sign of denitrification was found within this project at the location Stirniene, where sample no. 119 showed a high concentration of nitrous oxide (N_2O) that was fixed during analysis of CFCs (Annex 3).

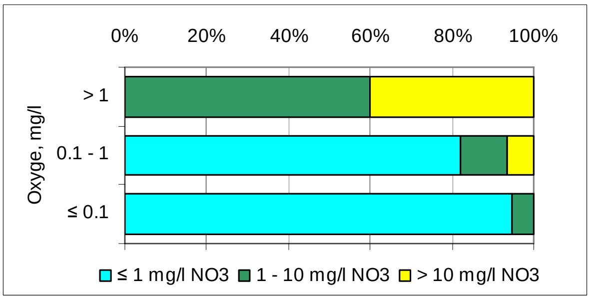

Figure 26. *Distribution of nitrates in groundwater depending on oxygen content (n = 105)*

One of the major factors influencing the groundwater Eh is the content of iron. High content of iron indicates anaerobic denitrification conditions (Figure 27).

Based on the data collected in frame of this project and within the Basic Groundwater Monitoring Programme it may be concluded that aerobic conditions in Latvian groundwater do not usually occur below depths of more than 5 – 20m. That means that deep water supply Latvian aquifers are well protected from nitrates.

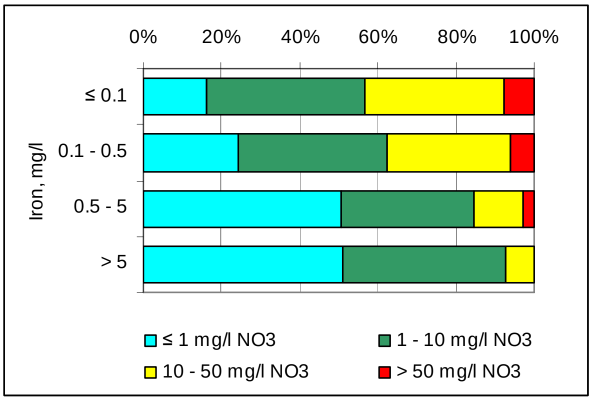

Figure 27. *Distribution of nitrates in groundwater depending on iron content (n = 675)*

Unfortunately, Eh or oxygen has only been directly measured at limited number of locations, including the measurements in this project. This very low density of measurements does not allow us to map the groundwater Eh even at a large scale. The indirect parameters of Red-Ox conditions like a high content of ferrous iron and the unusual low sulphates below 1 – 2 mg/l can not compensate the scarcity of direct Eh data, as the reliability of these data is limited[26]. Thus, in practice the Eh criterion can not be used for mapping of the groundwater vulnerability. Moreover, conversely to denitrification, anoxic conditions prevent the degradation of pesticides in aquifers, making the selection of vulnerability criterion difficult.

Based on the above mentioned it may be concluded that it is very difficult to select universal and in practice useful parameters for preparation of groundwater vulnerability maps. Therefore, the map of Contamination Risk of Important Water supply Aquifers (Figure 28) is based on a rather limited number of simple and understandable parameters. These are:

- Piezometric head – the territories of upward groundwater flow were delineated. The piezometric head in the (first from the surface) important aquifer within these territories is above ground surface, which prevents the downward flux of any pollutant;
- Denitrification potential – the territories with the high denitrification potential were delineated. These are territories covered by Holocene Litorina Sea and boggy deposits containing large quantities of organic matter and ferrous iron, and characterised by high groundwater table,
- Total thickness of low-permeable clayey deposits in the upper geological sections.

Mapping of the total thickness of Quaternary and Devonian clayey deposits in the upper part of the geological sections is a reasonable way of assessing the vulnerability of deep aquifers. As the superficial weathered part of the clayey layer often is well-permeable due to the vertical freeze-thaw fractures, root channels and worm hollows, the total thickness of the clayey deposits was calculated within the interval from 5 to 25m (Figure 29). The primary data of geological section and groundwater levels is taken from the database “Wells”.

Note that the resulting map depends heavily on the reliability and completeness of the database “Wells”, as well as on the total density of the borehole data. Danish experiences confirm that even the Danish density of borehole data - an average of approx. 2.5 bore-

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[26] Until recent years all analyses of sulphates in Latvian groundwater were conducted by the wet turbidimetric method, which does not allow quantification of sulphates content if the concentration is less than 10 mg/l. The majority of the electronically available data on iron, stored in the database “Wells”, is characterising by a poor quality due to typically inadequate storage of samples taken from the water supply wells.

holes per km^2, allows only a very general description of the geology and is even too sparse to establishing site-specific protection zones (Thomsen 2004). Therefore a spatially dense geophysical mapping of clay thickness and of distribution of sandy windows in the superficial layers overlying the aquifers has been started in Denmark. As the Latvian database “Wells” is yet not fully complete and the density of drilling points in Latvia is an average 3 times lower than in Denmark, the delineation of the clayey areas and the areas of upward groundwater flow is very approximate. Therefore the resultant map prepared in frame of this project shows the principles of vulnerability mapping, rather than presenting the definitive groundwater vulnerability.

In fact the data collected within this project demonstrate that, with increasing aquifer depth and degree of confinement, the concentrations of nitrates generally decrease rapidly (Table 11). High content of ferrous iron and reducing conditions within natural confinement of confined and semi-confined pre-Quaternary aquifers contribute to the protection of the aquifers from nitrates and heavy metals. No dangerous concentrations of agricultural pollutants were found in these aquifers, except for in few springs, which will be discussed separately in the next chapter, and for ammonia, which is mainly of natural origin[27]. Moreover, the groundwater contamination may just be emerging in main deep aquifers, because groundwater residence time in these are generally much longer than the duration of intensive agriculture (see chapter 2.3).

Table 11. *Maximum concentrations of main agriculture related elements and substances in groundwater outside the point-pollution plumes*

Parameters		**MAC for Drinking Water[28]**	**Max in ground-water**	**No. of analyses exceeding MAC, %**		
				Springs	**Wells in shallow unconfined aquifers**	**Wells in shallow confined aquifers**
N/NH$_4$	mg/l	0.39	5	9	26	27
N/NO$_2$		0.15	0.1	0	0	0
N/NO$_3$		11	90	5	6	0
Pesticides by GC / LC – MS	µg/l	0.1	1.2	(30) of 33 samples	(33) of 55 samples	(28) of 7 samples
U		20	67	0	1	0

The percentage of samples with pesticides above MAC is given in brackets because of the limited number of samples. The pesticide problem for Latvian groundwater will be discussed separately in chapter 3.5.

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[27] The natural concentrations of ammonium in groundwater very often exceed the MAC. However, a part of the ammonium in deep aquifers may originate from reduced agricultural nitrates, remained after denitrification. Nitrites are thermodynamically unstable in the all types of groundwater and can not reach the MAC.

[28] According the Drinking Water Directive, except for uranium taken from US EPA standards.

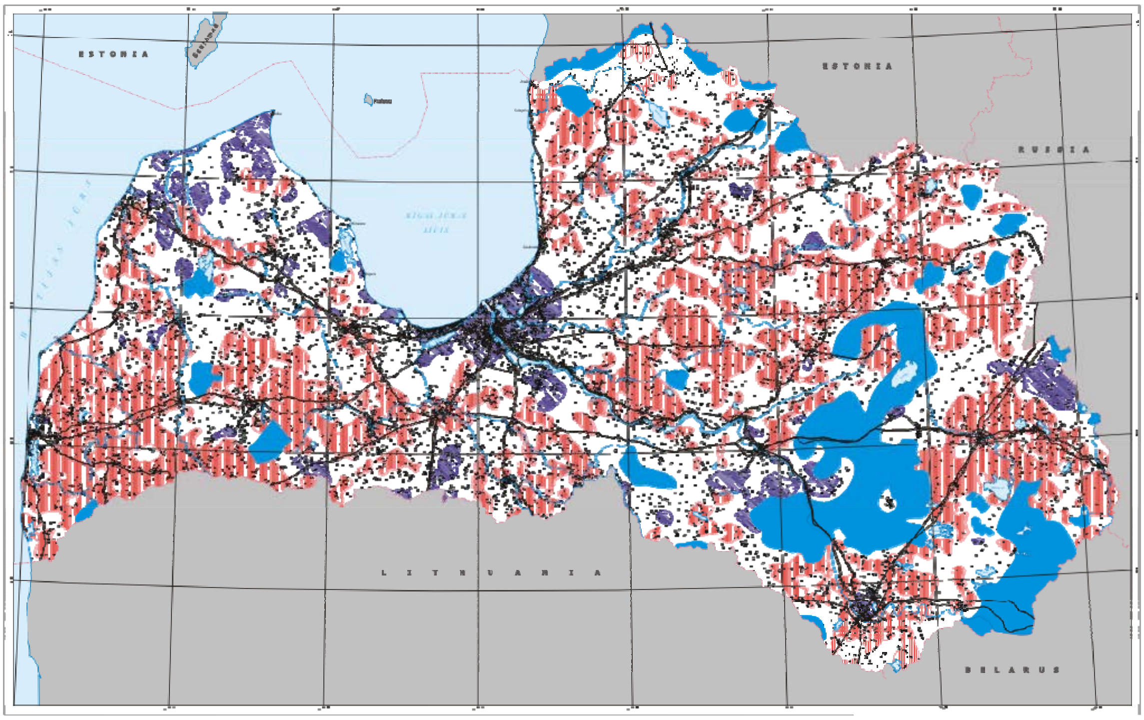

Figure 29. *Thickness of low-permeable deposits in upper pat of geological section and the density of the borehole data. Total thickness of clayey deposits within 5 – 25m below ground surface: red-shaded areas – more than 15 m, white areas – 5 – 15 m, blue-shaded areas – less than 5 m, dark blue areas – no borehole data. Point labels – boreholes already loaded in the database.*

3.4 Preferential flow

The phenomenon of preferential flow through the superficial clayey deposits of the unsaturated zone has shortly been discussed in previous chapters. However, the data collected in this project demonstrates the presence of other macro-scale types of preferential flow within the upper sections of aquifers.

Our investigations discovered quite surprising features regarding nitrate in shallow aquifers. Latvian springs are generally characterised by increased concentrations of nitrate and total nitrogen compared to the shallow wells drilled to the same aquifers (Figure 30).

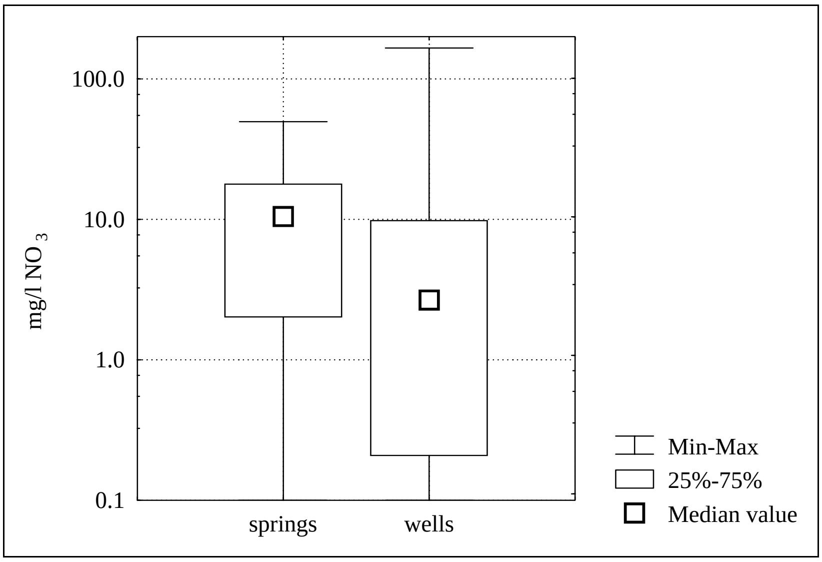

Figure 30. *Distribution of nitrates in 368 shallow wells and 85 springs within Latvian agricultural areas.*

In addition to the elevated concentrations of nitrate, the springs are characterising by a low content of As, Ba, Fe, Mn and Sr (Table 10). It is interesting that both artificial and natural (springs) drains have increased concentrations of main indicators of agricultural influence - nitrates and uranium, if compared with pre-Quaternary wells.

The difference of water quality in springs and wells confirms the presence of two different groundwater flows within same aquifers. The springs capture the youngest and most mobile part of the groundwater flowing in fractures and well-permeable zones, while the wells characterise the relatively “old” and “stagnant” or the matrix part of the groundwater. Thus younger water in fractures may be considerably different chemically from older water trapped in the matrix (Edmunds, 2003).

Note that increased concentrations of nitrate often occur even in springs located far of areas with obvious nutrients loading and in springs capturing pre-Quaternary confined aquifers in the bottom parts of 20 – 35m deep river valleys, which confirms the wide-spread occurrence of preferential flow in the upper aquifers.

After discovery of this phenomenon in 2004, several high-yielding springs were included in the regional groundwater monitoring network for better control of diffuse pollution.

3.5 Pesticides in groundwater

A selection of a spectrum of relevante pesticides have been analysed in this project. This list was collated based on an analysis of application of pesticides in Latvia, their stability and mobility in soils and groundwater, as well as on existing data of pesticides in Latvian environment (chapter 1.2, Annex 1). The data collected within this project basically confirm the previous theoretical assumption that atrazines, chlorophenoxy pesticides and TCA (trichloroacetic acid) are the most expectable pesticides in Latvian groundwater (Table 12).

The priority pesticides identified (in fact) in this project are:

- TCA;
- chlorophenoxy acids: MCPA, MCPB, 2,4-D;
- triazines: simazine, propazine, prometryn, metribuzin;
- bentazon.

So, only for one pesticide this theoretical prediction was not justified: bentazon. Bentazon was found in 6 groundwater samples, while its occurrence in Latvian groundwater was previously assumed to be low. Perhaps this is caused by missing data of application on this herbicide.

The herbicides TCA and MCPA were found most often and this is clarified by their high application rate and high mobility. As TCA is a former by-product of Latvian chemical industry, this was very cheap and the most widely utilised herbicide during the Soviet era. Due to the low-toxicity, this herbicide was applied in very large quantities. Note that TCA has not been utilised during the last decade, however this herbicide can remain many years in groundwater after application. The second champion - herbicide MCPA (4-chloro-2-methylphenoxy acetic acid) has been widely applied both in Soviet era and presently and is characterising by a high leaching potential.

As expected, organochlorine pesticides, organophosphorus pesticides, pyrethroids and amides were not found in groundwater due to the high adsorption capacity (organochlorine and organophosphorus pesticides, pyrethroids, and amides) and high degradation rate (organophosphorus pesticides, pyrethroids, amides). These pesticide groups have a large actuality for monitoring of the quality of soil and vegetables, rather than of groundwater.

Pesticides were found both in unconfined and shallow confined aquifers unlike nitrates found in unconfined aquifers only (Table 11). This indicates high pesticides stability in groundwater. Danish data show a substantial vertical variation in the degradation of pesticides when comparing topsoil and aquifers with the lowermost degradation potential in the aquifers, especially in anoxic aquifers (The Groundwater Group, 2000).

The distribution of pesticides in groundwater shows a very complicated pattern. There was found no correlation between pesticides, nitrate and other ingredients of agricultural diffuse contamination. For instance, high nitrate concentrations above MAC (11 mg $N\text{-}NO_3$/l) were observed in only 16% of the pesticide-containing samples, while in 47% of them nitrate were below background value (2 mg $N\text{-}NO_3$/l).

Pesticides were identified in 68 of 111 groundwater samples analysed by GC / LC - MS (61%); in 34 of them (31%) the concentration of pesticides exceeded the MAC (0.1 µg/l). In should be noted, that only the potentially most contaminated samples and samples with positive screening results by immunoassay tests (see chapter 1.4) were analysed for pesticides.

Table 12. *Results of pesticide analyses in groundwater by GC / LC – MS*

Analysed pesticides		Total no. of samples	No. of samples with identified pesticides	
			0.02 - 0.1 µg/l	0.1 - 1.0 µg/l
Triazines	Atrazine	111	5	
	Metribuzin	111	1	1
	Prometryn	111	2	3
	Propazine	111	3	1
	Simazine	111	3	2
Chloro-phenoxy acids	2,4 - D	111		5
	MCPA	111	10	22
	MCPB	111		2
Organochlorine pesticides	P,p-DDT, DDE, DDD	111		
	Lindane, a-HCH, b-HCH	111		
	Aldrin	111	1	
	Dieldrin, a,g-chlordane	111		
	Endrin, endrin aldehyde, endrin ketone	111		
	a,b-endosulfan, endosulfan-sulphate	111		
	Heptachlor, heptachlor-epoxide	111		
	Methoxychlor, vinklozolin, clopyralid	111		
Organo-phosphorus pesticides	Azinphos-ethyl, azinophos-methyl	111		
	Chlorpyriphos, diazinon, dimethoate	111		
	Malathion	111		
	Parathion-methyl	111		
Pyrethroids	Cyfluthrin	111		
	Cypermethrin, deltamethrin	111		
	Fenvalerate	111		
	Permethrin	111		
Amides	Dichlofluanid	111		
	Procymidone	111		
	Tolilfluanid	111		
Miscellaneous pesticides	Bentazon	111	2	4
	Metalaxyl	111		
	Pendimethalin	111		
	Propiconazole	111		
	TCA	111	25	3

It should be kept in mind, however, that the maximum flux of pesticides originating from the 1980s – the period of maximum application rate in Latvia – has still not reached the main Latvian aquifers with groundwater more than 50 years old. Note that the spectrum of pesticides identified in the groundwater beneath the presently utilised agricultural lands outside of the local contaminant plumes does not differ from the spectrum of pesticides found in the groundwater around the former agrochemical storehouses. This fact indirectly confirms that groundwater has a much delayed respond to superficial contamination, and that pesticides applied many years ago must have higher priority for groundwater monitoring compared to the recently applied pesticides.

3.6 Comparison of groundwater contamination in Latvia and Denmark

Latvia and Denmark are significantly different when it comes to agricultural load. The cultivated land covers more than 60% of Denmark and only 13% of Latvia. Moreover, the specific application of fertilisers within cultivated lands in Latvia is about half of the Danish figure.

As the investigations in this project focused on the uppermost groundwater, additional data of deeper aquifers were used for more correct comparison of groundwater contamination in Latvia and Denmark: data from the Latvian groundwater monitoring network and data of recently drilled water supply wells for the period 2000-2005.

The distribution of nitrates in Danish and Latvian groundwater differs considerably as expected (Figure 31). In shallow groundwater concentration of nitrates exceeds the maximum admissible concentration (MAC) for Drinking Water (50 mg/l NO_3) in 15% of the Danish compared to 3.5% of the Latvian monitoring screens. Furthermore, the decrease of concentration of nitrates with depth is much higher in the Latvian groundwater than in the Danish.

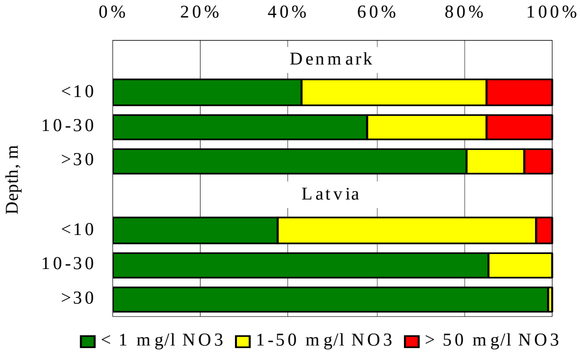

Figure 31. *Distribution of nitrates in Danish and Latvian wells compared to screen depth; Danish data from 719 monitoring screens for the period 1998-2003; Latvian data from 717 monitoring, investigative and water supply wells for the period 2000-2005*

The observed difference is caused not only by a lower agricultural load in Latvia, but also by a higher degree of confinement and denitrification potential of Latvian aquifers. These properties of Latvian aquifers are reflected by a longer residence time of groundwater and a lower content of oxygen, compared to Danish groundwater (Figure 32).

A statistical comparison of groundwater residence times is impossible due to the very limited number of age determinations of Latvian groundwater. However, it seems that Latvian groundwater is twice as old as Danish groundwater from the same depth. The observed difference may reflect both the lower abstraction rate of Latvian groundwater and a higher extent of preferential flow in fractured Latvian aquifers (see chapter 2.3).

Unlike Denmark the investigation of pesticides in Latvian groundwater has just begun and the extent of this problem is therefore not fully clear. In 30% of the samples concentrations of pesticides exceed MAC (0.1 µg/l). This figure is identical to the frequency observed in shallow Danish monitoring screens beneath cultivated lands (Stockmarr 2005).

Occurrence of different groups of pesticides in Latvia ad Denmark differs significantly. In Denmark triazines are the most common pesticide group, whereas in Latvia chlorophenoxy acids dominate (MCPA - 4-chloro-2-methylphenoyacetate), followed by trichloroacetic acid (TCA) and triazines.

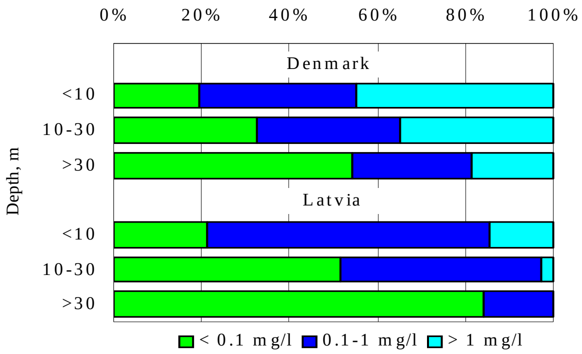

Figure 32. *Distribution of dissolved oxygen in Danish and Latvian wells compared to screen depth. Danish data of 706 monitoring screens for the period 1998-2003; Latvian data of 160 monitoring and investigative screens for the period 2003-2005*

As the investigations in this project focused on the potentially most contaminated Latvian groundwater, the occurrence of pesticides in 30% of the samples is not representative for the entire Latvian groundwater. Taking into account the smaller acreage of treated areas and a higher confinement degree of main aquifers the risk of contamination of water supply wells in Latvia by pesticides is significantly lower than in Denmark.

4. Groundwater contamination at selected locations

Some of the investigated locations are described in this chapter to characterise the most interesting cases of the groundwater contamination related to agriculture.

4.1 Agrochemical run-off monitoring station Jaunberze

The agricultural run-off monitoring station Jaunberze is located in central Latvia in the northeastern corner of the Dobele district. The catchment area of a small river with the total area 77 ha has been selected for the monitoring programme (Figure 33). The surface and drainage water at Jaunberze have been monitored since 1994, while the groundwater contamination was never investigated until 2005. In frame of this project 5 groundwater samples were taken, and four monitoring wells were established to improve the existing monitoring programme (chapter 1.7).

The catchment area is characterised by a relatively intensive crop production compared to the present average conditions in Latvia. Winter wheat and sugar beets are dominating crops, while the share of arable land reaches 80-90% of the catchment area. The average amounts of fertilisers applied vary from 15 to 80 kg N/ha.

Until the depth 12 – 16m the Quaternary glaciogenic deposits consist of sandy and loamy till with thin interbeds of sand (Figure 34). The glaciogenic deposits are underlain by clayey dolomite of the Upper Devonian Amula formation.

The depth to the local, shallow groundwater table is 1 – 2m which corresponds very well to the piezometric head in the deeper lying Amula aquifer: a little lower on the local hills in the western part of the catchment and a little higher in lowlands in the eastern part of the catchment. The groundwater flow both in the Quaternary and in the Amula deposits is toward east.

The observed interaction of the groundwater levels in Quaternary and pre-Quaternary aquifers show that the potential groundwater flow is downward in the western part of the catchment area and upward in the eastern part of the catchment area. The increased sulphate concentrations (200 mg/l) in the shallow groundwater in the eastern part of the catchment area confirm that saline groundwater flows upward from the Amula aquifer, containing 1300 mg/l sulphate.

The main feature at Jaunberze is the extremely high concentration of nitrate found in the shallow groundwater. The highest concentration of nitrate in sample no. 412 is 90 mg/l as nitrate nitrogen. This concentration is 8 times higher than the MAC and exceeds all nitrate concentrations found in Latvia outside of the local contaminant plumes within both this project and other investigations.

Additional to nitrate the contaminated groundwater contains anomaly high potassium concentrations (19 mg/l), manganese (0.39 mg/l) and zinc (2 mg/l), as well as chlorophenoxy pesticides (2.4-D up to 0.2 µg/l and MCPA up to 0.12 µg). Toward east or downstream of the groundwater flow the concentration of nitrate in shallow groundwater decreases to 20 mg N/l followed by a simultaneously decrease in concentrations of other pollutants (Figure 34).

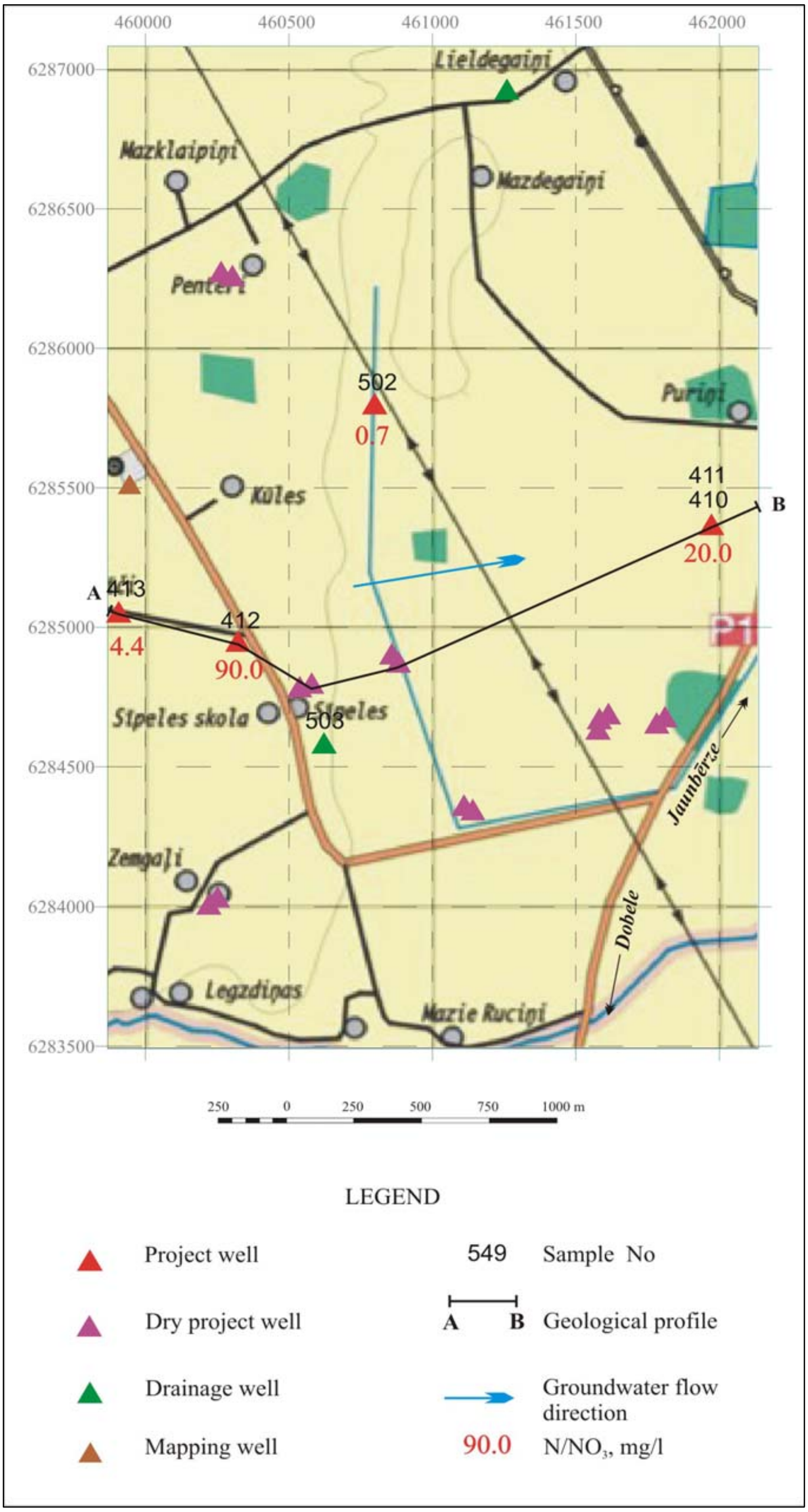

Figure 33. *Location of sampling points at Jaunberze*

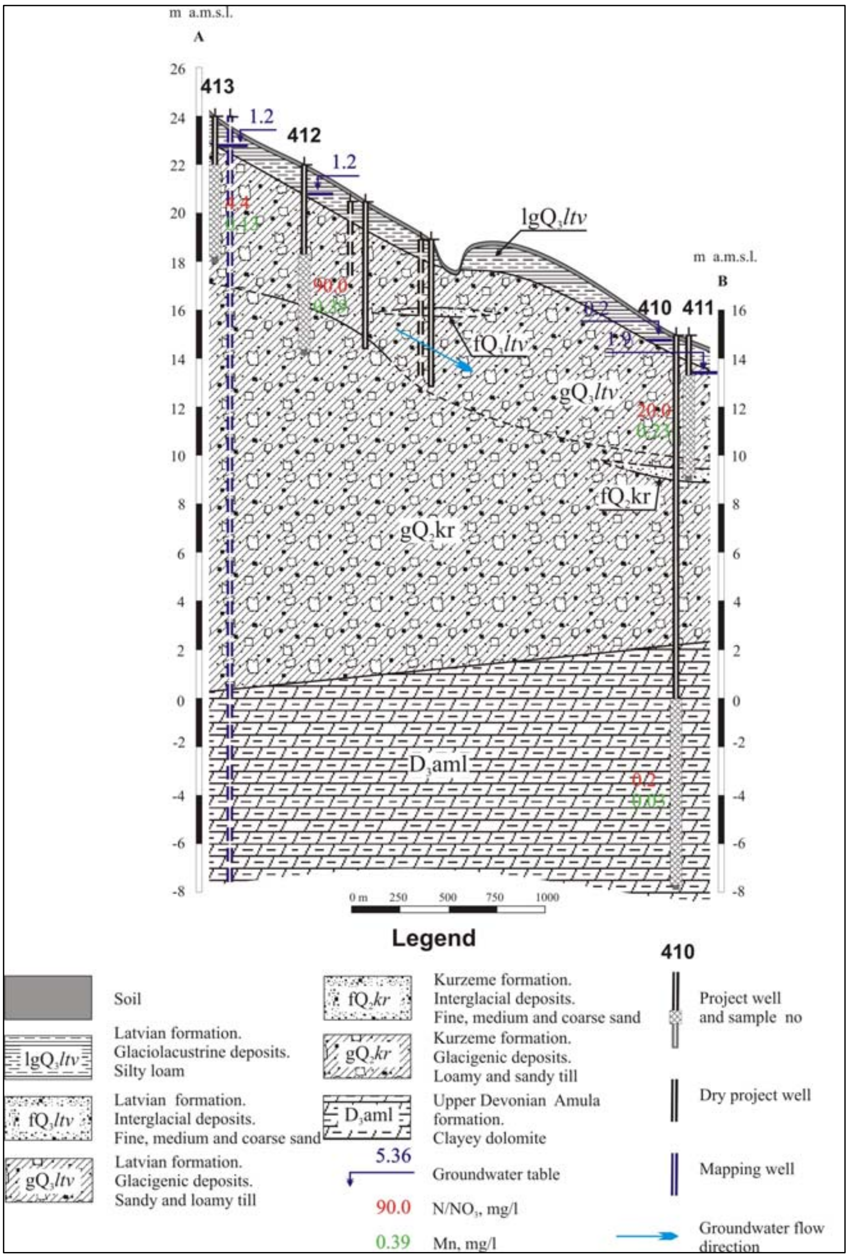

Figure 34. *Geological profile at Jaunberze*

In spite of the hydraulic connection between the Quaternary and pre-Quaternary aquifers, the concentration of nitrate and total nitrogen in moderately deep monitoring well screened in the Amula aquifer in the depth 15 – 22m (sample no. 410) are low and meet the natural background values. Note that this monitoring well is established east of the catchment area in the direction of the potential run-off of contaminated groundwater. That confirms the occurrence of denitrification in the Amula aquifer characterised by anoxic conditions (dissolved oxygen 0.17 mg/l, the concentration of ammonium exceeds the concentration of nitrate). When it comes to pesticides, the natural processes in groundwater in anoxic aquifers are not as effective as on nitrates, and the Amula aquifer contains pesticides (MCPA 0.12 µg/l).

4.2 Former agrochemical storehouse Vilani

The former agrochemical storehouse Vilani is located in eastern Latvia in the Rezekne district. This was one of the biggest pesticide storehouses during the Soviet era in Latvia. Around 200 tons of 100 different types of no longer utilised pesticides were collected from all over Latvia during 1969-1975 and stored until the end of 1980s at Vilani. In 1987-1988 two explosions and fires took place resulting in heavy contamination of the surroundings soils, mainly due to dispersion of contaminants during the rescue process. The concentration of organochlorine pesticides in soils samples reached 106 mg/kg (sum of DDT, DDE and DDD).

After the above mentioned incidents the groundwater quality was investigated in 1991, and this indicated a strong contamination of the groundwater by nitrogen compounds and other pollutants. However, due to limited capabilities of the Latvian laboratories, no pesticides were found in the groundwater. To clarify this question 9 groundwater samples (No 110 – 116, 301 – 302) were taken in frame of this project in the vicinity of the former agrochemical storehouse (Figure 35). The groundwater samples were collected from wells screened in depth until 8m mainly within the bottom part of the water table aquifer consisting of fine or medium sand underlain by till or clay (Figure 36).

The unconfined water table aquifer is contaminated by chloride (up to 670 mg/l), sodium (up to 670 mg/l), potassium (up to 22 mg/l), nitrogen (up to 22 mg/l) and phosphorus (up to 1.7 mg/l) and by pesticides. Various trace elements reaching extremely high concentrations were also found in shallow groundwater: REE up to 250 µg/l (500 times higher than the background value), aluminium up to 5,900 µg/l (200 times higher as background value), also zinc up to 480 µg/l and vanadium up to 40 µg/l. Apparently, this unique anomaly originates from mineral fertilisers rich in heavy metals. As the contaminated groundwater is strongly coloured and COD and alkalinity significantly exceeds background values, unidentified organic compounds must be present in the contaminant plume.

The ratios of the different nitrogen forms indicate that predominantly reducing conditions caused by slow water flow prevails in the unconfined water table aquifer at Vilani. Insignificant changes of the concentrations of pollutants have been observed since 1991 in the wells nearest to the storehouse. As the degree of groundwater contamination in the core of the contaminant plume has not decreased during more than 10 years, the presence of pesticides in contaminated groundwater was also highly expectable.

Nevertheless, organochlorine and organophosphorus pesticides, pyrethroids and amides were not found in the groundwater. The absence of organochlorine pesticides in groundwater in spite of very high concentrations of these substances in the soil is especially noteworthy. That confirms their extremely low movement rate due to high sorption capacity.

The spectrum of pesticides occurring in the groundwater contaminant plume basically is similar to the spectrum found in shallow groundwater beneath the recently cultivated lands (chapter 3.5). These are triazines, chlorophenoxy acids, bentazone and TCA. The concentration of MCPB and bentazone exceed the MAC: up to 0.35 µg/l and up to 0.25 µg/l respectively.

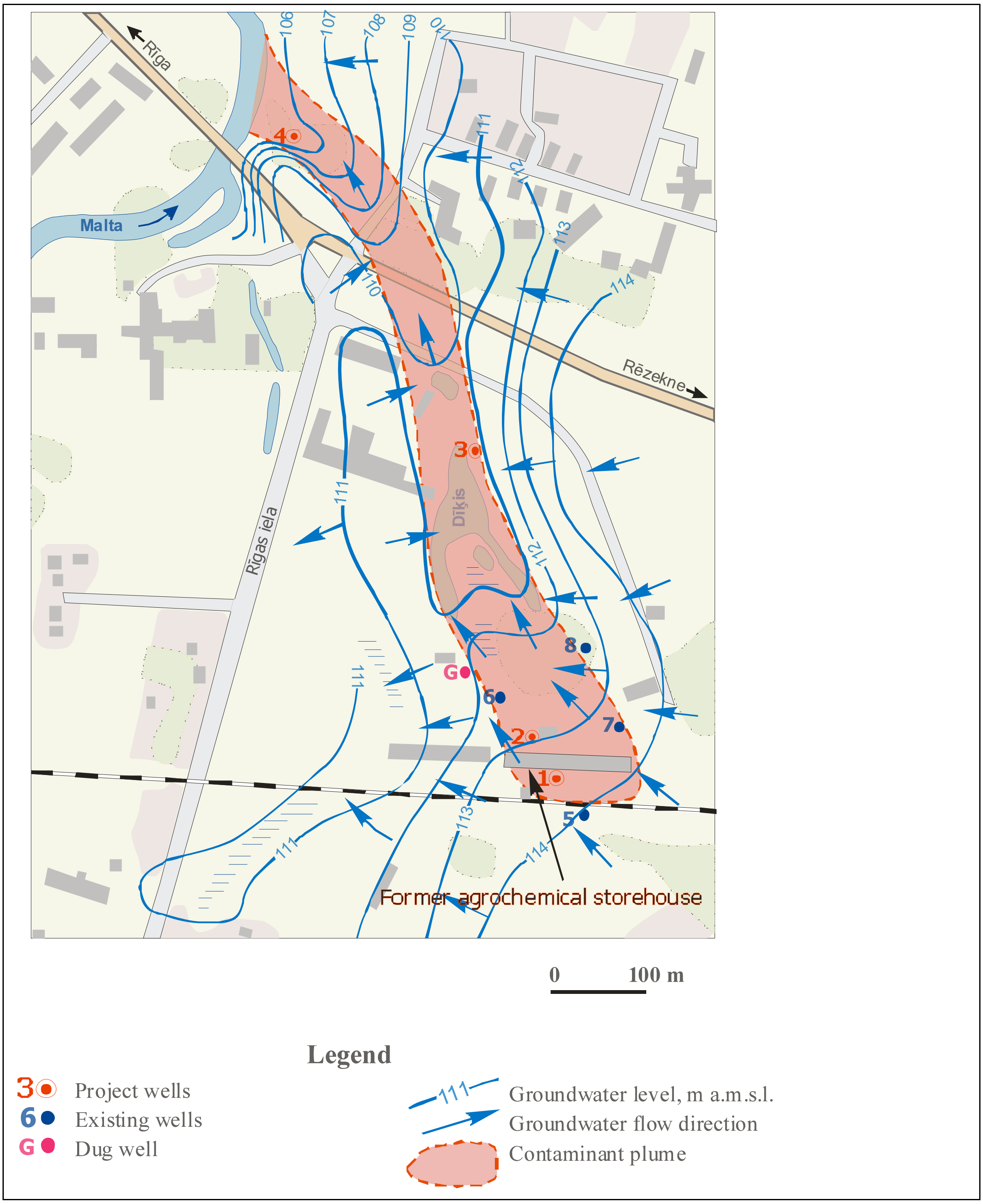

Figure 35. *Location of sampling points at Vilani*

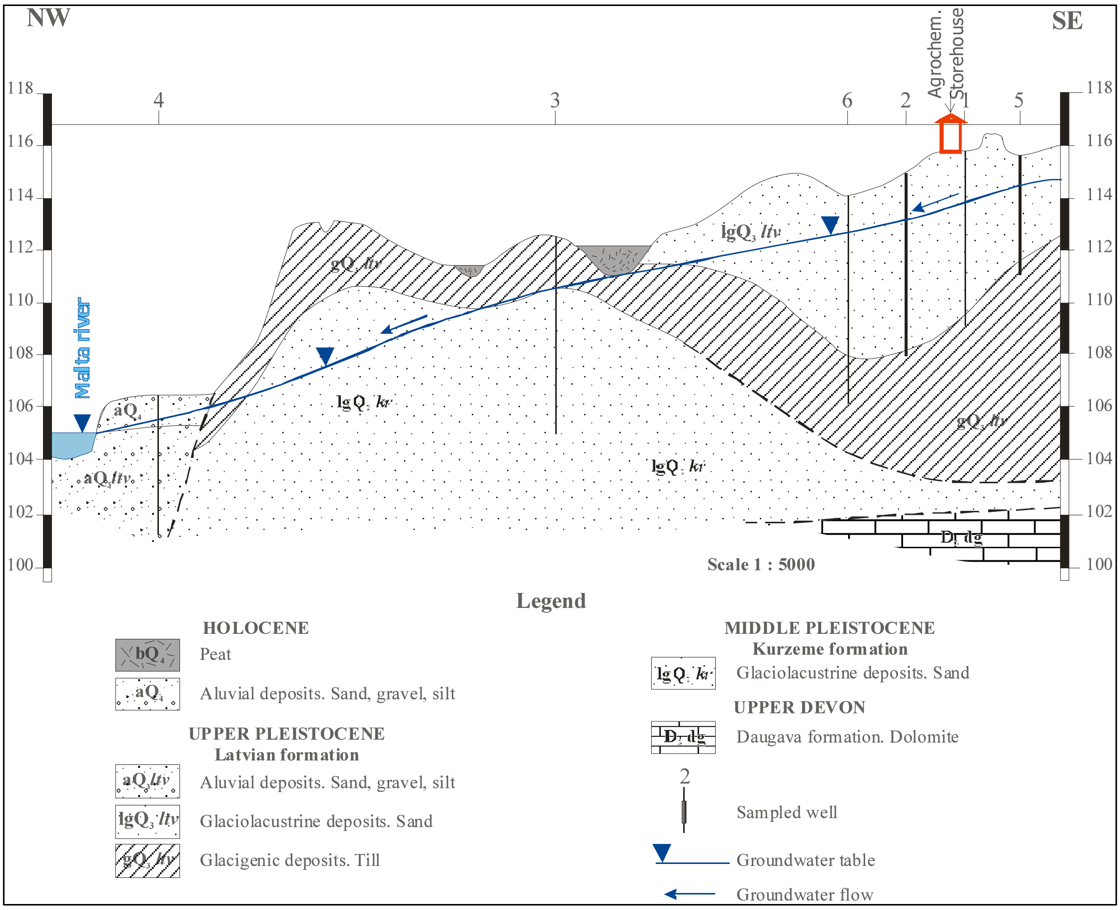

Figure 36. *Geological profile at Vilani*

The groundwater contaminant plume is stretching out towards NW reaching the Malta River located 800m from the former storehouse (Figure 35). The concentrations of contaminants step-by-step decreases downstream the groundwater flow. The contaminated groundwater on the river bank is diluted 5 times if chloride are measured, compared to the core of the contaminant plume. The concentrations of other reactive contaminants are reduced much higher due to the processes of sorption and degradation, i.e.: total nitrogen – 10 times, total phosphorus – 70 times, COD-Mn – 50 times, heavy metals – hundreds and thousands times. The concentrations of pesticides in the well located at the river bank are close to detection limit.

4.3 Kekava – location with heavy load of bird manure

The investigated site Kekava is located in the central part of Latvia 10 km SE of Riga (Figure 37). The earlier cultivated lands of this site were for a long period heavily fertilised by chicken manure provided by the largest chicken farm in Latvia. This input continued for several decades until the 1990s. As a result the unconfined water table aquifer has been seriously contaminated within an area of at least 100 ha.

Recently the area has been prospected for private dwellings. However, the groundwater contamination has not significantly decreased since the end of 1970s, when the first investigation of the groundwater contamination was carried out.

Groundwater at this location is highly vulnerable as the upper part of the geological section until the depths of 5 to 10m consists of high permeable sand-gravel deposits (Figure 38). The geochemical conditions of the aquifer are aerobic and generally unfavourable for denitrification (oxygen up to 2.2 mg/l, typically low iron).

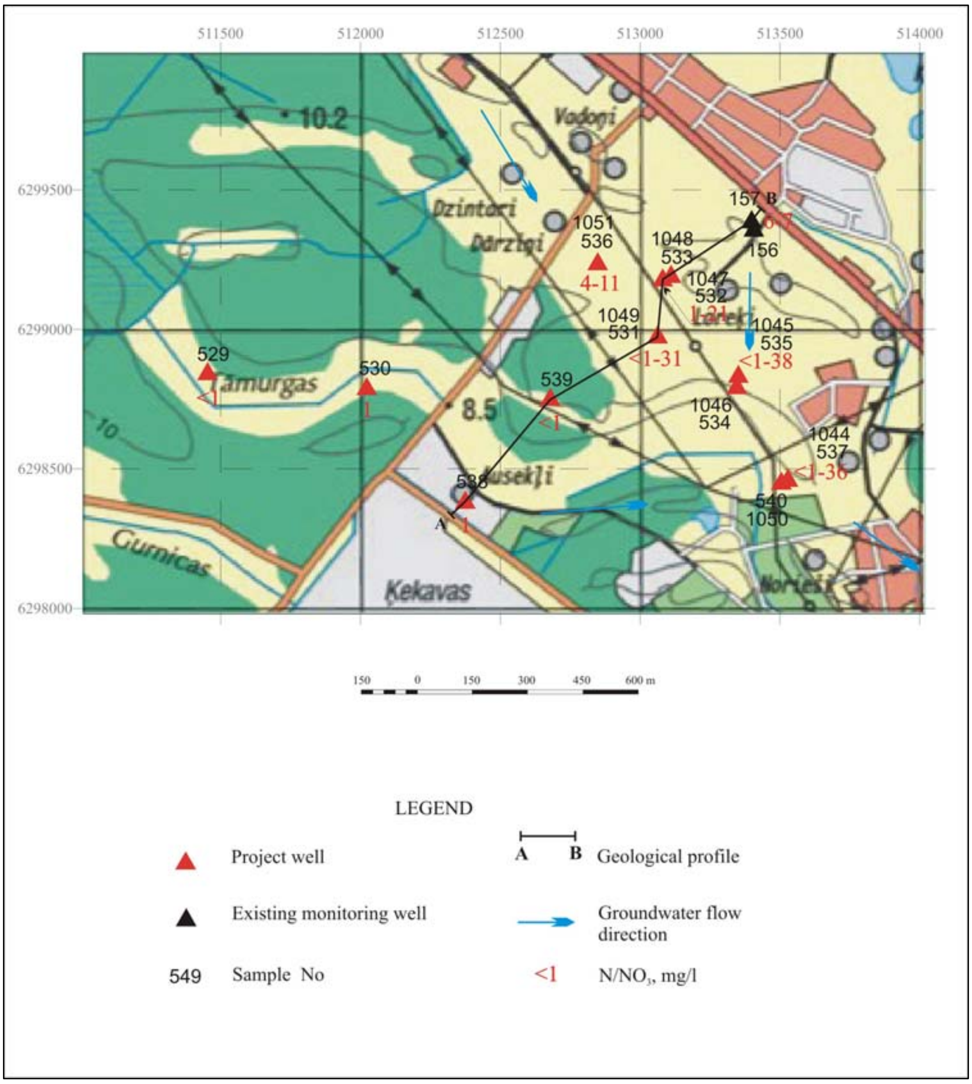

Figure 37. *Location of sampling points at Kekava*

One of the highest nitrate concentration in Latvia - up to 37 mg N-N0$_3$/l was found in the unconfined water table aquifer at Kekava, while the average concentration of nitrate was 12 mg/l. Also the concentration of potassium was significantly increased (20 – 53 mg/l). The concentrations of phosphorus, heavy metals and pesticides were low, except for manganese reaching 1.6 mg/l.

The concentrations of contaminants were very variable in the time, as well laterally as in a section of the contaminant plume (Table 13). The concentrations of nitrate within a rather small area and a rather thin unconfined water table aquifer varied from 0.6 to 37 mg N/l and decreased 3 – 7 times with increasing screen depth. Moreover, the concentration of nitrate in spring 2005 was 2 - 4 times lower than in autumn 2003.

Note that in spring 2005 the groundwater table was 0.3 – 0.9m higher compared to autumn 2003, and that a decrease of nitrate was accompanied by an increase of iron (Table 13). It may be assumed that the rising of the groundwater table conversed the strongly aerobic conditions to less aerobic, which resulted both in an increase of iron and in a short-time denitrification situation. So, incidental denitrification may still occur in the water table aquifer from time to time in spite of generally unfavourable geochemical conditions. Simultaneously with the denitrification some nitrate-reduction took place, which resulted in an increase of ammonium in the groundwater in May 2005 (Table 13). Nevertheless, the role of this process is secondary compared to the denitrification.

Table 13. *Variation of selected groundwater quality parameters in two clusters of the temporary wells drilled in the water table aquifer at Kekava*

Well cluster	**1**				**2 (300m SE of well cluster 1)**			
Date	**28-Sep-03**		**17-May-05**		**28-Sep-03**		**16-May-05**	
Water table, m.b.s.	3.1		2.8		3.5		2.6	
Depth of screen, m	3.5-5.0	6.9-8.4	3.5-5.0	6.9-8.4	3.4-4.9	6.9-8.4	3.4-4.9	6.9-8.4
Sample No	533	532	1048	1047	535	534	1045	1046
$N_{tot.}$, mg/l	22	3.2	12	3.4	38	11	10	1.0
N-NH$_4$, mg/l	0.04	0.1	0.1	1.5	0.04	0.08	0.1	0.3
N-NO$_3$, mg/l	21	3.0	10	1.2	37	10	9	0.6
Fe, mg/l	<0.1	0.4	0.2	7.1	<0.1	<0.1	0.2	0.9

The glaciolacustrine clay layer underlies the unconfined water table aquifer and confines the Upper Devonian Plavinas aquifer (Figure 38). However, the clay layer is only few meters thin and, perhaps, locally eroded. The elevated concentration of nitrate (6.1 mg N/l) was observed in the upper part of the Plavinas aquifer in the depth 8 – 9m (sample No 156). No signs of contamination were found in the bottom part of the Plavinas aquifer in the depth 18 – 16m (sample No 155, N-NO3 0.8 mg/l).

The contaminated groundwater is discharging into the small Kekava river located 1 km SE of the investigated site. As a result the concentration of nitrate in two springs in the river valley reaches 16 – 18 mg N/l (sample no. 603 and 604).

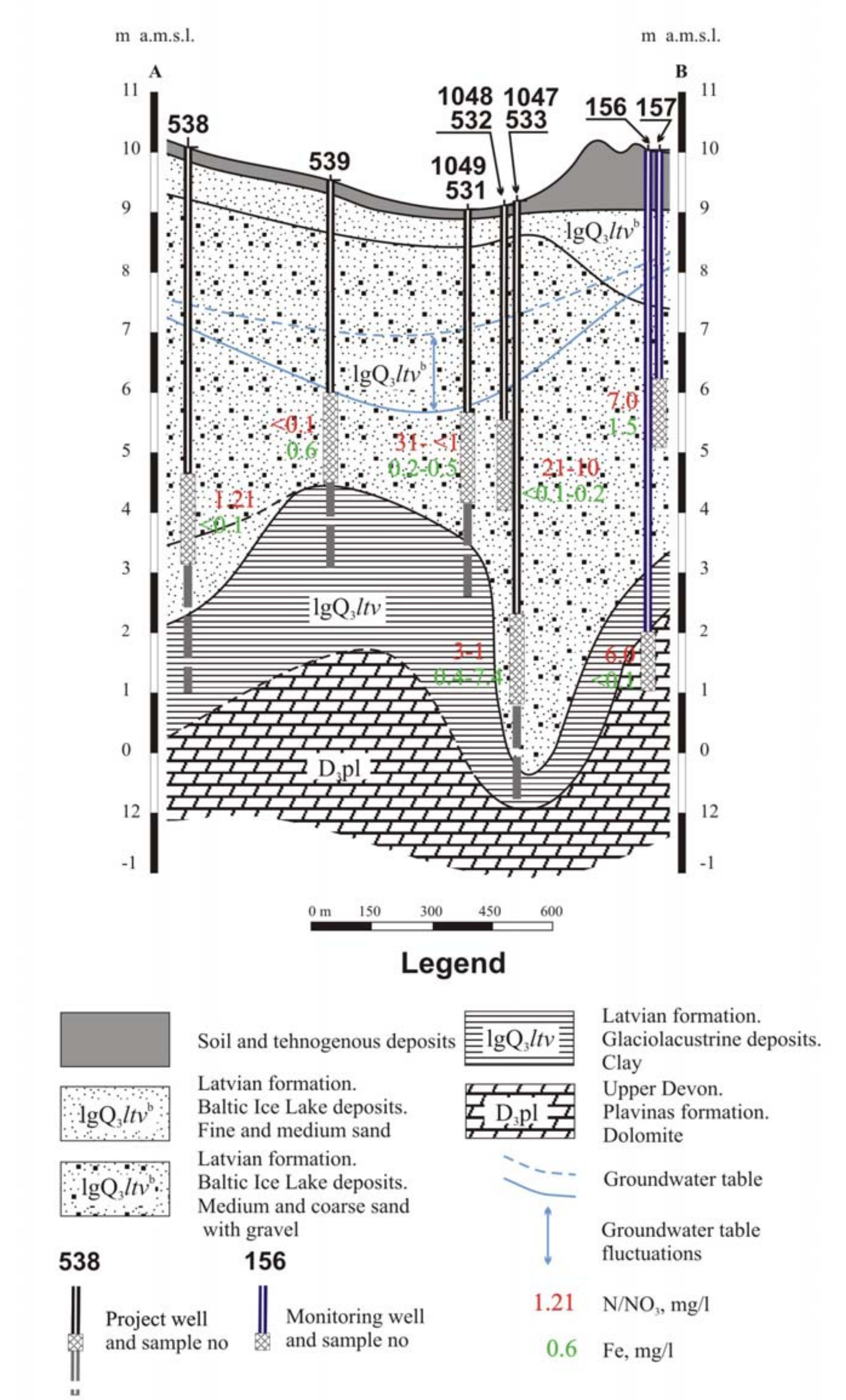

Figure 38. *Geological profile at Kekava*

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4.4 Griva – location with intensive pasturing

Within this project, five groundwater samples were taken from existing monitoring wells at Griva. Until recently and for several decades before, the investigated area has been used for intensive pasturing by cows.

At Griva, in eastern Latvia in the vicinity of the town Daugavpils, one of the stations of the Regional Groundwater Monitoring Network is situated. The station consists of a series of shallow wells oriented perpendicularly to the river Daugava (Figure 39). All the wells are screened in the depth 4 – 7m in the bottom part of the unconfined water table aquifer.

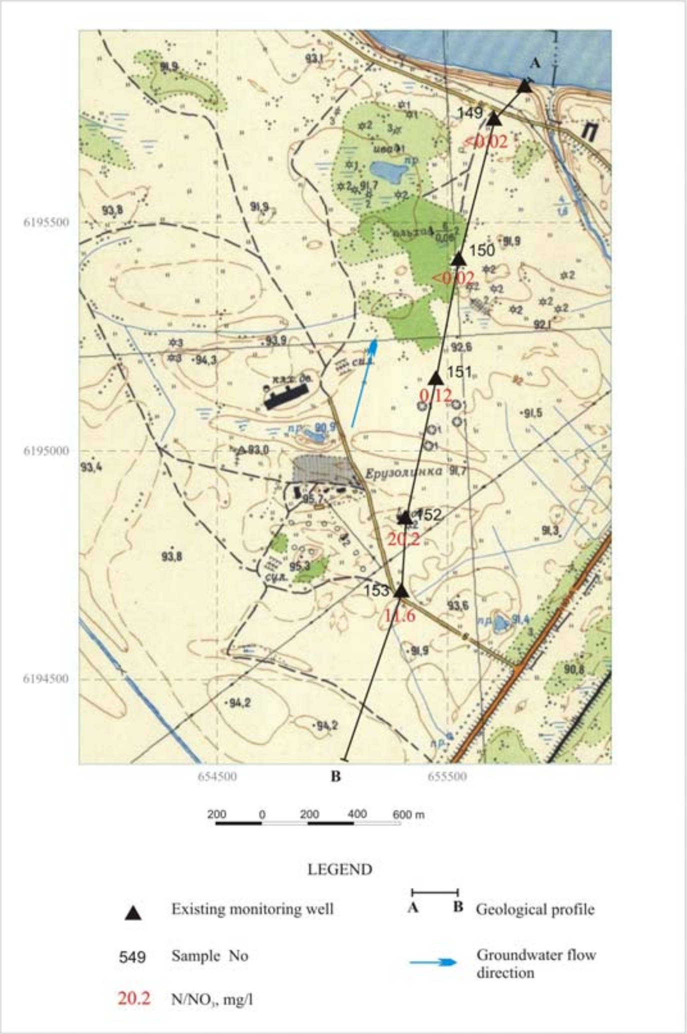

Figure 39. *Location of sampling points at Griva*

The unconfined water table aquifer consists of Quaternary glaciolacustrine medium-grained sand underlain by glaciogenic till (Figure 40). The depth of the water table is around 2 m. The groundwater flows toward north to the Daugava River.

The unconfined water table aquifer is seriously contaminated by nitrates reaching 20 mg N/l exceeding the MAC twice. Slightly elevated concentrations of chlorides, sulphates and potassium also occur in the contaminated groundwater, while the concentrations of phosphorus and heavy metals meet the background values. No pesticides were found in the groundwater.

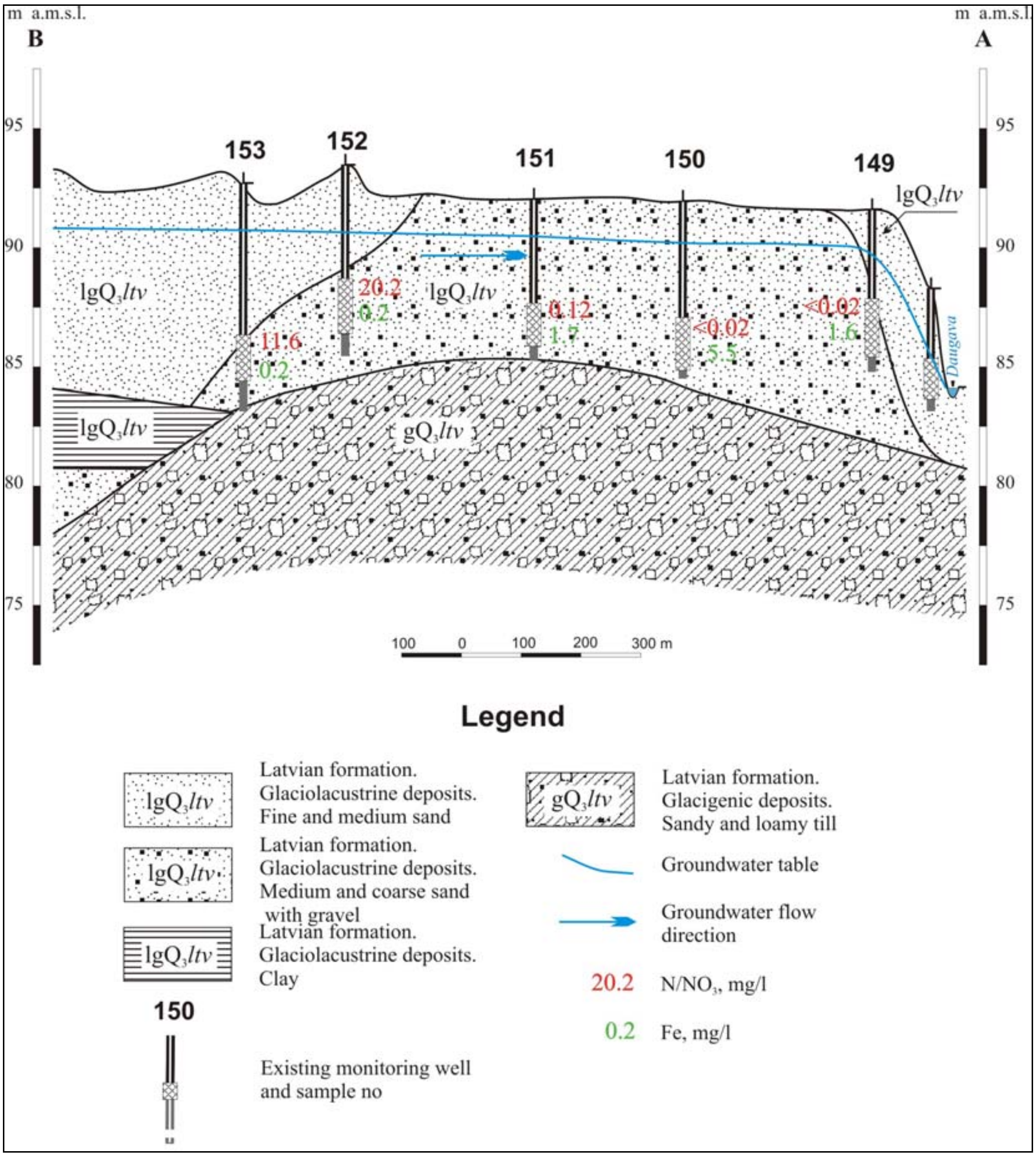

Figure 40. *Geological profile at Griva*

An increase of nitrate at Griva has been observed since the beginning of the 1980s and this tendency has remained until the recent years (Figure 41).

Downstream of the groundwater flow from the area of intensive pasturing the concentrations of chloride and sulphate decrease step-by-step, and the concentration of nitrate rapidly decreases. Simultaneously the concentrations of iron and ammonium increase (Figure 42).

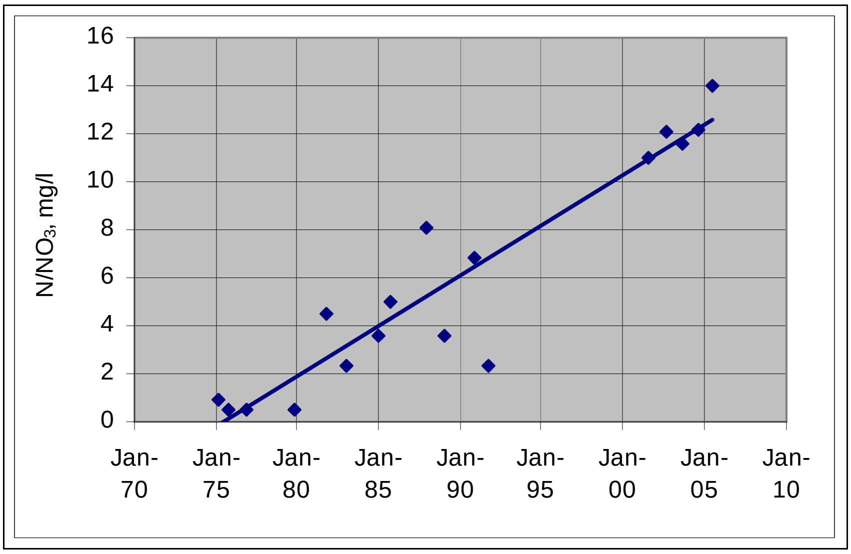

Figure 41. *Long-term variations of nitrate in shallow well No 228a at Griva*

The decrease of nitrate can not be explained by dilution, as concentration of nitrate decreases more than 2 thousands times, while the concentration of chloride concentration decreases 9 times only. The reduction of nitrate plays a secondary role, because the concentration of ammonium increases only by 0.5 mg/l. Thus, we observe a classic example of the denitrification process.

The concentration of dissolved oxygen is low in all of the wells and changes insignificantly from 0.13 to 0.18 mg/l, i.e. the slightly anoxic conditions favourable for denitrification occur in the unconfined water table aquifer. As the attenuation of nitrate is accompanied by a rapid increase of the dissolved iron, it may be assumed, that ferrous iron dissipated in the glaciolacustrine deposits is the main electron donor in the denitrification reaction.

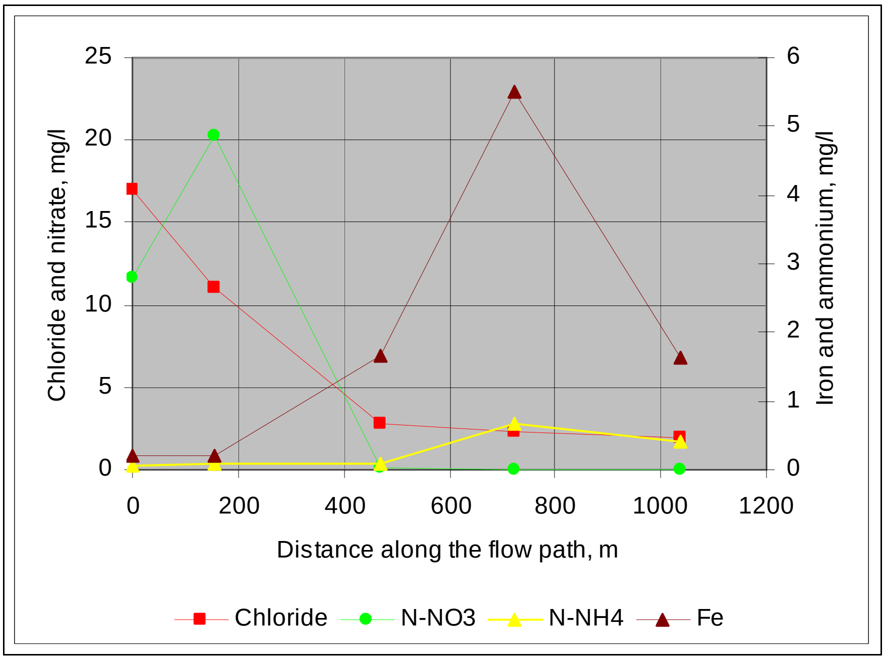

Figure 42. *Changes of the groundwater quality downstream of the groundwater flow at Griva*

5. Project outputs for different tasks related to the Water Framework Directive and for the improvement of several national guidelines as well as a national groundwater monitoring and protection program

5.1 Identification of groundwater bodies at risk and Recommendations for improvement of the Regional Groundwater Monitoring System

The EU Water Framework Directive requires that Member States identify groundwater bodies at risk. For these an extended groundwater monitoring programme must be established and implemented. The identification of groundwater bodies at risk requires knowledge of the anthropogenic pressures and of groundwater vulnerability as well as monitoring data concerning groundwater quality.

The data collected within this project demonstrates a very spotted pattern of the contamination of unconfined aquifers. An extensive agriculture practically does not influence the groundwater quality. Even within territories of intensive agriculture the concentrations of nitrates above MAC occur only sporadically within estimated 3% of the entire Latvian territory (chapter 3.2). The diffuse groundwater contamination is concentrated in the southern part of the central Latvia characterised by the highest agricultural loading: the southern part of the Jelgava district, the eastern part of the Dobele district and the south-western part of the Bauska district.

High confinement degree, low velocity of groundwater flow and anoxic conditions unfavourable for migration of nitrates and the majority of heavy metals prevent the downward percolation of contaminants in the main Latvian water supply aquifers (chapter 3.3). One of the main outputs of this project is that at present the risk of contamination by nitrates etc. of the main Latvian aquifers relevant for water supply is low. However, the distribution of pesticides is less predictable and is not completely investigated at the moment (chapter 3.5).

On the basis of the single-parameter maps of agricultural loading, the thickness of the superficial low-permeable deposits and other parameters related to the groundwater vulnerability, the most dangerous areas for downward infiltration of diffuse contamination into water supply aquifers were identified (Figure 29). These two areas, located south of the town Jelgava and south of the Auce settlement, can be defined as *the groundwater bodies at risk* related to agricultural contamination. Note that the delineation of the groundwater bodies at risk is approximate because this depends heavily on the density of the reliable borehole data (chapter 3.3).

On the basis of the results from this project, the following improvements of the Regional Groundwater Monitoring system are recommended:

- An improvement of the Regional Groundwater Monitoring Network by establishing a new monitoring station at the above mentioned highly vulnerable area south of Jelgava (Figure 28). This station should consist of 4 wells screened in the upper aquifers. The recommended approximate depths of the wells are 4, 10, 25 and 65m;

- An improvement of the agricultural run-off monitoring station Vecauce by establishing 3 additional deeper monitoring wells in the upper pre-Quaternary aquifers. The recommended approximate depths of the wells are 10, 20 and 40m. Station Vecauce is located close to the above mentioned second high-vulnerable area south of the Auce settlement. At this station 3 shallow monitoring wells in the superficial drift aquifer were installed in frame of this project (chapter 1.7). To control the downward migration of the contaminants, additional deeper monitoring wells are necessary;
- An improvement of the Regional Groundwater Monitoring Network by incorporation of selected high-yielding springs, because the springs are natural outlets of the youngest and potentially most contaminated groundwater (chapter 3.4), and the high-yielding springs capture groundwater flow from a large territory and can replace many monitoring wells;
- An improvement of the monitoring of diffuse contamination by including a limited number of the most actual micropollutants in the list of groundwater quality parameters analysed within the Regional Groundwater Monitoring Program, i.e.:
    1. pesticides: triazines (prometryn, simazin, propazine, metribuzin), chlorophenoxy acids (MCPA, 2,4-D, MCPB), miscellaneous pesticides (TCA, bentazon); these are the most likely to be found in the Latvian groundwater (chapter 3.5);
    2. arsenic, as this is the most mobile heavy metal, which can exceed the MAC both due to natural and anthropogenic reasons. Note that arsenic does not belong to the indicators of agricultural influence on the groundwater. However, uranium, cobalt, rubidium and other heavy metals – indicators of the agricultural influence on groundwater – do not reach a dangerous concentrations in the anoxic and neutral aquifers, and moreover, there are no MAC´s for these elements in Latvia or other EU countries;
- An improvement of the groundwater sampling frequency within the Regional Groundwater Monitoring Programme depending on the groundwater residence time. To select the optimal and individual frequency of the groundwater sampling, determination of CFCs in approx. 100 monitoring wells belonging to the Regional Groundwater Monitoring Network must be recommended. The first CFCs data obtained in frame of this project confirm the high effectiveness of the CFC method for evaluation of the groundwater residence time. Moreover, the even limited CFC data – just 27 samples, collected within this project demonstrate the rather high age of Latvian groundwater, which allow reducing the sampling frequency in many monitoring wells.

All these recommendations are included in the Basic Groundwater Monitoring Development Concept, prepared in 2005 (Levins 2005). 30 of 210 high-yielding springs found and sampled within this project were selected and has already been included in the Regional Groundwater Monitoring Network in 2006 (Annex 4).

5.2 Threshold values for minor and trace elements to distinguish pristine groundwater from contaminated groundwater and for assessing chemical status of the groundwater

The maximum natural concentrations of elements analysed in chapter 2.4 can be used as *the standards against which to measure anthropogenic impact*. The respective threshold values were prepared by the SGSL in 1998. However, threshold values for a number of microelements were not prepared due to the lack of relevant data on natural concentrations of these elements in Latvian groundwater.

Based on the comprehensive data obtained within this project (see chapter 2) both new and revised threshold values have been proposed (see Table 14).

Note that several exotic elements like REE and zirconium having a less importance for investigation of the groundwater contamination are not given in Table 14.

It is not expected that the proposed threshold values can be exceeded under natural conditions – except within strong geochemical anomalies. For instance, the concentration of uranium may exceed 0.005 mg/l if the well is screened directly within a nasturan[29] deposit (only one case for whole Latvia is identified recently).

The data collected within this project gives an important contribution to the establishment of threshold values according to the requirements of the Water Framework Directive (WFD). The WFD requires that Member States of the European Union determine the chemical status of groundwater bodies as “good” or “poor”. The draft Groundwater Directive (GD) defines a list of contaminants and substances that must be used as indicators of chemical status of groundwater.

When establishing threshold values, Member States shall consider the following guidelines:

- The extent of interactions between groundwater and associated aquatic and dependent terrestrial ecosystems,
- The interference with existing or future legitimate uses of groundwater,
- The toxicology and persistence of pollutants,
- The background concentrations.

This means that threshold values required by the GD must consider both the natural variability of the chemical composition of groundwater and the extent of environmental risks related to increased concentrations of elements. In terms of the WFD and GD a groundwater body is only polluted if pollutants are present at concentrations that may be harmful to humans, ecosystems etc. As the WFD and GD distinguish only between polluted groundwater and groundwater merely impacted by human activity, the threshold values required by the GD may be higher than the threshold values between pristine and contaminated groundwater.

The threshold values for nitrate and pesticides according to the GD are established at EU level. These are equal to the MAC´s for Drinking Water: N/NO3 – 11 mg, pesticides - 0.1 µg/l. It is noteworthy that the threshold value for nitrate is much higher than any natural background concentration.

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[29] Uranite, UO_2

Table 14. *Threshold values of minor and trace elements in shallow groundwater for distinguishing pristine from contaminated groundwater, mg/l*

Parameters	Latvian threshold values established in 1998[30]	Revised threshold values:			
		for a majority of groundwater	for organic rich groundwater	for strongly anaerobic groundwater of methanogenese stage[31]	for sulphate or chloride rich groundwater
K	12 – 23	10	25		25
$N_{tot.}$	10 – 15	4	6		
N/NH_4	3 – 10	1	5		
N/NO_3	4	3			
F	n.d.	0.5			2
Fe	n.d.	6	20		
$P_{tot.}$	n.d.	0.1	0.5		
Al	n.d.	0.2	3		
As	0.05	0.01	0.02	0.02	
B	n.d.	0.15			1.5
Ba	n.d.	0.5			
Cd	0.003	0.001			
Co	n.d.	0.002			
Cr	0.05	0.01			
Cu	0.05	0.01			
Mn	n.d.	0.5	1		
Ni	0.05	0.01			
Pb	0.03	0.001	0.01		
Sb	n.d.	0.0005			
Se	n.d.	0.001			0.01
Sr	n.d.	0.5			10
U	n.d.	0.005			
V	n.d.	0.002	0.02		
Zn	0.2	0.5			

At a national level threshold values must be established at least for trichloroethylene, tetrachloroethylene, arsenic, cadmium, lead, mercury, ammonium, chloride and sulphate. The additional individual threshold values can be established at the level of a groundwater body or group of the bodies, for pollutants that are indicative of possible specific environmental risk.

Trichloroethylene and tetrachloroethylene are not investigated within this project. Mercury data obtained within this project can not be utilised due to low accuracy of the ICP-MS data (see chapter 1.5). Data on chloride and sulphate obtained within this project is not representative for the entire Latvian groundwater, because the activities were concentrated on the investigation of shallow groundwater. Thus, the data obtained in this project are essen-

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[30] Investigation of groundwater contamination. Methodological recommendations. SGSL. State Geological Survey of Latvia. Riga, 1998.

[31] Confined aquifers with negative Red-Ox, oxygen, nitrates below detection limit and sulphate below 1 mg/l.

tial for the determination of threshold values for ammonia, arsenic, cadmium and lead only. Additional threshold values for the remaining minor and trace elements are not necessary, due to low natural concentrations and to the absence of dangerous diffuse contamination (see chapter 2).

The proposed threshold values of the above mentioned elements and substances, which consider the natural concentrations of elements and the Drinking Water Standards, are given in Table 15.

Table 15. *Proposed threshold values of selected minor and trace elements for Latvian groundwater according to the requirements of the Groundwater Directive, mg/l*

Parameters	Maximum natural value in shallow groundwater	Maximum Admissible Concentration for Drinking Water[32]	Proposed threshold values required by the Groundwater Directive
N/NH_4	1 to 5 in different groundwater bodies	0.39	1 to 5 in different groundwater bodies
As	0.01 to 0.02 in different groundwater bodies	0.01	0.01 to 0.02 in different groundwater bodies
Cd	0.001	0.005	0.005
Pb	0.001 – 0.01 in different groundwater bodies	0.01	0.01

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[32] According to the Drinking Water Directive.

5.3 Recommendations for prospecting of groundwater reserves and for determination of well field sanitary protection zones

The data collected within the frames of this project on background and on anthropogenic concentrations of elements as well as the data on groundwater age, provide an essential input for improvement of the national regulations of well field protection and for the prospecting of groundwater reserves intended for water supply. The basic groundwater quality parameters examined in each water supply well according the Latvian regulations (CMRL 2005)[33] are:

- EC, pH;
- Major ions: calcium, magnesium, sodium, potassium, bicarbonate, sulphate, chloride;
- Minor elements: iron, manganese;
- Nitrogen compounds: ammonia, nitrite, nitrate;
- Total content of organic matter: permanganate index or TOC.

The National Drinking Water Standard (CMRL 2003)[32] requires a wide spectrum of elements and substances, which must be examined in wells and springs intended for centralised water supply or for the bottling of the water. The full examination of the groundwater quality is extremely expensive and can only be conducted in few Latvian laboratories. In fact the full examination is almost never carried out and the list of quality parameters determined at various well fields is very random and somewhat subjective.

Note that the majority of Latvian well fields utilise deep aquifers containing old groundwater. A high confinement degree of the main Latvian aquifers is confirmed by the anoxic conditions, by residence time of groundwater above 50 years even in moderately deep aquifers, and by a very limited depth of contaminants percolation (see chapters 2 and 3). This means that in many cases the expensive determination of a number of anthropogenic contaminants is meaningless, and the examination of groundwater quality should be focused on naturally occurring compounds.

A list of elements and substances naturally occurring in Latvian groundwater or originating from agriculture, which concentrations may reach a level of harmfulness, is given in Table 16.

The priority pesticides identified within this project and which must be examined in water supply wells within rural areas are:

- Triazines (metribuzin, prometrym, propazine, simazine),
- Chlorophenoxy acids (2,4-D, MCPA, MCPB),
- Miscellaneous pesticides (TCA, bentazon).

Harmful concentrations of all microelements except arsenic occur only in groundwater with poor basic chemical composition – in groundwater with a high content of organic matter, sulphates and chlorides. Sulphate rich groundwater are widely utilised in central Latvia due

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[33] These national regulations were harmonised with the Drinking Water Directive and includes the same water quality parameters.

to absence of alternative water sources. On few locations with very unfavourable hydrogeological conditions, chloride rich groundwater and organic rich groundwater are also utilised in centralised water supply.

Table 16. *Elements and substances in Latvian groundwater may exceed the Maximum Admissible Concentration for Drinking Water*

Groundwater		**Elements and substances**
Pristine groundwater	any groundwater	ammonia iron manganese
	organic rich groundwater	permanganate index aluminium arsenic lead
	sulphate rich groundwater	sulphate fluoride boron
	chloride rich groundwater	chloride sulphate sodium selenium
	strongly anaerobic groundwater of methanogenic phase	arsenic
Groundwater with diffuse agricultural contamination		nitrate pesticides

The existing data on Latvian groundwater and the recent data obtained within this project confirm that - except those mentioned in the Table 16 – other parameters do not exceed the MAC in pristine groundwater and in the groundwater influenced by agricultural diffuse contamination. Therefore the determination of microelements like chromium, cadmium, copper, nickel, antimony and synthetic substances like organochlorine and organophosphorus pesticides is not necessary during prospecting of the groundwater reserves, except, of course, vulnerable aquifers beneath urbanised and industrial areas and in the vicinity of the historical contaminant plumes.

The optimised list of groundwater quality parameters that must be examined in groundwater intended for water supply is summarised in Table 17.

The confinement degree of aquifers must be estimated by assessment of the groundwater age, for instance by the CFC method, and by a complex of hydrogeological evaluation, including:

- Thickness and properties of confining layer,
- Direction and magnitude of groundwater flow under varying conditions (upward or downward),

- Characteristics of the chemical composition indicative of the aquifer confinement degree (Red-Ox, oxygen, nitrates, ammonia, organic matter, presence of pollutants, correspondence of the chemical composition to the pristine chemical composition).

Table 17. *Elements and substances to be examined in groundwater intended for water supply depending on aquifer type and basic groundwater chemistry*

<table>
<tr><th>Groundwater type / land use</th><th>Basic chemical composition of groundwater</th><th>Undeveloped and rural areas</th><th>Urbanised and industrial areas and surroundings of the contaminant plumes</th></tr>
<tr><td rowspan="3">Old groundwater
(confined aquifers)</td><td>chloride and sulphate below MAC</td><td colspan="2">• basic parameters
• As</td></tr>
<tr><td>chloride above MAC</td><td colspan="2">• basic parameters
• As, Se</td></tr>
<tr><td>sulphate above MAC</td><td colspan="2">• basic parameters
• As, B, F</td></tr>
<tr><td rowspan="4">Young groundwater (unconfined and semi-confined aquifers)</td><td>chloride and sulphate below MAC, permanganate index or TOC below 4 mg/l</td><td>▪ basic parameters
▪ As
▪ Pesticides</td><td rowspan="4">▪ basic parameters
▪ all parameters according to Drinking Water Standard[34]</td></tr>
<tr><td>permanganate index above 4 mg/l</td><td>▪ basic parameters
▪ Al, As, Pb
▪ Pesticides</td></tr>
<tr><td>chloride above MAC</td><td>▪ basic parameters
▪ Se
▪ Pesticides</td></tr>
<tr><td>sulphate above MAC</td><td>▪ basic parameters
▪ F, B
▪ Pesticides</td></tr>
</table>

The groundwater must be classified as “old” and less vulnerable if it does not contain CFCs and pollutants, and if the above mentioned hydrogeological indicators confirm the high confinement degree of the aquifer. In that case a limited number of groundwater quality parameters may be examined. If the groundwater contains CFCs or if the hydrogeological parameters do not indicate a high confinement degree of the aquifer, an extended list of the groundwater quality parameters shall be examined depending on a land use (Table 17).

The new data on residence time of Latvian groundwater and the concept of the aquifer confinement should be used for improvement of the existing regulations of well field protection.

The present Latvian legislation (CMRL, 2004) requires a three-belt protection zones around centralised water supply wells:

- The “strict regime zone”, which is 10 – 50m wide, where all economical activities are prohibited, except those related to the exploitation of water
- The “bacteriological protection zone”, which corresponds to 200-400-days catchment area of the considered well-field, where activities are restricted or prohibited,
- The “chemical protection zone”, equal to a 25-years catchment area of the well-field where the danger of all planned activities should be assessed and some may be restricted.

The “bacteriological” and “chemical” protection zones are typically determined using simplified calculations valid for idealised hydrogeological conditions. The total travel time of

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[34] Except, of course, parameters related to water treatment and transportation like acrilamide, trihalogenmethans etc.

groundwater is determined by piston-flow calculations (downward plus horizontal), taking into account the direction and gradient of the groundwater flow, the rate of groundwater abstraction, the permeability and porosity of aquifer sediments and the thickness, permeability and porosity of covering sediments.

The main problem of the existing concept of groundwater protection is an extremely high uncertainty on the calculation of the chemical protection zones for low-yielding well fields. These formally calculated capture zones for small-rate well fields that does practically not disturb the natural groundwater flow, makes the determination of the protection zones extremely uncertain, taking the limited knowledge of hydrogeological conditions into account.

The existing concept for delineation of chemical protection zones is not useful for the majority of small-rate Latvian well fields due to unjustified restrictions on land use within large areas. For Latvian conditions, where main aquifers are characterised by a high confinement degree, the configuration of these protection zones may be too restrictive and can have an unnecessary negative impact on economical activities.

Additionally this definition of groundwater protection zones inherited from the Soviet time, contradicts the general principles of the Water Framework Directive, which require protection of the entire water resources.

Note that the majority of Latvian well-fields are low-rate well fields yielding old groundwater from confined aquifers. In such situation there is no need to delineate chemical protection zones – particularly due to the fact that no reliable hydrogeological information can be provided.

Combinations of several types of aquifer conditions with different types of well-fields are shown in Table 18 together with recommendation for the need to delineate groundwater protection zones. It is stated that no such protection zones are necessary for cases where old groundwater (confined aquifers, low yield) is utilised for drinking water supply. If such recommendation is accepted, a large load of work associated with delineation of the chemical protection zones can be avoided. Furthermore, bureaucratic and technical procedures connected to permissions for business activities within the water supply catchments would by simplified.

Table 18. *Proposals for establishing of the chemical protection zones around the well fields*

Well-field influence on groundwater flow	**“Old” groundwater (confined aquifer)**	**“Young” groundwater (unconfined or semi-confined aquifer)**
low-rate well-fields not forming depression cones and not disturbed the natural groundwater flow	***chemical protection zone shall not be defined***	chemical protection zone shall be defined
high-rate well-fields disturbed the groundwater flow and forming depression cones	chemical protection zone shall be defined	chemical protection zone shall be defined

6. White spots" and objectives for future investigations

The finished project provides the first comprehensive data set on groundwater influenced by agricultural activities in Latvia. A spectrum of contaminants originating from agriculture has been identified, the extent of the agricultural contamination of groundwater has been evaluated, and some of the most vulnerable groundwater areas have been delineated. Moreover, this project provides the first wide-spread data on microelements in Latvian shallow groundwater, which allow the definition of some threshold values for Latvian groundwater according to the requirements of the Water Framework Directive and the draft Groundwater Directive. Finally the projects outputs allow improvement of national regulations.

However, some white spots still remain and they are the priority objectives of future investigations. Some of these white spots are:

- An insufficient knowledge of the distribution of the agricultural loading within the Latvian territory and the vulnerability of the main Latvian aquifers against surface contamination, which does not allow identifying of all groundwater bodies at risk,
- An insufficient knowledge of the pesticides in Latvian groundwater, and
- An insufficient knowledge of the background concentrations of several heavy metals in Latvian groundwater.

The insufficient knowledge of the distribution of the agricultural loading within the Latvian territory is caused by a too general character of the available GIS data of the fertilisation rate and, especially, of the application of pesticides. On the other hand, the lack of reliable soil maps and still not finished digitisation of the borehole data complicates the mapping of the most vulnerable groundwater areas.

One of the very important objectives for future investigations is to obtain more comprehensive data on groundwater residence time, which directly characterise the groundwater vulnerability and allows an assessment of the time of when the maximum flux of contaminants originating from the 1980s may reach the main Latvian water supply aquifers.

In frame of this project a priority list of pesticides occurring in the Latvian groundwater was identified, while the distribution of pesticides in Latvian aquifers is not fully clear. An extent of the pesticide problem for the main Latvian aquifers should be investigated in the future by comprehensive sampling of the moderately deep Latvian aquifers.

Low accuracy and sensitivity of applied ICP-MS method does not allow a determination of background concentrations of important heavy metals like mercury and cadmium. Another more robust and sensitive method must be used in the future to determine the threshold values of these metals according to the requirements in the Groundwater Directive.

As the groundwater sampling within this project were focused on shallow groundwater potentially impacted by agriculture, the distribution of many important heavy metals in confined Latvian aquifers typically used in water supply was studied insufficiently. A comprehensive sampling of moderately deep aquifers is recommended to assess natural concentrations of heavy metals, especially arsenic. The data collected within this project confirms the presence of high pristine concentrations of arsenic in some Latvian aquifers characterised by strong anaerobic conditions of methanogenese stage, but the extent of this problem is not clear.

ANNEXES

Annex 1: **The most widely applied pesticides**

Annex 2: **List of pesticides collected in the 1990s at the former agrochemical storehouse “Gardene”**

Annex 3: **Results of CFC dating**

Annex 4: **List of high-yielding Latvian springs found and sampled within this project, already included into the Basic Groundwater Monitoring Programme**

Annex 5: **Groundwater chemistry . Database in Excel format**

SEE THE ENCLOSED CD

Annex 6: **Site pictures**

SEE THE ENCLOSED CD

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Annex 1

The most widely applied pesticides

Common name	Application task	Application rate		Movement rating in soil	Relative probability of occurrence in ground-water
		Maximum - end of 1980-ties	Present - 2002 data		
2,4,5-TP	Herbicide	+		Very Low	Very Low
2,4-D	Herbicide	+++	+	Moderate	High
Alachlor (dimeth-achlor)	herbicide		+	Moderate	Very Low
Benomyl	fungicide	++		Low	Low
Bentazon	herbicide	++		Moderate	Low
Chlormequat chloride	plant growth regulator	+++	++	Very Low	Very Low
Chlorofos (trichlorfon)	insecticide	+		Moderate	Very Low
Clopyralid	herbicide	+	+	Very High	Low
Cypermethrin	insecticide	+		Extremely Low	Very Low
Dazomet	fungicide	+		Moderate	Very Low
Desmedipham	herbicide	+	+	Low	Very Low
Dicamba	herbicide		+	Very High	Very Low
Dichlorvos (DDVP)	insecticide	+		Extremely Low	Very Low
Dimethoate	insecticide	+	+	Low	Very Low
Diquat	herbicide	+		Extremely Low	Very Low
Epoxyconazole	fungicide		+	Low	Low
Ethephon	plant growth regulator	++	+	Low	Very Low
Ethofumesate	herbicide		+	Moderate	Low
Fenpropimorph	fungicide		+	Very Low	Very Low
Glyphosate	herbicide	++	+++	Extremely Low	Very Low
Kresoxim-methyl	fungicide		+	Very Low	Very Low
Lenacil	herbicide	+		High	Low
Lindane	insecticide	+		Moderate	High
Mancozeb	fungicide	++	++	Low	Low
MCPA + MCPB	herbicide	+++	++	High	High
Mecoprop (MCPP)	herbicide	++		High	Low
Mepiquat chloride	plant growth regulator		+	Extremely Low	Very Low
Metalaxyl	fungicide	+		High	Low
Metamitron	herbicide		+	Moderate	Very Low
Metazachlor	herbicide		+	Extremely Low	Very Low
Nitrofen	herbicide	+		Extremely Low	Very Low
PCNB	fungicide	+		Very Low	Very Low
Pendimethalin	herbicide		+	Very Low	Very Low
Pentachlorphenol	fungicide	+		Very High	Low
Permethrin	insecticide	+		Extremely Low	Very Low
Phenmedipham	herbicide		+	Very Low	Very Low
Phosalone	insecticide	+		Very Low	Very Low
Phosphamidon	insecticide	+		High	Very Low
Phoxim	insecticide	++		Very Low	Very Low
Pirimiphos-methyl	insecticide	+		Low	Very Low

Common name	Application task	Application rate		Movement rating in soil	Relative probability of occurrence in groundwater
		Maximum - end of 1980-ties	Present - 2002 data		
2,4,5-TP	Herbicide	+		Very Low	Very Low
Prochloraz	fungicide		+	Moderate	Low
Prometryn	herbicide	++	+	Moderate	High
Propamocarb	fungicide		+	Low	Very Low
Propiconazole	fungicide	++	+	Low	High
Pyrazon (chloridazon)	herbicide		+	Moderate	Very Low
Simazine	herbicide	++		High	High
TCA	herbicide	++++		Very High	Very High
Thiabendazole	fungicide	+		Very Low	Low
Thiram (TMTD)	fungicide	++		Low	Very Low
Triadimefon	fungicide	+		Moderate	Low
Triadimenol	fungicide	+		Moderate	High
Triallate	herbicide	+		Low	Very Low
Trifluralin	herbicide	++	+	Very Low	Very Low
Zineb	fungicide	++		Low	Low

Application rate, t/year	
++++	1000 - 2000
+++	100 - 300
++	10 - 100
+	1 - 10

Annex 2

List of pesticides collected in the 1990s at the former agrochemical storehouse “Gardene”

Name	**Prevailing organic pesticides stored at the waste depot Gardene (tons)**
Na TCA	279
DDT	173
HCH	131
TMTD (Thiram)	72
2,4-D	52
MCPA	49
Simazine	30
Polycarbamate	28
Prometryn	23
Nitrofen	23
DNOC	17
Cyneb	16
Cyram	14
Pyrazon	12
Dalapon sodium	10
Desmedipham	9
Parathion	8
Atrazine	7
Propachlor	7
Benomyl	7
Treflan	6
Dazomet	5
Toxaphene	5
Pentachlorophenol	5
Triallate	4
Dinocap	4
Malathion	4
Propazine	4
Dicofol	3
Carboxin	3

Annex 3

Results of CFC dating

Age-dating of groundwater using the CFC-method - Latvia June 2005

Location/ Well No.	Depth metres	Ampoul No.	Sampling Date	Hour	Concentration in water pg/kg CFC-11	pg/kg CFC-12	pg/kg CFC-113	Partial press. (calc.) in atmosphere, pptv CFC-11	CFC-12	CFC-113	CFC model infiltation year CFC-11	CFC-12	CFC-113	Remarks
Baltezers														
390	120-125	1	30-05-05	14.00	0.0	0.0	0.0	0.0	0.0	0.0	<1945	<1940	<1959,5	
do	do	4	30-05-05	14.55	0.0	0.0	0.0	0.0	0.0	0.0	<1945	<1940	<1959,5	
391	90-93	1	30-05-05	16.10	0.0	0.0	0.0	0.0	0.0	0.0	<1945	<1940	<1959,5	
do	do	2	30-05-05	16.15	0.0	0.0	0.0	0.0	0.0	0.0	<1945	<1940	<1959,5	
46	36-38	1	30-05-05	18.25	73.7	256.2	7.3	22.8	351.7	5.4	1964.0	1982.0	1969.0	
do	do	2	30-05-05	19.00	72.7	263.8	7.4	22.5	362.1	5.4	1964.0	1982.5	1969.0	
47	61-64	1	30-05-05	20.50	0.0	8.2	0.0	0.0	11.3	0.0	<1945	1952.0	<1959,5	
do	do	2	30-05-05	20.55	0.0	5.3	0.0	0.0	7.3	0.0	<1945	1949.5	<1959,5	
Incukalns														
357	158-175	1	31-05-05	14.25	0.0	0.0	0.0	0.0	0.0	0.0	<1945	<1940	<1959,5	
do	do	2	31-05-05	14.30	0.0	0.0	0.0	0.0	0.0	0.0	<1945	<1940	<1959,5	
359	46-59	1	31-05-05	16.40	44.1	71.2	6.8	13.7	97.7	5.0	1961.5	1967.5	1968.5	
do	do	2	31-05-05	16.50	42.2	70.3	6.8	13.1	96.5	5.0	1961.0	1967.5	1968.5	
358	108-128	1	31-05-05	18.00	0.0	5.0	0.0	0.0	6.8	0.0	<1945	1949.5	<1959,5	
do	do	2	31-05-05	18.10	0.0	3.5	0.0	0.0	4.8	0.0	<1945	1948.0	<1959,5	
Imanta														
6A	68-89	1	01-06-05	12.25	0.0	0.0	0.0	0.0	0.0	0.0	<1945	<1940	<1959,5	
do	do	2	01-06-05	12.30	0.0	0.0	0.0	0.0	0.0	0.0	<1945	<1940	<1959,5	
4A	40-52	1	01-06-05	13.55	0.0	0.0	0.0	0.0	0.0	0.0	<1945	<1940	<1959,5	
do	do	2	01-06-05	14.05	0.0	0.0	0.0	0.0	0.0	0.0	<1945	<1940	<1959,5	
3A	23-36	1	01-06-05	15.40	100.9	174.3	5.8	31.3	239.3	4.2	1965.5	1975.5	1967.5	PCE, trichloroethane
do	do	2	01-06-05	15.50	106.6	199.5	6.4	33.0	273.9	4.7	1966.0	1977.5	1968.0	PCE, trichloroethane
Tireli														
385	62-75	1	02-06-05	12.20	0.0	0.0	0.0	0.0	0.0	0.0	<1945	<1940	<1959,5	
do	do	2	02-06-05	12.25	0.0	0.0	0.0	0.0	0.0	0.0	<1945	<1940	<1959,5	
384	112-130	1	02-06-05	13.40	0.0	0.0	0.0	0.0	0.0	0.0	<1945	<1940	<1959,5	
do	do	2	02-06-05	13.50	0.0	0.0	0.0	0.0	0.0	0.0	<1945	<1940	<1959,5	
387	24-30	1	02-06-05	14.45	0.0	4.2	0.0	0.0	5.8	0.0	<1945	1948.5	<1959,5	
do	do	2	02-06-05	14.50	0.0	3.6	0.0	0.0	4.9	0.0	<1945	1948.0	<1959,5	

"Concentration in water" are measured CFC-concentrations
"Partial pressure" is the calculated CFC-concentration in the atmosphere at the time of infiltration
"CFC-model infiltration year" obtained by comparison with atmoshpere CFC-curve for individual CFCs
"Remarks" eg. Other halocarbons observed in the chromatogram

Age-dating of groundwater using the CFC-method - Latvia July 2005

Location/ Well No.	Depth metres	Ampoul Nr.	Sampling Date	Hour	Concentration in water pg/kg CFC-11	pg/kg CFC-12	pg/kg CFC-113	Partial press. (calc.) in atmosphere, pptv CFC-11	CFC-12	CFC-113	CFC model infiltation year CFC-11	CFC-12	CFC-113	Remarks
Kaitra														
27	47-49	3	15-06-05	11.35	0.0	1.0	0.0	0.0	1.4	0.0	<1945	1944.5	<1959,5	
do	do	4	15-06-05	11.45	0.0	1.0	0.0	0.0	1.4	0.0	<1945	1944.5	<1959,5	
Griva														
225	4,4-6,5	3	15-06-05	17.19	22.6	390.5	15.0	7.0	536.1	11.0	1957.5	1997.0	1974.5	
do	do	4	15-06-05	17.32	21.3	391.0	12.9	6.6	536.8	9.5	1957.0	1997.0	1973.5	
Stierniena														
10v	4,5-5,0	3	16-06-05	11.44	363.8	244.0	41.0	112.8	334.9	30.1	1974.5	1981.0	1982.0	N2O
do	do	4	16-06-05	12.05	366.2	265.8	38.7	113.5	364.9	28.5	1974.5	1983.0	1981.5	extra purge
10b	44-46	3	16-06-05	15.42	0.0	1.0	0.0	0.0	1.4	0.0	<1945	1944.5	<1959,5	
do	do	4	16-06-05	15.51	0.0	1.0	0.0	0.0	1.4	0.0	<1945	1944.5	<1959,5	
Trepe														
19	50-56	3	16-06-05	18.28	0.0	1.0	0.0	0.0	1.4	0.0	<1945	1944.5	<1959,5	
do	do	4	16-06-05	18.38	0.0	3.7	0.0	0.0	5.1	0.0	<1945	1948.0	<1959,5	
19a	12-21	3	16-06-05	19.30	0.0	1.0	0.0	0.0	1.4	0.0	<1945	1944.5	<1959,5	
do	do	4	16-06-05	19.42	0.0	1.0	0.0	0.0	1.4	0.0	<1945	1944.5	<1959,5	
Sasmaka														
28	17-22	3	05-07-05	19.13	0.0	2.0	0.0	0.0	2.8	0.0	<1945	1946.5	<1959,5	
do	do	4	05-07-05	19.26	0.0	7.3	0.0	0.0	10.1	0.0	<1945	1951.5	<1959,5	
27	53-58	3	06-07-05	11.37	0.0	1.6	0.0	0.0	2.1	0.0	<1945	1945.5	<1959,5	
do	do	4	06-07-05	11.50	0.0	2.0	0.0	0.0	2.8	0.0	<1945	1946.5	<1959,5	
Zakumizia														
15	48-50	3	08-07-05	14.45	0.0	3.1	0.0	0.0	4.3	0.0	<1945	1947.5	<1959,5	
do	do	4	08-07-05	14.55	0.0	3.6	0.0	0.0	4.9	0.0	<1945	1948.0	<1959,5	
16	21-26	3	08-07-05	17.03	0.0	1.7	0.0	0.0	2.3	0.0	<1945	1946.0	<1959,5	
do	do	4	08-07-05	17.23	0.0	1.5	0.0	0.0	2.1	0.0	<1945	1945.5	<1959,5	
Skrunda														
9	4-8	2	20-07-05	16.39	59.0	93.8	27.4	18.3	128.8	20.1	1963.0	1969.5	1979.0	
do	do	3	20-07-05	16.49	60.5	94.7	29.0	18.7	130.0	21.3	1963.0	1970.0	1979.0	
8	15-22	2	20-07-05	18.34	0.0	1.9	0.0	0.0	2.6	0.0	<1945	1946.5	<1959,5	
do	do	3	20-07-05	18.36	0.0	1.9	0.0	0.0	2.6	0.0	<1945	1946.5	<1959,5	
6	80-100	2	20-07-05	19.53	0.0	2.3	0.0	0.0	3.2	0.0	<1945	1947.0	<1959,5	
do	do	3	20-07-05	20.06	0.0	2.5	0.0	0.0	3.5	0.0	<1945	1947.0	<1959,5	
7	32-52	3	21-07-05	12.19	0.0	1.5	0.0	0.0	2.0	0.0	<1945	1945.5	<1959,5	
do	do	4	21-07-05	12.30	0.0	1.5	0.0	0.0	2.1	0.0	<1945	1945.5	<1959,5	

"Concentration in water" are measured CFC-concentrations
"Partial pressure" is the calculated CFC-concentration in the atmosphere at the time of infiltration
"CFC-model infiltration year" obtained by comparison with atmoshpere CFC-curve for individual CFCs
"Remarks" eg. Other halocarbons observed in the chromatogram
High concentration of N2O interfer with CFC-12, therefore extra purge is needed to remove N2O from the trap

Annex 4

List of high-yielding Latvian springs found and sampled within this project and already included into the Basic Groundwater Monitoring Programme

No	Spring name	X, km	Y, km	Aquifer
1	Bānūžu avots	57.158	25.571	Q
2	Brinku saltavots	57.451	25.271	D_3gj
3	Davida dz. avoti	57.268	25.388	D_3pl
4	Dukuļu avots	57.465	25.385	D_3gj
5	Govs avots	57.894	25.002	D_2br
6	Ķērpju avots	57.332	25.535	D_3pl
7	Līdumnieku avots	57.216	24.879	D_3gj
8	Lielas Ellites avots	57.384	25.427	D_3am
9	Mežmuižas avots	57.102	24.799	D_3pl
10	Rūcamavots	57.322	25.222	D_3gj
11	Saltavots	57.131	24.851	D_3pl
12	Spiģu avots	57.786	25.564	D_2br
13	Vecstrautu avots	57.399	25.949	Q
14	Zilu avots	57.530	26.709	D_3pl
15	Beipartu avots	56.401	24.154	D_3stp
16	Sauriešu avots	56.902	24.404	Q
17	Sērenes avots	56.570	25.221	D_3pl-dg
18	Sliseru avots	56.996	24.971	D_3og
19	Barbeles avots	56.434	24.592	D_3slp
20	Iecavas avots	56.593	24.195	D_3og
21	Plenku avots	56.869	22.999	Q
22	Vecmelderu avoti	56.186	25.729	D_3pl
23	Zebrus ezera avots	56.638	23.002	Q
24	Jaunpagasta avots	57.129	22.634	D_3pl
25	Kandavas avots	57.032	22.779	Q
26	Karaļu (Ķeveles) avots	56.483	22.821	Q + P_2 (?)
27	Kuldīgas avots	56.969	21.977	D_3pl
28	Lielbatas avots	56.446	21.854	Q
29	Sabiles avots	57.048	22.574	Q
30	Tukuma avots	56.975	23.197	Q

Annex 5 and 6 – see the enclosed CD rom