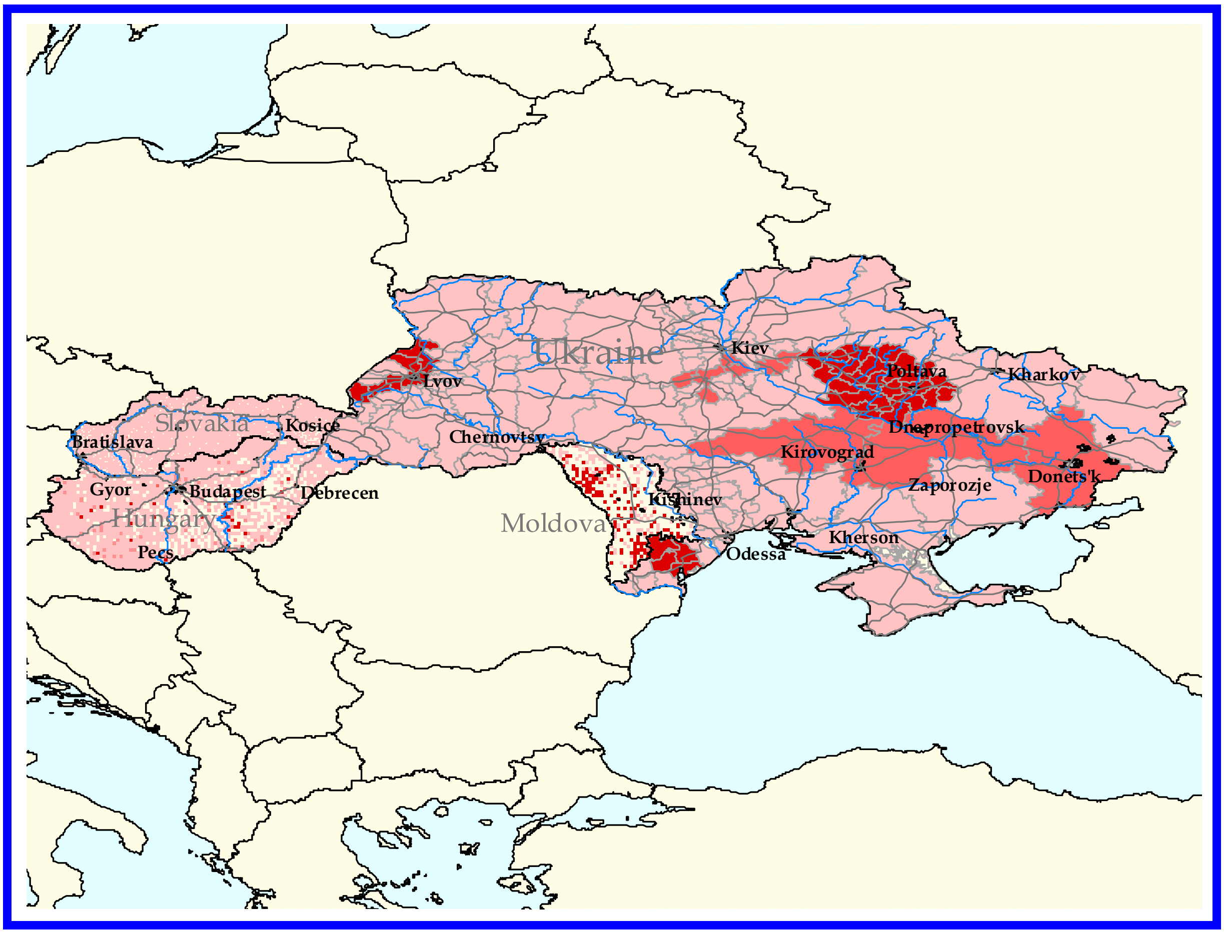
Water Quality Improvements through Fluoride Reduction in Groundwater of Central Europe

Inco - Copernicus 15-CT98-0139

Final Report December 2001

Development of a Fluoride Risk Assessment GIS for Central Europe



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Front Cover:
Map of high-fluoride risk in Central Europe

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Covering Notes

The information presented in this report and associated GIS represent the state of knowledge at the time of preparation in relation to an overview fluoride risks in Central Europe. It is beyond the scope of this project to consider cases of fluoride risk on a site-by-site basis. The purpose of this study is to highlight areas that in the opinion of Central European geochemical and health experts should be investigated further. As such, the indication in this report and GIS of an area as ‘high risk’ signifies that the area and possible fluoride remediation measures should be examined in more detail. Whilst substantial efforts have been made to incorporate all known problem areas into this report and GIS, due to the limited information available in some regions (Ukraine and Moldova in particular) other fluoride problem areas may exist in addition to those highlighted by this report and GIS.

It was not always possible to display all of the place names mentioned in the text of this report in the maps included as hard copy diagrams, however, the locations of all places mentioned in the text are available in the GIS.

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Glossary

ANOVA	Analysis of Variance
ASG	Association of State Geologists, Moldova
ASL	Above Sea Level
BGS	British Geological Survey
BUA	Broadband Ultrasound Attenuation
DMF-T	Decayed Missing and Filled Teeth Index
GIS	Geographic Information System
ESRI	Environmental Systems Research Institute
FW	Fresh Weight
IDW	Inverse Distance Weighting
IGAMS	Institute of Gerontology, Ukraine
IGMOF	Institute of Geochemistry and Ore Mineral Formation, Ukraine
IPR	Intellectual Property Rights
MAC	Maximum Admissible Concentration
MAG	Monitoring and Advisory Group
MAFI	Hungarian Geological Survey
OHI-S	Oral Cavity Hygiene Index
OM	Organic Matter
PBM	Peak Bone Mass
PMA	Papillary Marginal Alveolar Index
SHI	State Health Institute, Slovakia
SGUDS	State Geological Institute of Dionyz Stur, Slovakia
SOS	Speed of Sound
SPITN	Silness-Loe Index
STF	Bone Stiffness Index
TDS	Total Dissolved Solids
WHO	World Health Organisation
ZSNP	Ziar nad Hronom Company

Summary

Introduction

This report outlines the development of a risk assessment geographic information system (GIS) for Central Europe carried out as part of a project to assess and develop remediation technologies to mitigate high concentrations of fluoride (F) in drinking water in Ukraine, Moldova, Hungary and Slovakia: INCO-COPERNICUS IC15-CT98-0139 'Water Quality Improvement Through Fluoride Reduction in Groundwater of Central Europe'. The primary aim of the project was to develop technologies to remove fluoride from drinking waters. The second aim of the project was to develop a risk assessment GIS to predict areas were high-fluoride waters or fluorosis (fluoride toxicosis) may occur in Central Europe so that remediation technologies can be deployed most effectively. Hydrogeological, geochemical, medical and GIS experts from Ukraine, Moldova, Hungary, Slovakia and the UK were involved in the development of the risk assessment GIS between December 1998 – December 2001. In the original project plan, the geographic focus centred on Ukraine, Moldova and Hungary, however, information for Slovakia was included in the project as excellent geochemical data were available for Slovakia and enhanced the overview of fluoride risks in the study region.

The development of the project risk assessment GIS was based upon the collation and digitisation of existing information relevant to fluoride risk in Ukraine, Moldova, Hungary and Slovakia assembled for the first time in a readily accessible form to aid water management. In addition, geochemistry and health studies to examine in more detail the relationships between high-fluoride drinking waters and health effects in the population were carried out in Moldova and Ukraine. This is the first time that dental-skeletal status, physiological status and hydrogeochemistry have been investigated simultaneously in these countries and the data contribute to a state-of-the-art assessment of fluoride risks in Central Europe.

During the course of the study it was apparent that in addition to human health problems associated with high fluoride, many areas of Central Europe were at risk from dental caries related to low fluoride concentrations in drinking water. Therefore, a dental caries risk assessment was included in the project.

Fluoride and Health

During the initial phases of the project, background information on the occurrence and controls on fluoride in the environment and influences on health were collated from Central European expertise and from a review of international literature. Approximately 380 references were compiled into a project bibliography to aid the development of the GIS and to act as a reference source for future users of the fluoride risk assessment in Central Europe. The results of the review are summarised as follows:

Fluoride is one of the most abundant natural substances found on Earth and is a constituent of the rocks, soils, waters and air that make up the planet. Like several other naturally occurring elements, fluorides can enter the human body via inhalation of air and ingestion of food and water and have an effect on health.

Studies carried out in the USA and Europe in the 1950's demonstrated a link between improved dental health and the introduction of fluoridated toothpaste and fluoridated drinking water to local communities. Scientists are still uncertain whether fluoride is essential to human health but the mechanisms of dental benefaction are thought to be two-fold. Firstly, teeth are formed from the calcium mineral hydroxylapatite. During the pre-eruptive stage (i.e. during tooth formation in children up to 12 years old) fluoride can enter the mineral lattice forming fluorapatite, which is stronger than hydroxylapatite. Secondly, fluoride acts as an anti-bacterial agent in the mouth helping to minimise acid-attack on teeth.

In contrast to the possible benefits from low intakes of fluoride, health problems (known as fluorosis) associated with too much fluoride have also been widely reported. Fluoride is a powerful calcium-seeking element and can interfere with the structure of teeth (dental fluorosis) and bones (skeletal fluorosis) in the human body.

Dental fluorosis is an irregular calcification disorder of the enamel-forming cells. Fluorosed enamel is porous, often stained and has brown pits and in its more severe form, is brittle and prone to erosion and breakage.

Endemic skeletal fluorosis is a chronic metabolic bone and joint disease caused by intake of large amounts of fluoride either through water or rarely from foods/air in endemic areas. Human bone tissue is constantly resorbed and redeposited during a lifetime and fluoride is a cumulative toxin, which can enter the bone mineral structure altering the accretion and resorption rates leading to over-calcification of the bone structure and immobilisation of the joints. Although skeletal fluorosis commonly affects older people following long years of exposure, crippling forms of the disease are also seen children in endemic areas.

No effective cures are available for either form of fluorosis; however, the diseases are preventable if fluoride intake is controlled.

Fluoride concentrations in the environment are highly variable and are often controlled by the presence of particular types of rocks or minerals or water. For example, endemic dental and/or skeletal fluorosis has been reported in the East African Rift Valley associated with volcanic rocks and thermal waters. In India and Sri Lanka, fluorosis is linked to alkaline groundwaters and in China problems are associated with particular types of coal. The concentration of fluoride in most waters is controlled by the solubility of the main fluoride-bearing mineral calcite (CaF_2); hence waters that are sodium (Na), potassium (K) and chloride (Cl) rich and calcium (Ca) -poor tend to contain high fluoride concentrations. In general, groundwaters contain more fluoride than surface water resources due to greater contact times with fluoride-bearing minerals in rock-water interactions. In addition to natural sources, man disperses fluoride into the environment. Industrial sources include aluminium and coal industries, fertiliser use and manufacturing processes.

The development of fluoride related diseases in the population not only depends upon the fluoride concentration in the water but on the overall fluoride exposure including inhalation and intake from foods, drinks such as tea and inadvertent sources such as dental products. There is also evidence to suggest that the adverse health effects of fluoride are enhanced by a lack of Ca, vitamins and protein in the diet. In most normal (non occupational) circumstances, fluoride exposure from air is very low (1 ug/m^3) and although the fluoride contents in some food products such seafood (0.01 - 24 mg/l fresh weight) and tea (3.2 - 400 mg/l fresh weight) can be high, in most circumstances, water is the most important human exposure route. Approximately 90% of fluoride ingested in water is absorbed in the gastro-intestinal tract compared to only 30 – 60% of fluoride in food.

In response to the potentially harmful effects of high-fluoride waters, the World Health Organisation (WHO) has set an upper drinking water quality guideline of 1.5 mg/l. Conversely, the WHO also recommend intakes of water containing > 0.5 mg/l in the prevention of dental caries.

In Central Europe, groundwater resources that exceed the upper guideline value of 1.5 mg/l are widespread and dental fluorosis associated with high fluoride concentrations in water has been reported in Ukraine, Moldova and Hungary.

Development of the Risk Assessment Scheme

The overall aim of the risk assessment scheme was to combine geochemical, environmental, and health information to produce fluoride risk avoidance maps for water resource management planning in Central Europe. In order to assess the risks associated with fluoride in the study area, the first phase of the project involved the development of a theoretical risk framework identifying the most likely controls on fluoride so that these factors could be considered for the region and the final GIS scheme devised and risk avoidance maps prepared. The following main controls were included in the framework:

- Geology and Tectonics
- Hydrogeology
- Water Supply
- Fluoride Concentrations in Water
- Water Type
- Anthropogenic Sources of Fluoride
- Disease Prevalence and Other Health Criteria
- Population Density

These controls were assessed in terms of the data available for Slovakia, Ukraine, Moldova and Hungary and the final risk scheme derived as follows:

Population Density - Although an area of high population density constitutes an inherently greater risk than an area of low population density, the risk related to fluoride exposure also depends upon the source of drinking water in an area. For example, a high population density in a region with high-fluoride waters is not necessarily a high-risk area if the population is supplied with low-fluoride waters from elsewhere. Detailed water supply information was not known in all countries and population density information was not available in a consistent format for the whole study region therefore the population data were included in this report and the GIS for background information only.

Geology-Tectonics - Information was not available in a consistent format for all four countries and although the mineral composition of different rock types exerts a fundamental control on fluoride concentrations in water, fluoride concentrations in the same rock-unit can vary considerably and it is difficult to generalise across whole units. Investigations carried out during the project revealed a strong association between high-fluoride waters and tectonically active fault zones in Ukraine, however, not all fault zones are characterised by high-fluoride waters. Whereas geological and tectonic information could give a broad indication of risk in situations were no water chemistry data are available, geological data were included as background information only in the risk assessment scheme developed for the present project as water chemistry data were available in all countries.

Hydrogeology - In any location, the aquifer properties and the hydrogeological regime, exert a major control on water fluoride contents, which can be fundamentally different between aquifers at various depths. However, concentrations also vary within the same aquifer unit and it is difficult to generalise across aquifers. Information about the hydrogeological regimes and high-fluoride aquifers was not available in a consistent format for all four countries and has not been included in the project GIS but has been incorporated into this report. Although major aquifer units used for drinking water supply present an inherently greater risk than minor or local aquifer units, the risk in terms of fluoride exposure also depends on the extent of the water supply network. Detailed water supply information was not known in all countries therefore maps of the main hydrogeological units classified by aquifer importance in Moldova, Slovakia and Hungary were included in the GIS scheme for background information only. No data were available for Ukraine.

Water Type - Chemistry

Physio-chemical controls on fluoride in groundwater dictate that high fluoride waters are generally associated with high alkalinity-Na-K-Cl, low Ca and Mg waters as a lack of Ca inhibits the precipitation of the main fluoride bearing mineral fluorite (CaF_2) hence more fluoride remains in solution. During the present study, a strong association between high fluoride contents and mineralised Na-K-Cl waters was noted in Hungary, Moldova and Ukraine, however high fluoride concentrations (> 1.5 mg/l) occur over a range of water types. In areas where the fluoride contents of waters are unknown, the type of water could be used to give a broad indication of likely fluoride risks, however, during the present project, fluoride water chemistry data were available for the four study countries and information on water types was included in this report for background information only.

Water Type - Uptake

Many studies have shown that the development of dental fluorosis is not only dependent on the total fluoride concentration in the water but is enhanced by low Ca contents and depends upon the speciation of fluoride in the water. Thermodynamic modelling studies of selected Ukrainian waters carried out during the present study suggest that the ratio of F^- to MgF^+ and CaF^+ ionic species may be an indicator of potential health risk, however, these results are preliminary and require further investigation to assess the relationships between health outcomes and different water types.

Water Fluoride -

Water fluoride contents are a fundamental control on disease incidence in the study region and water chemistry data were available nationally for Slovakia, Hungary and Moldova and in the Lvov, Kiev, Odessa and Poltava Regions of Ukraine. These data were categorised according to WHO health risk limits for fluoride in water as follows:

< 0.5 mg/l = dental caries risk
0.5 – 1.5 mg/l = no adverse health effects
≥ 1.5 mg/l = fluorosis risk

and incorporated into the final risk assessment GIS.

Anthropogenic - Sources

High environmental fluoride concentrations in the region are associated with industrial activities such as aluminium production, fertilizer use and coal mining and the locations of these industries were incorporated into the final risk assessment GIS as these sites present potential problem areas. The risks of high fluoride associated with the Ziar nad Hronom aluminium plant in Slovakia were examined in more detail as part of the project.

Disease and Health –

No national surveys of dental fluorosis prevalence have been carried out in Moldova or Ukraine, however prevalence data derived from a number of studies carried out by previous investigators and during the present project were collated. This information and data on fluorosis incidences in Hungary were incorporated into the final risk scheme as the occurrence of dental fluorosis is a fundamental indicator of high-fluoride risk areas where water defluoridation methods may be required. In contrast to these three countries, no incidences of dental fluorosis have been reported in Slovakia. Although the project also considered the risks of dental caries related to low fluoride concentrations in water, this was not the principal topic of investigation, and these data were not purposely collated for the project. Dental caries prevalence data, where readily available, were included in the report and GIS as background information only. The relationships between dietary factors and dental fluorosis were examined in detail in the Falesti Region of Moldova as part of the project and this information was included in the final risk assessment GIS for information. Average dietary fluoride intakes across Ukraine were considered as part of the project and biogeochemical experts demonstrated that in general, intake increases from the north to the south of the country due to increased water consumption in warmer climates. Regional variances in dietary composition were incorporated into the final national risk assessment scheme for Ukraine. It was beyond the scope of this project to examine the relationships between dietary factors and disease in all four study countries, but in addition to the dietary studies in Moldova and Ukraine, general information on the levels of Ca, Mg, P, vitamin and protein intakes for the study countries was incorporated into this report for background information.

Water Supply - Basic information on the water supply regime in the four study countries was incorporated into the risk assessment GIS. In terms of dental caries risk, waters in Hungary, Ukraine and Moldova are not fluoridated before supply to the pubic whereas waters in Slovakia are fluoridated. Information about whether or not high-fluoride waters were utilised for drinking in potential problem areas was taken into account in the high-fluoride risk assessment. For example in terms of high-fluoride risk, if historical incidences of fluorosis associated with high-fluoride waters are known in an area, the area is categorised as high risk in the scheme. However, if the population are now supplied with low-fluoride drinking water from elsewhere, the final risk categorisation is reduced to moderate indicating that although no immediate health problems are evident, the situation should continue to be monitored in the future.

The above datasets were incorporated into the project risk assessment GIS based on the ArcView® software package, which was chosen as it is readily available and widely used in Central Europe. Due to data confidentiality issues, two GIS were developed during the project. Firstly, a generic GIS (called Central.apr) designed for general distribution contains the final risk avoidance maps of each of the study countries. The second GIS (called Country.apr) contains the final risk avoidance maps and all the background data sets and is designed for dissemination by the project partners. Both of the GIS contain two levels of information. Firstly, national data are included providing an overview of fluoride risks at the country level. Secondly, more detailed data are presented for regions examined more fully during the preset project including the following:

- Industrial fluoride contamination and ecological impacts in the Ziar nad Hronom area of Slovakia
- Geochemistry and health relationships in the regions of Falesti, Moldova and Lvov and Odessa in Ukraine
- The hydrochemistry of Lvov, Odessa, Kiev and Poltava regions in Ukraine

With the exception of the national maps of Ukraine, the final risk avoidance maps of dental caries and high-fluoride were based upon a grid-square scheme. In each case the territory of interest was divided into a series of grid squares, the size of which was determined by the sample density of water fluoride data available for the region. Utilising the GIS ability to combine different data layers, for each square, water fluoride content, fluorosis incidence and industrial sources data were coupled with water supply information to determine the overall risk as follows:

Dental Caries Risk -	Water F mg/l < 0.5	= High Risk
	If water is fluoridated (as in the case of Slovakia) the risk is reduced	= Moderate Risk
	Water F mg/l ≥ 0.5	= Low Risk
High –fluoride Risk -	Water F mg/l ≥ 1.5 Or Industrial Source is present Or Fluorosis Incidence is present	= High Risk
	If high-fluoride water is no longer used for drinking, the risk is reduced	= Moderate Risk
	Water F mg/l < 1.5	= Low Risk

Final Risk Avoidance Maps

Due to the limited amount of hydrochemical and fluorosis prevalence information available at the national scale in Ukraine, the national risk avoidance maps were prepared by categorising each region of the country into likely fluoride contents in water and uptake in the population. Although these maps look complete, they are based on very limited information and provide a very generalised picture, as fluoride risks within regions can vary markedly. For example, detailed information for the regions of Lvov, Poltava, Odessa and Kiev was incorporated into the final maps and demonstrates that although the majority of the territory of Lvov, Odessa and Kiev is classified as low-fluoride, dental fluorosis hotspots occur in these regions. Dental fluorosis incidence is associated with mining activities and the upwelling of mineralised waters in tectonically active fault zones in the Chervonograd district of Lvov, with mining contaminated waters in Kiev and with upwelling mineralised waters in fault zones in the Arciz area of southern Odessa Region. The Poltava Region of Ukraine lies in the centre of the Buchak-Kaniv fluoride hydrogeochemical province in the Dnepro-Donetsk basin where high-fluoride waters (containing up to 18 mg/l) are associated with shallow deposits of fluoride-bearing phosphorites. Although lower-fluoride waters are available at depth in this region, drilling costs prevent exploitation of these alternative sources. In addition to Poltava Region, fluoride concentrations in waters are generally high in the Dnepro-Donetsk basin affecting Dnepropetrovsk, Donetsk and Kirovograd but the extent of fluorosis prevalence in the latter three regions is currently unknown.

Dental fluorosis has been reported in all the above regions of Ukraine and detailed geochemistry and health studies carried out during the present project in Lvov and Odessa Regions indicate prevalence rates of 64% among adolescents and children in Chervonograd, Lvov (water fluoride up to 3.8 mg/l) and 90% in Arciz, Odessa (water fluoride 2 – 7 mg/l). In contrast, low-fluoride regions where dental caries may be a problem are located in the west, northwest and south of the country.

High-fluoride risks are also identified in the Falesti, Prut and Chadyr-Lunga regions of Moldova associated with deeper mineralised Na-K dominated waters. Although shallow water resources generally contain much lower fluoride concentrations in these regions, it is desirable that the population use the deeper waters for drinking as the shallow waters are heavily bacterially contaminated. Dental fluorosis has been reported in all these regions of Moldova and geochemistry and health investigations carried out during the present project in Falesti Region indicate prevalence rates of 60% among adolescents and children in the towns of Falesti (water fluoride up to 5.3 mg/l) and Kalarash (water fluoride up to 3.6 mg/l). However, in the town of Cornesti, low fluoride waters are utilised for drinking and dental fluorosis is not prevalent. Areas of Moldova were low-fluoride waters prevail and dental caries may be a problem are located in the north of the country.

High-fluoride waters (containing up to 6.2 mg/l) are a feature of the central Great Hungarian Plain region of Hungary due to migration of deeper thermal waters into shallow Quaternary aquifers. No fluorosis incidence has been reported in this region but it is recommended that the situation be monitored in the future. High-fluoride waters are also associated with the Mosonmagyarovar, Almasfuzito, Ajka Redmud, Ajka Alufactory, Varpalota Alufactory red-mud and aluminium production plants but the extent of environmental contamination and effects on health have not been investigated. Dental fluorosis has been reported historically in the towns of Bar, Dunaszekcso and Herceghalom but alternative low fluoride waters have been supplied to these localities in recent years and the disease is no longer prevalent. However, it is recommended that the situation be monitored in the future. The majority of drinking waters in Hungary contain low fluoride concentrations (< 0.5 mg/l) and dental caries risk is of concern over most of the territory as drinking water is not fluoridated before supply to the public.

High fluoride concentrations in surface and groundwaters (up to 9 mg/l) occur in the immediate vicinity of the Ziar nad Hronom aluminium factory in the Ziarska Kotlina Basin of Slovakia. Previous investigators have carried out detailed environmental studies in this region and no incidences of fluorosis have been reported. The population is supplied with water from elsewhere, therefore, the final risk assessment for this region is reduced to moderate indicating that the situation should continue to be monitored in the future. Apart from this one region, over almost the whole territory of Slovakia, water contents are less than 0.5 mg/l and high fluoride risks are not a problem in this country. Dental caries would be of concern but water is fluoridated before supply to the public and risks are therefore reduced to moderate in the assessment scheme indicating that the situation with regard to low fluoride contents should continue to be monitored in the future.

Geochemistry and health investigations incorporating assessments of drinking water fluoride concentration, dental status and the structural functional state of bone tissue were carried out for the first time in Moldova and Ukraine as part of the present project in Falesti Region and Lvov Region respectively. The results of these studies indicate that intakes of water containing 3 – 4 mg/l fluoride cause dental fluorosis in the population, however, no detrimental effects on bone tissue formation were observed. These results confirm international studies, which indicate that skeletal fluorosis does not manifest until fluoride concentrations of 5 mg/l in water are consumed. Results of dietary surveys carried out in Falesti Region also demonstrate that diets are Ca, protein and vitamin poor, which probably enhances the severity of fluorosis in this region.

Risk Prioritisation and Recommendations

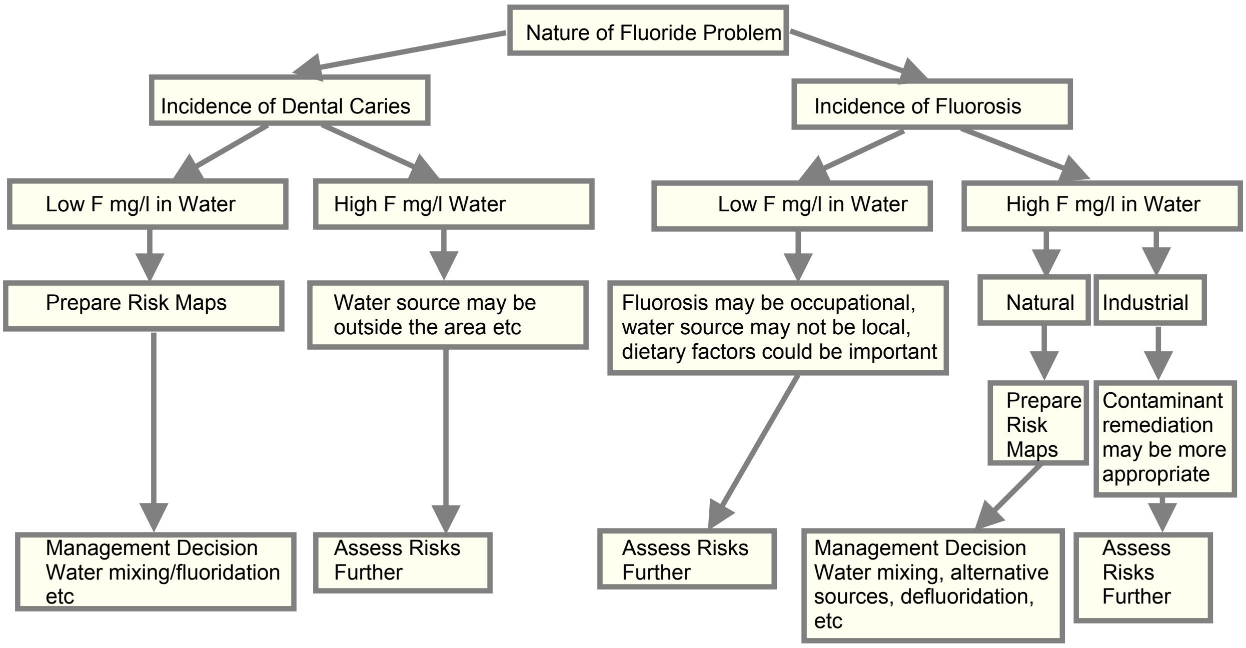
On the basis of the high-fluoride risk assessment, the following areas are prioritised for defluoridation technology:

1. Arciz District, Odessa Region, Ukraine
2. Falesti, Prut and Chadyr-Lunga Regions of Moldova
3. Poltava Region, Ukraine
4. Chervonograd Mining District, Lvov Region, Ukraine
5. Dnepropetrovsk, Donetsk and Kirovograd Regions of Ukraine, however further investigations are necessary to establish the extent of high-fluoride risks in these regions.

It should be noted that the information presented in this report is based on generalised data and any follow-up implementation of defluoridation technologies should incorporate detailed local assessments of environmental fluoride conditions and health effects in the population. In particular, information on fluorosis incidence and water chemistry are sparse for Ukraine and Moldova and it is recommended that these areas should be the focus of future investigations.

Although detailed geochemistry and health studies were carried out for the first time in Ukraine and Moldova during this project, these data are preliminary and it is recommended that more extensive investigations are carried out to elucidate the relationships between water type and fluoride content, diet, physiological status and fluoride –related diseases.

Based on the evidence of this study, the following generic risk assessment scheme is proposed for identifying water fluoride risks in other areas:



1 Introduction

Fiona Fordyce and Kamil Vrana

This report outlines the development of a risk assessment geographic information system (GIS) for Central Europe carried out as part of a project to assess and develop remediation technologies to combat high fluoride (F) concentrations in drinking water in Ukraine, Moldova, Hungary and Slovakia: INCO-COPERNICUS IC15-CT98-0139 'Water Quality Improvement Through Fluoride Reduction in Groundwater of Central Europe'. Like many naturally occurring elements, fluoride can cause human health problems if ingested in excess and the primary aim of the project was to develop technologies to remove fluoride from drinking waters. The second aim of the project was to develop a risk assessment GIS to predict areas were high-fluoride waters or fluorosis (fluoride toxicosis) may occur in Central Europe so that remediation technologies can be deployed most effectively. Between December 1998 and December 2001, hydrogeological, geochemical, medical and GIS experts from Ukraine, Moldova, Hungary, Slovakia and the UK were involved in the development of the risk assessment GIS. In the original project plan, the geographic focus centred on Ukraine, Moldova and Hungary, however, information for Slovakia was also included in the project as excellent geochemical data were available for Slovakia and enhanced the overview of fluoride risks in the study region. The risk assessment scheme and GIS have been developed on the basis of data available for each country. During the course of the project it was apparent that in addition to human health problems associated with high- fluoride waters, many areas of Central Europe were at potential risk from dental caries related to low fluoride concentrations in drinking water. A dental caries risk assessment was also devised as part of the study.

The development of the project risk assessment GIS was based upon the collation and digitisation of existing information relevant to fluoride risk in Ukraine, Moldova, Hungary and Slovakia assembled for the first time in a readily accessible form to aid water management. In addition, geochemistry and health studies to examine in more detail the relationships between high-fluoride drinking waters and health effects in the population were carried out in Moldova and Ukraine. This is the first time that the dental-skeletal and physiological status of the population and the hydrogeochemistry have been investigated simultaneously in these countries and the data contribute to a state-of-the-art assessment of fluoride risk in Central Europe.

This report contains an overview of the human health problems associated with fluoride in drinking water and outlines the development of a theoretical risk assessment framework for the project. Results of an international literature review are discussed in the context of the study area and the information available for each country is described. The rationale behind the final risk assessment scheme for Central Europe is presented and fluoride risks in each country are reviewed. Recommendations for future follow-up and the development of similar risk assessment schemes in other areas are also suggested.

2 Environmental Fluoride and Health

Fiona Fordyce, Vladislav Povorosnuk, Edward Zhovinsky and Kamil Vrana

2.1 INTRODUCTON

This chapter provides background information on the occurrence and controls on fluoride in the environment and influences on health collated from Central European expertise and from a review of international literature. Data from these two data sources have been combined into a project bibliography (Chapter 10) designed to aid the development of the GIS and to act as a reference source for future users of the fluoride risk assessment in Central Europe.

2.2 FLUORIDE INTERNATIONAL LITERATURE REVIEW

The review of international literature was carried out on existing references held by the British Geological Survey (BGS) and on the electronic bibliographic databases BIDS ISI® (scientific citation index) and MEDLINE® (medical citation index). Information on these latter two databases was available from 1981 – 2000 and 1966 – 2000 respectively. The keywords used in the searches are listed in Table 2.1.

Table 2.1 Keywords used in digital database searches

List of Keywords			
Moldova (n)	Fluoride	Fluorosis	Water
Ukraine (ian)	Calcium	Diet	Hydrogeochemistry
Slovakia (n)	Vitamin D	Dental	Hydrogeology
Hungary (ian)	Vitamin C	Pollution	Groundwater

Words were used individually and in combination during the search

Approximately 26,000 references to fluoride and 1000 references to fluorosis were returned from the electronic database search. The majority of these references reflect the scientific processes involved in the development of dental products and the on-going debate in the United States and other Western Countries on the use of fluoride in dental practice. A significant proportion of the literature also refers to the benefits and hazards associated with the use of fluoride to combat osteoporosis. There is a wealth of literature on the effects of fluoridated dental products and drinking water on dental health and on the uptake of fluoride in children. The literature contains arguments both for and against the fluoridation of water to aid dental health reflecting increasing concern in the United States over elevated fluoride intakes.

Pertinent to this study, 170 references from the international literature were collated in the review. Of these, several were references to dietary intakes and dental uses of fluoride in Hungary but no information on fluoride in groundwater or fluorosis in Hungary, Ukraine or Slovakia was returned in the international searches. Two references to fluoride in soils in Moldova were retrieved. Only a small proportion of the literature, largely from developing countries, was concerned with the uptake of fluoride from natural waters and the factors controlling fluoride intake in humans such as hydrochemistry and diet. This information and data from approximately 210 references from Central Europe are summarised in the following sections of this report.

2.3 OCCURRENCE OF FLUORIDE IN THE ENVIRONMENT

2.3.1 Geochemical Distribution

Fluorine, is a naturally occurring chemical element, which exists in the rocks, soils, waters, air, plants and animals on Earth. It is the lightest member of the halogen elements and is the 13^{th} most abundant naturally occurring element in the Earth's crust. It is the most electronegative and reactive of all the elements. As a result, elemental fluorine does not occur in nature but is found as fluoride mineral complexes. Fluorides account for 0.06 – 0.08% of the Earth's crust but their average crustal abundance is low (300 µg/g, Tebbutt, 1983, Table 2.2). Unlike some of the other halogen elements, the majority of fluoride in the Earth's surface environment is derived from rock minerals whereas other sources such as airborne seawater and anthropogenic activities constitute a relatively small proportion (Fuge, 1988; Lahermo, 1991) (Tables 2.2 and 2.3).

Table 2.2 Average fluoride concentrations in selected materials

Material	Fluoride Content	Reference
Earth's Crust	300 µg/g	(Tebbutt, 1983)
Igneous Rocks	715 µg/g	(Hem, 1992)
Sandstones	392 µg/g	(Hem, 1992)
Shales	575 µg/g	(Hem, 1992)
Limestones	842 µg/g	(Hem, 1992)
Seawater	1.3 mg/l	(Hem, 1992)
Freshwater	0.5 mg/l	(WHO, 2000a)
Groundwater	< 10 mg/l	(WHO, 2000b)
Sodic Lakes (East Africa)	690 – 2800 mg/l	(WHO, 2000a)
Air (non industrial)	0.05 – 1.90 ng /m^3	(WHO, 1986)
Air (including industrial)	3 ng/ m^3	(WHO, 2000b)
Air (industrial)	70 ng/m^3	(WHO, 2000b)
Vegetables and Fruit	0.1 – 0.4 µg/g	(WHO, 1986)
Kale	≤ 40 µg/g fresh weight (FW)	(WHO, 2000b)
High F Barley and Rice	2 µg/g	(WHO, 1986)
Meat	0.2 – 1.0 µg/g	(WHO, 1986)
Fish	2 – 5 µg/g	(WHO, 1986)
Milk	0.02 – 0.05 mg/l	(WHO, 1986)
Tea	≤ 400 µg/g dry weight	(WHO, 2000a)
Toothpaste	1000 – 1500 µg/g	(WHO, 1986)
Dental Gel	2500 – 2400 µg/g	(WHO, 1986)
Fluoride Tablets	250 – 1000 µg/ tablet	(WHO, 1986)

WHO = World Health Organisation

Table 2.3 Range of fluoride concentrations in some natural materials (Zhovinsky, 1979a)

Material	Fluoride Content
Earth's Crust	25 – 10 000 µg/g
Rocks	300 – 800 µg/g
Soil	30 – 320 µg/g (mean 200 µg/g)
Fresh Water	0.01 – 0.8 mg/l (more rarely 0.8 – 20 mg/l)
Saltwater	0.7 – 1.4 mg/l
Air	$2 \times 10^{-6} – 4 \times 10^{-4}$ mg/m^3
Vegetable Tissue	0.05 – 3 µg/g
Soft Animal Tissue	0.05 – 3 µg/g
Hard Animal Tissue	100 – 800 µg/g

Fluorine has a propensity to acquire a negative charge and in solutions forms F^- ions. The geochemical behaviour of fluoride ions resembles that of hydroxyl ions (OH^-) due to the similarities in charge and radius and fluoride often substitutes for hydroxyl ions in mineral structures (Hem, 1992). Approximately 150 fluoride-bearing minerals have been identified. Calcium fluoride known as fluorite (CaF_2), the most common fluoride mineral has low solubility and occurs in both igneous and sedimentary rocks. Other minerals that contain significant concentrations of fluoride include apatite ($Ca_5(Cl,F,OH)PO_4$); cryolite (Na_3AlF_8); amphiboles such as hornblende; pyroxenes; micas and aragonite (WHO, 2000a). Table 2.4 lists the number of fluoride-bearing minerals in some different chemical groups and examples of the most important mineral types in each group.

Table 2.4 Fluoride bearing minerals (Frencken, 1990)

Mineral Group	Number of Minerals	Most Important Minerals
Silicates	63	Amphiboles, Micas
Halides	34	Fluorite, Villiaumite
Phosphates	22	Apatite
Others	30	Aragonite

Fluoride is commonly associated with volcanic activity, fumarolic gases, volcanic glasses (obsidian), geothermal thermal waters and granitic rocks. Although the total volume of hydrogen fluoride (HF) in volcanic gases amounts to only 1 or 2 %, the fluoride concentration may reach several thousand g/cm^3. High pH thermal waters such as those of the East African Rift, contain exceptionally high fluoride concentrations (Edmunds, 1995) Table 2.2.

2.3.2 Hydrogeochemistry

Fluoride in most waters is predominately in the free F^- ionic form although at low pH, hydrogen fluoride (HF) may be produced (Hem, 1992). Fluoride also forms complexes with aluminium (Al), beryllium (Be), iron (Fe^{3+}), boron (B) and silica (Si), however, the main control on dissolved fluoride in most waters is fluorite (CaF_2) solubility such that in waters containing sufficient Ca concentrations, fluorite will be in equilibrium. Hem (1992) demonstrated that in the presence of 10^{-3} M/l Ca, fluorite concentrations should be limited to 3.1 mg/l assuming a solubility product of $10^{-10.58}$ for fluorite. It is therefore an absence of Ca in solutions, which favours the stability of high-fluoride waters (Edmunds and Smedley, 1996). It is estimated that cryolite (Na_3AlF_6) solubility is not a limiting factor for fluoride concentrations in most waters. For example, in a solution containing 2300 mg/l sodium (Na) and 2.7 mg/l Al (only possible in very low pH waters) the concentration of fluoride would only be limited to 30 mg/l (Hem, 1992). High-fluoride waters can therefore be expected in the following situations (Edmunds and Smedley, 1996):

- *Fluoride minerals (or F-substituted minerals such as biotite) are present*
- *Ca-poor waters*
- *Waters where cation exchange of Na for Ca occurs*

There are many examples worldwide where fluoride problems have been linked to these particular types of waters. In India, studies demonstrate that high-fluoride waters have high alkalinity (bicarbonate (HCO_3) > Ca and Mg), low water hardness, low Ca and Mg contents and very often, greater Mg than Ca contents. In these waters, calcite and dolomite precipitation removes Ca and Mg whereas fluorite is the last mineral to reach equilibrium and precipitate (Bhagan et al., 1996a) (Bhagan et al., 1996b) (Jacks et al., 1993). Similarly, (Teotia et al., 1981) report that high-fluoride waters in India are Na-Cl (chloride) rather than Ca-Mg dominated and have low hardness and increased alkalinity. High fluoride contents in Chinese waters (up to 45 mg/l) occur in low-Ca, high-Na thermal waters of pH > 7.5 (Fuhong and Shuqin, 1988). Lui and Hua (1991) also noted a relationship between fluoride-rich waters in China and Na-dominance due to the high solubility of cryolite (Na_3AlF_6). High-fluoride waters in Kenya are also reported to contain high HCO_3-CO_3 and low Ca-Mg (Nanyaro et al., 1984).

In areas where geological formations contain fluoride minerals, the groundwater through its direct contact with the rocks usually has higher fluoride contents than adjacent surface waters. Fluoride concentrations in most waters are usually below 1 mg/l, however, in groundwater, contents can vary between 0.1 to over 100 mg/l depending factors such as:

- *Seasonal recharge - in shallow groundwater, the fluoride content is usually lower during the wet season than the dry season due to dilution by infiltrating rainwater.*
- *Depth - deep groundwaters generally contain more fluoride due to greater contact times with fluoride-bearing minerals and the influence of deep hydrothermal waters*
- *Fluoride minerals - groundwater fluoride concentrations may be highly variable at the same locality depending on the presence or absence of fluoride-bearing minerals at different depths.*

Fluoride concentrations in surface waters and groundwaters are commonly controlled by the following natural and man-made processes (Mjengera, 1998):

- *Leaching of rocks in areas where lithologies such as volcanic ash, exhalations and sublimates contain very high concentrations of soluble fluorides.*
- *Rainwater may acquire low concentrations of fluoride from marine aerosols and continental dusts.*
- *Industrial emissions such as freons, organofluoride compounds produced by burning fossil fuels and dust from cryolite processing*
- *Industrial effluents from processes using fluoride-bearing compounds.*
- *Fluoride in the run-off from agricultural processes using phosphatic fertilisers*

In addition to these factors, fluoride concentrations in waters are controlled by the presence or absence of sorbant materials. The clay minerals gibbsite, kaolinte and halloysite are effective sorbants of fluoride in water and can limit the amount of fluoride in solution, especially under low pH conditions.

2.3.3 Soil Chemistry

The mineral, chemical and mechanical composition of soil-forming rocks greatly influences the distribution and concentration of fluoride in most soil horizons. Other common sources of fluoride in soils include fluoride-bearing minerals, volcanic gases, atmospheric precipitation and mineral fertilizers. Fluoride from the atmosphere is dissolved in soil pore waters and is distributed in the redox zone. The main factor controlling fluoride accumulation in soils is sorption by clay minerals, hydroxides and organic substances. In general terms, there is a close association between the acidity of soil and its ability to retain fluoride (Zhovinsky, 1994c). Bowen (1979) suggests an average fluoride concentration of 200 µg/g for most soils.

2.3.4 Fluoride in the Biomass

Fluoride is found in fluoroacids and nucleocidine but is not essential to bacteria, algae, fungi and higher plants. The element accumulates in the plant species *Accacia georginae, Dichapetalum ssp., Gastrolobium grandiflorum* and *Porifere Dysudea crawshayi.* Fluoride toxicity in plants causes chlorosis or yellowing of young leaves and growth reduction and generally manifests at contents above 5 µg/g (Mankovska, 1996).

Bowen (1979) suggests average fluoride concentrations of 0.02 - 24 µg/g in most plants, whereas the total fluoride content of the world biomass has been estimated by Markert (1992) as 3.682 x 10^6 tonnes.

2.3.5 Anthropogenic Sources

In addition to natural sources of fluoride, anthropogenic sources include coal burning, the production of coke, glass, ceramics and electronics; steel and aluminium processing and pesticide, fertiliser and electroplating operations (Bartram and Balance, 1996). Cryolite is used as a catalyst to facilitate aluminium electrolysis and environmental contamination with fluoride around aluminium plants has been well documented in many countries. The industrial processing of fluoride is rising sharply around the world. During the last two decades, fluoride usage in the USA increased four times from 0.4 to 1.5 million tonnes. In the year 2000, the global use of fluoride reached 15 million tonnes. During the 1970s of 6.4 million tonnes of fluoride processed by world economies, it is estimated only 0.4 tonnes became industrial products and the remainder was dispersed to the environment as waste and losses (Okunyev et al., 1987).

2.4 FLUORIDE DEFICIENCY AND EXCESSS - EFFECTS ON HUMAN HEALTH

Biogeochemical processes and human industrial activity determine the distribution and dispersion of fluoride in the environment. Like several other naturally occurring elements, fluorides can enter the human body by ingestion, inhalation and skin absorption via air, water, food, medicines and cosmetics and have an effect on human health.

2.4.1 Deficiency

Dental caries is one of the most widespread diseases affecting mankind. It is estimated that in economically advanced countries, dental caries prevalence is currently 95 – 98% and these rates are rising in all cultures around the world. Caries is the most common cause of tooth loss, inhibited mastication and poor digestion. During the 1930s - 1950s, studies carried out in the USA and Europe demonstrated a link between improved dental health and the introduction of fluoridated toothpaste and fluoridated drinking water to local communities. Caries prevalence in residents of localities where the water fluoride content was 1 mg/l or more was found to be almost half that of communities where drinking water contained 0.1-0.3 mg/l fluoride (Dean et al., 1942a) (Dean et al., 1942b). These observations led to further studies into the prophylaxis of caries by endogenic use of fluoride compounds. Scientists are still uncertain whether fluoride is essential to human health but the mechanisms of dental benefaction are thought to be two-fold. Firstly, teeth are formed from the calcium mineral hydroxylapatite. During the pre-eruptive stage (i.e. during tooth formation in children up to 12 years old) fluoride is thought to accelerate the mineralisation process and can enter the mineral lattice forming fluorapatite, which is stronger (less soluble) than hydroxylapatite. Experiments on rats have demonstrated activation of mineralisation and increases in dental cement growth in animals receiving higher fluoride concentrations. Secondly, fluoride acts as an anti-bacterial agent in the mouth helping to minimise acid-attack on teeth (Brown and Konig, 1977; Jenkins, 1967; Lukomsky, 1955; Pashayev et al., 1990; Petrovich et al., 1995; Voynar, 1960).

2.4.2 Excess

The detrimental effects of high-fluoride intake on the structure of dental hard tissue were established by Smith et al., (1931) who proved a connection between mottled enamel and excess fluoride in drinking water. This condition, named dental fluorosis, is an irregular calcification disorder of the enamel-forming cells. Fluorosed enamel is porous, often stained and has brown pits and in its more severe form, is brittle and prone to erosion and breakage.

Subsequent investigations revealed that fluoride also affects the human skeletal structure as it is a powerful calcium-seeking element. Endemic skeletal fluorosis is a chronic metabolic bone and joint disease caused by intake of large amounts of fluoride either through water or rarely from foods/air in endemic areas. Human and other animal bones are composed of hydroxylapatite but this mineral and fluorapatite are end-members in the apatite solid solution series therefore fluoride exchanges readily with the OH^- ion in the apatite structure increasing the brittleness and decreasing the solubility of the bone structure (Dissanayake and Chandrajith, 1999; Skinner, 2000). The bones of the human body are constantly resorbed and redeposited during a life-time and high fluoride intakes increase the accretion, resorption and Ca-turnover rates of bone tissue affecting the homeostasis of bone mineral metabolism (Krishnamachari, 1986a). Calcification of soft tissues such as ligaments can also occur. Although approximately 80% of fluoride entering the body is excreted mainly in the urine, the remainder is adsorbed into body tissues from where it is released very slowly (WHO, 1996a). Repeated or continuous exposure to fluoride therefore causes accumulation of fluoride in the body. Fluoride is a cumulative toxin and although skeletal fluorosis commonly affects older people following long years of exposure, crippling forms of the disease are also seen children in endemic areas. Hyperthyroidism is a secondary effect of the condition (WHO, 1996a).

In terms of effects on soft tissues, problems associated with *occupational* exposure have been well documented. At very high doses fluoride interferes with carbohydrate, lipid, protein, vitamin, enzyme and mineral metabolisms and can lead to haemorrhagic gastroenteritis, acute toxic nephritis and damage to the liver and kidneys. The acute lethal dose is 2 g (WHO, 1996a). Long-term exposure to fluoride reduces the iodine accumulation activity of the thyroid resulting in a reduction in triiodothyronine production, an increase in thyrotropic hormone levels in blood-serum and irregularities of the androgen status (subclinical hypothyrosis).

In contrast, data on the effects of *general environmental* fluoride exposure on human soft tissue homeostasis are equivocal. There is some evidence to suggest that continuous fluoride intoxication provokes hypertension and chronic ischemic heart disease (Krishnamachari, 1986b). Some studies have shown that clinically acute fluoride intoxication manifests as nausea, sickness, diarrhoea, stomach ache and heart rate disorders at concentrations of 6.5 –20 mg/l in water. Due to the inhibition of cholinesterase glycolysis and the formation of complex fluoride and Ca compounds in extracellular fluids, such metabolic disorders are observed as hypercalcemia, hypocalcemia and hypomagnesemia.

2.5 ENVIRONMENTAL EXPOSURE AND FLUORIDE UPTAKE

2.5.1 Fluoride in Drinking Water

The World Health Organisation (WHO) estimate that in most situations, the major pathway for fluoride to enter the human body is via drinking water and in response to the potentially harmful effects of the element, have set a drinking water quality maximum admissible concentration (MAC) of 1.5 mg/l (Table 2.5). Numerous clinical and experimental studies show a variety of influences of fluoride on human health depending upon the content in drinking water (Gnatyuk, 1988) (Grigoryeva et al., 1993), (Rozier, 1999). Research has shown that fluoride concentrations between 0 – 0.5 mg/l favour dental caries development whereas concentrations between 1.5 - 5 mg/l can result in dental fluorosis. Ingestion of 5 - 40 mg/day fluoride via drinking water can produce skeletal deformities, and knock knees (genu valgum) have been reported in adolescents receiving > 10 mg/day in water accumulated from birth (WHO, 1996b). However, fluoride contents of between 0.5 – 1.5 mg/l have a beneficial effect, reducing caries development. The relationships between water fluoride content and fluorosis prevalence determined in some previous investigations are outlined in Table 2.6.

Table 2.5. International guidelines for fluoride concentrations in drinking water and possible health effects

Guideline Value	F mg/l Water	Possible Health Effects
Recommended Minimum	0.5	Dental cavities may occur at lower concentrations
Optimum Range	0.5 – 1.5	No adverse health effects, cavities decrease
Recommended Maximum	1.5	Mottling of teeth and dental fluorosis may occur at higher concentrations. Association with skeletal fluorosis at > 3 mg/l concentrations

From: Guidelines for Drinking Water Quality. 1996. World Health Organisation, Geneva.

Table 2.6 Relationships between water fluoride content and fluorosis prevalence from previous studies

F mg/l Water	Fluorosis Prevalence %
0.8	10 – 12 (mild forms)
1.0 – 1.5	20 – 30
1.5 – 2.5	30 – 45
> 2.5	> 50

(Eklund et al., 1987; Gabovych and Ovrutsky, 1969; Gnatyuk et al., 1988; Grigoryeva et al., 1993; Heller et al., 1997a+b; Jackson et al., 1999; Kasyanenko et al., 1981; Larsen et al., 1987; Mascarenhas, 1999; Nikolishyn, 1999; Pavlyenko et al., 1987; Rozier, 1999)

It is estimated that more than 260 million people across the world consume drinking water containing more than 1.5 mg/l fluoride many of which live in tropical countries (WHO, 1984). Endemic dental and/or skeletal fluorosis have been reported in the East African Rift Valley associated with volcanic rock types and thermal waters (Bhagan et al., 1996a). In India and Sri Lanka, fluorosis is linked to alkaline groundwaters (Susheela, 1999; Dissanayake, 1996) and in China problems are associated with high-fluoride groundwaters and inhalation of fluoride from coal smoke (Zheng et al., 1999). Approximately 25 million people suffer from fluorosis in India alone (WHO, 2000a). Table 2.7 lists some of the countries where health problems associated with > 1.5 mg/l fluoride in drinking water have been identified.

Table 2.7 Some countries where human health problems associated with > 1.5 mg/l fluoride in water have been reported

Region	Country
Africa	Ethiopia, Sudan, Kenya, Tanzania, South Africa, Nigeria, Senegal, Algeria, Egypt, Zimbabwe, Malawi, Morocco, Uganda, Somalia
Asia	India China, Korea, Thailand, Sri Lanka, Indonesia, Yemen, Pakistan
South America	Mexico, Peru, Ecuador, Chile, Argentina
Europe	Ukraine, Moldova, Finland, Sweden, Greece, UK, Germany, Poland, Hungary

The WHO water quality guidelines are based on consumption of 2 l/day and an average intake of 1.2 - 3.4 mg fluoride from water. However, conditions may vary between climatic regions and socio-economic groups and total fluoride exposure should be considered when assessing the affects of fluoride in water. In tropical countries for example, water consumption is much higher than in temperate regions as the ambient temperatures are higher and the physical workload generally greater. Adults consume on average 2 to 5 litres per capita per day and sometimes up to 10 litres per capita per day. Therefore the MAC need to be lower in these conditions. A study carried out in Senegal, for example, found dental fluorosis occurred in populations consuming water with only 0.6 mg/l fluoride and skeletal fluorosis was endemic in areas where water fluoride contents were greater than 7.0 mg/l (Frencken, 1990). In both tropical and temperate regions, a number of studies indicate that dental fluorosis can occur when water fluoride concentrations are below 1.5 mg/l (Weeks et al., 1993; Bhagan et al., 1996b; Dissanayake and Chandrajith, 1999) and dental mottling in children has been reported when fluoride concentrations in water are as low as 0.8 mg/l. Conversely some communities who intake water with more than 1.5 mg/l fluoride do not suffer dental fluorosis. This may be because health outcomes are not just dependent upon the total fluoride concentration in the water but may be influenced by other water chemistry and dietary parameters. In addition to the international water guidelines, the WHO recommend that the total intakes at 1, 2 and 3 years of age should be limited to 0.5, 1.0 and 1.5 mg/day respectively with not more than 75% in soluble water form and that adult intakes of > 5 mg/day from all sources pose a health threat (WHO, 1996b).

2.5.2 Fluoride in Air, Foodstuffs and Other Sources

In addition to water consumption, total fluoride uptake also depends upon dietary sources and inhalation. Due to the presence of continental dusts, the industrial production of phosphate fertilisers, coal ash and gases from burning fuels and volcanic activity, fluoride is widely distributed in the atmosphere, however, in non-industrial areas, typical concentrations in air are low ranging from 0.05 to 1.90 mg/ m^3. Average fluoride exposures from air are estimated at 1 ug/m^3 and are insignificant in normal circumstances (WHO, 1996a). In areas where high-fluoride coal is burned or phosphatic fertilisers are produced and used, exposure via inhalation can cause health problems. For example, high concentrations of atmospheric fluoride occur in areas of Morocco and in China where it is estimated that more than 10 million people suffer from fluorosis related to the burning of high-fluoride coal (Zheng et al., 1999). In gaseous and particulate form, the degree of toxicity of different fluoride chemical species is in the order $F_2 > F_2O > H_2F_2 > H_2SiF_6 > BF_3$ whereby gaseous fluoride species are more toxic than particulates in air.

Exposure to fluoride in foodstuffs is normally less important than water as the fluoride content of most foods is low (< 10 mg/kg). However, seafood (0.01 - 24 mg/l FW), tea (3.2 - 400 mg/l FW) and some wines (0 - 6.34 mg/l) can contain relatively high quantities. Despite the fact that fish protein may contain up to 370 mg/kg fluoride and fluoride accumulates in the bones of canned fish, even in mixed diets with relatively high fish consumption, it is estimated that average daily fluoride intakes are only about 0.2 mg (WHO, 1996b). Vegetables and fruits normally contain low concentrations of fluoride, but some fruit juices have elevated concentrations as fluoride is used as a pesticide during crop growth (Kiritsy et al., 1996). High levels of fluoride have also been reported in barley, rice, taro, yams and cassava (WHO, 1996b). A study in two endemic fluorosis regions in Tanzania with water supplies containing 0.2 – 0.8 mg/l fluoride demonstrated that the impact of dental fluorosis was lower in coastal communities despite the fact that they consumed fish and tea (fluorosis rate 7-46%, no severe forms) than in inland villages where a high-fluoride magadi salt was used in cooking (fluorosis rate 53-100%, severe forms highly prevalent 18-97%) emphasising the need to consider all sources in exposure assessments (Mabelya et al., 1997).

Significant quantities of fluoride can also be absorbed inadvertently from dental applications. Toothpastes typically contain 1.0 – 1.5 g/kg fluoride and studies estimate intakes of 50 ug per brushing and 2 mg per use with mouthwash (Sabeiha and Rock, 1997). It is also estimated that swallowing of toothpaste may contribute between 0.5 – 0.75 mg/day fluoride in children (WHO, 1996b) and as a result, low fluoride child-toothpaste is now available in many countries.

There is increasing evidence to suggest that the fluoride content of infant formulas can have a negative impact on teeth. In a study carried out in six countries, infant formula made with distilled water was found to supply 30 µg/day fluoride and the average daily fluoride intake of 3-month-old babies was estimated at 3-74 µg (WHO, 1996b). Heilman et al. (1997) report evidence of dental mottling in infants receiving 0.5 mg/day fluoride from baby formula and after weaning, in children given 1 mg/day fluoride as dental supplements. In areas of low fluoride concentrations in water, fluoride levels in breast milk are approximately 5 µg/l, however, human milk containing 7 µg/l has been reported in an area where the fluoride content of water was 1 mg/l (WHO, 1996b).

Some daily dietary intake estimates for different countries are listed in Table 2.8.

Table 2.8 Estimates of daily dietary fluoride intake (WHO, 1996b).

Country	F mg/l Water	Adult Intake mg/day	Children Intake mg/day
USA	-	0.2 – 3.1	0.5
Germany	-	0.51	0.25
USA	< 0.3	0.86	0.21 – 0.23
USA	0.7	1.85	0.42 - 0.62
Japan	-	1.12 - 1.34	
India	2 – 11	6 - 30	

2.5.3 Fluoride Uptake

More than 90% of the fluoride present in water is absorbed in the human body compared to only 30 – 60% of fluoride in foodstuffs (WHO, 1996b). Even fluoride in liquid products (milk, etc) is assimilated 10% less than in water (Zhovinsky, 1994d). Interestingly, experiments on rats have shown that in small quantities, solid fluoride compounds (NaF, Na_2SiF_6, K_2SiF_6, Na_3AlF_6, $NH_4.2SiF_6$, CaF_2) are absorbed more readily than at higher concentrations, for example, 96% adsorption of fluorite and 93% adsorption of cryolite (Krishnamachari, 1986b). In the stomach under acid conditions, up to 40% of the ingested fluoride can be absorbed following conversion to hydrogen fluoride (HF). Fluoride that is not absorbed in the stomach is subsequently ingested in the upper intestine independent of pH (Whitford, 1997). Dental fluorosis is thought to develop when more than 0.1 – 0.15 mg per 1 kg of body weight fluoride is adsorbed (Zhovinsky, 1994d).

Total fluoride absorption in the human body not only depends upon the concentration in water but on the proportion of liquid to solid matter (food) consumed and the composition of the food. Studies have shown that Ca contents up to 200 mg/l, Mg contents up to 160 mg/l, Fe contents up to 20 mg/l, and PO_4^{2-} contents up to 80 mg/l have little influence on fluoride absorption independently but in combination, these elements can have an effect (Zhovinsky, 1994d). The intake of cations such as Ca, Mg and Al, which form insoluble complexes with fluoride has a protective effect against absorption (Jowsey and Riggs, 1978) (Whitford, 1997) whereas the presence of PO_4^{2-}, Fe, SO_4^{2-} and Mo enhances absorption (Zhovinsky, 1994d).

Many studies demonstrate that the prevalence and severity of fluorosis are influenced by complex interactions between dietary factors. Protein deficiency is thought to enhance the effects of fluorosis as proteins aid the absorption of Ca in the body (Zheng et al., 1999; Jacks et al., 1993). In a nutritional study of Chinese children suffering fluorosis, protein intake was found to be above the national standards, however, children with Ca-poor diets who did not consume milk displayed the most severe forms of the disease (Chen and Lin, 1997). In another Chinese study of two communities with similar fluoride intake but differing nutritional status, the community with lower Ca and protein diets suffered more fluorosis (Li et al., 1996). In addition to the influence of proteins, there is some evidence to suggest that high fat diets may exacerbate the adverse health affects of fluoride (Krishnamachari, 1986b).

Vitamins C, D and E have also been implicated in the pathogenesis of fluorosis. Vitamin C aids the hydroxylation of prolein, one of the most important amino acids of the basic bone building material collagen. Hence, healthy collagen is required if bones are to be calcified correctly (Susheela, 1999). Vitamin D is known to aid Ca absorption in the body and deficiency has been both suggested (Misra et al., 1992; Rajyalakshmi and Rao, 1985; Teotia and Teotia, 1994) and disputed (Mithal and Godhole, 1992) as a contributory factor in fluorosis in India. Evidence for the prophylactic effect of vitamin E against fluorosis has also been demonstrated in rats (Burgstahler, 1985).

In summary, the absorption of fluoride in the gastrointestinal tract depends upon:

1. *The type of fluoride compound (organic, inorganic, etc), its form and solubility*
2. *The concentration of fluoride ingested*
3. *The nature and volume of accompanying compounds*
4. *Nutritional status*
5. *Physiological status (age etc)*

Once absorbed, the majority of fluoride (approximately 60–80%) is retained in the skeleton and the average fluoride content of human bones is 300 - 7000 ug/g dry tissue. In contrast, fluoride levels in blood are normally very low typically ranging from 0.04 mg/l in normal circumstances to 0.5 – 0.8 mg/l in fluorosis populations. For example, studies in Algeria report 0.6 mg/l in blood in an area with 3 μg/l fluoride in water (WHO, 1996b). The retention of fluoride in bones versus secretion via the kidneys (and partly the skin) plays the most important role in the homeostatic mechanism responsible for maintaining the fluoride concentration in blood. A certain proportion of fluoride (data from different studies estimates 15 – 50%) remains in an ionic state and the remainder forms albumin bonds with Ca acting as a bond mediator. The lowest fluoride concentrations are found in body soft tissues, which generally contain 0.5-1mg/kg however; concentrations of 3 – 50 mg/kg are not uncommon in epidermal tissues. Even in cases of chronic fluorosis, only very slight increases in soft tissue fluoride concentrations are observed (Zhovinsky, 1994d).

2.6 PATHOGENESIS OF DENTAL AND SKELETAL FLUOROSIS AND DENTAL CARIES

2.6.1 Mechanisms of Dental Fluorosis

It is thought that dental fluorosis manifests during enamel formation in the pre-eruptive phase of tooth development and can affect both temporary and permanent teeth. At the end of tooth development and mineralisation, the enamel and dentin become less penetrable for fluoride ions therefore the rate of inclusion and mobilisation of fluoride slows dramatically. Fluoride is incorporated into dental tissues hematogenically through pulp and saliva (or water) contact with upper layers of enamel. The fluoride content in different sections of enamel from the same tooth can vary greatly (from 50 to 560 μg/g) and teeth in the same jaw can have differing fluoride contents (Gnatyuk, 1988; Krylov and Pyettsold, 1982; Redinov, 1984; Warren et al., 1999; Zhylenko and Dyeshchyuk, 1975).

The mechanism of change in dental hard tissue due to fluoride excess is still open to debate. Sodium fluoride (NaF) is known to inhibit protein synthesis (Avtsyn and Zhavoronkov, 1981a+b; Holland, 1980), which has lead some workers to believe that fluoride cytotoxicity is related to a reduction in protein synthesis. Fluoride is thought to affect the enameloblasts while the dental epithelial organ is under development, disrupting the formation of normal enamel (Den Besten, 1999; Den Besten et al., 1992; Gerlach et al., 2000; Patrikyeyev, 1958).

According to Lukomsky (1955) dental fluorosis occurs as a result of fluoride interaction with Ca, Mg, manganese (Mn) and other elements in the dental hard tissues destroying the biological activity of the these elements leading to enamel injuries. Voynar (1960) and Smolyar (1974) found a reduction in alkaline phosphatase activity in unformed dental tissues resulting in mineralisation disorders, however, this finding is not supported by other researchers (Babyel et al., 1968; Ericson and Angamar-Mansson, 1983). Fedorov et al. (1972) suggest that dental fluorosis is related to the more aggressive chemical activity of fluoride compared to iodine such that fluoride reduces the amount of iodine in the thyroid gland resulting in functional disorders. Studies demonstrate that ingested fluoride is absorbed quickly into the blood and blocks thyroid activity. It should be noted, however, that even if fluoride is both chemically and biologically iodine-antagonistic, it does not influence goitre prevalence (Avtsyn et al., 1991; Smolyar, 1989).

There is some evidence to suggest that fluoride influences the collagen metabolism. Collagen is the most widespread protein in the human body and its synthesis is suppressed by fluorosis. Fluoride induces the formation of active oxygen metabolites, which disturb collagen biogenesis. Since collagen is one of the most important foundations of bone formation, interruption of the collagen metabolism could also affect dental development.

Another potentially important factor in dental fluorosis is the possible reduction in Ca content during tooth mineralisation, which leads to the destruction of hard dental tissue structure. Babyel et al. (1968); Fejerskov et al. (1994); Fejerskov et al. (1990); Fejerskov et al. (1977); Ovrutsky (1962) and Smolyar (1970; 1974) have all demonstrated that mineralisation disorders of hard dental tissues were associated with changes in Ca and P content. However, other workers report no significant difference in Ca and P contents in enamel from patients suffering fluorosis. Redinov (1981) obtained contradictory data on Ca and P, human patients with fluorosis showed no change in element contents whereas experiments on rats proved that the Ca content of enamel was much lower when excessive fluoride was introduced.

In addition to affects on dental hard tissues, both extremely low and extremely high fluoride concentrations can result in pathological changes in periodontal tissues (gums). In an experimental study on rats fed water with 1, 2 and 10 mg/l fluoride, the greatest prevalence of periodontal disease and dental fluorosis was observed in the high-fluoride group and the lowest prevalence in the 2 mg/l group. Animal sensitisation with pertussoiddiphtherial vaccine aggravated the inflammatory-dystrophic changes in the periodontium (Maksimenko et al., 1988; Skripnikova et al., 1993). Zhavoronkov (1976) found osteoporosis of the alveolar process in rats fed water with high fluoride concentrations and Vyesnina (1993) noted changes in periodontal antioxidant enzymes indicating stress of the defence mechanisms at high fluoride concentrations.

Studies of maxillodental deformations caused by fluoride are few in number and open to debate. At low fluoride intakes, Zhavoronkov and Avtsyn (1989) noted the late eruption of teeth whereas Akhmyedov and Gusyeynov (1971) revealed a reduction in the abnormal occlusion rate at higher intakes. Kotsyubinksy et al. (1989) explained a high prevalence of maxillodental deformations and loss of occlusion height by the rapid loss of the first permanent molars caused by fluoride deficiency. However, Radochina et al. (1989) found no systematic relationship between maxillodental deformations and fluoride intake. In an experimental study on rats Andryeyev (1981) observed a correlation between fluoride concentrations in water and the size of jaws such that a larger amount of fluoride led to a reduction in upper maxilla size.

2.6.2 Severity of Dental Fluorosis

Depending on the severity of fluorosis, dental injuries can manifest as chalk-like lines (line form) and spots (spot form) in various places over the tooth-crown; spot pigmentation from light yellow to dark brown; small defects in the enamel on the background of spots (chalk-like-dot form); more pronounced defects (erosive form) and the complete destruction of dental enamel and wearing down of teeth (destructive form) (Gabovych, 1950; Groshikov, 1985; Moller, 1965; Patrikyeyev, 1968; Wong, 1991). Increased fragility of hard dental tissues during fluorosis leads to the brittle fracture of crowns. Various schemes to assess the severity of dental fluorosis have been devised. The schemes adopted in this report are outlined in Tables 2.9 – 2.11.

Table 2.9 R.D. Gabovych dental fluorosis classifications (orignally presented at the 5th All-USSR Meeting of Hygenists (Gabovych and Ovrutsky, 1969))

Severity	Description
I Degree	Slight injury, with 1/3 of labial (glossal) incisors or first molars masticatory tuber surface covered with small chalk-like dots. They are practically undetectable by the naked eye.
II Degree	Similar chalk-like or tinted yellow spots (solitary or numerous) cover half of the crown and spread to a large number of teeth.
III Degree	Moderate injury of many dental crowns, spots become larger, they occupy more space and have a brighter colour (dark-yellow or dark-brown). Teeth become fragile, they are easily worn down.
IV Degree	Heavy injury. In addition to the above-mentioned changes, many small, pitted erosions occur, which sometimes join together. Chalk-like changes in the enamel create a “dead look” and the surface of the teeth become uneven. Increased fragility of the hard tissue leads to wearing down of teeth and broken enamel. Some teeth may even lose their natural form, affecting occlusion.

Table 2.10 V.K. Patrikyeyev dental fluorosis classifications (Patrikyeyev, 1958)

Dental Fluorosis Type	Description
Line form	Characterized by the appearance of small chalk-like lines on the enamel. This form of fluorosis primarily affects the central and lateral incisors of the upper jaw and more rarely, incisors of the lower jaw. The main effect is to the vestibular surface.
Mottled form	Changes in the enamel of incisors, canine teeth and more rarely of premolars and molars are more pronounced. They are associated with the appearance of chalk-like spots located on different parts of the crown. The intensity of colour increases towards the centre of the spot and on the periphery; the spot gradually dissolves into normal enamel. The surface near the chalk-like spot is even and shiny. Sometimes a weak yellow pigmentation covers the crown in various places.
Chalk-like-spotted form	As a rule, it affects teeth of all groups. Clinical features are variable. Sometimes the entire surface of the crown lacks pigmentation or has a chalk-like tint, preserving a shiny aspect. More often the surface acquires a mat look. Both cases can also include light-brown or dark-brown pigmentation of the enamel. Spots are located on the vestibular surface of the front teeth. When enamel loses its shine and becomes mat, it can also be covered with small round defects – spots with a diameter of 1.5 mm and depth of 0.1—0.3 mm. Their base has a light-yellow or dark colour.
Erosive form	Greater injury to the dental tissues with more pronounced dystrophy (chalk-like changes of the enamel layer) and enamel pigmentation. Small spots are replaced by larger and deeper defects called erosions. Unlike spots, erosions may have various forms. The enamel is usually worn down to the dentin.
Destructive form	Occurs in endemic fluorosis hotspots with high fluoride content in water (10—20 mg/l). Along with typical but more pronounced fluorosis manifestations, the form of the crown is changed due to erosion, dental wearing and breakage. This form of fluorosis is associated with enamel and dentin injuries.

Table 2.11 I. Moller dental fluorosis classifications (Moller, 1965)

Dental Fluorosis Form	Description
I form — Questionable fluorosis	Enamel is covered with small white spots
II form — Very mild fluorosis	Enamel is covered with small opaque white spots that occupy no more than 25% of the crown surface
III form — Mild fluorosis	Opaque white spots become larger, still occupying no more than 50% of the enamel
IV form — Moderate fluorosis	Characterized by the appearance of brown spots and enamel damage
V form — Severe fluorosis	Entire dental surface is injured, large areas have brown pigmentation, and the enamel is partly destroyed.

There are many studies (Bardsen and Bjorvatn, 1998; Lalumandier and Rozier, 1995; McGill, 1995; Pendrys et al., 1994; Rwenyonyi et al., 1999; Rybakov and Baziyan, 1972), which demonstrate that the severity of dental fluorosis depends primarily on the following factors:

1. *Fluoride uptake (particularly in water)*
2. *Duration of exposure*
3. *Child nutritional characteristics age 1 – 2 years*
4. *Physiological status*
5. *Sensitivity to fluoride intoxication*

Thus, at the peak of endemia children who have suffered other somatic diseases are more susceptible to severe forms of fluorosis compared to healthy controls (Redinov, 1984). Experiments on rats fed water with fluoride concentrations of 2.0-5.0 mg/l showed a more pronounced inhibition of ameloblast functional activity in animals whose unspecific resistibility was weakened by horse serum sensitisation (Ovrutsky et al., 1985).

Endemic fluorosis regions are often characterized by a reduction in the prevalence and intensity of caries affecting temporary and permanent teeth (Jackson et al., 1995; Maksimenko et al., 1987; Pashayev, 1976; Selwitz et al., 1995). However, during intake of very high concentrations of fluoride, the anti-caries effect is lost due to the prevalence of severe fluorosis causing increased fragility and breaking of enamel. Under these conditions, the dentin becomes exposed and destructive processes, which closely resemble dental caries are observed (Rybakov and Baziyan, 1972).

2.6.3 Dental Caries

Many studies have shown a relationship between low concentrations of fluoride in water and the prevalence and severity of dental caries (Eldarushyeva, 1989; Grigoryeva et al., 1993; Kotsyubinksy et al., 1989; Maksimenko et al., 1987; Selwitz et al., 1998; Todorashko, 1989; Zhavoronkov and Avtsyn, 1989).

In terms of the influence of fluoride on periodontal tissue, most research has shown an increase in periodontal disease with low fluoride intake. Studies of the periodontium in children drinking water with high fluoride contents (1.6-2.0 mg/l) and low fluoride contents (0.09-0.20 mg/l) demonstrated greater prevalences of periodontal diseases and higher periodontal index values among children in the low-fluoride area. Studies carried out on rats (Politun, 1996) showed the destruction of the maxillary alveolar processes and inflammation of the jaws and periodontium during fluoride and iodine deficiency. The main mechanisms that destroy the protective function of periodontal tissues provoking inflammatory-destructive changes are thought to be a reduction in the bactericidal activity of neutrophilic granulocyte cation proteins in peripheral blood and the inflamed zone; disruption to intracellular cooperative action and imperfect reparative regeneration causing repeated chronic pathological changes and gingivitis. Maksimenko et al. (1987) found no significant difference between periodontal disease prevalence in persons aged 35-44 years drinking water with high fluoride contents (1.5-2.4 mg/l) and low fluoride contents (0.3-0.5 mg/l) but the severity of periodontal destruction was significantly higher in the low-fluoride group.

2.6.4 Mechanisms of Skeletal Fluorosis

The negative impacts of fluoride on the skeletal system have been extensively studied. Some early works include A. Bartolucci in Italy (1912) and H. Hristiani in Switzerland (1930) who described skeletal fluorosis and joint diseases in cattle grazing near aluminium plants. The surrounding localities were polluted with atmospheric emissions containing fluoride and cows developed a painful lameness and their joints were covered with diffusive painless hyperostoses. Whilst carrying out experiments on calves, dogs, rats and other animals receiving foods with high fluoride, K. Rokholm (1934) observed pathological bone and cartilage changes in all cases.

Within the bone structure, fluoride accumulates most effectively in growing cells due to better hydration of the tissues and richer blood supply. Small apatite crystals on the bone surface also enable rapid inter-crystal and surface fluoride metabolism. Within the same skeleton, fluoride contents in different types of bone vary. Most fluoride is found in bones containing abundant spongy tissue (for example rib – 204 μg/g, vertebra – 213 μg/g and tibia – 335 μg/g). Even within different segments of the same bone (sometimes several mm apart) large variations in fluoride content can occur.

Bone becomes richer in fluoride with age. There is an almost linear correlation between age (on a logarithmic scale) and bone fluoride content. Although ingestion of fluoride may occur over a lifetime, after a number of years bones become 'saturated' with fluoride (although the human organism can never create 100%-pure fluorapatite) and a dynamic equilibrium is established. Some studies suggest a fluoride "plateau" appears after 50-55 years but there are other data that show fluoride contents in bones in older people continue to increase very slowly. If the fluoride intake drops, then the concentration in blood is reduced and the body remobilises fluoride deposited in bones. Two stages of mobilisation are established. The first stage lasts about a month and during this time fluoride from the surface of bone crystals is resorbed. During the second stage, fluoride is mobilised from deep within the bone crystal structure. Over this time, which lasts about 2 years, fluoride secretion reduces exponentially. Animal experiments have shown that fluoride secretion halves over the two-year period. Reduced metabolic rates in later life increase the resorbtion time of fluoride from bones (Zhovinsky, 1994d).

The connection between water fluoridation and the state of bone tissue and femoral fractures has been investigated in many studies (Cauley et al., 1995; Chavassieux and Meunier, 1995; Hillier et al., 1996; Raheb, 1995). Fluoride has a strong attraction for Ca ions in the body and binds Ca in the bone structure. Ca excretion from other tissues is increased resulting in an almost constant negative Ca balance. Fluoride ions enhance bone turn-over and increase osteoblast activity in bone formation zones (Hillier et al., 1996; Okano, 1996). Several studies have also shown that skeletal fluorosis patients retain far more Ca in bone than control groups (32 - 53 % and 17% Ca respectively) (Krishnamachari, 1986b).

Previous investigations in Ukraine have demonstrated a correlation between adult bone fluoride contents and fluoride concentrations in drinking water (Table 2.12). However, the bone fluoride concentration also depends upon personal characteristics (age, health etc.)

and living conditions including total daily dietary intake of fluoride, length of exposure to fluoride, nutritional status and exposure to ultra-violet-light, etc.

Table 2.12 Relationships between bone and water fluoride content in Ukraine (Zhovinsky, 1994d)

Male Hip Bone (Age: 30 – 40 years) F mg/kg	Drinking Water F mg/l
326	0.2
810	1.0
980	1.5
1530	2.2
3160	4.1
5700	9.0

Experiments carried out on rats also showed that under conditions of low Ca consumption and a fixed fluoride content in water of 100 mg/l osteomalacia and osteoporosis developed and bone turnover was accelerated followed by increases in the activity of serum alkaline phosphatase, osteocalcine and parathyroid hormones. Rats receiving adequate amounts of Ca with high-fluoride water over a period of 2 months suffered no significant augmentation of osteoblast activity, however, the width of the trabecular bone and the activity of serum alkaline phosphatase both increased in rats receiving these doses over a period of a year. The main effect of high-fluoride water consumption was an increase in bone turnover, which was exacerbated when the Ca intake was low (Li and Ren, 1997).

Other studies have shown that fluoride contents in drinking water of more than 5 mg/l cause bone remodeling and provoke disorders of the bone tissue structural-functional state promoting osteoporosis. Insufficient Ca consumption in conjunction with high fluoride intake can result in rachitis and osteomalacia development (Grigoryeva et al., 1993).

2.6.5 Skeletal Fluorosis in Children

In children, due to the rapid rate of growth and bone tissue metabolism, changes in the skeletal structure can be induced by relatively small doses of fluoride. Children are therefore more susceptible to fluoride intoxication than adults. Child clinical symptoms include rachitis, osteoporosis and disorders of the Ca homeostasis balance (Teotia et al., 1998). Studies have shown that in children with Ca deficient diets, bone tissue disorders were observed in 90% of subjects whereas in children receiving more than 800 mg/day Ca only 25% developed symptoms of fluoride intoxication. In areas of Ca deficiency, evidence of skeletal fluorosis has been found in children consuming water with less than 2.5 mg/l fluoride.

The pharmacokinetics of fluoride in children are characterised by a positive balance. Under normal conditions, fluoride mobilisation from blood plasma to bone tissue is greater than between plasma and excretion in urine. The amount of fluoride resorbed into plasma from the bone tissue in children is greater than and conversely the amount of fluoride entering the bone from blood plasma is less than that in adults. Although, the fluoride balance is normally positive in children, factors such as age, fluoride content in dinking water, food and air, etc. can result in either positive or negative balances (Whitford, 1999).

Bone mass accumulation in children is very dependant on age, genetic factors and gender. Periods of intensive growth and active accumulation of bone mass occur simultaneously. The rate of growth and final body height are determined primarily by genetic coding in more than 100 genes (Vorontsov, 1986). Child growth is also strongly influenced by the intensity of muscle use; presence of static loading (if directed along the body axis, it may give rise to growth delays and may halt the growth process); nutritional status, sleep, presence of chronic diseases, climatic conditions, etc. (Vorontsov, 1986).

During longitudinal bone growth, bone tissue density increases with age until reaching a maximum at 30 years. Beyond this age, bone density begins to reduce. Increases in bone tissue density over the first 30 years of life are not constant but are characterised by a series of stages. At ages of 4-8 years (girls) and 4-12 years (boys), the rate of bone mass accumulation is constant (Milinarsky et al., 1998). The period between 10-14 years is crucial for bone tissue formation (as is the period of early pre- and postnatal ontogenesis) and is characterized by the rapid accumulation of bone mass at rates of 7 - 8 % a year corresponding to 45% bone mass accumulation over the 4 year period (Lloyd et al., 1992; Slemenda et al., 1994). The rapid accumulation of bone mass in the prepubertal period begins with the acceleration of physical development and reaches a maximum in puberty. According to Magaray et al. (1999), bone tissue mineralisation happens more quickly in girls than in boys and reaches a maximum in the period of menarche (commonly age 12 years). By the age of 17 years, girls have 93% of the bone tissue maxima of adult women whereas boys have only 86% of the bone tissue maxima in men (Magaray et al., 1999).

Peak bone mass formation (PBM) requires physical activity, adequate Ca consumption and sufficient levels of oestrogen production in girls. It has been established that Ca intake and physical activity can increase PBM by 3-5 % and 4-7 %, respectively (Toss, 1992). Similarly (Bailey et al., 1999) reports an increase in bone tissue density of 9% and 17% (boys and girls respectively) in children with high levels of physical activity compared to a group with low level activity monitored over a two year period of intensive bone mass accumulation amounting to 26% of the total accumulation. Milinarsky et al. (1998) noted a greater accumulation rate of bone mass in boys than in girls during PBM formation.

There is a wealth of evidence to suggest that the level of physical activity in pubertal age is the main predictor of osteoporosis development in later life (Bailey et al., 1999; Bidoli et al., 1998; Kristinsson et al., 1994; Slemenda et al., 1994) and that there is a inverse relationship between bone tissue density at the age of 18 and the risk of osteoporotic fractures beyond the age off 70 (Slemenda et al., 1994).

As a consequence of the importance of skeletal development in childhood, children dwelling in territories with increased fluoride contents in drinking water very often exhibit problems with harmonious physical maturity and bone formation due to exposure at sensitive developmental stages particularly the pre- and postnatal ontogenesis period, the first year of life and during puberty (Vyeltishchyev, 1995). Several studies comparing children with identical social and domestic conditions in endemic fluorosis regions and control groups demonstrate the greater prevalence of children of below average height in fluorosis areas.

2.6.6 Benefits of Fluoride in Osteoporosis

There is much evidence to suggest the prophylactic action of fluoride consumed in moderate doses against osteoporosis. For example, epidemiological research carried out on Italian and East German populations with identical living standards, economic, social and employment status and different fluoride contents in drinking water revealed that the prevalence of femoral fractures was significantly higher in a population with low-fluoride waters. The higher fluoride content in drinking water of the other population group was found to play a protective role against fractures (Fabiani et al., 1999; Lehmann et al., 1998). Fluoride prophylaxis is increasingly used to combat osteoporosis in many Western Countries.

2.7 CURRENT STATUS OF KNOWLEDGE

Whereas the effects of environmental fluoride exposure on human soft tissues are open to debate, many studies have proved both positive and negative influences on human hard tissues, including the processes of dental development and dentin formation; bone formation and Ca and P metabolism in both adults and children (Heller et al., 1997a+b; Hillier et al., 1996; Jackson et al., 1999; Mascarenhas, 1999; Okano, 1996; Rozier, 1999). Although the exact biological mechanisms may be multi-factorial, the links between high environmental fluoride and human dental and skeletal fluorosis and low environmental fluoride and dental caries have been established. The severity of clinical response to high fluoride intakes is determined by a variety of factors such as general nutritional status (Ca and P in particular), length and timing of exposure in relation to the body developmental growth stage, gender and genetic status.

No effective cures are available for either form of fluorosis, however, the diseases are preventable if fluoride intake is controlled. In all these diseases, one of the most important exposure routes to be considered is drinking water.

Despite the overwhelming evidence for effects of fluoride intake on human health, there are surprisingly few studies that truly combine geochemistry and health information investigating factors such as the peak bone mass (PBM) status, bone structural functional state, maxillodental status, physical development status, gender, nutritional status (Ca, P and Mg in particular) gastrointestinal status, socio-economic and lifestyle factors in relation to environmental fluoride exposure. Geochemistry and health investigations carried out in Ukraine and Moldova as part of the present project aim to address these knowledge gaps in the Central Europe region.

3 Development of the Fluoride Risk Assessment for Central Europe

Fiona Fordyce, Kamil Vrana, Gyorgy Toth, Edward Zhovinsky and Vladislav Povorosnuk

3.1 INTRODUCTION

On the basis of the current state of knowledge identified from the international literature review and geochemistry and health expertise in the four study countries, an initial theoretical risk framework for Central Europe was devised to aid data collation. The framework was subsequently modified into a final risk assessment scheme in light of the research carried out and data available for the study countries. This chapter outlines the basic structure of and discusses each factor in the risk assessment and charts the development of the final risk assessment scheme. In the original project plan, the focus of the risk assessment was to identify high-fluoride areas with which to target the fluoride-removal technology. During the development of the risk assessment scheme for Central Europe, it became evident that much of the region is also at risk from dental caries and an overview of this risk is included in the final scheme.

3.2 THEORETICAL RISK ASSESSMENT FRAMEWORK

The overall aim of the risk assessment scheme was to combine geochemical, environmental, and health information to produce fluoride risk avoidance maps for water resource management planning in Central Europe. The first stage of this process was to identify the main factors controlling environmental fluoride and fluoride-related disease and the main indicators of fluoride-related risk on the basis of existing information on the occurrence of fluoride-related diseases in Ukraine and Moldova and elsewhere. The main factors under consideration in the initial theoretical framework were identified as follows:

1. Water Quality
    - *Geochemical information for surface and groundwaters from the study area used to define regions with naturally occurring fluoride concentrations that exceed known WHO water quality guidelines.*
    - *Assessment of other water quality parameters such as alkalinity and Ca content, which have a fundamental effect on the amount and chemical form of fluoride in water.*
    - *Delineation of areas of anthropogenic contamination.*
    - *Determination of relationships between water quality parameters, volume of water consumed and health effects.*

2. <u>Health Criteria</u>
   - *Information on fluorosis prevalence and the severity of fluorosis in the study countries used to indicate areas of high risk.*
   - *Consideration of other dietary factors that control the uptake of fluoride in humans, such as fluoride intake from non-water sources and the amount of Ca, Vitamin D and Vitamin C in the diet.*
   -
3. <u>Hydrogeology</u>
   - *Consideration of the importance of water resources as part of the scheme*
   - *Inclusion of water supply information*

4. <u>Population</u>
   - *Consideration of population density, as a high-density population living in an area of high-fluoride drinking water represents a greater risk than a sparse population exposed to high-fluoride waters.*

5. <u>Geological Factors</u>
   - *Rock geochemistry exerts a major control on fluoride concentrations in groundwater. Volcanic and granitic rock types, geothermally active areas and tectonically active zones tend to contain high concentrations of fluoride. Some rock types therefore present a higher potential risk than others.*

On the basis of these criteria, the following initial framework was devised (Figure 3.1):

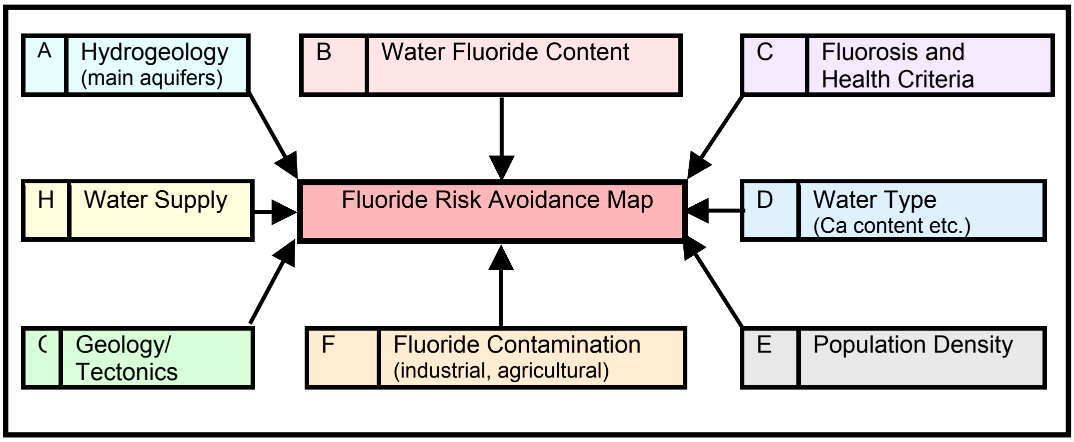


Figure 3.1 Initial theoretical framework for the assessment of fluoride risk

Each of these factors, were assigned an importance category based on the significance of the factor as a fluoride-risk indicator. The factors were also graded according to relative importance in terms of controlling environmental fluoride or the incidence of fluoride-related diseases. This framework was designed to create the final risk assessment by combining the importance and influence categories for each of the factors as follows:

Risk assessment = Importance category x Influence category

The initial importance and influence categories assigned to each factor are outlined in Table 3.1.

Table 3.1 Different importance and influence categories for each of the controlling factors and risk indicators considered in the development of the fluoride-related risk assessment scheme.

Controlling Factor/ Risk Indicator	Importance Category		Influence Category	
A – Hydrogeology	Low	*The importance of the hydrogeological resource as an indicator of risk is less than that of knowing the water supply regime*	High	*Major aquifer unit used for drinking water supply more people are exposed to this water therefore the risk is higher*
			Moderate	*Minor units or units not used directly for drinking but connect to drinking water units*
			Low	*Impermeable units or units not used for drinking water*
B - Fluoride Concentration in Water	High	*The concentration of fluoride in water is one of the most important risk indicators*	High Fluorosis*	*Concentration of fluoride > 1.5 mg/l*
			Low*	*Concentration of fluoride 0.5 – 1.5 mg/l*
			High Dental Caries*	*Concentration of fluoride < 0.5 mg/l*
C – Fluorosis and Health Criteria	High	*If fluorosis is already known to occur, this is an important indicator of high risk*	High	*Evidence of fluorosis incidence and low Ca/ protein diets etc*
			Low	*No evidence of fluorosis incidence*
D – Water Type	Low	*Major element chemistry of waters can be an indicator of likely risk but is not as important as knowing the fluoride content of water*	High	*Na+ K dominated , Ca-poor waters, thermal waters, waters in fluoride mineralised zones*
			Low	*Waters with normal to high Ca content*
E – Population Density	Low	*Gives an approximate indication of risk but information on the water supply regime is a more important indicator*	High	*High population density*
			Moderate	*Medium population density*
			Low	*Low population density*
F –Fluoride Contamination	High	*Industrial and agricultural sources enhance environmental fluoride contents and are indicators of potential risk*	High	*Source of fluoride exists and impacts upon the environment*
			Moderate	*Source of fluoride exists but does not impact upon the environment*
			Low	*No source of fluoride exists*
G – Tectonic/ Geological Conditions	Low	*Tectonic and geological information can give an indication of risk but are not as important as knowing the fluoride content of water*	High	*Area evaluated includes rock types/ tectonic regions which may contain high fluoride concentrations*
			Low	*Area evaluated does not contain rock types/ tectonic zones with fluoride potential*
H – Water Supply	High	*The nature and type of water supply is a key factor in the risk assessment*	High	*Water is used for drinking and is not fluoridated*
			Moderate	*Water has high (fluorosis)/low (caries) fluoride content but is not used for drinking*
			Low	*Water is not used for drinking*

* Based on WHO Drinking Water Quality Guidelines (WHO, 1996b)

Once the overall framework for the risk assessment was completed, the second stage of the project was to collate the relevant information from Central Europe. This information is discussed in the context of the framework and derivation of the final risk assessment GIS for the project in the following sections of this report.

3.3 EVALUATION OF FACTORS AFFECTING FLUORIDE RISK IN CENTRAL EUROPE

3.3.1 Geological and Tectonic Controls

Geology exerts a fundamental influence on water fluoride concentrations. Certain rock types commonly contain high concentrations of fluoride and on this basis it is possible to define a crude relative risk assessment scheme based on geology (Table 3.2). However, geological maps are a two-dimensional representation of the rock units appearing at surface and could give a misleading indication of likely fluoride risk as fluoride-rich horizons may be present at depth and deeper waters often contain more fluoride than shallow waters. Furthermore, high-fluoride waters are not restricted to individual rock units and even within the same rock unit fluoride concentrations in water can be highly variable. Therefore, it is not possible to predict, other than in general terms, the fluoride content of water on the basis of geology alone.

Table 3.2 Examples of relative fluoride-risk from different geological rock types and settings

Geological Conditions	Risk Influence Factor
Volcanically active/thermally active area Obsidian Acid volcanic/igneous rock types including granite Acid metamorphic rock types including gneiss	High
Sedimentary rocks containing fluorite, apatite, francolite, topaz, cryolite, hornblende, mica, rock phosphate	High
Basic igneous rocks Basic metamorphic rocks	Low
Sedimentary rocks with no appreciable F-bearing minerals	Low

Tectonically active fault zones are commonly the focus of hydrothermal water movement near the Earth’s surface and as such, waters in these regions often contain high fluoride concentrations. In Ukraine, high-fluoride groundwaters are associated with faults in the Odessa and Lvov regions (see Chapter 8). However, not all tectonic zones produce high-fluoride groundwaters and in Ukraine, there are many other tectonic zones where high-fluoride waters are not a problem. Therefore, geological and tectonic information should only be used to predict fluoride risk in areas where no other information such as water chemistry data is available.

During the present project, digital maps of geology for Hungary (Hungarian Geological Survey (MAFI) data (Pecsi, 1989)) and tectonic regions for Ukraine (Institute of Geochemistry and Ore Mineral Formation (IGMOF) data) and Slovakia (State Geological Institute of Dionyz Stur, Slovak Republic (SGUDS) data (Rapant et al., 1996)) were collated but similar information was not available for Moldova therefore coverage for the study region was incomplete. For the reasons outlined above, it was the opinion of the geochemistry and health experts that fluoride risk could not be predicted from geological and tectonic information alone therefore these data were not incorporated into the final risk assessment scheme. Water chemistry information was available in all four countries and was considered a far more important indicator of risk. The geological and tectonic maps of Hungary, Slovakia and Ukraine are included in this report as useful background information only.

3.3.2 Hydrogeological Controls

Information on the location and importance of the main aquifers in each country was also considered as part of the risk assessment. On a countrywide basis, maps of the major hydrogeological units of Slovakia (SGUDS, (Rapant et al., 1996))and Hungary (MAFI, (Siposs and Toth, 1989)) and of the main younger aquifers in Moldova (Association of State Geologists (ASG) data) were made available to the project. No national hydrogeological map was available for Ukraine. From information gathered during the project it was possible to classify the national hydrogeological maps of Slovakia, Hungary and Moldova into aquifer importance according to the scheme outlined in Table 3.1. Although major aquifers used for public drinking water supply constitute an inherently greater risk than minor or non-aquifer units, it was not possible to include this information alone in the fluoride risk assessment because the actual risk to the population depends upon where the water is used and on the water quality (fluoride content). Hydrogeological maps of Slovakia, Hungary and Moldova classified by aquifer importance are therefore not included in the final risk assessment but are incorporated for background information in the reports prepared for each country (Chapters 5-8).

In terms of assessing the fluoride contents of waters from each aquifer, national groundwater chemistry data were available in Slovakia and Moldova only. In Hungary, national groundwater chemistry data were defined on the basis of water temperature rather than aquifer source. In Ukraine, information on aquifer chemistry was collated in specific regions of study (Lvov, Odessa, Kiev and Poltava) but no maps of aquifer locations were available. Using the existing data, it was possible to categorise aquifer units by water fluoride content in Slovakia, Moldova and in the regions of Ukraine (Table 3.3), however, this information can only be used as a broad indication of risk as fluoride concentrations within aquifer units vary markedly. Therefore, maps of the fluoride contents of different aquifers were not included in the final risk assessment but the fluoride contents of different water-bearing horizons are discussed in the reports prepared for each country (Chapters 5 - 8).

3.3.3 Water Fluoride Content

The concentration of fluoride in water is one of the most important risk indictors. National hydrochemical data were available for Moldova (ASG data), Slovakia (SGUDS data, (Rapant et al., 1996)) and Hungary (MAFI data, (Toth, 1989)) (Table 3.3). The distribution of data points in Slovakia and Hungary (1 per 3 km^2) were of sufficient sample density to provide information for the whole country whereas data in Moldova were not evenly distributed, therefore in some areas of the country it was not possible to make an assessment of fluoride risk on the basis of water chemistry.

No national hydrogeochemical data were available in Ukraine, however, geochemical experts have estimated the likely fluoride content in water and potential for fluoride-related health problems in different regions of the country as part of this project.

More detailed water chemistry information was available for the Ziarska Kotlina Basin, a region with industrial sources of fluoride in Slovakia and for four regions of Ukraine (Kiev, Lvov, Poltava and Odessa)**,** which have been examined more fully as part of this project.

The framework outlined in Table 3.1 bases the risk assessment of fluoride concentrations in water on the current WHO drinking water quality guidelines of > 1.5 mg/l for dental fluorosis and < 0.5 mg/l for dental caries (see also Table 2.5). Geochemistry and health investigations carried out as part of the present study in Moldova confirmed that dental fluorosis occurred when water concentrations exceeded 1.5 mg/l (see Chapter 7). Therefore, the water fluoride data collated for the project were included in the final risk assessment GIS categorised according to the WHO guidelines.

However, in Ukraine, evidence from previous investigations suggests that in the south of the country where the climate is warmer, people drink more water and fluorosis can occur at concentrations of below 1.2 mg/l. The national assessment of fluoride risk for Ukraine carried out by Central European experts therefore takes account of fluorosis incidence at fluoride concentrations below the WHO recommended guideline of 1.5 mg/l (Chapter 8).

Table 3.3 Fluoride concentrations in different waters from the study region

Country	Coverage	Aquifer/ Source Name	Aquifer Type	F mg/l Min	F mg/l Max	F mg/l Av.	N
Slovakia	National¬	Quaternary – loess, loams, impermeable beds	Rock complexes without water sources, generally impermeable	0.05	4.0	0.2	1829
		Quaternary – sands + gravels, intragranular permeability	Extensive aquifers with very significant water sources	0.05	2.5	0.2	3575
		Neogene - clays, impermeable beds	Rock complexes without water sources, generally impermeable	0.05	0.3	0.2	4
		Neogene - conglomerates, sandstones	Aquifers with significant water sources	0.05	0.9	0.3	35
		Neogene - gravels, sands interlayered with clays	Aquifers with significant water sources	0.05	0.5	0.2	307
		Neogene – volcanics, fissure permeability	Aquifers containing local and less important water sources	0.05	1.3	0.1	2140
		Palaeogene - sandstones, conglomerates	Aquifers with significant water sources	0.05	3.0	0.1	912
		Palaeogene - carbonate conglomerates + breccias	Extensive aquifers with very significant water sources	0.05	3.0	0.1	157
		Palaeogene - sandstones with claystones	Aquifers containing local and less important water sources	0.05	2.4	0.1	2745
		Palaeogene-Mesozoic - impermeable beds	Rock complexes without water sources, generally impermeable	0.05	1.0	0.1	335
		Triassic-Jurassic - limestones, dolomites	Extensive aquifers with very significant water sources	0.05	3.0	0.1	1946
		Triassic - quartzites, fissure permeability	Aquifers containing local and less important water sources	0.05	0.2	0.1	28
		Palaeozoic undifferentiated - fissure permeability	Aquifers containing local and less important water sources	0.05	3.0	0.1	617
		Intrusions - granitoids, crystalline schists	Aquifers containing local and less important water sources	0.05	3.0	0.1	1526
	Ziarska	Groundwater	-	0.01	3.6	0.1	107
	Kotlina`	Surface water	-	0.03	9.0	0.4	126
		Snow¬	-	0.02	1.3	0.3	20
Hungary	National^	Lowland porous aquifers	Excellent conductivity	Unknown	Unknown	Unknown	
		Mesozoic karst rocks	Excellent conductivity	Unknown	Unknown	Unknown	
		Fissured volcanic rocks	Medium conductivity	Unknown	Unknown	Unknown	
		Hilly porous aquifers	Medium conductivity	Unknown	Unknown	Unknown	
		Hilly porous aquifers	Low conductivity	Unknown	Unknown	Unknown	
		Lowland porous aquifers	High conductivity	Unknown	Unknown	Unknown	
		Lowland porous aquifers	Low conductivity	Unknown	Unknown	Unknown	
		Lowland porous aquifers	Medium conductivity	Unknown	Unknown	Unknown	
	National^	Thermal Wells > 25°C	-	0.60	6.2	1.4	344
		Cold Wells < 25°C	-	0.30	3.3	0.2	532
		Tap Water	-	0.00	1.8	0.2	3266
Moldova	National#	Unconfined – Quaternary , Pliocene Pontic + Levantin Sediments	Low - local water supplies	1.4	7.6	3.1	45
		Mid Sarmatian – Conherian	Important - 16.5% of drinking water	0.20	3.5	1.0	35
		Baden Sarmat (Lower Sarmatian)	Very important - 66% of drinking water	0.17	15.7	2.4	161
		Silurian-Cretaceous Chalk	Important - 16.5% of drinking water	0.10	16.2	2.9	86
	Falesti*	Tap and well water	-	0.39	5.3	1.3	10
	Kalarash*	Tap and well water	-	0.19	3.6	1.6	9
	Cornesti*	Tap and well water	-	0.25	0.88	0.41	8
Ukraine	Odessa~	Neogene	-	0.05	0.8	0.4	58
	Kiev~	Quaternary	-	0.00	0.3	0.2	28
		Palaeogene	-	0.00	1.15	0.3	26
		Cretaceous	-	0.18	0.6	0.2	15
		Jurassic	-	0.06	1.1	0.4	18
		Proterozoic	-	0.2	0.9	0.4	6
	Poltava~	Quaternary	-	0.00	3.2	0.6	37
		Palaeogene	-	0.00	8.8	2.8	53
		Cretaceous	-	0.18	2	1.1	21
	Lvov~	Quaternary	-	0.00	0.9	0.2	39
		Cretaceous	-	0.00	3.8	0.9	20
	Khar'kov*	Well Water	-	0.4	1.8	1.1	2
	Dnepropetrovsk*	Well Water	-	0.12	2.7	1.0	34
	Donetsk*	Well Water	-	0.05	1.5	0.5	36
	Zaporozh'ye*	Well Water	-	0.04	2.2	0.7	36
	Podgorny*	Tap water	-	0.71	7.1	2.5	13
	Arciz*	Tap water	-	-	-	2.54	1
	Izmail~	Tap water	-	-	-	0.24	1
	Tarutino*	Tap water	-	-	-	1.14	1

¬SGUDS National Groundwater Data (Rapant et al., 1996); ‘ Ministry of the Environment (1988); ^MAFI National Groundwater Data(Toth, 1989),; # ASG Groundwater Data; ~ IGMOF Groundwater Data, *Data from the present study. Min = minimum, Max = maximum, Av = average, N = number

3.3.4 Water Type - Hydrogeochemical Controls

As outlined in Chapter 2, the solubility of fluoride in waters is controlled by the presence or absence of other elements and the major element chemistry in particular. Waters that are Na+K-dominated tend to contain more free fluoride in solution than Ca-dominated waters. Human fluoride absorption from water is also inversely related to dietary Ca intake and high concentrations of other cations that form insoluble complexes with fluoride such as Mg and Al can markedly reduce gastrointestinal fluoride absorption (Jowsey and Riggs, 1978; Whitford, 1997).

The relationships between these factors were examined in more detail during the present study but the extent of these investigations was limited by the data available to the project, (summarised in Table 3.4).

3.3.4.1 Water Type and Fluoride Content

On the basis of the information available it was possible to examine the relationships between water types and fluoride content in more detail in the following datasets:

- *Slovakia – Ziarska Kotlina Basin – surface water*
- *Hungary – Whole Country – groundwater data for cold wells and thermal wells*
- *Moldova – Whole Country – groundwater data*
- *Ukraine – Regions - Kiev, Lvov, Poltava, Odessa – groundwater data*

In order to determine water type, the data were plotted on trilinear Piper Diagrams (Piper, 1944), which are commonly used by hydrochemists to express the ionic composition of different waters. The major cation data (Na, K, Ca, Mg) were converted from mg/l concentrations to milli-equivalents per litre and percentages of cation abundances were calculated for each sample.

Results demonstrate that the majority of surface waters from the Ziarska Kotlina basin in Slovakia are Ca-dominated and high fluoride contents (> 1.5 mg/l) are associated with lower Ca and higher Na+K-dominated waters in 2 out of 5 cases (Figure 3.2).

In Hungary, the majority of groundwaters from cold wells are Ca-dominated but high fluoride contents (> 1.5 mg/l) are associated with lower Ca, higher Na+K waters in 5 out of 6 cases. In contrast, groundwaters from thermal wells range from Na+K- to Ca-dominance and many of these waters contain high fluoride concentrations (> 1.5 mg/l) (Figure 3.3).

In Moldova, the majority of groundwaters are Na+K- or Mg-dominated with very few Ca-dominated waters. High fluoride contents (> 1.5 mg/l) are associated with waters from the shallow unconfined aquifer and with strongly Na+K-dominated waters from the Baden-Sarmatian and Silurian-Cretaceous horizons. Waters of the Mid-Sarmatian horizons do not contain high fluoride contents despite Na+K-dominance of these waters (Figure 3.4)

Table 3.4 Summary of water chemistry information available to the current project

Country	Coverage	Water Type	Chemical Determinants
Slovakia	National¬	Groundwater	TDS, pH, F, Ca
	Ziarska Kotlina`	Groundwater	F, Ca
		Surface water	COD, BOD, Na, K, Ca, Mg, NH_4, Fe, Mn, Cl, F, NO_2, NO_3, PO_4, SO_4, HCO_3, CO_3, OH, H_2SiO_3, CO_2, Li, Sr, Cr, Cu, Zn, As, Cd, Se, Pb, Hg, Ba, Al, Sb, TDS
		Snow¬	pH, COD(Mn), conductivity, NH_4, Cl, F, NO_3 NO_2 , SO_4, M n, Fe, Al, Zn, Cu, Pb, Cr, Ni, Cd
Hungary	National^	Cold wells < 25°C	K, Na, NH_4, Ca, Mg, Fe, Mn, Cl, HCO_3, SO_4, NO_3, F, Temp
		Thermal wells > 25°C	K, Na, NH_4, Ca, Mg, Fe, Mn, Cl, HCO_3, SO_4, NO_3, F, Temp
		Tap water	F, Ca
Moldova	National#	Groundwater	F , Na+K , Ca , Mg , Cl , HCO_3 , CO_3 , SO_4 , Sr , Se, pH, Eh, TDS
	Falesti*	Tap and well water	F, Ca, pH
	Kalarash*	Tap and well water	F, Ca, pH
	Cornesti*	Tap and well water	F, Ca, pH
Ukraine	Kiev~	Groundwater	pH, F, Ca, Mg, Na+K, Fe^{2}+, Fe^{3}+, NH_4, NO_2, NO_3, Cl, SO_4, HCO_3, CO_3, CO_2, HBO_2, I, Br, Se, Zn, Pb, Mn , Mo, Be, B, Co, Ni I, As, U
	Lvov~	Groundwater	pH, F, Ca, Mg, Na+K, Fe^{2}+, Fe^{3}+, NH_4, NO_2, NO_3, Cl, SO_4, HCO_3, CO_3, CO_2, HBO_2, I, Br
	Poltava~	Groundwater	pH, F, Ca, Mg, Na+K, Fe^{2}+, Fe^{3}+, NH_4, NO_2, NO_3, Cl, SO_4, HCO_3, CO_3, CO_2, HBO_2, I, Br, Se, Zn, Pb, Mn , Mo, Be, B, Co, Ni I, As, U
	Odessa~	Groundwater	pH, F, Ca, Mg, Na+K, Fe^{2}+, Fe^{3}+, NH_4, NO_2, NO_3, Cl, SO_4, HCO_3, CO_3, Cu, Zn, Pb, Ni, U
	Arciz*	Tap water	Na, K, Ca, Mg, Fe, CO_3, HCO_3, SO_4, Cl, Mn, Ni, V, Cr, Mo, Zr, Cu, Pb, Ag, Bi, Zn, F
	Vilkovo*	Tap water	Na, K, Ca, Mg, Fe, CO_3, HCO_3, SO_4, Cl, Mn, Ni, V, Cr, Mo, Zr, Cu, Pb, Ag, Bi, Zn
	Izmail~	Tap water	Na, K, Ca, Mg, Fe, CO_3, HCO_3, SO_4, Cl, Mn, Ni, V, Cr, Mo, Zr, Cu, Pb, Ag, Bi, Zn, F
	Podgorny*	Tap water	F, pH
	Tarutino*	Tap water	F
	Khar'kov*	Well water	F, NO_3, NO_2, As, Pb, Zn, Se, U, Cd, V, Hg, Cr, Sr, Pa, Phenols, C
	Dnepropetrovsk*	Well water	F, NO_3, NO_2, As, Pb, Zn, Se, U, Cd, V, Hg, Cr, Sr, Pa, Phenols, C
	Donetsk*	Well water	F, NO_3, NO_2, As, Pb, Zn, Se, U, Cd, V, Hg, Cr, Sr, Pa, Phenols, C
	Zaporozh'ye*	Well water	F, NO_3, NO_2, As, Pb, Zn, Se, U, Cd, V, Hg, Cr, Sr, Pa, Phenols, C

¬SGUDS National Data (Rapant et al., 1996); ‘ Ministry of the Environment (1998); ^MAFI National Data(Toth, 1989); #ASG Data; ~IGMOF Data; *Data from the present study

In Ukraine, the majority of waters from the Odessa region derived from a Neogene aquifer are Mg-Ca-dominated, only 8 of these waters are Na+K-dominated and do not have high fluoride contents (> 1.5 mg/l). Samples of tap water from the Odessa region towns of Arciz, Izmail and Vilkovo demonstrate that only in Arciz is water strongly Na+K-dominated with high fluoride contents, waters from the other settlements are Mg-Ca-dominated with low fluoride concentrations. Groundwaters from Quaternary and Cretaceous aquifers in the Lvov region are generally Ca-dominated and do not contain high fluoride contents with the exception of 5 very highly Na+K-dominated Cretaceous aquifer waters. In the Kiev region, groundwaters from Quaternary, Palaeogene, Cretaceous, Jurassic and Proterozoic aquifers are all Ca-Mg dominated and do not contain high fluoride contents. Groundwaters from Quaternary aquifers in the Poltava region show a range of anion dominance, Ca-Mg waters do not contain high fluoride contents but Na+K-dominated waters contain elevated levels of fluoride. Palaeogene aquifer waters in Poltava region are generally Na+K-dominated and contain high fluoride contents as do Na+K-dominated Cretaceous aquifer waters (Figure 3.5).

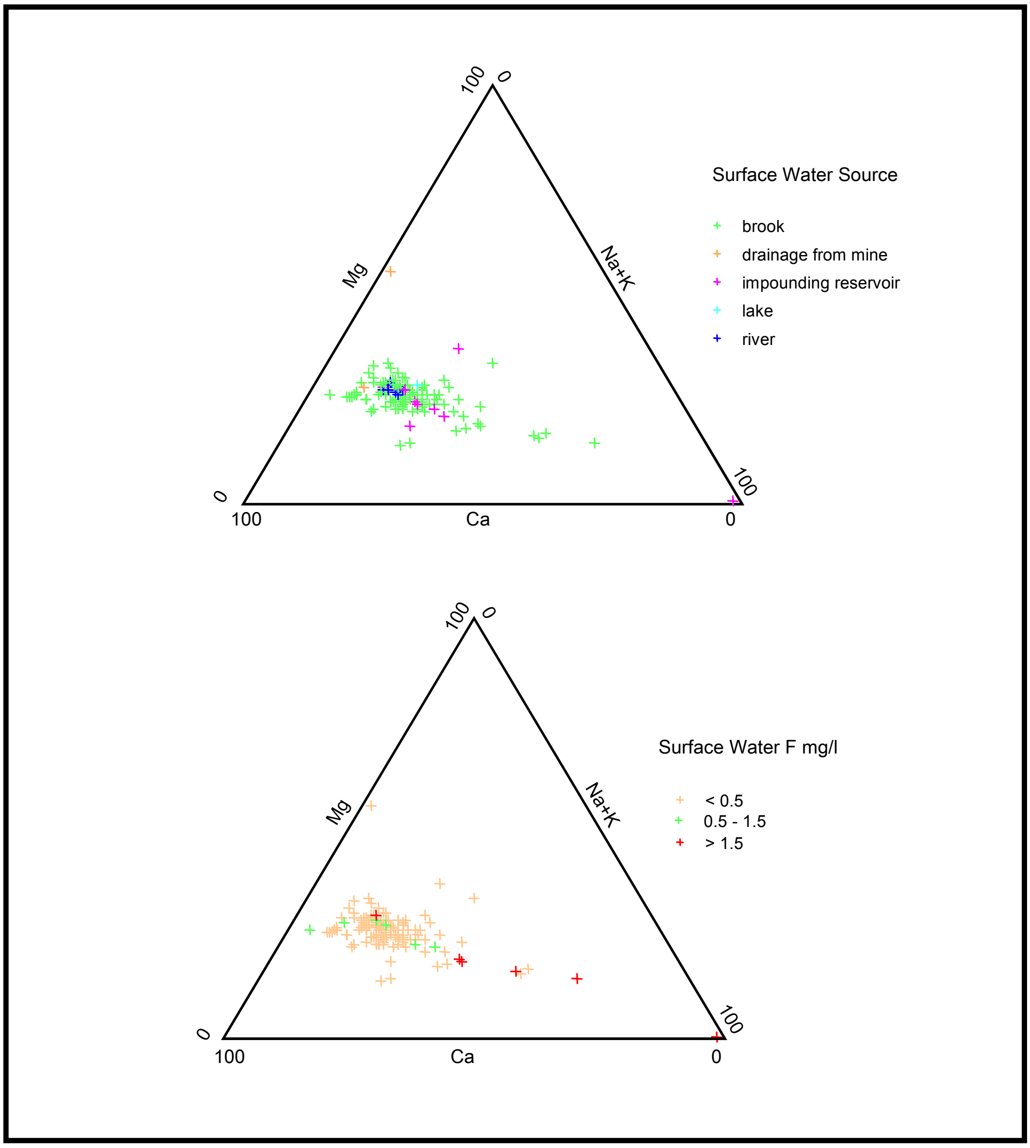


Figure 3.2 Piper diagrams showing the relationships between cation dominance and fluoride concentration in surface waters from the Ziarska Kotlina Basin, Slovakia

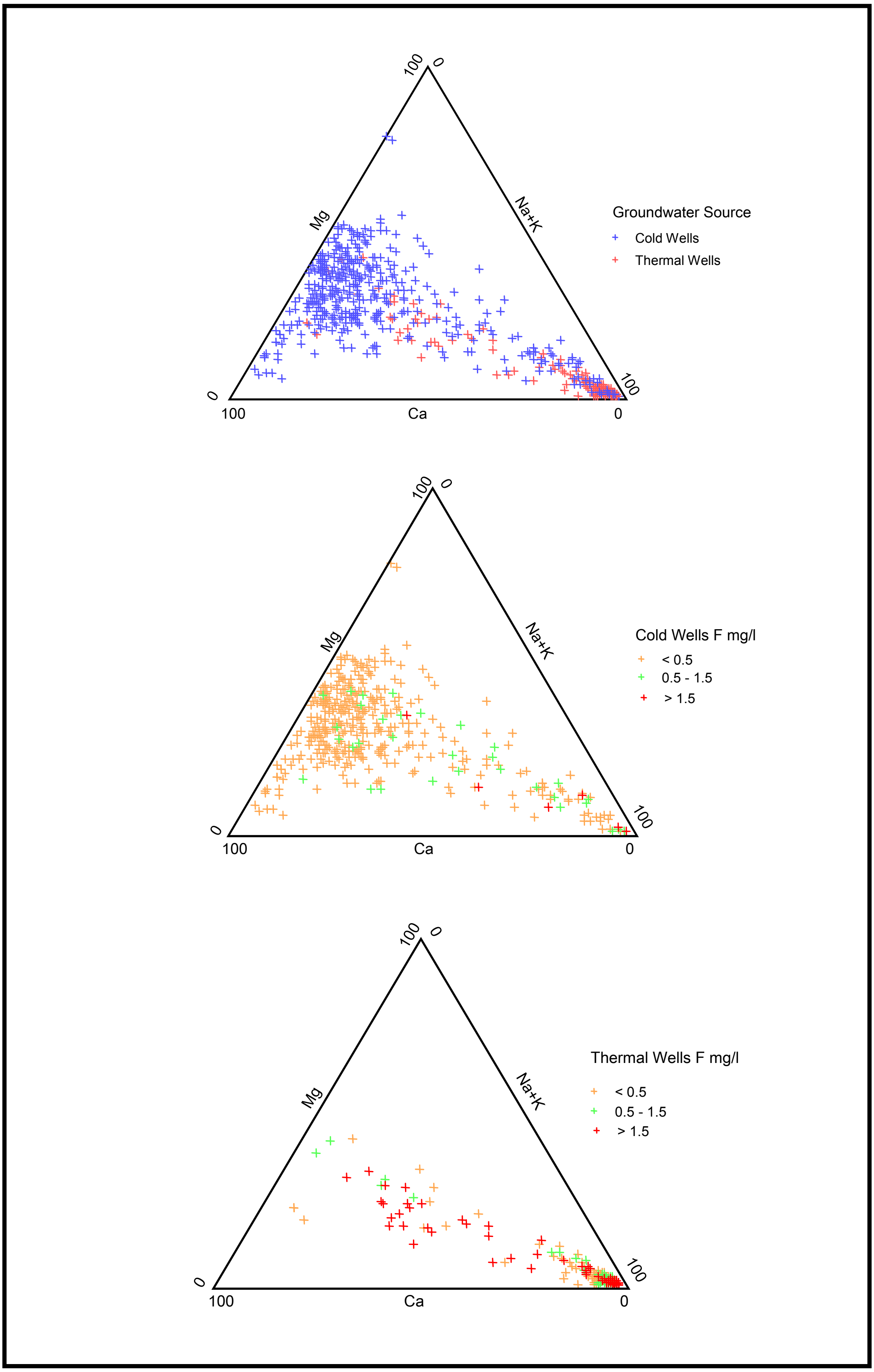


Figure 3.3 Piper diagrams showing the relationships between cation dominance and fluoride concentration in cold (< 25°C) and thermal (> 25°C) groundwaters in Hungary

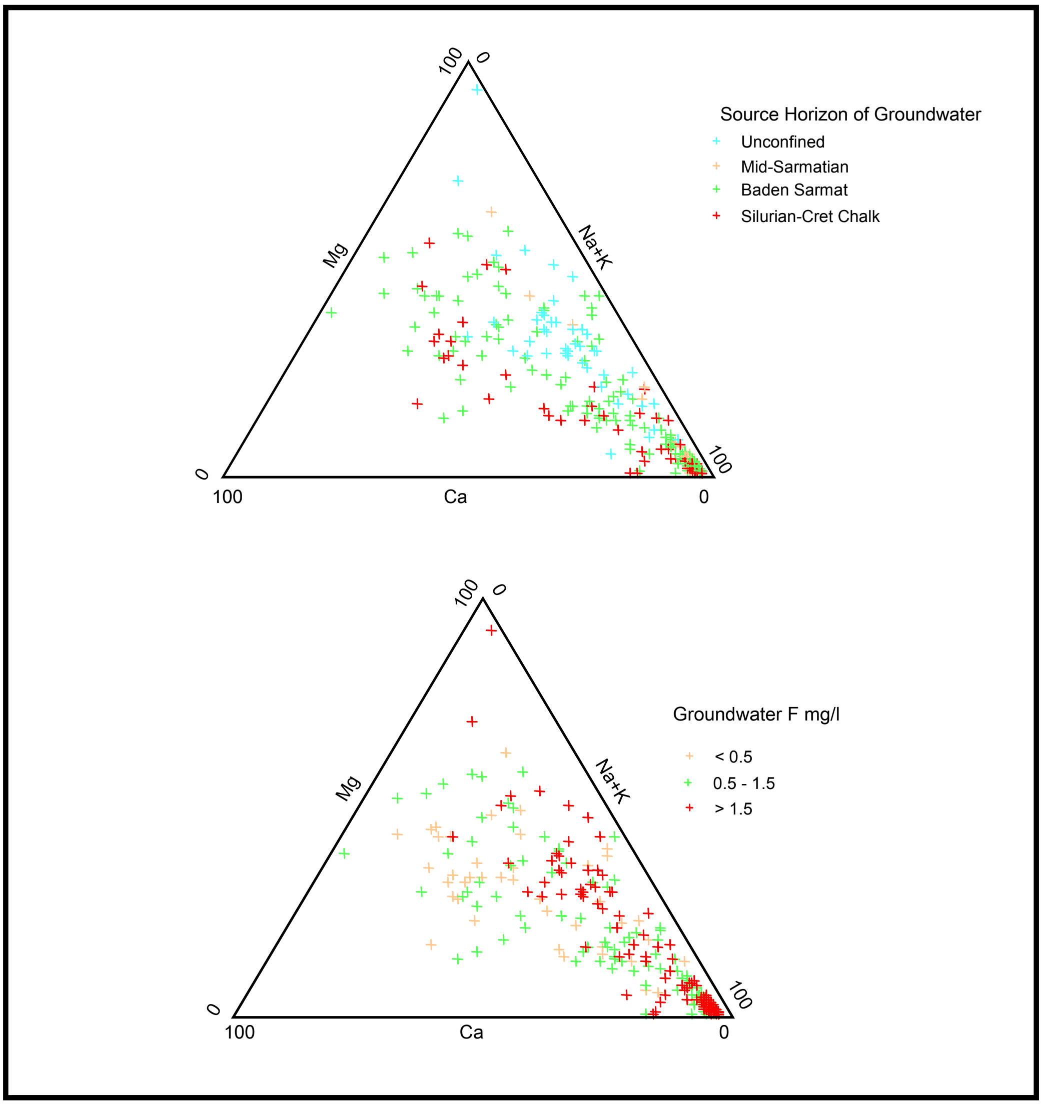


Figure 3.4 Piper diagrams showing the relationships between cation dominance and fluoride concentration in groundwaters in Moldova

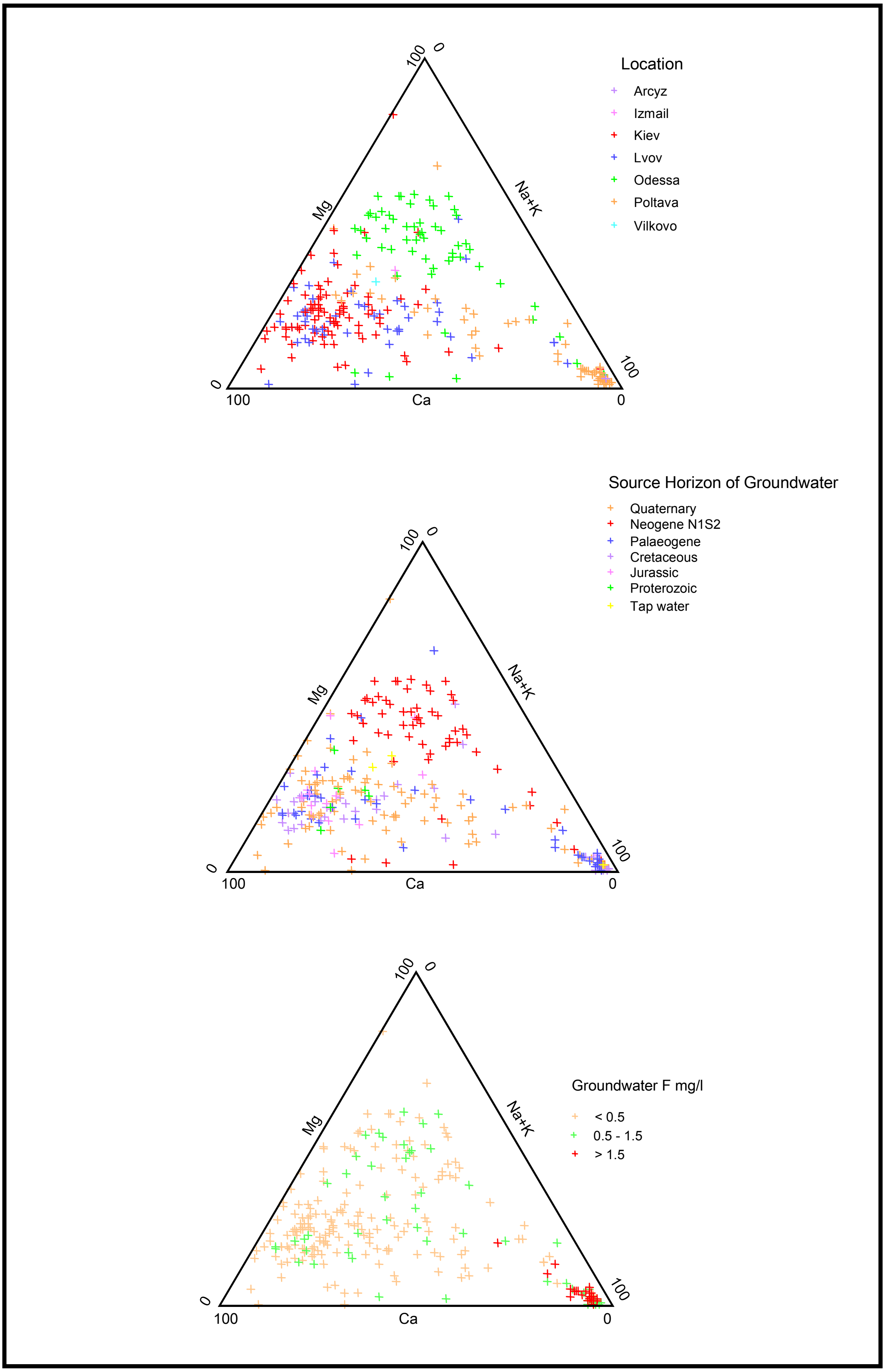


Figure 3.5 Piper diagrams showing the relationships between cation dominance and fluoride concentration in groundwaters in Kiev, Lvov, Odessa and Poltava, Ukraine

In general, the investigations carried out during the present study confirm an association between high fluoride concentrations in water and Na+K-dominated water types. In particular, groundwaters in Moldova and in the Poltava region of the Ukraine show low Ca-dominance and high fluoride contents and present a significant high-fluoride threat in these regions. However, high fluoride waters (> 1.5 mg/l) occur across a broad range of Ca/Na+K anion dominance ratios and not all Na+K-dominated waters contain high fluoride contents.

It is possible in many areas of the world that information on the fluoride content of water may not be available whereas data on the major ion chemistry of water may have been collected. In these circumstances, based on the evidence of the present study and many other investigations carried out around the world, water type could be used as a guide to the likely risk of high fluoride contents in water. For the purposes of the present study, however, fluoride water chemistry data are available therefore water type was not included in the final risk assessment but is incorporated into this report for background information.

3.3.4.2 Water Type and Health

Many studies have demonstrated that in locations with similar fluoride contents in water, the prevalence of fluorosis can show marked variation and one factor thought to control the development of the disease is the form of the fluoride in the water. Fluorite (CaF_2) solubility is generally considered to control the mobility of fluoride in most waters and low Ca also enhances the uptake of fluoride during ingestion (bioavailability). Mineral saturation indices are a way of examining the likely speciation or form of elements in water and can be represented by calculations for major dissolved phases via geochemical speciation codes or by simple graphical formats. During the present study, fluorite saturation indices were calculated using the latter method for examples of groundwater data from Slovakia and from the Poltava Region, Ukraine. Estimates of mineral stability and solute saturation derived from the chemical compositions of waters assume a pure closed system and the hydrolysis reaction of a primary mineral phase. In simple cases such as the dissolution or precipitation of fluorite, this generates a single linear boundary with a slope of 2 and an intercept that may be calculated from the equilibrium constant of the reaction:

$$Ksp\ (CaF_2) = [Ca^{2+}][F^-]^2$$

where Ksp = solubility product constant
[ ] = ionic activities of the elements

The ionic activities depend upon temperature and the ionic strength of the solutions, however, most natural waters are assumed to be pure dilute solutions therefore the ionic activity equals the element concentration. Due to the lack of temperature data available to the present project, the water temperature for fluorite saturation index calculations was assumed to be 25°C. The ionic activities of fluoride and Ca were calculated by converting the mg/l concentrations to moles per litre and taking the –log (activity). These data were compared to the theoretical activity of Ca calculated using the equilibrium constant equation above rearranged as follows:

$$pCa = pKsp - 2pF$$

where Ksp = solubility product constant at 25°C = $10^{-10.58}$ (Brown and Robertson, 1977)
p = -log

The results of these calculations are presented graphically in Figures 3.6, 3.7 and 3.8. The theoretical calculations of pCa plot on a straight line and points below the line meet the condition that $[Ca^{2+}][F^-]^2 < Ksp$, therefore CaF_2 will dissolve (undersaturated with respect to fluorite). Points above the line meet the condition that $[Ca^{2+}][F^-]^2 > Ksp$, therefore CaF_2 will precipitate (saturated/oversaturated with respect to fluorite).

Results for Slovakian groundwaters show a broad range between undersaturation and saturation with respect to fluorite. Several thousand data records lie below the detection limit for fluoride and plot on a vertical line in the saturated zone. Despite the large number of undersaturated data points, fluoride concentrations rarely exceed 1.5 mg/l in Slovakian groundwaters. The fluorite saturation data should be treated with caution, however, as it is likely that these shallow groundwaters were not at temperatures of 25°C.

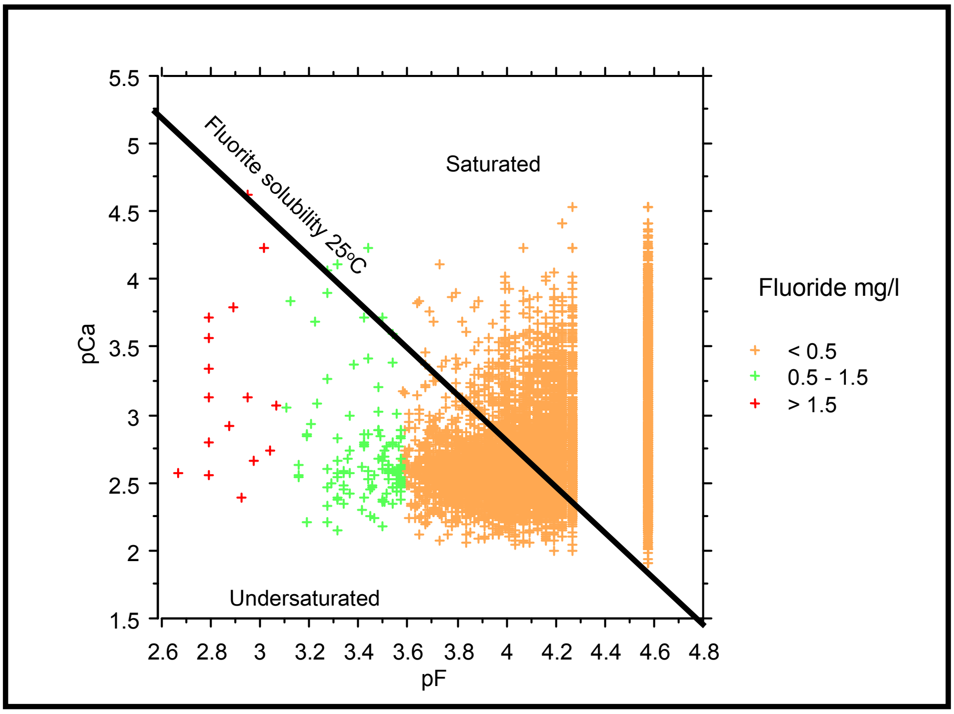


Figure 3.6 Fluorite saturation data for Slovakian groundwaters compared to the formation constant of (Brown and Robertson, 1977) for the system pCa = pKsp – 2pF. The total fluoride content (mg/l) of the waters is also shown. (saturated = saturated/oversaturated)

Data for Poltava indicate that almost all of the Palaeogene and Cretaceous aquifer waters and the majority of the Quaternary aquifer waters are undersaturated with respect to fluorite (Figure 3.7). All these waters, and the Palaeogene in particular, are known to contain high fluoride contents and cause fluorosis health problems in this region.

Whilst these examples of fluorite saturation indices provide interesting background information, these data were not included in the final risk assessment scheme as it is assumed that fluorite saturation is the main controlling factor in the mobility of fluoride. The chemical data made available to the project were not sufficient to check whether this assumption was valid in all the regions and the relationships between mineral saturation indices and medical outcomes in the population would require further investigation before a risk scheme using these data could be established.

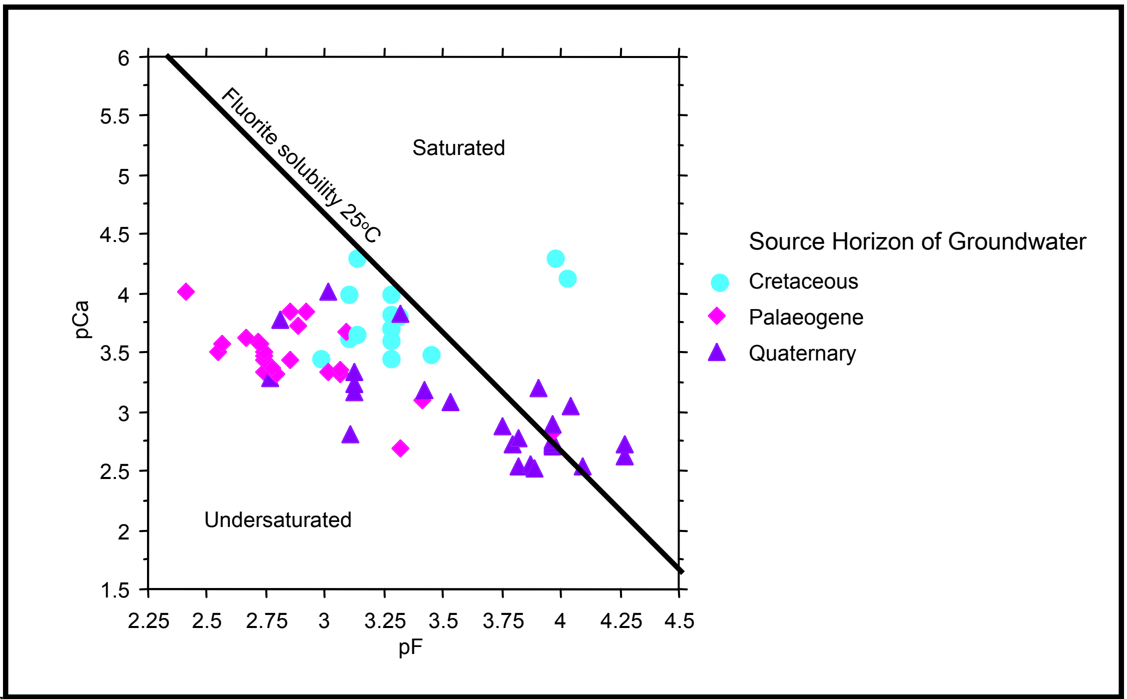


Figure 3.7 Fluorite saturation for different Poltava groundwaters compared to the formation constant of (Brown and Robertson, 1977) for the system pCa = pKsp – 2pF. (saturated = saturated/oversaturated)

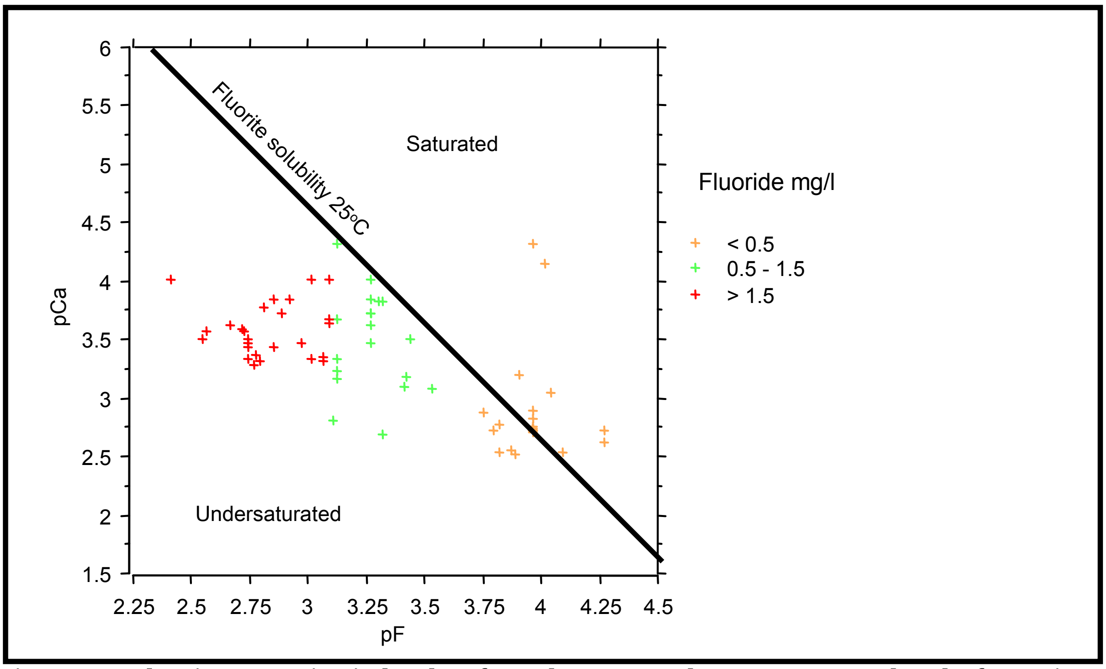


Figure 3.8 Fluorite saturation index data for Poltava groundwaters compared to the formation constant of (Brown and Robertson, 1977) for the system pCa = pKsp – 2pF. The total fluoride content (mg/l) of the waters is also shown. (saturated = saturated/oversaturated)

The bioavailability of fluoride in the human organism is very dependant on the amount and forms of soluble fluoride and Ca in the diet. Previous investigations carried out in Moldova demonstrated a correlation between the ratio of these two elements in water and disease prevalence (Table 3.5). The following ratio was calculated for several waters in different regions:

$$\frac{\text{F mg/l}}{\text{Ca mg/l}} \times 100 \text{ (expressed as \%)}$$

In general, the prevalence of fluorosis was greater in areas with high F/Ca ratios. However, not all areas affected by fluorosis followed this pattern, in the Chadyr-Lunga region of southern Moldova, the population were supplied with water containing 1.2 – 7.6 mg/l fluoride with F/Ca ratios of 1 to 4%. However the fluorosis incidence in this area was 80%. It was suggested that other factors such as the high mineralisation (1.5 – 6 g/l) of these waters may affect fluorosis prevalence and further studies are required to elucidate these relationships. Simple comparisons of the total element concentrations in water do not take account of the different charges and weights of the ionic species present and when trying to estimate the likely inhibitory effect of Ca on fluoride absorption due to the ability to form insoluble mineral species, converting the concentrations from mg/l to chemical equivalence units such as moles/l may give more meaningful results.

Table 3.5 Relationships between fluoride and calcium ratios and fluorosis prevalence rates from Moldova

F/Ca Ratio %	Fluorosis Prevalence %
< 25	0
25 – 80	< 50
> 100	60 – 70
1 – 4	80

During the present study, many of the water chemistry datasets did not contain enough information to examine the ionic forms of fluoride and other elements in solution in any detail. However, fluoride speciation was determined in selected waters from Ukraine (see Chapter 8).

Several water chemistry modelling programmes and databases such as PHREEQC (Parkhurst, 1995) and WATEQ4F (Ball and Nordstrom, 1991) are available to determine the likely speciation of elements in water. These programmes rely on the input of parameters such as pH, Eh, temperature, total element chemistry, organic content etc. and use thermodynamic calculations to estimate the likely element species present. The programme PHREEQC assumes that the system under investigation is in a state of thermodynamic equilibrium namely, that the speed of all physio-chemical processes is greater than the speed of the kinetic and diffusion processes. It calculates the equilibrium compositions of multi-component systems, which can be of aqueous, gaseous, solid (mineral), ion-exchange and/ or sorption phases simultaneously. For the purposes of this study, it was assumed that only one water solution phase was present. The following data were entered into the model to perform the calculations:

- *Thermodynamic equilibrium constants for chemical reactions taken from the WATER4F database*
- *Major and trace element and pH composition of selected Ukrainian groundwaters*

Results show that as expected, in most Ukrainian waters the free fluoride ion (F^-) is the most dominant species accounting for 90 – 98% of the total fluoride present. Interestingly, in almost every case, MgF^+ is more dominant (1 – 9%) than CaF^+ (1%). In waters from the Neogene Sarmatian horizon in Odessa and the Cretaceous horizon in the Poltava region NaF is a stable aqueous form (Figure 3.9). Closer examination into the relationships between soluble forms of fluoride and total water fluoride contents indicated that although the percentage of fluoride present in free F^- form shows little variation between waters with very differing total fluoride contents (0.05 – 7.65 mg/l), the proportion of MgF^+ and CaF^+ forms decrease in high-fluoride waters (Figure 3.10). On the basis of this evidence it is suggested that further investigations into the relationships between fluoride bioavailability and disease outcomes should focus on the following ratios:

$$\text{Ratio K} = \frac{F^-}{MgF^+ + CaF^+} \quad \text{or more correctly} \quad \frac{F^{-}}{\sum \text{F-species}}$$

Although water type does exert an important influence on the amount and forms of fluoride in the water and subsequent uptake into the population, the relationships between these factors has not yet been established in enough detail to include in the risk assessment scheme, therefore these data are included in this report for information only.

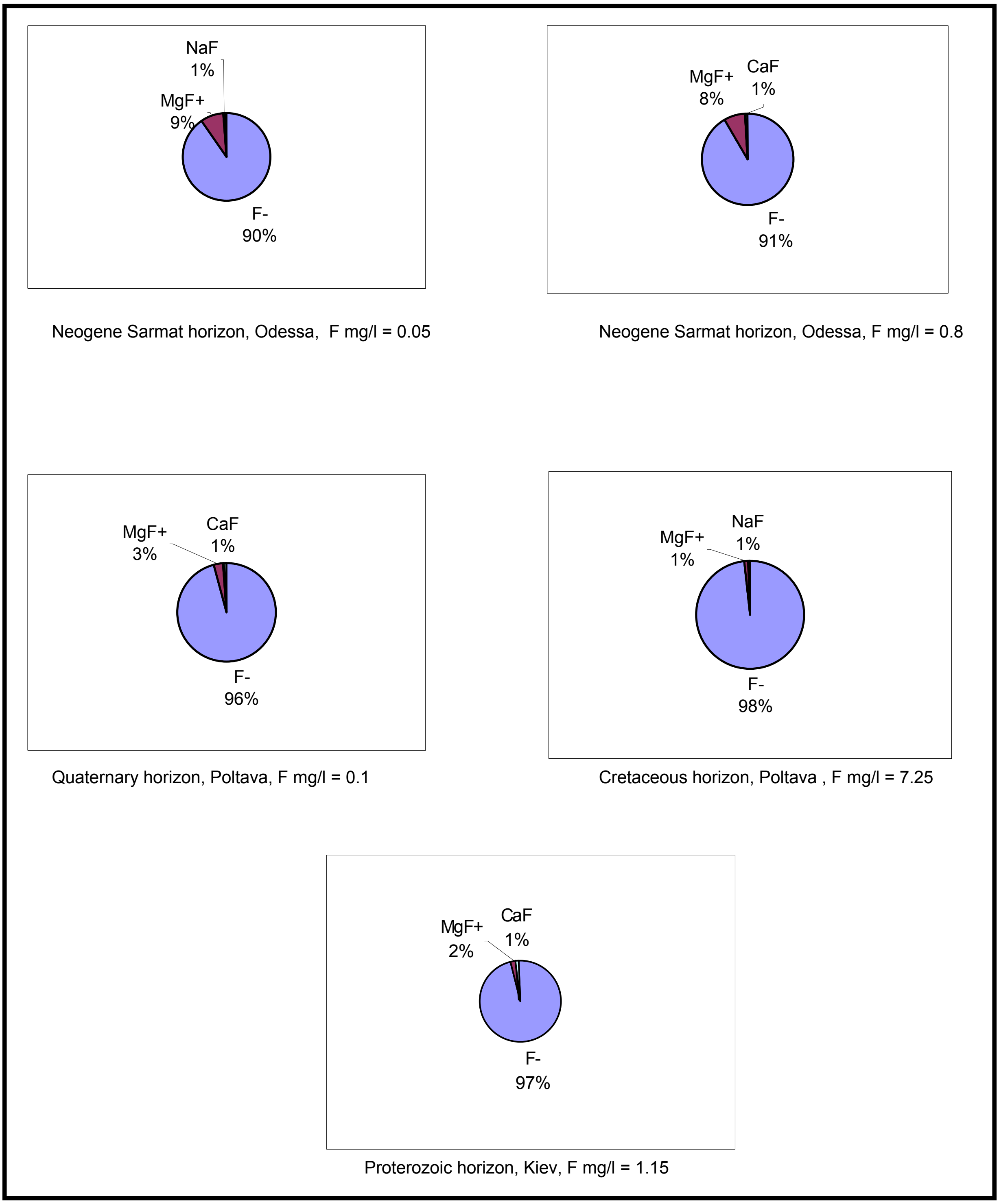


Figure 3.9 Speciation of aqueous forms of fluoride in selected Ukrainian waters with a range of total fluoride contents determined using the PHREEQC chemical modelling programme

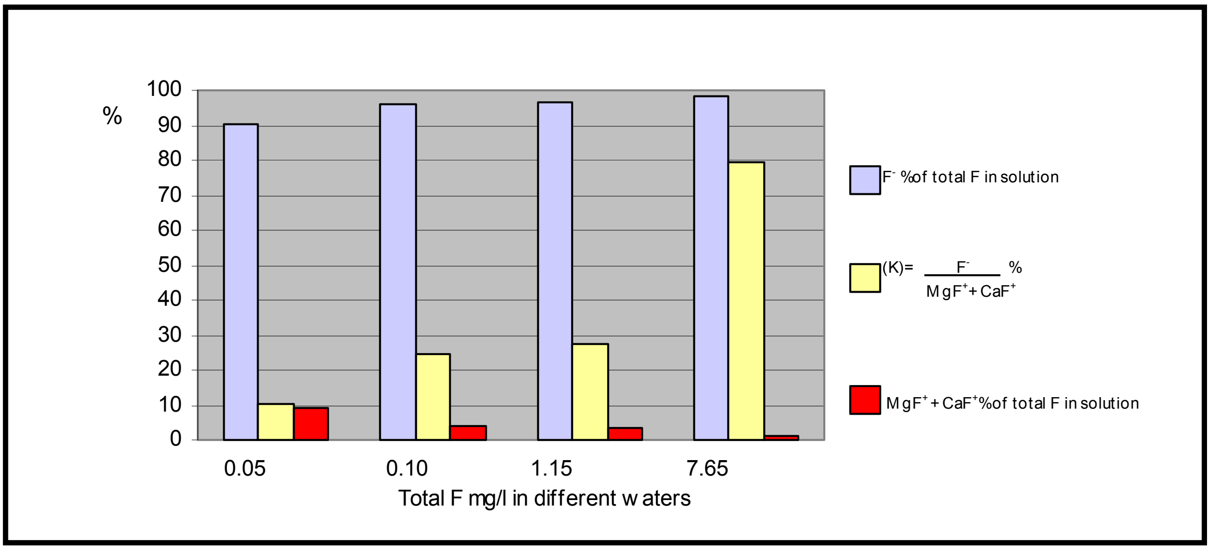


Figure 3.10 Percentage of aqueous forms of fluoride as a proportion of total fluoride content in selected Ukrainian waters showing the ratios of free F^- ions to MgF^+ and CaF^+ forms

3.3.5 Fluorosis Prevalence

Information on fluorosis prevalence in the study countries was limited. In Slovakia, no human incidences of fluorosis have been recorded and dental caries is more of a concern (see Chapter 5). Dental fluorosis has been reported historically in three locations in Hungary associated with high-fluoride waters, the water sources in these areas have since been altered and the disease is no longer prevalent (see Chapter 6). In a study of 3 groups of Hungarian children aged 14 exposed to contrasting fluoride concentrations in drinking water, (Schamschula et al., 1985) demonstrated a link between high fluoride contents and community fluorosis index values but the index values were too low (< 0.6) to constitute a public health problem (Table 6.7).

No national surveys of fluorosis prevalence have been carried out in Moldova or Ukraine. Therefore, fluorosis prevalence data for these countries were derived from previous studies of particular areas and information generated by the present project. The absence of information for large areas of these countries does not indicate a low risk of fluorosis, rather that the problem has yet to be fully investigated. The prevalence information available for the study countries demonstrate that the relationships between fluorosis and fluoride concentrations in the water are not simple (Table 3.6). Although it is often the case that waters containing > 1.5 mg/l cause disease, the disease also occurs in areas where water fluoride contents are below 1.5 mg/l and this may be due to other water chemistry factors, other non-water sources of fluoride and dietary or physiological factors in the areas concerned. However, all available fluorosis prevalence information was incorporated into the risk assessment scheme as this is one of the most important indicators of potential water fluoride problem areas.

3.3.6 Dental Caries Prevalence

Whilst some information on dental caries prevalence was collected as part of the present study (Table 3.7), caries problems were not the main focus of the study. Therefore, prevalence information was not collated consistently for the study region and is not included in the final dental caries risk assessment scheme but is included in the report for information only.

3.3.7 Population Data

In the theoretical framework outlined in Table 3.1, population density was highlighted as a risk parameter whereby densely populated areas have inherently higher risks of fluoride exposure than sparsely populated areas. Population statistics were available for Slovakia and Hungary but not for Moldova and Ukraine therefore population density data was difficult to quantify for the study region, Furthermore, relationships between populations at risk and fluoride in water depend upon the source of the water supply. For example, an area may contain high fluoride contents in groundwaters and a high population density, but if the population is supplied with low-fluoride water from elsewhere, the risk is significantly reduced. As a result, population density was not included the final risk assessment scheme but was included in this report as useful background information.

3.3.8 Industrial Sources

Information on industrial sources of fluoride in the study countries was made available to the project for Slovakia Hungary and Ukraine. There are no major industrial sources of fluoride in Moldova, however, dispersion in the environment does occur from agricultural products (see Chapter 7). In the case of Slovakia, industrial contamination poses one of the most likely risks of high fluoride in waters and more detailed investigations have been carried out in the affected region (Chapter 5). The presence of industry has been included in the final risk assessment as many of these sources do cause elevated concentrations of fluoride in surrounding surface and groundwaters. In Ukraine, an assessment of two industrial regions, Chervonograd in the West and Khar'kov-Dnepropetrovsk-Donetsk-Zaporozh’ye in the Centre-East of the country revealed that industrial sources related to coal mining do cause increased fluoride in the environment in the Chervonograd region but industrial sources have little impact on water fluoride concentrations in the Khar’kov-Dnepropetrovsk-Donetsk-Zaporozh’ye region. These findings were incorporated into the national risk assessment for Ukraine (Chapter 8).

Table 3.6 Dental caries and fluorosis prevalence information collated for the present study

Country	Location	Water F mg/l	Fluorosis Prevalence Rate %	Dental Caries Rate %	Healthy Teeth %
Hungary	Bar	>4`	Unknown		
	Dunaszekcso	2.2-2.4`	Unknown		
	Herceghalom	2.0-2.2`	Unknown	DMF-T = 2.0 at 1.3 - 2 mg/ F in water DMF-T = 2.82 - 3.52 at low F in water#	38 - 60% at 1.3 - 2 mg/l F in water 20 - 37% at low F in water#
	Kaptalanfa	1.3 - 2.0#	None	DMF-T = 2.0 at 1.3 - 2 mg/ F in water DMF-T = 2.82 - 3.52 at low F in water#	38 - 60% at 1.3 - 2 mg/l F in water 20 - 37% at low F in water#
	Csepa	1.3 - 2.0#	None	DMF-T = 2.0 at 1.3 - 2 mg/ F in water DMF-T = 2.82 - 3.52 at low F in water#	38 - 60% at 1.3 - 2 mg/l F in water 20 - 37% at low F in water#
	Szeleveny	1.3 - 2.0#	None	DMF-T = 2.0 at 1.3 - 2 mg/ F in water DMF-T = 2.82 - 3.52 at low F in water#	38 - 60% at 1.3 - 2 mg/l F in water 20 - 37% at low F in water#
	Tiszakurt	1.3 - 2.0#	None	DMF-T = 2.0 at 1.3 - 2 mg/ F in water DMF-T = 2.82 - 3.52 at low F in water#	38 - 60% at 1.3 - 2 mg/l F in water 20 - 37% at low F in water#
Moldova	Hyncheshty		30^		
	Gaydar		32^		
	Naslava Oknits		40^		
	Ungheny		40^		
	Komrat		40^		
	Congas, Komrat		40^		
	Beshgioz		40^		
	Bulboka, Nov. Aneny	0.6 - 1.0^	40^		
	Kiseliea, Komrat	0.6 - 1.0^	40^		
	Djoltay		45^		
	Falesti	0.39 - 5.3*	50^/ 61*		
	Kalarash	0.19 - 3.6*	50^/ 60*		
	Chadyr-Lunga		50^		
	Baurchi		50^		
	Ishkalevo, Falesti		50^		
	Glodeany		60^		
	Fegedeu, Falesti		60^		
	Falesti		62^		
	Beltsy		66^		
	Edintsy		72^		
	Pyrlitsa, Ungheny	1.2 – 17^	74^		
	Skuleany, Ungheny	1.2 – 17^	10^		
	Chadyr-Lunga		80^		
	Kazakliea		80^		
	Cornesti	0.2 - 0.88*	0*		
Ukraine	Sosnovka	0.2 - 3.5*	71.4*		
	Silyets	0 - 0.5*	0	66.7*	
	Zhovkva + Kulykiv	0 - 0.5*	0	29*	
	Peremyshlyany	0 - 0.5*	0	31.3*	
	Chervonograd	3 - 3.8*	38 – 68^		
	Lvov	3 - 3.8*	38 – 68^		
	Stryii	3 - 3.8*	38 – 68^		
	Drogobech	3 - 3.8*	38 – 68^		
	Odessa	0.01 - 0.6*		35 – 85^	
	Arciz	2 - 7*	92.78*	37.11*	
	Tatarbunary	2 - 7*	90^		
	Tarutino	2 - 7*	90^		
	Kiev	< 0.7*		90^	
	Podgorny	2.5 – 7.1*	85.71*	14.29*	
	Kiev	0.7 - 1.0*	4	0^	
	Girnik	3 - 3.8^	Unknown		
	Dimer	0 - 3*	Unknown		
	Dimer	1 – 2^	Unknown		
	Dimer	0 – 1^		30^	
	Ivanovsky			90^	
	Buchak	3.4 - 3.5^	100^		
	Polesky			90^	
	Stavishe	1 – 2^	Unknown		
	Stavishe	0 - 3*	Unknown		
	Stavishe	0 - 0.12^		30^	
	Tarashansky	0 - 0.12^		30^	
	Volodarsky	0 - 0.12^		30^	
	Jagotinsky	1 – 2^	Unknown		
	Poltava	1.4^	20^		
	Poltava	> 5^	100^		
	Poltava	1.8^	30^		
Slovakia			0		

DMF-T = Decayed, missing and filled teeth index `Baker (2000) ^ IGMOF data * Data from present study # (Farkas et al., 1999)

3.3.9 Dietary Factors

As indicated in previous sections of this report, fluorosis prevalence is not only dependent on fluoride intake from water by is influenced by other fluoride sources in the diet and dietary composition. There are very few dietary surveys available for the study countries but from the limited dietary information available it is likely that Ca, Mg and vitamin deficiencies are prevalent in communities at risk from fluorosis.

In Slovakia, a dietary study of children indicated Ca and P intakes were lower than recommended values (Kajaba and Bucko, 1968) and it was estimated that water accounts for 60%, food 40% and air a very minor component of the daily dietary intake of fluoride. Detailed dietary studies carried out in the Ziarska Kotlina Region of Slovakia associated with industrial sources of fluoride showed no evidence of elevated concentrations in food (see Chapter 5).

A study carried out by (Biro et al., 1996) demonstrated that Mg intakes were just adequate, but Ca and Vitamin E intakes were generally deficient in Hungarian diets. There is also some evidence to suggest that in low-fluoride areas, food is a more important source than water, air or dust (58 – 90% of intake in food, 0.01 – 0.17 % of intake in air, 0.03 – 0.37% intake in dust) (Schamschula et al., 1988a+b). Other studies carried out in Hungary showed that Ca, Al and Mg in food inhibit the uptake of fluoride but the mechanisms were not clear. Maize flour and leafy vegetables such as parsley and celery were found to contain the highest fluoride contents, but the highest concentrations in foodstuffs did not always correspond to regions with high-fluoride waters. However, the use of high-fluoride waters in cooking was found to enhance levels in prepared foods (Schamschula et al., 1988c+d). Toth and Sugar (1978) concluded that the daily dietary intakes of fluoride in Hungary from foodstuffs including the effect of cooking water were 0.096 - 0.567 mg/kg/ day (see Chapter 6).

Poor dietary Ca intakes have also been reported in the Chernobyl Region of Ukraine (Zaichick et al., 1996) whereas daily dietary intakes of fluoride are estimated at 0.5 – 1.1 mg in Ukraine. At low concentrations of fluoride in water (< 0.4 mg/l), food is a more important source in the diet, however, above this concentration, water is the dominant source. Several studies have demonstrated that the fluoride content of basic foodstuffs such as cabbage and potatoes can rise during cooking due to evaporation of cooking water. Based on dietary information, it is possible to approximate the daily amount of fluoride intake in different regions of Ukraine. In non-fluorosis-endemic areas, intakes of fluoride from food range from 0.7 – 1.2 mg. Total dietary intakes including water are estimated at 0.5 mg in fluoride-poor regions, 0.8 mg in fluoride-optimal regions and 1.2 mg in high-fluoride regions. Biogeochemical experts in Ukraine have demonstrated that fluoride intake varies with climate (higher in the south of the country due to greater water intakes in the hotter climate) and with the degree of physical activity of the person. Dietary intake has therefore been taken into account in the national risk assessment of potential problem areas in Ukraine (Chapter 8).

No dietary information from previous studies for Moldova was available to the project. Detailed dietary assessments in three towns, Kalarash, Falesti and Cornesti were carried out as part of the geochemical and health investigations of the present study. Results demonstrate high fluoride intakes, and low Ca, P, vitamin and protein dietary contents in towns (Kalarash and Falesti) affected by fluorosis (Chapter 7).

The absence of detailed information about the relationships between diet and fluorosis on a national scale for Slovakia, Hungary and Moldova make the impact of these factors difficult to quantify in the final risk assessment. Dietary factors have, however, been included in the national risk assessment of Ukraine based on previous studies carried out by biogeochemical experts. The general relationships between dietary factors and fluorosis are highlighted in this report to aid decision-making and risk management. The detailed dietary studies carried out as part of this project in Moldova are described in Chapter 7 and constitute a valuable contribution to the knowledge and understanding of the links between fluorosis and diet of which very few studies have been carried out internationally.

3.3.10 Water Supply Information

In addition to examining the potential for natural surface and ground- waters to contain high fluoride concentrations, in order to assess risk it is important to determine an exposure route to the population, namely whether or not the waters are used for drinking and if any treatments are carried out on the water prior to drinking. Comprehensive water supply information for each country was not available to the project but is held by local water engineers and operators who are in a position to examine the results of this study in more detail to initiate mitigation actions. In Slovakia and Hungary, for example, water is supplied by a complex mains pipeline system therefore relationships between natural groundwaters and tap drinking waters are difficult to quantify at the national scale. The following broad-scale information on water supplies has been incorporated into the final risk assessment scheme (Table 3.7).

Table 3.7 Water supply information for each country included in the final risk assessment scheme

Country	Water Sources	Water Used for Drinking	Water Fluoridation
Slovakia	Water mains supply	Water adjacent to industrial sources is not used for drinking	Water is fluoridated before supply to the public
Hungary	Water mains supply. High and low fluoride waters from cold and thermal wells can be available in the same location and are often mixed in the mains system	Water in areas of historic fluorosis incidence is no longer used for drinking	Water is not fluoridated before supply to the public
Moldova	Water mains supply and local supplies. High and low fluoride waters from different aquifer horizons can be available in the same location	Waters from several aquifer horizons are used for drinking	Water is not fluoridated before supply to the public
Ukraine	Water mains supply and local supplies. High and low fluoride waters from different aquifer horizons can be available in the same location	Waters from several aquifer horizons are used for drinking	Water is not fluoridated before supply to the public

3.4 DESIGN OF THE FINAL RISK ASSESSMENT SCHEME

It was evident from the data collation phase of the project that different types and levels of information exist for each of the study countries and some of the criteria outlined in the initial assessment framework were not available in geographic format on a national basis. For example, none of the study countries had complete coverage of the combination, fluorosis prevalence, dietary intake and water chemistry data. Many of the factors identified in the initial assessment framework such as water type and diet have an impact on fluoride risk but further studies are required to quantify the influence of these factors on disease. Therefore factors such as geology, hydrogeology, tectonically active zones, diet, water type and population density outlined in the initial framework were included in the final scheme for information only. In each country, different data sets were available nationally and for more detailed study areas, requiring two levels of risk assessment at national and local scales.

On the basis of the information available for Central Europe, a final simplified risk assessment scheme incorporating the water fluoride content, incidence of fluorosis, industrial sources of fluoride and water supply information was developed for high-fluoride and dental caries risk as follows.

3.4.1 Dental Caries Risk Scheme

As outlined in Section 3.3.6, although some dental caries prevalence data were available, this health problem was not the main focus of the project and these data were not included in the risk analysis. The final risk assessment scheme for dental caries is based upon the fluoride concentrations in water categorised by the WHO water quality guideline for caries < 0.5 mg/l combined with water supply information relating to fluoridation. For example, if water fluoride contents are < 0.5 mg/l the initial phase of the risk assessment categorises these waters as high risk. However, if these waters are fluoridated before supply to the public then the risk is reduced to moderate indicating that although potential health problems are not immediately evident, the situation should be monitored in the future. In some locations, both low and high fluoride waters are present both of which are used for drinking, these locations are highlighted in the scheme to show that although the risk from caries may be high, alternative water sources are locally available. The scheme and rationale are outlined in Table 3.8.

Table 3.8 Final risk assessment scheme for dental caries

Caries Risk					
Phase 1		**Phase 2**		**Final Risk**	**Assessment Rationale**
If water F mg/l < 0.5	**Potential Risk**	**If Water Fluoridated**	**Potential Risk**		
No	Low	Yes	Low	Low	Fluoride content is sufficient
No	Low	No	Low	Low	Despite no fluoridation, water fluoride content is sufficient
Yes	High	Yes	Low	Moderate	Although water is fluoridated, if fluoridation stops for any reason there will be a risk of dental caries, these areas should be monitored in the future
Yes	High	No	High	High	Fluoride content is insufficient
Yes and No	High/low			High/low	Water has low fluoride content but higher fluoride water is available in the vicinity
Unknown				Unknown	If the water fluoride content is unknown the risk is not assessed.

3.4.2 High-Fluoride Risk Assessment Scheme

The final risk assessment scheme for high-fluoride is based upon the presence or absence of fluoride in the environment indicated by water fluoride contents ≥ 1.5 mg/l (the WHO water quality guideline for fluorosis), the locations of fluorosis incidence and industrial sources. The scheme adopts a precautionary principle approach to the risk assessment whereby if any one of or a combination of these conditions is met in a location, the location is initially assigned a high risk. During the second phase of the assessment, this information is combined with water supply data to determine the overall risk. For example, an area of historic fluorosis incidence is categorised as high risk during the first phase of the assessment, however, if the population in this region no longer drink the high-fluoride water, the overall risk is reduced to moderate indicating that although no immediate problems are evident, the situation should be monitored in the future. Similarly if an industrial source is present and is known to cause high fluoride in the surrounding environment, the initial risk assigned is high. However, if the local population drink water from elsewhere, the overall risk is reduced to moderate. As in the case of caries risk, high- and low-fluoride waters can occur in the same vicinity. These locations are highlighted in the scheme to show that although the risk of fluorosis is high, alternative low-fluoride water sources are available locally. The scheme and rationale are outlined in Table 3.9.

The final dental caries and fluorosis risk schemes were transformed into a GIS data management system as outlined in the following chapter of this report and were applied to each of the study countries (Chapters 5-8).

Table 3.9 Final risk assessment scheme for high-fluoride

High-Fluoride Risk					
Phase 1		**Phase 2**		**Final Risk**	**Assessment Rationale**
If water F mg/l ≥ 1.5	**Potential Risk**	**If Drinking Water**	**Potential Risk**		
No	Low	Yes	Low	Low	Fluoride content should not normally cause problems, but may do under certain circumstances in hot climates
No	Low	No	Low	Low	Fluoride content should not normally cause problems, but may do under certain circumstances in hot climates
Yes	High	No	Low	Moderate	Although water is not currently used for drinking, if it were to be used in the future, health problems could arise
Yes	High	Yes	High	High	Fluoride content may cause health problems
Yes and No	High/low			High/low	Water has high fluoride content but lower fluoride water is available in the vicinity
Unknown				Unknown	If the water fluoride content is unknown and there is no evidence of fluorosis incidence or industrial sources, the risk is not assessed.
Or If Fluorosis Incidence	**Potential Risk**				
No	Low			Low	No history of fluorosis in the area therefore low risk
Yes	High	No	Low	Moderate	There is a history of fluorosis in the region but the water is no longer used for drinking therefore the risk is moderate indicating the situation should be monitored in case high fluoride waters are used for drinking in the future
Yes	High	Yes	High	High	There is evidence of fluorosis in the region and the waters are still used for drinking therefore high risk
Unknown				Unknown	If the prevalence of fluorosis is unknown and there is no evidence of high-fluoride waters or industrial sources, the risk is not assessed.
Or If Industrial Source					
No	Low			Low	No industrial sources of fluoride in the area therefore low risk
Yes	High	No	Low	Moderate	Although there is an industrial source of fluoride in the area, the waters are not used for drinking therefore the risk is moderate indicating the situation should be monitored in case high fluoride waters are used for drinking in the future
Yes	High	Yes	High	High	An industrial source of fluoride is present and the waters are used for drinking therefore high risk

4 Development of the Risk Assessment GIS

Bryony Hope and Fiona Fordyce

4.1 PRINCIPLES OF GEOGRAPHIC INFORMATION SYSTEMS (GIS)

A GIS is a computer system for capturing, storing, checking, integrating, manipulating, analysing and displaying data related to positions on the Earth's surface. Typically, a GIS is used for handling maps of one kind or another. These might be represented as several different layers where each layer holds data about a particular kind of feature. Each feature is linked to a position on the graphical image of a map. Layers of data are organised to be studied and to perform statistical analysis. GIS have become a very powerful tool in recent years and are used extensively by government, town planners, local authorities, public utility managers, environmental and resource managers, engineers, businesses, and marketing and distribution networks. A number of GIS are commercially available and the ArcView® (Environmental Systems Research Institute (ESRI)), system has been selected for the present study, as it is readily available in Central Europe.

GIS require input of geographic data, namely data that record the shape and location of a feature as well as associated characteristics, to define and describe the feature. For example, hydrogeological units can be located according to co-ordinate grid system references, and their attribute data such as aquifer type, or water quality can be recorded. GIS rely on data that are correctly georeferenced such that page co-ordinates on a planar map correspond to known real-world co-ordinates. It is essential that the type of locational co-ordinate system (for example latitude-longitude or national grid co-ordinates) and map projections are known. The projection is a method of representing the Earth's three-dimensional surface as a flat two-dimensional surface. This normally involves a mathematical model that transforms the locations of features on the Earth's surface to locations on a two-dimensional surface. Such representations inevitably distort some parameter of the Earth's surface, be it distance, area, shape, or direction. As a result, the rectification of different data sets, involving the rotation and scaling of map data may be required to spatially co-register data from different sources.

Information for the current project was derived from a number of sources including printed and digitally held topographic, hydrogeological and geological maps, geo-coded geochemical, hydrogeological and fluorosis prevalence information and area-based population information. It has been necessary to establish a common locational co-ordinate system based on latitude-longitude for all these different data sets and to spatially co-register these data via a process of rectification. Therefore maps developed in the GIS and presented in this report are in unprojected format unless otherwise stated, however, the data can be readily transformed from latitude-longitude to national grid coordinates within the GIS framework should this be required by future users of the system.

Geographic data are normally captured in the GIS in two main formats known as raster and vector information that deal with topology differently. Topology is the relative location of geographic phenomena independent of their exact position. In digital data, topological relationships such as connectivity, adjacency and relative position are usually expressed as relationships between nodes, links and polygons. Topology is useful in GIS because many spatial modelling operations don't require co-ordinates, only topological information. For example, to find an optimal path between two points requires a list of the lines or arcs that connect to each other and the cost to traverse each line in each direction. Co-ordinates are only needed for drawing the path after it is calculated.

Raster data are an abstraction of the real world where spatial data is expressed as a matrix of cells or pixels. Each cell must be rectangular in shape, although not necessarily square. Each cell within this matrix contains an attribute value as well as location co-ordinate. The spatial location of each cell is implicitly contained within the ordering of the matrix, unlike a vector structure, which stores topology explicitly. With the raster data model, spatial data is not continuous but divided into discrete units. This makes raster data particularly suitable for certain types of spatial operation, for example overlays or area calculations. Areas containing the same attribute value are recognised as such; however, raster structures cannot identify the boundaries of such areas as polygons. Also raster structures may lead to increased storage in certain situations, since they store each cell in the matrix regardless of whether it is a feature or simply 'empty' space.

Vector data are an abstraction of the real world whereby positional data are represented in the form of co-ordinates. In vector data, the basic units of spatial information are points, lines and polygons. Each of these units is composed simply of a series of one or more co-ordinate points, for example, a line is a collection of related points, and a polygon is a collection of related lines.

Point data are a zero-dimensional abstraction of an object represented by a single X, Y co-ordinate. A point normally represents a geographic feature too small to be displayed as a line or area; for example, the location of a water well on a small-scale map. Line data comprise a set of ordered co-ordinates that represent the shape of geographic features too narrow to be displayed as an area at the given scale (for example, contours, streets, or streams) or linear features with no area such as county boundaries. Finally, polygons are a feature used to represent areas. A polygon is defined by the lines that make up its boundary and a point inside its boundary for identification. Polygons have attributes that describe the geographic feature they represent. For example, the outcrop of a geological rock unit can be represented by a polygon whose boundaries define the extent of the unit. Attributes such as the rock type and geochemistry can be also attached to the polygon.

Vector information is of most use in the current study as it allows the attachment of risk attributes to polygons and points etc.

Once data are entered into the GIS, spatial querying and spatial modelling can be performed. There are three categories of spatial modelling functions that can be applied to geographic features within a GIS as follows:

(i) *geometric models, such as calculating the straight-line distance between features, generating buffers and calculating areas and perimeters*
(ii) *coprevalence models, such as overlays*
(iii) *adjacency models (pathfinding, redistricting, and allocation)*

For the purposes of this project, two key functions were the assigning of polygon or point attributes and overlay co-prevalence models. The ability to assign attributes to polygons or points can be used to define likely risk in particular areas. For example, a water well containing high fluoride concentrations can be assigned a 'high-risk' attribute. Overlaying is the process of superimposing two or more maps, through registration to a common co-ordinate system, such that the resultant maps contain the data from both maps for selected features. This technique was used to develop the overall risk avoidance maps whereby different features such as groundwater fluoride maps and fluorosis prevalence maps were combined together.

In the GIS, the various data layers are held within an ArcView® workspace called a *'project'*. For each layer of data (called a '*theme'* in ArcView®) a *shapefile* is generated. ArcView® *shapefiles* are a simple, non-topological format for storing the geometric location and attribute information of geographic features. The *shapefile* format defines the geometry and attributes of geographically-referenced features in as many as five files with specific file extensions that should always be stored in the same *project* workspace. ArcView® *projects*, display geographic data in interactive maps called '*views*'. Each feature in the *view* is listed in a '*table of contents'*. Within each *project*, the attributes of features displayed in a *view* are held in '*tables*' and by selecting features in a *view*, the attribute records in the *table* are automatically highlighted. The *tables* also have a full range of functions for obtaining summary statistics, sorting and querying data. ArcView® *projects* can also contain legend and symbol files, which aid data presentation. These different file types, which should always be stored in the same *project* for the GIS to work, are outlined as follows:

- *.apr – ArcView® project, the workspace that contains all the data layers*
- *.shp - the file that stores the feature geometry.*
- *.shx - the file that stores the index of the feature geometry.*
- *.dbf - the dBASE file that stores the attribute information of features. When a shapefile is added as a theme to a view, this file is displayed as a feature table.*
- *.sbn and .sbx - the files that store the spatial index of the features. These two files may not exist unless a theme on theme selection, spatial join, or an index on a theme shape field is created.*

- *.ain and .aih - the files that store the attribute index of the active fields in a table or a theme's attribute table. These two files may not exist unless tables have been linked.*

- *.avl – an ArcView® legend, a file, which stores the classifications, symbols and colours applied to a theme.*

- *.avp - ArcView® palette, a file, which loads extra symbols.*

- *.ave – ArcView® script file written in the programming language Avenue, these files are macros allowing customisation of the ArcView® programme*

4.2 GIS DESIGN

The overall aim of the GIS was to combine various geographic datasets from Central Europe to produce final dental caries and high-fluoride risk avoidance maps according to the assessment scheme developed for the project.

Risk assessment GIS have been developed previously for fluoride in Durango, Mexico where concentrations determined in tap water were used to categorise the city into zones of low to high risk. Exposure assessments were calculated for infants, adults and children on the basis of body weight and water consumption and demonstrated that 95% of the population had high fluoride intakes in excess of 0.05 mg kg day^{-1} (Ortiz et al. 1998). Similarly Apambire et al. (1997) investigating prevalence rates of 62 % dental fluorosis in school children in the Bolgatanga and Bongo Districts of Ghana demonstrated that 23 % of the groundwater wells in the region had concentrations above 1.5 mg/l F^-. Due to the climatic conditions, daily water consumption in the population was approximately 3 to 4 1. In addition, dietary intake was higher than WHO baseline values (0.2-0.5 mg/day). 'Geochemical health-risk maps' were generated by contouring the water fluoride data using intake interval guidelines more closely aligned to regional climatic and dietary conditions, to aid health officials in the assessment of fluorosis risk.

These two fluoride risk assessment investigations focussed on relatively small survey areas where water data, exposure information and disease prevalence rates could be collected and examined simultaneously, allowing exposure risk assessments to be calculated. During the present study it was not possible to collate this type of information at the national level for Central Europe. However, information on water supply and fluorosis prevalence were included to give some indication of exposure in the GIS risk assessment adopted.

As outlined in the previous chapter of this report, different information was available for each of the study countries at both national and regional scales. As a result, the project GIS was designed to incorporate two different levels of information. The first or basic level of the risk assessment covers the whole country in each case of Ukraine, Slovakia, Hungary and Moldova. The purpose of this level is to provide an overview of the risks of high-fluoride and of dental caries and highlight areas that in the opinion of the geology and health experts from Central Europe, present a known or suspected threat to human health from fluoride.

The second or more detailed level of risk assessment incorporates information from the current project where the links between environmental and health factors have been more closely examined at the local scale. Information at this level is available for the Ziarska Kotlina Basin in Slovakia, the Falesti Region of Moldova and the Kiev, Lvov, Poltava and Odessa Regions of Ukraine. No detailed study area information was available in GIS format for Hungary, however, further information on high-fluoride waters in the Central Great Hungarian Plain is described in this report (Chapter 6).

Due to the different nature, quantity and intellectual property rights (IPR) of the data for each of the study countries, two types of GIS were developed for the project. In the first instance a detailed GIS containing all the was developed for the Central European project partners for use within their continued studies of water management and fluoride mitigation and for dissemination by them in each country. This GIS is called **Country.apr**. The second type of GIS is a generic system called **Central.apr** designed for general distribution, which contains the final risk assessment maps from the four study countries only.

Within the Country.apr GIS, the hydrogeological units in Slovakia, Hungary and Moldova were classified according to aquifer importance by assigning low, moderate and high categories to each of the aquifer polygons depending on the use of the aquifer for drinking water. These data and other layers such as tectonic zones, geology, hydrogeology, population centres and dental caries incidence were included in the GIS for background information. The data layers used in the final risk assessment were also incorporated- water fluoride content, industrial fluoride sources and fluorosis incidence. The overall GIS scheme developed by the project and the different data layers held in each type of GIS are detailed in Tables 4.1 and 4.2 .

Much of the locational information incorporated into the GIS (roads, rivers, railways, country boundaries, cities etc.) was derived from geographic resource packages available via the ArcView® web-site: www.esri.com.

Within the GIS, the final risk avoidance maps for Slovakia, Ziarska Kotlina, Hungary, Moldova, Kiev, Poltava, Lvov and Odessa were developed using a grid-square system. Countries and local study regions were divided into a series of grid square polygons by creating a new grid theme or shapefile using the ArcView® script *planimetry.ave* (www.esri.com). The size of the grid was selected on the basis of the sample density of the water chemistry information as in all cases this was the most comprehensive data set in each location (Table 4.3).

Table 4.1 Summary of information layers in the Generic GIS – Central.apr

Country	National Layer	Information Category	Regional Layers	Information Category
Slovakia	Roads	Locational	Ziarska Kotlina	
	Railways	Locational	Roads	Locational
	Lakes	Locational	Railways	Locational
	Rivers	Locational	Rivers	Locational
	Islands	Locational	Towns	Background
	Country Boundary	Locational	Buildings	Background
	Cities	Background	Industrial Source	Risk Assessment
	Main Towns	Background	Dental Caries Risk Map	Final Map
	Industrial Sources	Risk Assessment	High-Fluoride Risk Map	Final Map
	Dental Caries Risk Map	Final Map		
	High-Fluoride Risk Map	Final Map		
Hungary	Roads	Locational	-	-
	Railways	Locational		
	Lakes	Locational		
	Rivers	Locational		
	Country Boundary	Locational		
	Cities	Background		
	Main Towns	Background		
	Dental Caries Risk Map	Final Map		
	High-Fluoride Risk Map	Final Map		
Moldova	Roads	Locational	Falesti	
	Railways	Locational	Roads	Locational
	Rivers	Locational	Cities	Background
	Country Boundary	Locational	Main Towns	Background
	Cities	Background	High-Fluoride Risk Map	Final Map
	Main Towns	Background		
	Dental Caries Risk Map	Final Map		
	High-Fluoride Risk Map	Final Map		
Ukraine	Roads	Locational	Lvov	
	Railways	Locational	Roads	Locational
	Rivers	Locational	Regional Boundaries	Locational
	Country Boundary	Locational	Main Towns	Background
	Region Boundaries	Locational	Dental Caries Risk Map	Final Map
	Cities	Background	High-Fluoride Risk Map	Final Map
	Main Towns	Background	Kiev	
	Fluoride Biogeochemical Risk Map	Final Map	Roads	Locational
	High-Fluoride Risk Map	Final Map	Regional Boundaries	Locational
			Main Towns	Background
			Dental Caries Risk Map	Final Map
			High-Fluoride Risk Map	Final Map
			Odessa	
			Roads	Locational
			Regional Boundaries	Locational
			Main Towns	Background
			Dental Caries Risk Map	Final Map
			High-Fluoride Risk Map	Final Map
			Poltava	
			Roads	Locational
			Regional Boundaries	Locational
			Main Towns	Background
			Dental Caries Risk Map	Final Map
			High -Fluoride Risk Map	Final Map

Table 4.2 Summary of information layers in the Project Partner GIS – Country.apr

Country	National Layer	Information Category	Regional Layers	Information Category
Slovakia	Roads	Locational	Ziarska Kotlina	
	Railways	Locational	Roads	Locational
	Lakes	Locational	Railways	Locational
	Rivers	Locational	Rivers	Locational
	Islands	Locational	Towns	Background
	Country Boundary	Locational	Buildings	Background
	Cities	Background	Snow Chemistry	Background
	Main Towns	Background	Surface Water Chemistry	Risk Assessment
	Resident Population	Background	Groundwater Chemistry	Risk Assessment
	Tectonic Zones	Background	Industrial Source	Risk Assessment
	Hydrogeology Units	Background	Water Supply	Risk Assessment
	Aquifer Importance	Background	Dental Caries Risk Map	Final Map
	Groundwater Chemistry	Risk Assessment	High-Fluoride Risk Map	Final Map
	Industrial Sources	Risk Assessment		
	Water Supply	Risk Assessment		
	Dental Caries Risk Map	Final Map		
	High-Fluoride Risk Map	Final Map		
Hungary	Roads	Locational	-	-
	Railways	Locational		
	Lakes	Locational		
	Rivers	Locational		
	Country Boundary	Locational		
	Cities	Background		
	Main Towns	Background		
	Resident Population	Background		
	Geology	Background		
	Recharge/ Discharge Zones	Background		
	Hydrogeology Units	Background		
	Aquifer Importance	Background		
	Industrial Sources	Risk Assessment		
	Fluorosis Incidence	Risk Assessment		
	Drinking Water Chemistry	Risk Assessment		
	Thermal Well Chemistry	Risk Assessment		
	Cold Well Chemistry	Risk Assessment		
	Water Supply	Risk Assessment		
	Dental Caries Risk Map	Final Map		
	High-Fluoride Risk Map	Final Map		
Moldova	Roads	Locational	Falesti	
	Railways	Locational	Roads	Locational
	Rivers	Locational	Cities	Background
	Country Boundary	Locational	Main Towns	Background
	Cities	Background	Fluorosis Prevalence Girls	Background
	Main Towns	Background	Fluorosis Prevalence Boys	Background
	Hydrogeology Units	Background	Dietary Ca Intake Girls	Background
	Aquifer Importance	Background	Dietary Ca Intake Boys	Background
	Fluorosis Incidence	Risk Assessment	Dietary F Intake Girls	Background
	Groundwater Chemistry	Risk Assessment	Dietary F Intake Boys	Background
	Water Supply	Risk Assessment	Water Supply	Risk Assessment
	Dental Caries Risk Map	Final Map	Tap Water Chemistry	Risk Assessment
	High-Fluoride Risk Map	Final Map	Fluorosis Incidence	Risk Assessment
			High-Fluoride Risk Map	Final Map
Ukraine	Roads	Locational	Lvov	
	Railways	Locational	Roads	Locational
	Rivers	Locational	Regional Boundaries	Locational
	Country Boundary	Locational	Main Towns	Background
	Region Boundaries	Locational	Tectonic Zones	Background
	Cities	Background	Caries Prevalence	Background
	Main Towns	Background	Fluorosis Prevalence	Risk Assessment
	Tectonic Zones	Background	Fluorosis Hotspots	Risk Assessment
	Tectonic Regions	Background	Groundwater Chemistry	Risk Assessment
	Fluorosis Incidence	Background	Dental Caries Risk Map	Final Map
	Dental Caries Incidence	Background	High Fluoride Risk Map	Final Map
	Groundwater Chemistry	Background	Kiev	
	Fluoride Biogeochemical Risk Map	Final Map	Roads	Locational
	High-Fluoride Risk Map	Final Map	Regional Boundaries	Locational
			Main Towns	Background
			Tectonic Zones	Background
			Caries Prevalence	Background
			Fluorosis Prevalence	Risk Assessment
			Fluorosis Hotspots	Risk Assessment
			Groundwater Chemistry	Risk Assessment
			Dental Caries Risk Map	Final Map
			High Fluoride Risk Map	Final Map
			Odessa	
			Roads	Locational
			Regional Boundaries	Locational
			Main Towns	Background
			Tectonic Zones	Background
			Caries Prevalence	Background
			Fluorosis Prevalence	Risk Assessment
			Fluorosis Hotspots	Risk Assessment
			Groundwater Chemistry	Risk Assessment
			Dental Caries Risk Map	Final Map
			High Fluoride Risk Map	Final Map
			Poltava	
			Roads	Locational
			Regional Boundaries	Locational
			Main Towns	Background
			Tectonic Zones	Background
			Caries Prevalence	Background
			Fluorosis Prevalence	Risk Assessment
			Fluorosis Hotspots	Risk Assessment
			Groundwater Chemistry	Risk Assessment
			Dental Caries Risk Map	Final Map
			High Fluoride Risk Map	Final Map

Table 4.3 Grid sizes used for the preparation of final risk assessment maps in Central Europe

Location	Water Chemistry Data Sample Density per km^2	Grid Square Size km^2
Slovakia	1 per 2-3	2
Ziarska Kotlina, Slovakia	1 per 0.5	0.5
Hungary	1 per 3	3
Moldova	1 per 5	5
Lvov, Ukraine	1 per 6.5	6.5
Poltava, Ukraine	1 per 6.5	6.5
Odessa, Ukraine	1 per 6.5	6.5
Kiev, Ukraine	1 per 6.5	6.5

Creating the grids as polygons allowed the risk attributes of the basic data layers to be assigned to each grid polygon according to the final GIS risk assessment scheme, which is outlined in Table 4.4 and Figure 4.1.

For each grid, the attribute table was edited to contain columns (known as fields in ArcView®) for dental caries risk (C_Risk), high-fluoride water (F_Risk), fluorosis incidence (F_Incidenc) and industrial sources (Industry) (Table 4.4). During the first phase of the risk assessment, the grids were overlain on the water chemistry, industrial source and fluorosis incidence base data layers, which were interrogated using the ArcView® *Query Function.* Risk codes were assigned to the above attribute fields for every grid square based on the fluoride contents in water (< 0.5 mg/l for C_Risk) (≥ 1.5 mg/l for F_Risk); the presence or absence of fluorosis incidence (F_Incidenc) and the presence or absence of industrial sources (Industry) (Tables 4.4 and 4.5, Figure 4.1). In cases where both high and low fluoride waters were present in the same square, the scheme adopts a precautionary principle approach, taking the highest fluoride value in the case of high-fluoride risk and the lowest fluoride value in the case of dental caries risk.

During the second phase of the risk assessment, two more fields were added to the grid attribute tables called 'Drink' and 'Treat'. Water supply information indicating whether or not water was used for drinking ('Drink') and whether or not water was fluoridated before supply to the public ('Treat') was then added to these fields for each grid square (Tables 4.4 and 4.5, Figure 4.1).

The final phase of the assessment used the ArcView® *Query Function* to combine information about fluoride sources (Phase 1) with the water supply information (Phase 2) to assign the final risk code to each square. This information was entered into two new fields called 'RISK_C' for dental caries risk and 'RISK_F' for high-fluoride risk. The data were combined such that in squares were high-fluoride risks were identified but the water was not used for drinking, the final risk code assigned was moderate; in squares were dental caries risks were identified but water was fluoridated before supply to the public, the final risk code assigned was moderate and in squares with both high high-fluoride risk and high dental caries risk, the presence of alternative water sources were highlighted (Tables 4.4 and 4.5, Figure 4.1).

Table 4.4 GIS risk assessment based on assigning high-fluoride and dental caries risk attributes to grid squares for each of the study regions Slovakia, Ziarska Kotlina, Hungary, Moldova, Lvov, Kiev, Odessa and Poltava

Grid Attribute Field	Data	Risk Category	Initial Grid Square Risk Code	Final Grid Square Risk Code
Phase 1				
C_Risk	Water Fluoride ≥ 0.5 mg/l Water Fluoride < 0.5 mg/l Water Fluoride unknown	Low High Unknown	L H U	
F_Risk	Water Fluoride < 1.5 mg/l Water Fluoride ≥ 1.5 mg/l Water Fluoride unknown	Low High Unknown	L H U	
F_Incidenc	Fluorosis Incidence = No Fluorosis Incidence = Yes	Low High	L H	
Industry	Industrial Source = No Industrial Source = Yes	Low High	L H	
Phase 2				
Drink	Water used for drinking = Yes Water used for drinking = No	Yes No	Y N	
Treated	Water fluoridated = Yes Water fluoridated = No	Yes No	Y N	
Final Risk				
RISK_C	If C_Risk = H If C_Risk = H + Treated = Y If C_Risk = L If C_Risk = U If RISK_F = H + RISK_C = H	High Moderate Low Unknown Alternative water source available		H M L U A
RISK_F	If F_Risk = H If Industry = Y If F_Incidenc = Y If F_Risk = H + Drink = N If F_Risk = L If F_Risk = U If RISK_F = H + RISK_C = H	High High High Moderate Low Unknown Alternative water source available		H H H M L U A

Table 4.5 Examples of risk attribute data assigned to grid polygons in the GIS

Grid Shape	Phase 1				Phase 2		Final Risk Category	
	F_Risk	C_Risk	Industry	F_Incidenc	Drink	Treated	RISK_F	RISK_C
Polygon	U	U	N	N	N	N	U	U
Polygon	L	H	N	N	N	N	L	H
Polygon	H	L	Y	Y	N	Y	M	L
Polygon	H	H	N	N	N	N	A	A
Polygon	L	H	N	N	N	Y	L	M
Polygon	H	L	N	N	Y	N	H	L

The grid squares were displayed in map format and colour coded according to the final dental caries (RISK_C) and high-fluoride (RISK_F) (Table 4.4) to produce the final risk avoidance maps. The ArcView® procedure for creating the final risk avoidance maps is outlined in Section 4.3 Appendix 1 of this report.

In the case of the detailed study region in Falesti, Moldova, geochemistry and heath data were available for three population centres in the region, Falesti, Cornesti and Kalarash. It was not possible to adopt a grid square approach for the preparation of the final risk avoidance maps in this case due to the limited spatial distribution of the data. The final maps follow the same risk assessment scheme but the data are presented as point locations rather than in a grid format (Chapter 7).

Due to the lack of national geochemistry and health data available for Ukraine, the final countrywide risk assessment map is not based on the GIS risk assessment scheme or on the gird square system but has been compiled on the basis of the biogeochemical characteristics of the different Regions of Ukraine determined by local experts. The map takes into account the likely fluoride content in drinking water, likely total dietary fluoride intake, likely dietary intake from water (which is more in the south of the country than in the north), likely industrial sources of fluoride; the presence of high-fluoride waters associated with tectonically active zones and information on the prevalence of dental caries and fluorosis.

This map, which presents both high-fluoride and dental caries risks has been incorporated as a layer in the country.apr and central.apr GIS. For the purposes of the final presentation of high-fluoride risk across the whole study region, the map of Ukraine was reclassified according to the project risk assessment scheme and combined with the grid-based maps of Slovakia, Moldova and Hungary (Chapter 9).

A guide to the using the GIS developed by the project is outlined in Section 4.4 Appendix 2 of this report.

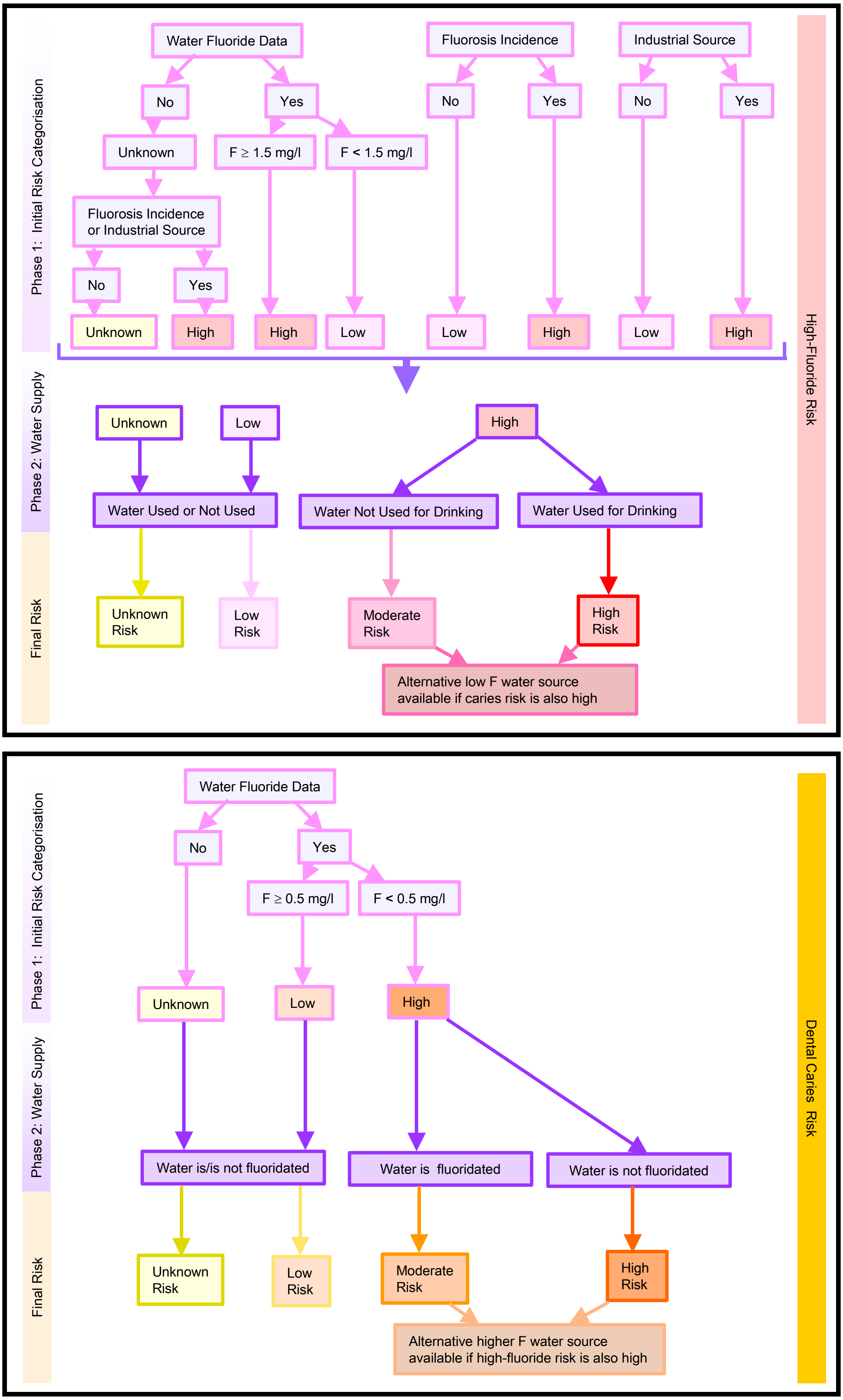


Figure 4.1 Flow diagram of the GIS-based high-fluoride and dental caries final risk assessment schemes

4.3 APPENDIX 1: ARCVIEW® PROCEDURE FOR CREATION OF THE FINAL RISK AVOIDANCE MAPS

Creating the Grid

1. Within the GIS containing the background data layers, create a grid (using the ArcView® script, *planimetry.ave*, downloaded from www.esri.com) approximating to the required grid cell size.

2. Create a new polygon theme within ArcView® and paste in the grid to create a grid theme.

3. Clip the grid theme to the country or region boundary using the ArcView® *Geoprocessing Wizard* extension.

4. Open the grid theme attribute table and add in the following string fields with a width of 1:

	Explanation
C_Risk	(relates to water F mg/l)
F_Risk	(relates to water F mg/l)
F_Incidenc	(relates to fluorosis incidence)
Industry	(relates to industrial sources)
Drink	(relates to use of water for drinking)
Treated	(relates to water fluoridation)
RISK_C	(Final dental caries risk code)
RISK_F	(Final high-fluoride risk code)

Phase 1: Dental Caries Initial Risk Assessment

5. With the background water data set open using the ArcView® *query button* select all locations where fluoride concentrations in the background water dataset < 0.5 mg/l.

6. Use the *select by theme* function from the *Theme* menu to highlight all grid cells containing the data selected above.

7. Open the grid theme attribute table and use the *field calculator button* to assign the initial risk value “H” (High) to the C_Risk field for all the selected cells.

8. Make a new selection of water fluoride data to highlight all locations where fluoride concentrations are ≥ 0.5 mg/l.

9. Use the *select by theme* function again to highlight all grid cells containing the new set of data selected above.

10. Use the *query button* on the grid theme to highlight all cells where (C_Risk <> “H”) from the current selection so as not to overwrite the existing ‘High’ cell values.

11. Use the *field calculator button* to assign the initial risk value “L” (Low) to all the selected cells in the C_Risk field.

12. Use the *query button* to make a new selection (C_Risk <> “H”) and (C_Risk <> “L”) to select all cells without a value.

13. Use the *field calculator button* to assign the value “U” (unknown) to these unclassified cells in the C_Risk field.

Phase 1: High-Fluoride Initial Risk Assessment

14. With the background water data set open, using the ArcView® *query button* select all locations where fluoride concentrations ≥ 1.5 mg/l.

15. Use the *select by theme* function from the *Theme* menu to highlight all grid cells containing the data selected above.

16. Open the grid theme attribute table and use the *field calculator button* to assign the initial risk value "H" (High) to the F_Risk field for all the selected cells.

17. Make a new selection of water fluoride data to highlight all locations where fluoride concentrations are < 1.5 mg/l.

18. Use the *select by theme* function again to highlight all grid cells containing the new set of data selected above.

19. Use the *query button* on the grid theme to highlight all cells where (F_Risk <> "H") from the current selection so as not to overwrite the existing 'High' cell values.

20. Use the *field calculator button* to assign the initial risk value "L" (Low) to all the selected cells in the F_Risk field.

21. Use the *query button* to make a new selection ((F_Risk <> "H") and (F_Risk <> "L") to select all cells without a value.

22. Use the *field calculator button* to assign the value "U" (unknown) to these unclassified cells in the F_Risk field.

23. With the industrial source base data set open, use the *select by theme* function to select all grid cells, which contain an industrial source.

24. Use the *field calculator button* to assign "Y" (Yes) to the selected cells in the Industry field, click the *switch selection button* and assign "N" (No) to all other cells.

25. With the fluorosis incidence base data set open, use the *select by theme* function to select all grid cells, which contain fluorosis incidence.

26. Use the *field calculator button* to assign "Y" (Yes) to the selected cells in the F_Incidenc field, click the *switch selection button* and assign "N" (No) to all other cells.

Phase 2: Water Supply Information

27. If it is known that water is or is not used for drinking or if water is fluoridated or non-fluoridated, for different locations, assign "Y" (Yes) or "N" (No) in the Drink and Treated fields as necessary.

Final Risk Assessment: High-Fluoride

28. Using the *query* and *field calculator buttons*, populate the RISK_F field according to the following criteria (note: assign the final risk values in the order shown below - if a value has already been assigned by previous criteria, then overwrite it):

    i. If F_Risk = "H" then "H" (High Risk)
    ii. If F_Risk = "L" then "L" (Low Risk)
    iii. If F_Risk = "U" then "U" (Unknown Risk)
    iv. If F_Incidenc = "Y" then "H" (High Risk)
    v. If Industry = "Y" then "H" (High Risk)
    vi. If F_Risk = "H" and Drink = "N" then "M" (Moderate Risk)

Final Risk Assessment: Dental Caries

29. Using the *query* and *field calculator buttons*, populate the RISK_C field according to the following criteria (note: assign the final risk values in the order shown below - if a value has already been assigned by previous criteria, then overwrite it):

    i. If C_Risk = "H" then "H" (High Risk)
    ii. If C_Risk = "L" then "L" (Low Risk)
    iii. If C_Risk = "U" then "U" (Unknown Risk)
    iv. If C_Risk = "H" and Treated = "Y" then "M" (Moderate Risk)

Alternative Water Sources

30. Finally, using the *query button*, select all cells that have both 'High' RISK_F and 'High' RISK_C classifications and assign both these fields with "A" rather than 'High' as an alternative water source is available in these locations.

4.4 APPENDIX 2: GUIDE TO USING THE RISK ASSESSMENT GIS

The project GIS are distributed on CD-Rom. The ArcView® GIS software package must be loaded onto the host computer before the CD-Rom versions of the GIS will operate.

Generic GIS – Central.apr

The CD-Rom has a folder called Central_Europe which contains the **Central.apr** GIS and associated ArcView® files. Within this folder are four sub-folders for each of the study countries (Hungary, Slovakia, Ukraine and Moldova) containing the data layers for each country.

To open the GIS, click on the file **Central.apr**. The GIS should open automatically. The first level of information displayed is a map of the whole study region. The final risk assessment maps for each country and each of the study regions and the background locational data sets such as roads and railways appear in the table of contents list to the left of the view screen. Any of these layers can be viewed by ticking the check-box in the table of contents list.

In CD-Rom, format, the **Central.apr** GIS is read-only. The GIS can be copied to a new host computer for use in future studies.

Project Partner GIS – Country.apr

The CD-Rom has a folder called Central_Europe which contains the **Country.apr** GIS and associated ArcView® files. Within this folder are four sub-folders for each of the study countries (Hungary, Slovakia, Ukraine and Moldova) containing the data layers for each country.

To open the GIS, click on the file **Country.apr**. The GIS should open automatically. The first level of information displayed is a map of the whole study region. The final risk assessment maps for each country and each of the study regions and the background locational data sets such as roads and railways appear in the table of contents list to the left of the view screen. Any of these layers can be viewed by ticking the check-box in the table of contents list.

In the menu bar across the top of the view, is an option called 'Central Europe'. Under this menu, the background data layers included in the GIS for each country can be accessed by clicking on the country required. Once a country is selected, the set of data layers available for that country will appear in the table of contents list to the left of the view screen. Any of these layers can be viewed by ticking the check-box in the table of contents list.

In CD-Rom, format, the **Country.apr** GIS is read-only. The GIS can be copied to a new host computer for use in future studies.

5 Fluoride Risk Assessment for Slovakia

Kamil Vrana, Fiona Fordyce and Bryony Hope

5.1 INTRODUCTION

As outlined at the start of this report, the assessment of fluoride risks in Slovakia was not included in the original project concept, however, due to the excellent national geochemical data available, Slovakia has been included in the risk assessment scheme for Central Europe to broaden the scope of this study. No evidence of dental fluorosis in the population has been recorded in Slovakia and low fluoride contents in most waters mean that the risk of dental caries is more of a problem in this region. However, industrial fluoride contamination has been well documented in the Ziarska Kotlina Basin of Slovakia and presents an excellent example of risk assessment associated with an industrial source. Information for Slovakia as a whole and for the Ziarska Kotlina Basin study area is presented in this chapter.

5.2 NATIONAL RISK ASSESSMENT

The data incorporated into the Project Partner GIS (Country.apr) for Slovakia are listed in Table 5.1. At the national level, the map of hydrogeological units (SGUDS (Rapant et al., 1996)) (Figure 5.1), hydrogeology classified according to aquifer importance (Figure 5.2), the population of the main towns (Figure 5.3) and the location of tectonic features (Figure 5.4) were included in the GIS for background information only.

The national fluoride risk assessments for Slovakia were carried out on the basis of the groundwater chemistry database for the whole country (SGUDS (Rapant et al., 1996)), water supply information and the location of industrial sources of fluoride (Tables 5.2 and 5.3).

The 16359 records in the national groundwater chemistry database (SGUDS (Rapant et al., 1996)) provide excellent detailed (1 sample per 2.5 - 3 km^2) information on the fluoride contents in Slovakian waters (Figure 5.5). During the initial phase of the risk assessment these data were categorised by fluoride concentration according to the WHO guideline values of < 0.5 mg/l caries risk and ≥ 1.5 mg/l fluorosis risk. The WHO guidelines are similar to Slovak Standard 757111 which recommends that drinking water should contain 0.8 – 1.0 mg/l fluoride (unless fluoride intake from different sources is ensured) but should not exceed 1.5 mg/l fluoride.

Due to the litho logical and mineralogical characteristics of the rocks in Slovakia, very little fluoride is released to groundwaters from primary sources. The map of groundwater fluoride distribution (Figure 5.5) indicates that in over half of the samples, the fluoride content is below the limit of detection (0.1 mg/l). Concentrations below the detection limit occur in groundwaters with total dissolved solid (TDS) contents of 250 – 300 mg/l. Only 21% of samples contain fluoride contents of more than 0.18 mg/l and the maximum concentration is an exceptional value of 4 mg/l. The average highest concentrations of fluoride occur in the south-eastern Danube Basin and East Slovakian Basin and are seasonally variable. Therefore, depending on the time of year the samples are collected, the fluoride contents may or may not exceed the 1.5 mg/l threshold.

In Slovakia it is estimated that water accounts for 60%, food 40% and air a very minor component of the daily dietary intake of fluoride therefore water is the most important source. In addition, dietary studies have shown that in general Ca and P intakes are lower than recommended values (Kajaba and Bucko, 1968). Despite these facts, no incidences of fluorosis related to environmental exposure have been reported in Slovakia therefore the only other information incorporated into the national risk assessment was the location of industrial sources (Figure 5.4).

Very few waters present a risk of in terms of high fluoride and on the basis of the water chemistry information alone, the majority of the country would be at risk from dental caries. However, the water supply in Slovakia is fluoridated before provision to the population reducing the risk of dental caries.

The dental caries and high-fluoride risk avoidance maps for Slovakia are based on a grid size of 2 km^2 compatible with the sample density of the water chemistry data set used in the risk assessment. In each grid square, water fluoride content data were combined with water supply information to produce the final risk maps (Annex 1 and 2).

Across most of Slovakia, the dental caries risk is classified as moderate indicating that although the majority of waters have low fluoride contents the overall risk classification is reduced to moderate as the water supply is fluoridated. The moderate rather than low classification indicates that the situation should be monitored as if at any time in the future, water fluoridation was interrupted, the risks of dental caries associated with low-fluoride waters would increase (Annex 1).

Risks from high-fluoride occur in very few isolated localities and due to the seasonal variability in groundwater fluoride contents in these regions do not pose a significant threat to human health. In the majority of locations, alternative low-fluoride water sources are also available with the exception of one high-fluoride area in the western extremity of Slovakia. Although water fluoride in these locations does not impact adversely on health the final risk avoidance map highlights these areas so that they can be monitored in the future (Annex 2).

In addition to natural fluoride contents, industrial contamination represents one of the main sources of fluoride in water in the Ziarska Kotlina Basin of Slovakia (Annex 2) and risks in this region were examined in more detail as part of this project.

Table 5.1 Data included in the Project Partner Country.apr risk assessment GIS for Slovakia

		GIS Risk Assessment
Data	Groundwater Chemistry Data for Slovakia	Data categorised according to WHO fluoride water quality guidelines: < 0.5 mg/l Caries Risk, ≥ 1.5 mg/l Fluorosis Risk in risk assessment scheme
Data Source	From the database of the Geochemical Atlas of Slovakia – Part 1. Groundwater (Geological Survey of the Slovak Republic (SGUDS) (Rapant et al., 1996)).	
Data Type	16 359 analyses of groundwater (first water reached) collected at a sample density of approximately 1 sample per 2.5 km^2 over the whole of Slovakia. Data for: X, Y, Longitude, Latitude, Map Number, Type of Source, Locallity, Date of Sampling, Ca, F, TDS, pH, Geology	
Data	Hydrogeological Units for Slovakia	Data categorised according to aqufer importance for drinking water and included as background information layer only
Data Source	From the database of the Geochemical Atlas of Slovakia – Part 1. Groundwater (Geological Survey of the Slovak Republic (SGUDS), (Rapant et al., 1996))	
Data Type	Digital map of the main hydrogeological units of the whole of Slovakia.	
Data	Groundwater Chemistry Data for the Ziarska Kotlina Basin	Data categorised according to WHO fluoride water quality guidelines: < 0.5 mg/l Caries Risk, ≥ 1.5 mg/l Fluorosis Risk in risk assessment scheme
Data Source	82 analyses from the database of the Geochemical Atlas of Slovakia – Part 1. Groundwater (Geological Survey of the Slovak Republic (SGUDS), (Rapant et al., 1996)) and 25 analyses of groundwater from the project: 'Evaluation of Ecological Sustainability of the Ziarska Kotlina Basin', 1997.	
Data Type	107 analysis of groundwater in total. Data for: Map Number, Y, X, Longitude, Latitude, Locality, Type of Source, Date of Sampling, Ca (mg/l), F (mg/l)	
Data	Surface Water Chemistry for the Ziarska Kotlina Basin	Data categorised according to WHO fluoride water quality guidelines: < 0.5 mg/l Caries Risk, ≥ 1.5 mg/l Fluorosis Risk in risk assessment scheme
Data Source	95 analyses of surface water from the database of the project: 'Collection of Maps of Geofactors of the Environment of the Ziarska Kotlina Basin and Banskostiavnicka Oblast', 1993 and 31 analyses of surface water from the project: 'Evaluation of Ecological Sustainability of the Ziarska Kotlina Basin', 1997.	
Data Type	126 analysis of groundwater in total. Data for: Map Number, Y, X, Longitude, Latitude, Locality, Type of Source, Date of Sampling, Depth of Source (m), Yield (l/s), Water Temperature °C, Air Temperature °C, pH, Conductivity (μS/cm), Alkalinity, Acidity, Alkalinity in Field, Alkalinity in Laboratory, Dissolved oxygen, COD, BOD, Na, K, NH4, Ca, Mg, Fe, Mn, Cl, F, NO2, NO3, PO4, SO4, HCO3, CO3, OH, H2SiO3, Free CO2, Aggressive CO2, Heyer, Li, Sr, Cr, Cu, Zn, As, Cd, Se, Pb, Hg, Ba, Al, Sb, Filtrated Al, Filtrated Fe, TPH, Fluoranthene (μg/l), TDS (mg/l), Water Quality Classes, Ca (mg/l), F (mg/l)	
Data	Snow Chemistry for the Ziarska Kotlina Basin	Data used to generate contour maps of F, Al and Fe content in snow, included as background information layers only
Data Source	20 analyses of snow from the project: 'Evaluation of Ecological Sustainability of the Ziarska Kotlina Basin', 1997.	
Data Type	Map Number, Locality, X, Y, Longitude, Latitude, Date of Sampling, pH, COD(Mn), Conductivity, NH_4, Cl, F, NO_3, NO_2, SO_4, Mn, Fe, Al, Zn, Cu, Pb, Cr, Ni, Cd	
Data	Population of Slovakia	Data included as background information layer only
Data Source	Census of Slovakia	
Data Type	Digital map of towns with population statistics	
Data	Industrial Sources	Data included in risk assessment scheme
Data Source	Map of Slovakia	
Data Type	Coordinates of the Ziar nad Hronom Aluminium Factory in the Ziarska Kotlina Basin	
Data	Water Supply Information	Data included in risk assessment scheme
Data Source	Water Supply of Slovakia	
Data Type	Knowledge of water fluoridation and use of water for drinking	
Data	Tectonic Features	Data included as background information layer only
Data Source	From the database of the Geological Survey of the Slovak Republic (SGUDS)	
Data Type	Digital map of main tectonic features	

Table 5.2 Dental caries risk assessment scheme for Slovakia

Caries Risk						
Location	**Phase 1**		**Phase 2**		**Final Risk**	**Assessment Rationale**
	Ground water F mg/l < 0.5	**Potential Risk**	**Water Fluoridated**	**Potential Risk**		
Slovakia	No	Low	Yes	Low	Low	Fluoride content is sufficient
	Yes	High	Yes	Low	Moderate	Although water is fluoridated, if fluoridation stops for any reason there will be a risk of dental caries, these areas should be monitored
	Yes and No	High/low			Moderate/ low	Water has low fluoride content but higher fluoride water is available in the vicinity
	Unknown				Unknown	If the water fluoride content is unknown the risk is not assessed.

Table 5.3 High-fluoride risk assessment scheme for Slovakia

High-Fluoride Risk						
Location	**Phase 1**		**Phase 2**		**Final Risk**	**Assessment Rationale**
	Ground water F mg/l ≥ 1.5	**Potential Risk**	**Water used directly for drinking**	**Potential Risk**		
Slovakia	No	Low	Yes	Low	Low	Fluoride content should not normally cause problems, but may do under certain circumstances in hot climates
	Yes	High	Yes	Low	High	Water contains high fluoride which may cause health problems
	Yes and No	High/low			High/ low	Water has high fluoride content but lower fluoride water is available in the vicinity
	Unknown				Unknown	If the water fluoride content is unknown and there is no evidence of fluorosis incidence or industrial sources, the risk is not assessed.
	Fluorosis Incidence					
	None	Low			Low	No history of fluorosis in the area therefore low risk
	Industrial Source					
	Yes	High	No		Moderate	Although there is an industrial source of fluoride in the area, the waters are not used for drinking therefore the risk is moderate but the situation should be monitored in case high fluoride waters are used for drinking in the future

5.3 ZIARSKA KOTLINA BASIN STUDY AREA

The only area of concern in terms of high-fluoride in Slovakia is associated with the Ziar nad Hronom Aluminium Factory (ZSNP) in the Ziarska Kotlina Basin (Figures 5.4 and 5.6). The factory has been in operation for many years producing Al from the raw material bauxite and has created a significant ecological debt to society and the surrounding natural environment. The state of the Ziarska Kotlina Basin was examined by a Monitoring and

Advisory Group (MAG) established in 1997 via an agreement between ZNSP and the European Bank for Reconstruction and Development that contributed to the modernisation of the factory. The main reason for establishing the MAG was to enable citizens to obtain information about and discuss the environmental programme of the ZSNP Company. Citizens' opinions, comments and suggestions became part of the environmental programme. The ZSNP company has been running an extensive remediation programme in Ziar nad Hronom since 1994. The main aim is to comply with strict environmental standards required by the Slovak Republic and the European Union. The progress of this programme has been evaluated by a project entitled 'The Evaluation of Ecological Sustainability of the Ziarska Kotlina Basin' (Ministry of the Environment, 1998).

The environmental strategy of ZSNP includes several tasks as follows:

- *Modernization of aluminium production as well as the approval of the Green Program of ZSNP.*

- *Environmental upgrading of present production lines, potentially cancelling those that do not comply with the strictest environmental criteria.*

- *Removal of historical contamination resulting from over 40 years of Al production, aluminium oxide, carbonaceous materials, and Al processing in individual plants.*

- *Introduction of improved methods of Al production, which fully utilise its excellent qualities as a light-weight construction material achieving considerable savings in energy consumption. This aspect also includes solving the problem of liquidation or further use of ZSNP alumina products after their lifespan has elapsed.*

- *Preparation of detailed environmental best practice manuals for the ZSNP complex and the implementation of individual rules.*

The Slovalco Company outlined new technologies for Al production and the results of environmental monitoring. The results prove that after completion of a pilot study, Al production will comply with Slovak and EU environmental standards.

The Al plant stopped production of Al_2O_3 from bauxite on December 31 1997. The realization of the above-mentioned projects in the framework of the remediation programme of ZSNP has had a positive impact on the environment in the Ziar nad Hronom area. The following facts are relevant to the process of project realization.

5.3.1 Air Pollution

According to the index of air pollution, which describes the total impact of pollutants, monitoring programmes have shown the following trends in the Ziarska Kotlina Basin:

- *1993 - 1994 Ziarska Kotlina was an area with some of the highest degrees of pollution*

- *1995 - 1996 Ziarska Kotlina was an area of medium pollution*
- *1997 onwards Ziarska Kotlina was an are of low pollution*

The State Health Institute (SHI) in Ziarska Kotlina has a specialised laboratory for measuring fluoride in all components of the environment except for soil, i.e. in air, water, food and biological substances. The SHI annually examines approximately 460 air samples in the region to determine the fluoride content. Prior to 1990, some 15 - 20 % of cases exceeded the MAC in air.

In 1953, the factory emitted approximately 13 000 tonnes of exhalents, in which fluoride was bound to around 400 compounds. Emissions of fluoride were highest at the beginning of the 1960s and dramatically decreased from the beginning of 1970s after the installation of absorbers in the technological process. The average concentration of fluoride in air decreased from 8 $\mu g/m^3$ in 1973 to 3 $\mu g/m^3$ in 1987, but was still 3 times higher than the Slovak MAC. In 1991 the factory emitted 10 871 tonnes of exhalents of which, 7.1% contained solid and gaseous fluoride compounds. New technology installed in 1995 lowered fluoride emissions to levels below the 1 $\mu g/m^3$ Slovak MAC, which are not considered harmful for the environment.

5.3.2 Fluoride in Soils

The most contaminated area of land in the Region is found over alluvial deposits of the River Hron close to the factory. A study of water-soluble fluoride concentrations in soil carried out across the Ziarska Kotlina Region revealed concentrations range from 0.2 - 33.0 µg/g (median 1.9 µg/g). A further study in 1998, detected concentrations of water-soluble fluoride in the range 3 - 26.4 µg/g in the Region. The average contents of water-soluble fluoride in a 2.5 km zone around the factory were 12.45 µg/g in top soil and 12.75 µg/g in sub-soil, which exceed recommended maximum limits for water-soluble fluoride in soil of 10 µg/g (Mocik, 1986). In the vicinity of the ZSNP factory, water-soluble contents of 11.49 µg/g in soil correspond to total fluoride contents of 1256 µg/g. The German and Slovak recommended MAC for total fluoride concentrations in agricultural soil are 200 µg/g and 500 µg/g respectively. In total, 9000 ha of soil is contaminated by fluoride emissions from ZSNP.

5.3.3 Fluoride in Stream Sediments

In the Ziarska Kotlina Basin, concentrations of fluoride in stream sediments range from 300 to 500 µg/g (equivalent to the MAC for soil). The highest concentrations are typical found in ponded channels of the River Hron close to the ZSNP factory.

5.3.4 Fluoride in the Biomass

The arithmetic mean of total fluoride contents in foliage of all forest tree species reported in the Geochemical Atlas of Slovakia (Mankovska, 1996) is 6.2$\pm$ 4.8 µg/g (median 6.1 µg/g). Average contents in foliage of individual tree species are as follows (in µg/g): *F. sylvatica* 5.8$\pm$ 2.6 (median 5.9), *Q. species* 4.7$\pm$ 2.1 (median 4.9), *P. abies* 6.3$\pm$ 4.2 (median 6.2), *P. sylvestris* 7.8$\pm$ 14.9 (median 6.3) and *A. alba* 8.3$\pm$ 5.1 (median 8.0). Exogenic fluoride was absent from stomata of all analysed foliage of forest tree species. Mankovska (1980) suggests MAC for fluoride in larch needles of 8.7 μg/g and Markert (1993) a MAC of 2.0 μg/g for pine-tree needles.

The national map of all tree species shows that fluoride contents exceed 5 μg/g in two-thirds of the Slovak territory and are clearly associated with industrial plants. Total fluoride contents above 10 μg/g have been determined in needles of *P. abies, P. sylvestris* and *A. alba* in the Ziarska Kotlina Basin and central Spis region (Mankovska, 1996).

5.3.5 Water Quality

Part of the remediation programme consists of projects related to the management of drinking, ground and waste-waters. Between 1988 and 1997 the amount of water taken from the River Hron was reduced by 65% by the introduction of a water recycling programme. Industrial water usage fell by 57 % and the consumption of groundwater and the volume of waste water generated fell by 50 %. In total, 15 water-economy projects focussing on recycling the industrial water and increasing water quality were initiated. The ZSNP industrial complex now meets the required Slovak standards regarding waste-water discharges into the River Hron. In addition to waste-waters, the ZSNP complex generates many other kinds of waste and in July 1998 a new stockyard for storing solid wastes was created.

Although the water quality in streams has recently considerably improved, according to monitoring of the River Hron catchment in Ziar nad Hronom District, the River Hron is still classified as polluted or even considerably polluted. The number of pollution indicators monitored in the District has increased from 25 in 1966 to 50 at the present time. The findings are published annually in the summary report "Water Quality in Streams" by the Slovak Hydrometeorological Institute in Bratislava. The monitoring of water quality is carried out according to Slovak Technical Standards STN 75 7221.

Municipal sewage systems are among the largest producers of contaminants, because some municipalities in the Ziarska Kotlina Basin lack sewage treatment plants. The town of Ziar nad Hronom uses a sewage treatment plant, which was put into operation recently.

In 1997, 89.78 % of the 48,509 inhabitants of the town of Ziar nad Hronom received drinking water from the public water main. The SHI found that the quality of water from the public supply had the following attributes (based on 155 samples):

- *Physical and chemical parameters – 2.58 % exceeded the water quality MAC*
- *Microbiological – 38.71 % exceeded the water quality MAC*
- *Biological – 8.39 % exceeded the water quality MAC*
- *Total - 44.71 % exceeded the water quality MAC*

These results show that microbiological factors are the most important cause of water quality degradation in the area. The hygiene of the water supply is also negatively influenced by irregularities in the water supply resulting from water-main breaks and by a lack of water during dry periods. Municipalities lacking water mains are in an unacceptable position, with respect to sources of drinking water, relying chiefly on private or public wells. Most of these wells (80 - 100%) have unsuitable water. The quality of well water is affected by the location of the water sources, adjacent to street gutters polluted streams, toilets, and gardens where fertilizers are used, and by factors such as inadequate treatment of areas surrounding wells, unsuitable casing of wells, etc. Monitoring of private and public wells revealed that the water is largely unsuitable for consumption by infants, in particular, because of the high nitrate contents (MAC 15 mg/l) and in some cases is unsuitable for adults also. Some wells might improve with technical treatment, removal of pollution sources and application of appropriate disinfections. The most important remedy, however, is to build public water mains. Since the Ziarska Kotlina Basin lacks quality drinking water it is necessary to lengthen and interconnect the water-main network.

A detailed study of water quality in the Ziarska Kotlina Basin was completed in 1988 (Vrana and Kusikova, 1998). Data collected during this study have been incorporated into the current project GIS (Table 5.1). Fluoride concentrations in various sample types in the region are listed in Table 5.4.

Table 5.4 Fluoride concentrations in waters of the Ziarska Kotlina Basin

Data Type	Fluoride Range mg/l	Fluoride Average mg/l	Number
Surface waters	0.03 – 9.0	0.4	126
Snow	<0.02 – 1.3	0.3	20
Groundwater	0.01 – 3.6 (average 0.17)	0.1	107
Wells (private houses)	0.03 – 0.27	-	-

Ziar nad Hronom town is supplied by drinking water from public sources (pipeline) outside the Region. This is not high-fluoride water. In 1991 the following concentrations of fluoride in drinking water were documented by the SHI in the Region:

Ziar nad Hronom	0.05 mg/l
Hlinik nad Hronom	0.08 mg/l
Lovcica-Trubin	0.05 mg/l
District Ziar nad Hronom	0.09 mg/l

According to the SHI monitoring of fluoride in drinking water over the past 10 years, values vary between 0.15 – 1.45 mg/l and do not exceed the MAC (Slovak limit 1.5 mg/l). According to the Geochemical Atlas of Slovakia (Rapant et al., 1996) the average concentration of fluoride in groundwater for the Ziarska Kotlina Basin is 0.10 mg/l. Small individual sources (e.g. in Lovca), which extract local shallow groundwater, contain higher concentrations of fluoride (0.45 mg/l). Snow samples taken from the ZSNP factory area revealed fluoride concentrations of 11.5 mg/l (Horne Opatovcec) compared to 0.04 mg/l in reference samples from a mountainous ‘clean air’ locality (Bansky Studenec).

5.3.6 Impacts on Agricultural Production, Wildlife and Food

In 1955 the municipalities of Lovca, Ladomierska Vieska, Horne Opatovce, Lehotka pod Brehmi, Dolna Zdana, Hliník nad Hronom and Ziar witnessed the occurrence of a disease affecting mainly cattle and goats resulting in a large number of dead animals, particularly young animals. The first species to be affected were bees. Although it was a serious disease it was neither infectious nor parasitic. Symptoms included the inability to stand and move, reduced production of milk, respiratory and digestive organ trouble and reproduction disruptions. A group of veterinary experts concluded that the disease was caused by a serious disruption of the internal organs of animals related to fluoride poisoning or fluorosis. Dental fluorosis has also been reported in deer in the Ziar nad Hronom area (Kierdorf, 2000).

Between the years 1990 and 1992, complex environmental monitoring was carried out by a team of veterinary surgeons from the University of Veterinary Medicine in co-operation with specialist veterinarians from Ziar nad Hronom. The 1992 results showed the following:

- *Analysis of fodder and water*
    - *The highest contents of contaminant elements (cadmium) were present in hay and in silage grass (arsenic)*
    - *Fluoride concentrations were below normal levels*
    - *Water did not contain high amounts of any of the monitored elements*

- *Analysis of milk*
    - *Increased contents of arsenic were discovered on farms in the vicinity of ZSNP*
    - *Increased values of cadmium were noted in Kremnica, Janova Lehota and Banska Stiavnica*

- *Analysis of meat and organs of cattle and swine*
    - *Content of fluoride was above normal values*

- *Wild game, fish and bees*
    - *Increased amounts of fluoride above normal levels were found in all kinds of wild game*
    - *Values for carp were within recommended limits*
    - *Bees showed different element contents depending on the region*

Wild game and domestic cattle are the best indicators of the state of the environment since they consume natural foods. Results showed that harmful substances were particularly concentrated in the inner organs of these animals. The highest concentrations of potentially harmful elements were generally found within a distance of 10 - 15 km from the centre of Ziar nad Hronom.

Subsequent improvements to the Al production technology removed the source of pollution. Environmental monitoring demonstrates that the food sold to consumers (including meat and fodder products) in the Region complies with Slovak and EU standards and limits. Proper processing ensures that the milk produced in the Region is not harmful to health. Imported products also meet the required food quality standards. The limits are exceeded for cadmium and mercury only in case of hunting and wild game, however, this situation is typical across the globe as a result of increased environmental pollution and is not specifically related to local industrial contamination in the Region.

Measurements of fluoride contents in food (1985 - 1997) demonstrated that in 57 % of samples the MAC were not exceeded in contrast to previous years (1985 – 1993) whereby 50 - 100 % of potato samples contained excess fluoride. The Slovak MAC for fluoride in potatoes is 2.5 µg/g. This value was exceeded in Stara Kremnicka (2.6 µg/g), Hlinik nad Hronom (3.4 µg/g), Kremnica (2.8 µg/g) and Janova Lehota (3.2 µg/g) in the Region. As a precautionary measure, from 1960 onwards, legislation ensured that potatoes grown in the Region were distributed elsewhere. No fluoride excesses in corn, flour and bakery produces have been reported.

5.3.7 Health Status

According to data released in 1997 from the SHI for the Ziarska Kotlina Basin, cardiovascular diseases were the most frequent causes of death in the previous year (l996) (55.15 %), followed by cancer (19.85%), respiratory diseases (8.71%) and injuries and intoxication (7.02%). The mortality rate due to cardiovascular diseases in the Ziar nad Hronom District is not and has never been the highest in Slovakia (ranked 8th - 12th in Slovakia over the last 10 years) but it is higher than the national average. A high prevalence of allergic diseases had been reported previously in Ziar nad Hronom District. However, the SHI monitored the symptoms of allergic diseases among 6 to 14 year old children in the District in co-operation with 16 other regions. The Ziar nad Hronom District ranked 15th with 29.4% of boys and 14th with 29.9% of girls suffering from allergic diseases out of 17 regions in the Slovak Republic. The most frequent causes of worker disability in the region are respiratory diseases, followed by diseases of the muscles, bones and flesh and then by injuries and intoxication incurred outside of work. The majority of demographic data indicate a generally poor state of health of inhabitants in Ziar nad Hronom. The demography development trends and the population health indicators reveal an undesirable situation but this cannot be attributed only to polluted living and working environments. The causes of poor health comprise higher incidence of chronic non-infectious conditions, generally known as civilization diseases, such as cardiovascular diseases, cancer, chronic respiratory diseases and others, which result mainly from the following:

- *Degraded living and working conditions*
- *Improper or unhealthy life-styles, including bad habits like improper diet, smoking, drinking too much alcohol and improper daily routines and regimes*
- *Low levels of health consciousness among the Region's population, who generally display little interest in taking care of their health and living environment*
- *The living environment and social conditions influence the state of children’s health (from 3 years of age children attend nursery where they spend 7 - 9 hours in big groups and the disposition to illness high)*

- *High numbers of services involving risk and high numbers of workers regularly occupied in dangerous industries*

- *Poorly implemented preventative medical regimes and inadequate health education (increased preventive examinations, diagnosis and therapy are preferred)*

- *Delays in building of a health care information system*

Medical investigations relating to fluoride in the Ziarska Kotlina Basin were summarised in the project 'The Evaluation of Ecological Sustainability of the Ziarska Kotlina Basin'(Ministry of Environment, 1998). For the purposes of the present study, these data were interpreted in cooperation with M Khun from the Department of Geochemistry, Comenius University, Bratislava (Khun 2001a+b+c). The medical data were derived from the archives of the SHI, Ziar nad Hronom. The following interesting relationships between high environmental fluoride and heath factors were noted:

As the main indicators of long-term exposure to fluoride, hair and urine samples were taken from the local population. Between 1958 and 1965 differences in blood composition, and statistically significant higher fluoride contents in urine, hair, teeth and nails compared to reference samples were noted in children living close to ZSNP factory.

However, studies carried out on children during 1970 – 1975 showed that hair fluoride concentrations in the Ziarska Kotlina Basin (4.1 – 5.7 µg/g) were similar to control areas with no fluoride exposure (4.2 – 5.9 µg/g). Further studies in 1988 showed slightly higher concentrations in hair than in 1970 – 1975.

As a more accurate measurement of fluoride exposure, urine samples were also tested. A MAC for fluoride in urine of 1 mg/l has been set in Slovakia. Between 1958 and 1965, urine fluoride contents in children ranged between 0.66 –0.78 mg/l. In further studies carried out between 1970 and 1975, the fluoride values in urine for boys (age 6-9 years) living adjacent to the ZSNP factory ranged from 0.33 – 0.38 mg/l and for girls 0.36 – 0.38 mg/l, higher than reference samples (0.28 - 0.31 mg/l and 0.2 - 0.27 mg/l respectively) but lower than the 1958 – 1965 levels and lower than the MAC. Data from recent studies show that no samples in the region exceed the MAC for fluoride in urine. In 10 – 14 year-old girls urine fluoride contents ranged from 0.25 – 0.61 mg/l and in 10 – 14 year-old boys from 0.28 – 0.89 mg/l.

Results of fluoride determinations in nails were less clear but data from 1965 showed an average fluoride content 297 µg/g in children close the ZSNP factory compared to 198 µg/g in control areas.

Analyses of teeth samples carried out between 1965 and 1975 revealed that the concentrations were higher close to the ZNSP factory than in control areas and that levels had increased compared to values reported in the period 1950 – 1958. The majority of values in the area close to the factory exceeded the recommended maximum value of 300 µg/g (Table 5.5).

Table 5.5 Fluoride contents in children's teeth 1965 - 1975

	Fluoride Teeth µg/g			
	ZSNP Factory		Control Area	
	Range	Average	Range	Average
Boys	102-776	363	58-790	280
Girls	195-738	408	112-603	-

In terms of stomatology, the percentage of children with minor white-chalky-patches on teeth has been decreasing with time but is still higher in the Region than in control areas and this factor is related to higher environmental fluoride in the Region:

Year	% Children with white-chalky-patches
1965	44.8
1970	31.17
1975	22.25
Control	3.63

No fluorosis related to environmental exposure (drinking, water, air, food, soil) has been reported in the Region. One case of occupational fluorosis was reported in 1991 in a worker from the ZSNP factory but the situation prior to 1989 is not known.

In relation to cancer, the prevalence rate in men is 4.88 % and in women 12.97% higher than the Slovak average but the reasons are not understood. The prevalence of the types of cancers that could be related to contaminants in the environment is decreasing in the Region.

5.3.8 Risk Avoidance Maps

The information presented in the previous section of this report demonstrates that although there is evidence of fluoride contamination associated with the ZNSP factory, the impacts on human health are low in the Region. In order to carry out the current project risk assessment, data for snow chemistry, groundwater chemistry and surface water chemistry were included in the GIS (Table 5.1). Interpolated surface maps showing the distribution of F, Al and Fe contents in snow around the ZNSP factory demonstrate the extent of atmospheric contamination and are included in this report for background information (Figures 5.7 – 5.9). The interpolated surfaces were created from the point-source snow chemistry data using the ArcView® *Spatial Analyst* extension and the inverse-distance-weighting (IDW) interpolation function default settings (cell size =0.000629 degrees; 227 rows, 250 columns, 12 nearest neighbours, IDW power 2). The interpolated surfaces were not included in the project partner GIS (Country.apr) as the *Spatial Analyst* extension is additional to the basic ArcView® programme.

The fluoride risk assessments for Ziarska Kotlina were carried out on the basis of the groundwater and surface water chemistry databases for the Region (Table 5.1), water supply information and the location of industrial sources of fluoride (Tables 5.6 and 5.7).

Table 5.6 Dental caries risk assessment scheme for the Ziarska Kotlina Basin

Caries Risk						
Location	**Phase 1**		**Phase 2**		**Final Risk**	**Assessment Rationale**
	Ground or surface water F mg/l < 0.5	**Potential Risk**	**Water Fluoridated**	**Potential Risk**		
Ziarska Kotlina Basin	No	Low	Yes	Low	Low	Fluoride content is sufficient
	Yes	High	Yes	Low	Moderate	Although water is fluoridated, if fluoridation stops for any reason there will be a risk of dental caries, these areas should be monitored
	Yes and No	High/low			Moderate/ low	Water has low fluoride content but higher fluoride water is available in the vicinity
	Unknown				Unknown	If the water fluoride content is unknown the risk is not assessed.

Table 5.7 High-fluoride risk assessment scheme for the Ziarska Kotlina Basin

High-Fluoride Risk						
Location	**Phase 1**		**Phase 2**		**Final Risk**	**Assessment Rationale**
	Ground or surface water F mg/l ≥ 1.5	**Potential Risk**	**Water used directly for drinking**	**Potential Risk**		
Ziarska Kotlina Basin	No	Low	No	Low	Low	Fluoride content should not normally cause problems, but may do under certain circumstances in hot climates
	Yes	High	No	Low	Moderate	Although water is not currently used for drinking, if it were to be used in the future, health problems could arise.
	Yes and No	High/low			High/ low	Water has high fluoride content but lower fluoride water is available in the vicinity
	Unknown				Unknown	If the water fluoride content is unknown and there is no evidence of fluorosis incidence or industrial sources, the risk is not assessed.
	Fluorosis Incidence					
	None	Low			Low	No history of fluorosis in the area therefore low risk
	Industrial Source					
	Yes	High	No		Moderate	Although there is an industrial source of fluoride in the area, the waters are not used for drinking therefore the risk is moderate but the situation should be monitored in case high fluoride waters are used for drinking in the future

The final risk avoidance maps for the Region were based on a grid size of 0.5 km^2 compatible with the sample density of the ground and surface water datasets. Groundwater and surface water chemistry data were combined in the GIS so that problem waters from any possible source in the Region would be highlighted. In each grid square, the water fluoride data were assessed with water supply information to produce the final risk maps (Annex 3 and 4).

The majority of waters in the Region have low fluoride concentrations and dental caries would be of concern, however, since the drinking water supply in Slovakia is fluoridated, the final risk assessment is moderate indicating that the situation should be monitored as if at any time in the future, water fluoridation was interrupted, the risks of dental caries associated with low fluoride waters would increase (Annex 3).

High fluoride concentrations exceeding the 1.5 mg/l MAC in ground and surface waters in the Region are restricted to the immediate vicinity of the ZNSP plant. The extent of water contamination from the plant is very limited (Figure 5.10 and Annex 4). Although these waters pose a potential problem, the local population in Ziar nad Hronom are supplied with drinking water from elsewhere therefore the final assessment classifies these areas as moderate risk indicating that the situation should continue to be monitored in the future to ensure these waters are not used for drinking (Annex 4).

5.4 CONCLUSIONS

In general, natural waters used for drinking in Slovakia contain very low concentrations of fluoride and dental fluorosis is not a problem in this region. At the national scale, there are very few locations where water fluoride contents exceed 1.5 mg/l and in all but one of these cases, lower fluoride waters are available in the vicinity. High fluoride concentrations in Slovakia are seasonably variable and do not pose a threat to human health. Environmental contamination in a very limited area around the Ziar nad Hronom Aluminium Factory in the Ziarska Kotlina Region results in high fluoride contents in groundwater and surface water, however these waters are not used for drinking and present little immediate risk to health.

The majority of Slovakian waters contain less fluoride than the recommended minimum contents for dental caries prevention (< 0.5 mg/l); however, the water supply is fluoridated in Slovakia reducing the immediate risk of dental caries in this region.

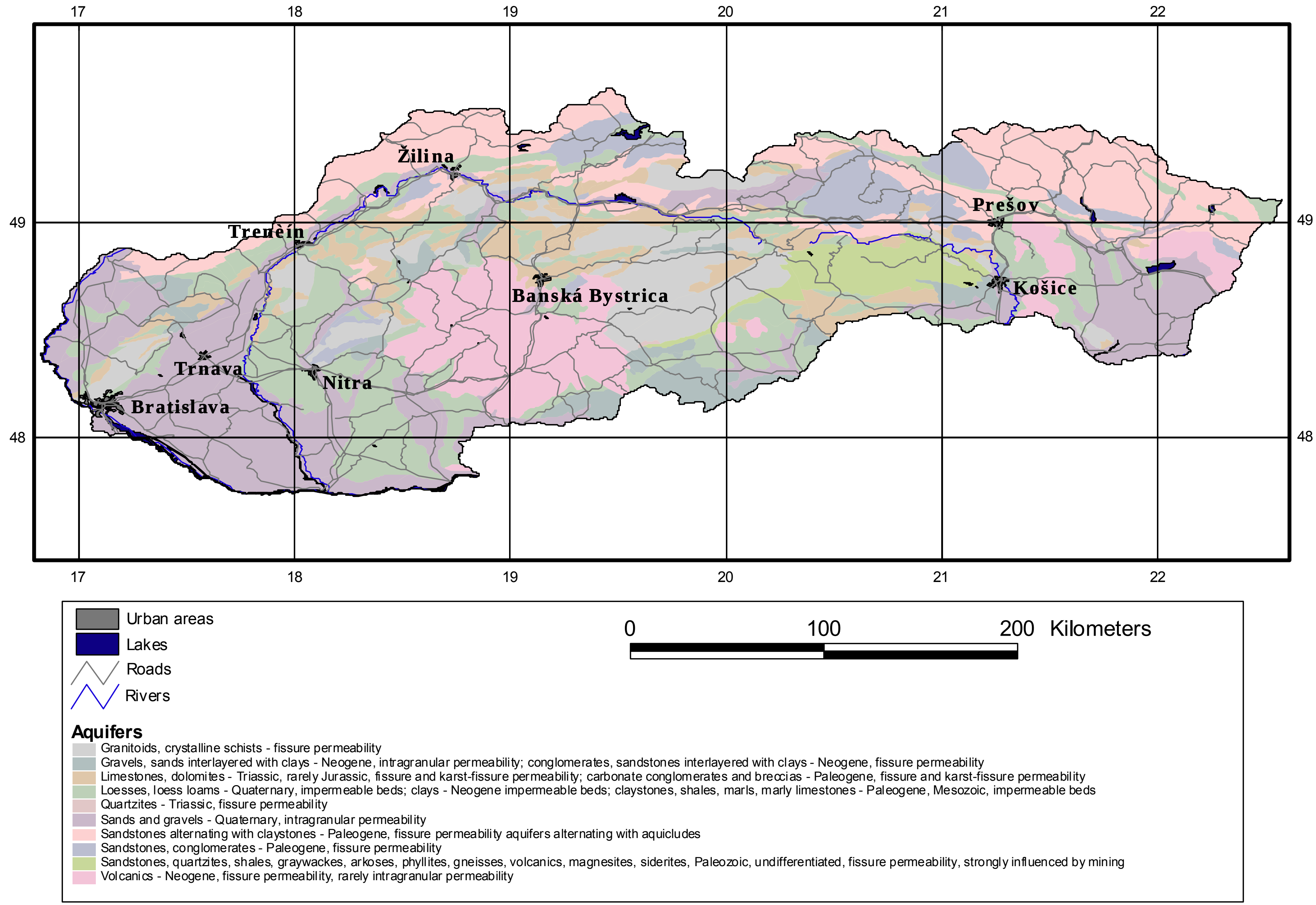


Figure 5.1 Main hydrogeological units of Slovakia (SGUDS (Rapant et al., 1996))

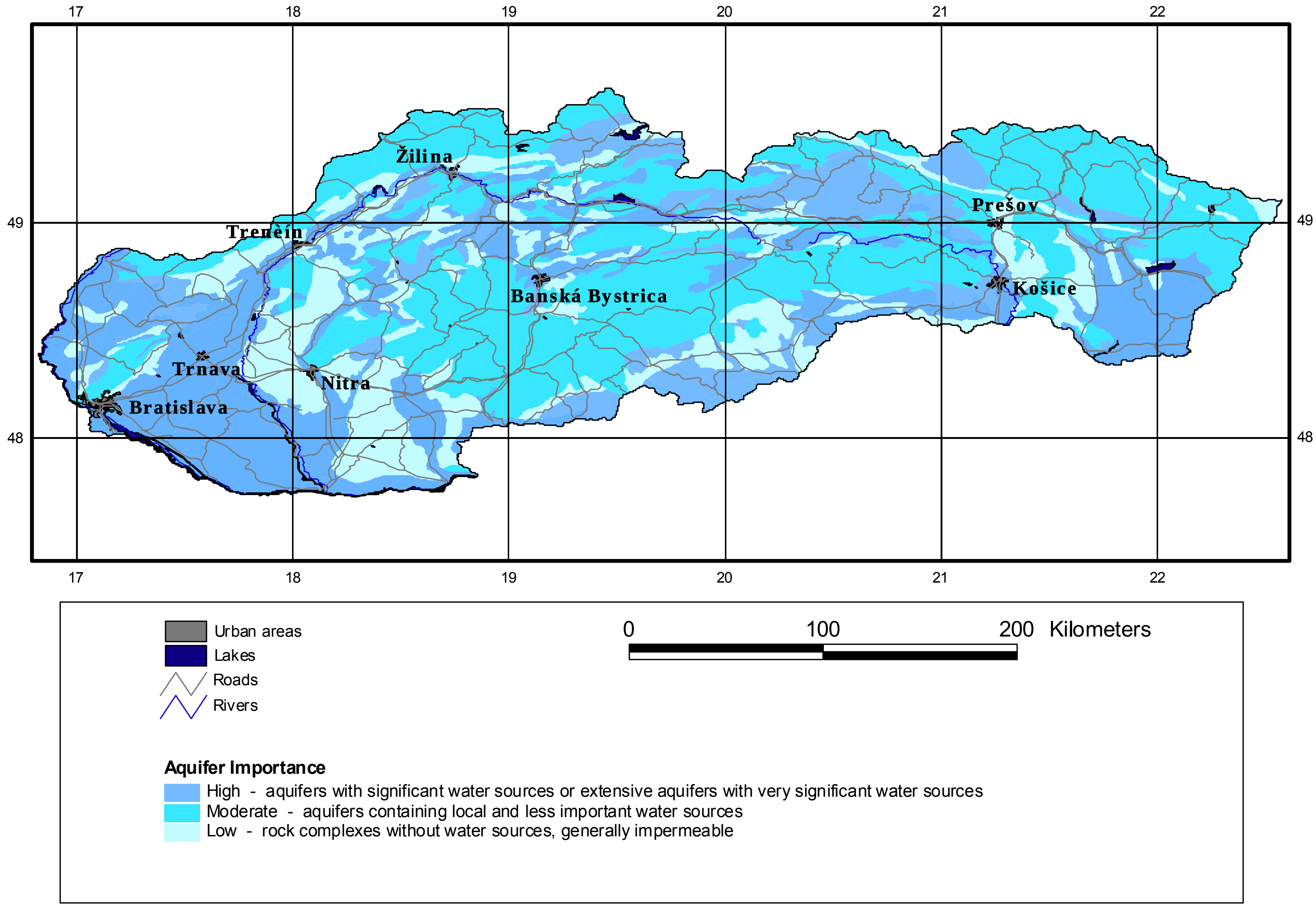


Figure 5.2 Main hydrogeological units of Slovakia classified according to aquifer importance

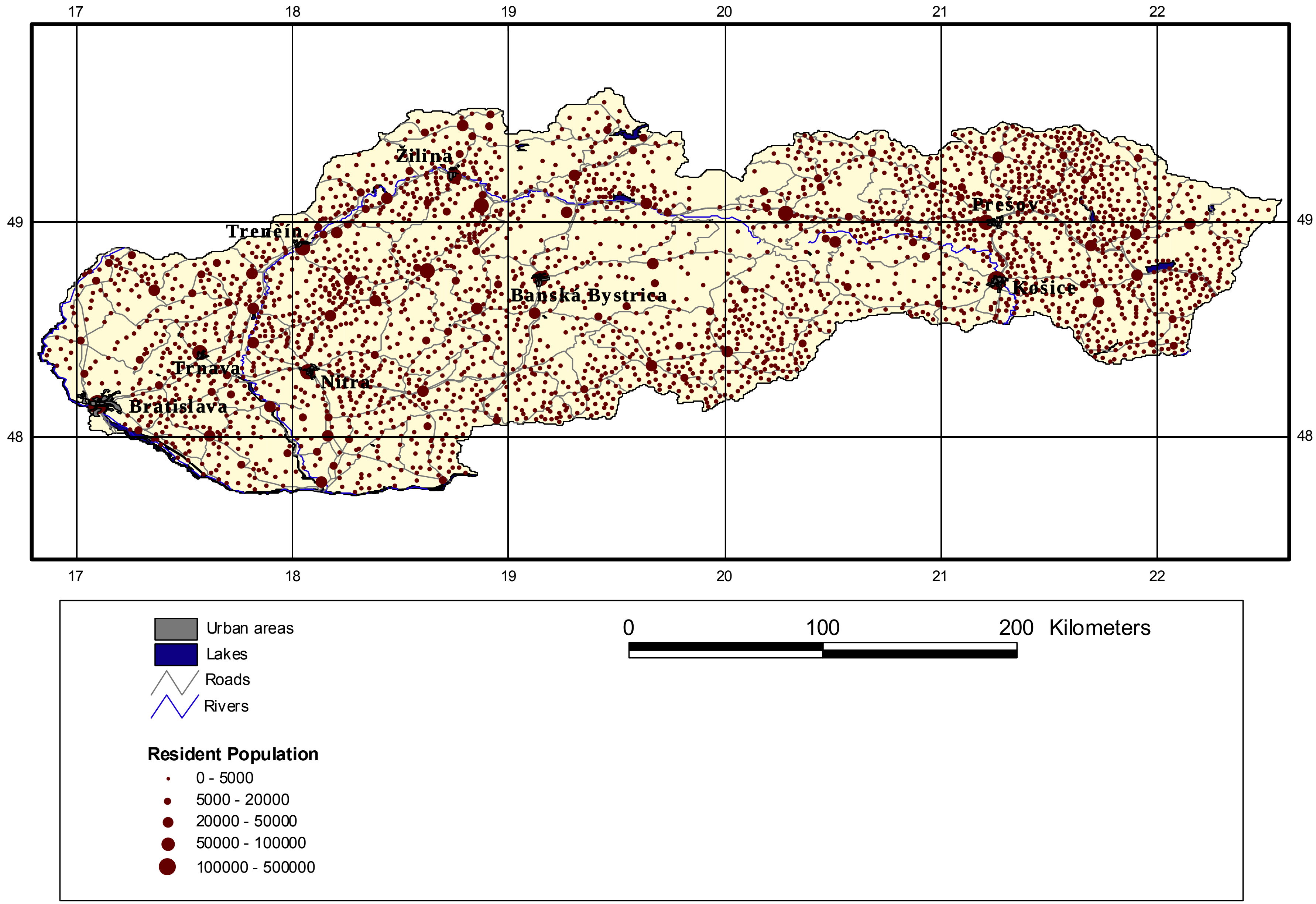


Figure 5.3 Population of the main settlements in Slovakia

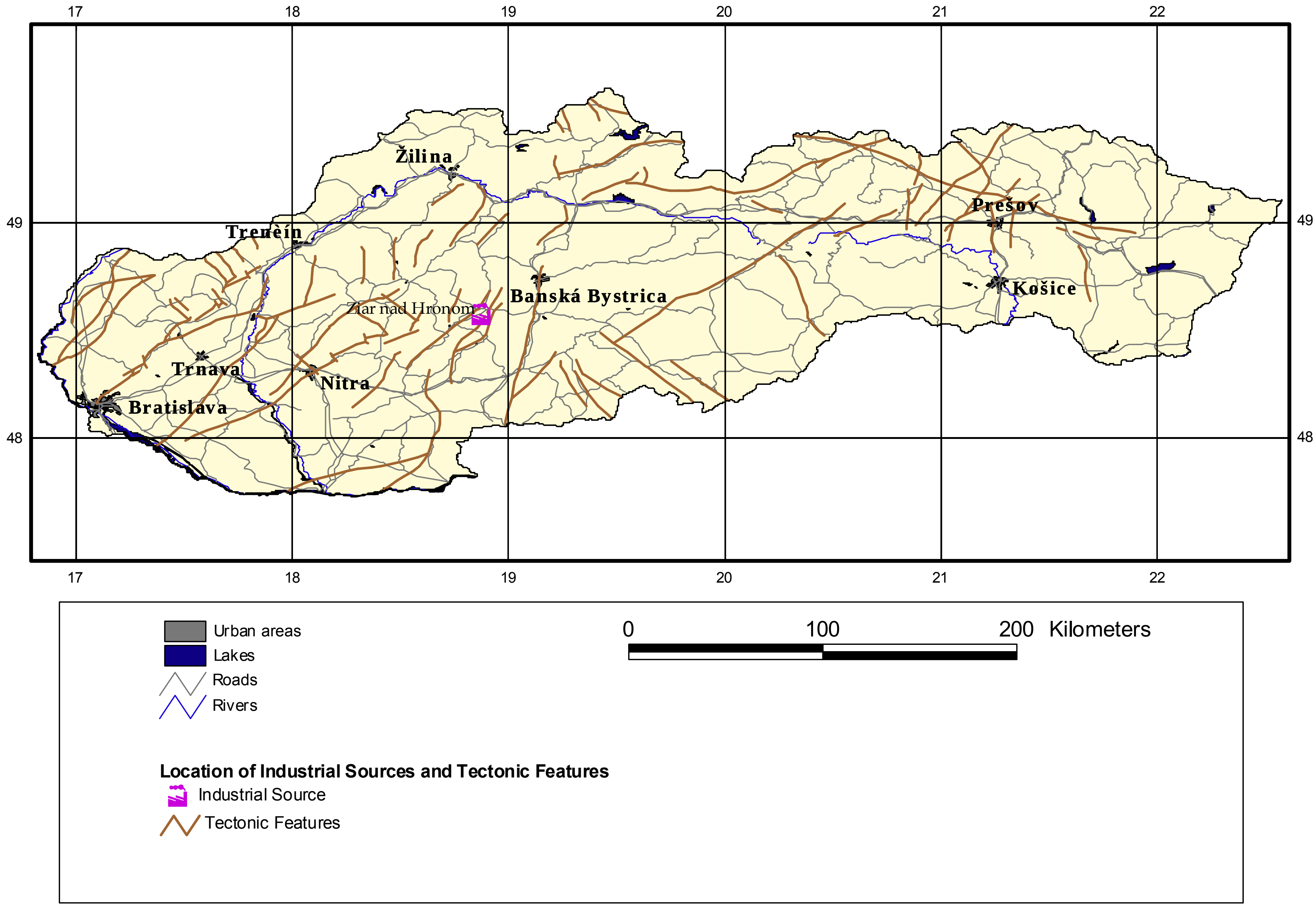


Figure 5.4 Location of the Ziar nad Hronom Aluminium Factory (industrial source) and major tectonic features in Slovakia

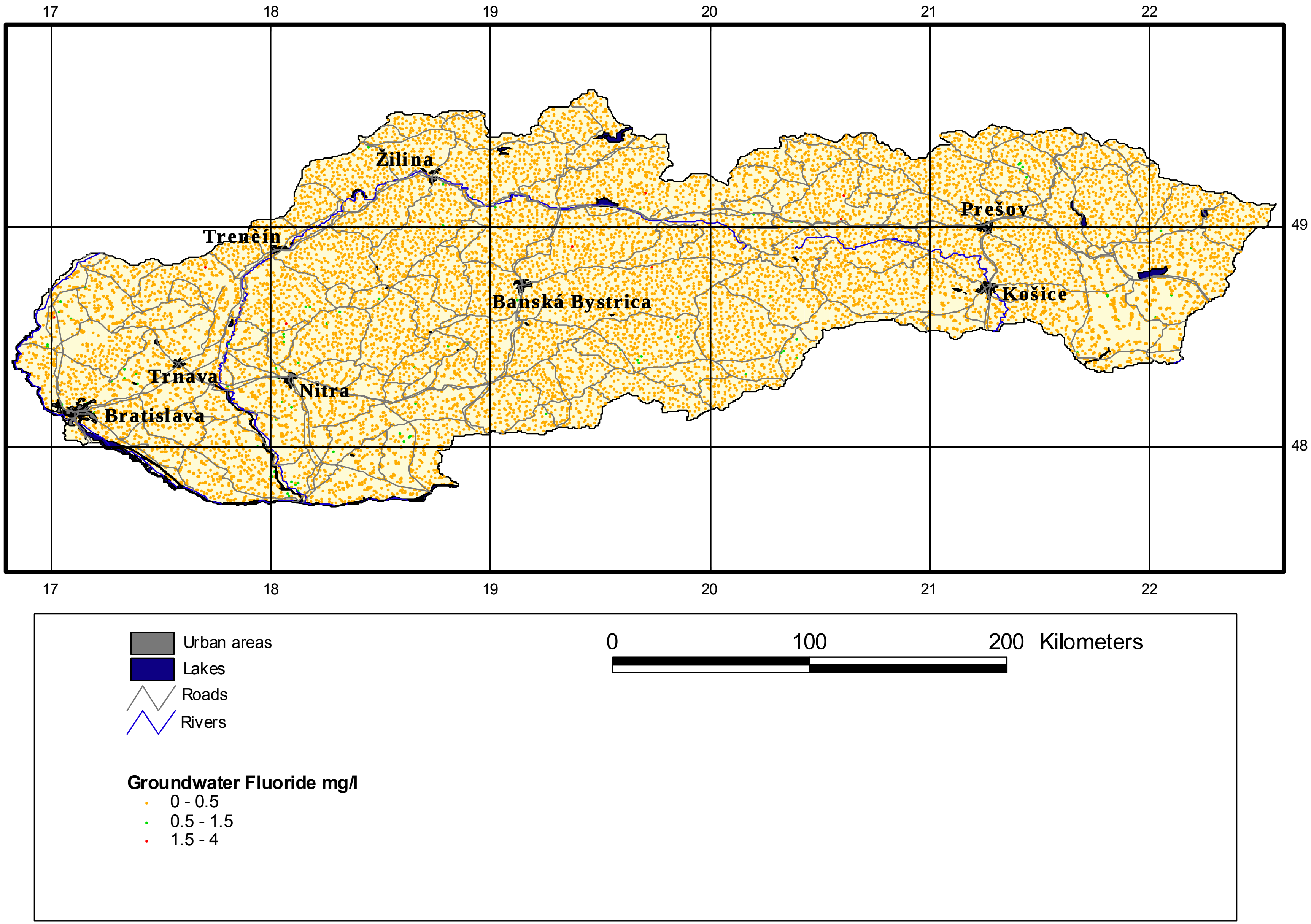


Figure 5.5 Groundwater fluoride concentrations in Slovakia (SGUDS (Rapant et al., 1996)) classified according to water quality guidelines (WHO, 1996b)

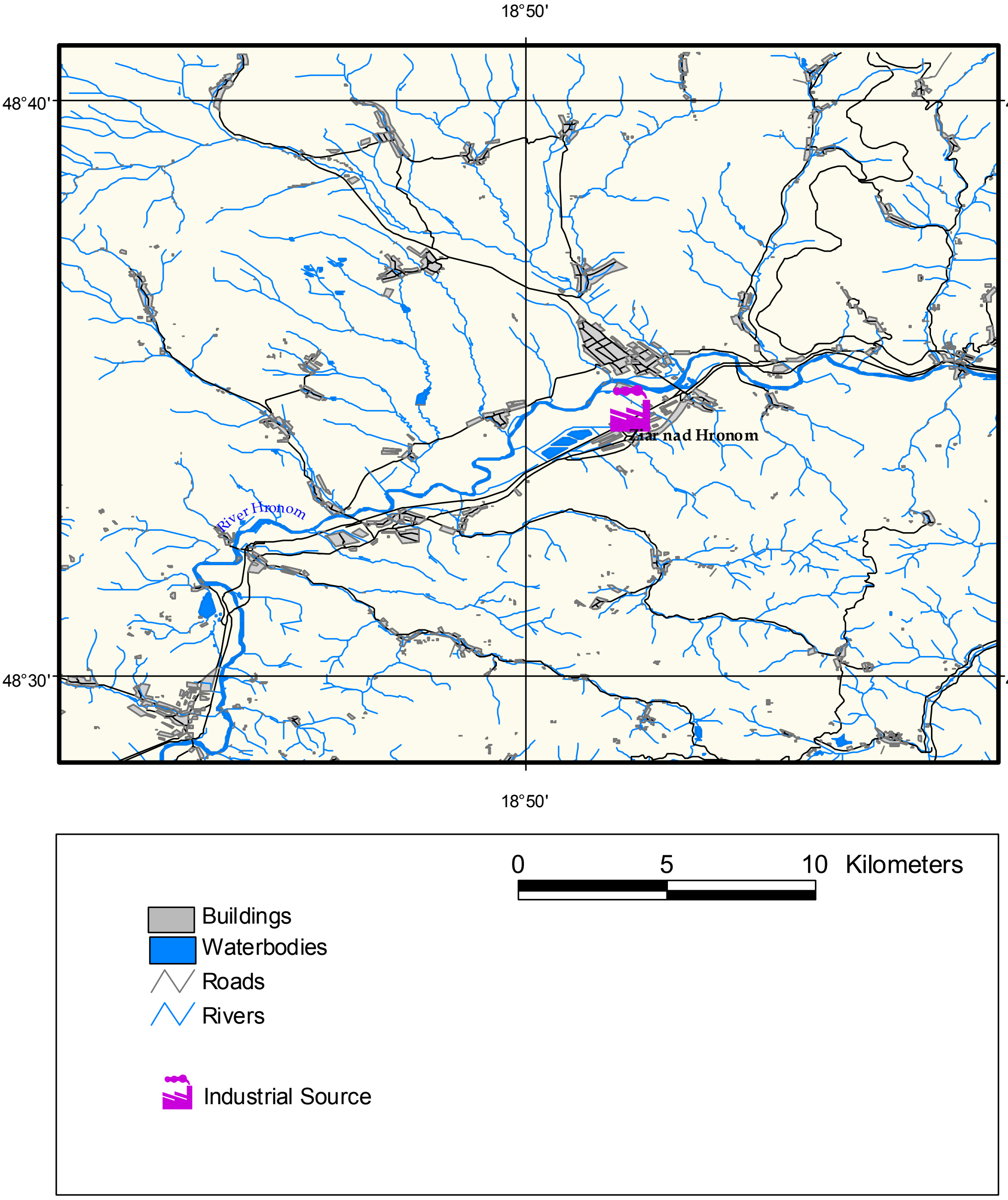


Figure 5.6 Map showing the location of the Ziar nad Hronom aluminium factory in the Ziarska Kotlina Basin, Slovakia

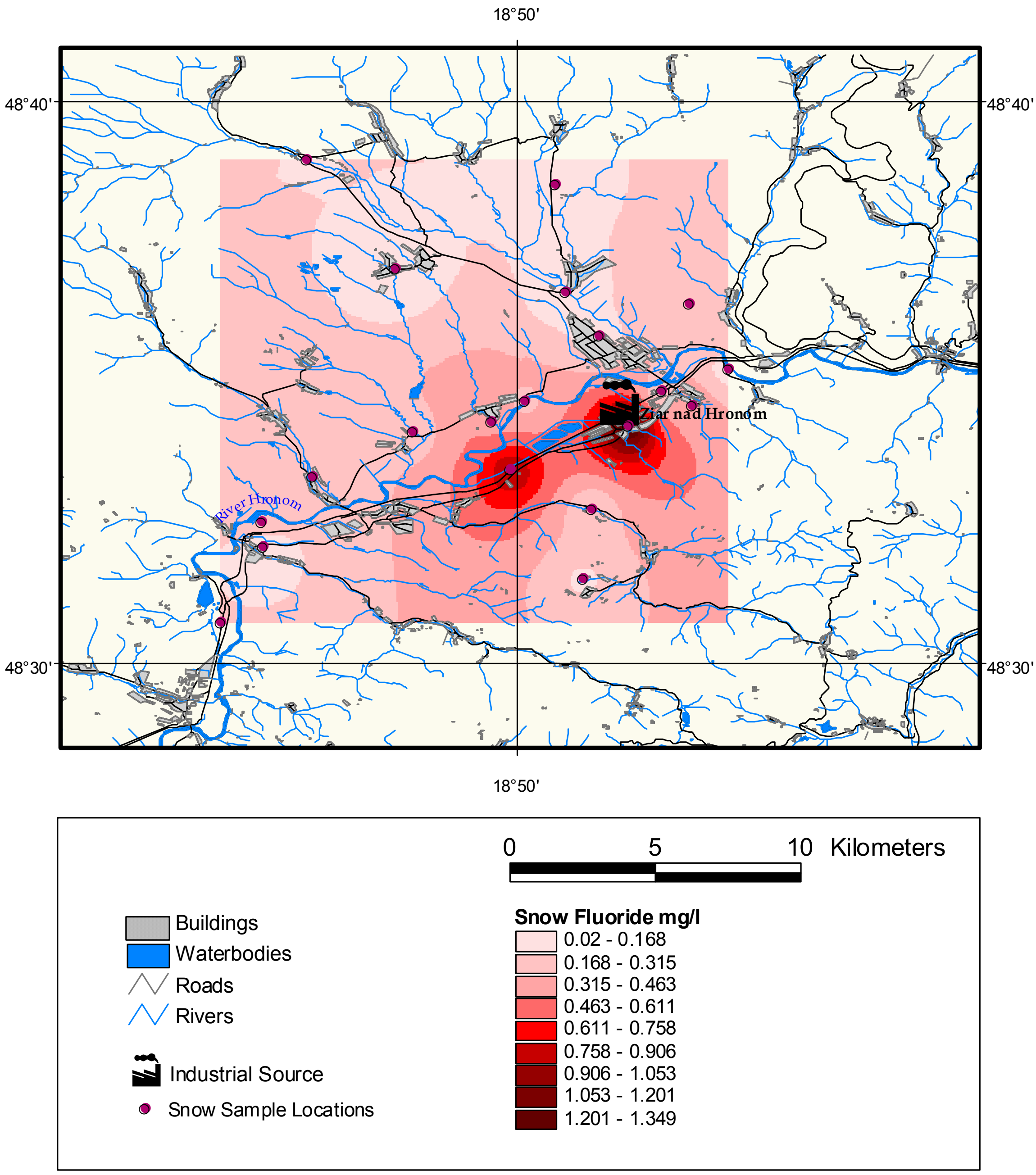


Figure 5.7 Interpolated surface map showing fluoride contents in snow around the Ziar nad Hronom aluminium factory in the Ziarska Kotlina Basin, Slovakia

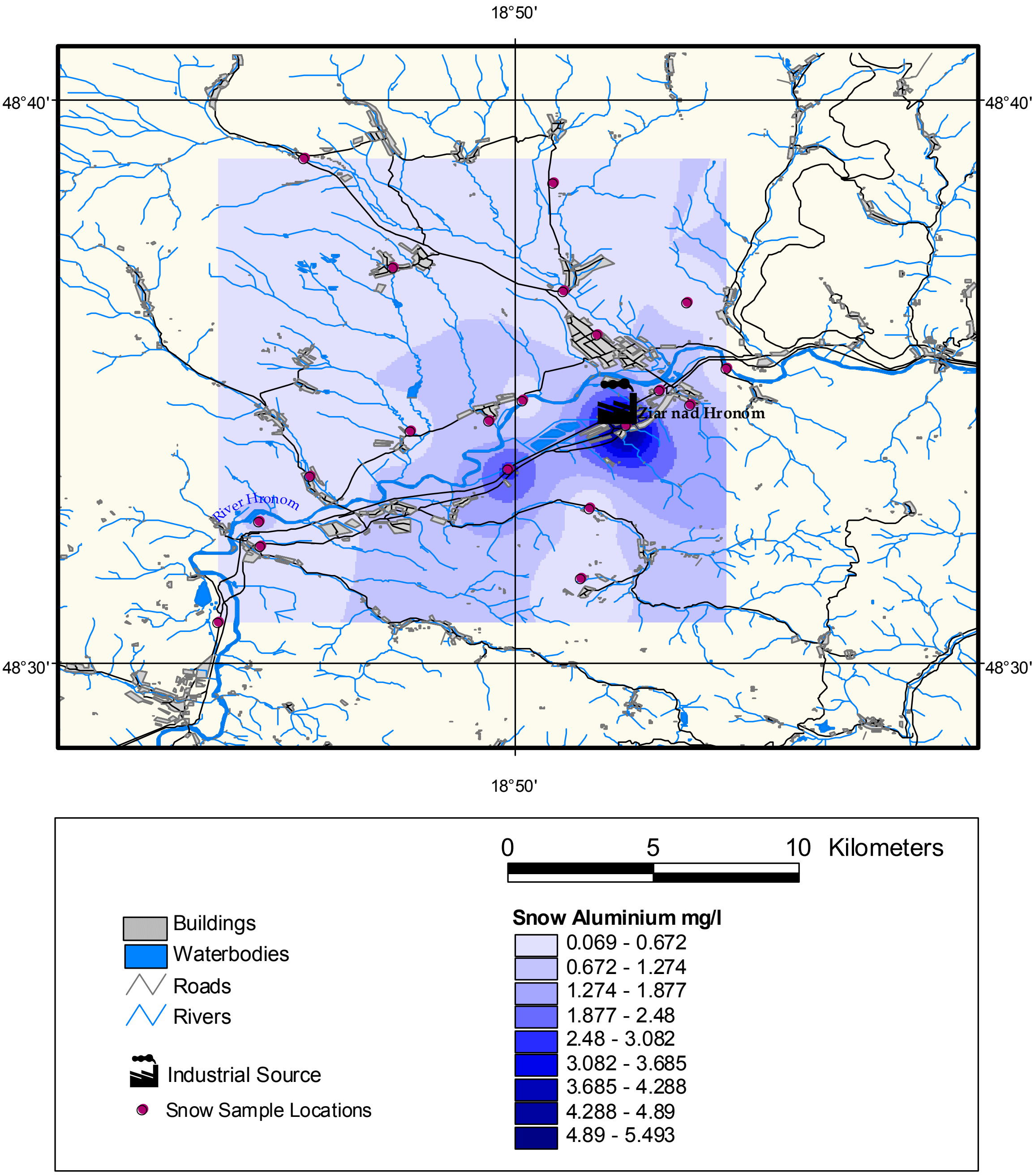


Figure 5.8 Interpolated surface map showing aluminium contents in snow around the Ziar nad Hronom aluminium factory in the Ziarska Kotlina Basin, Slovakia

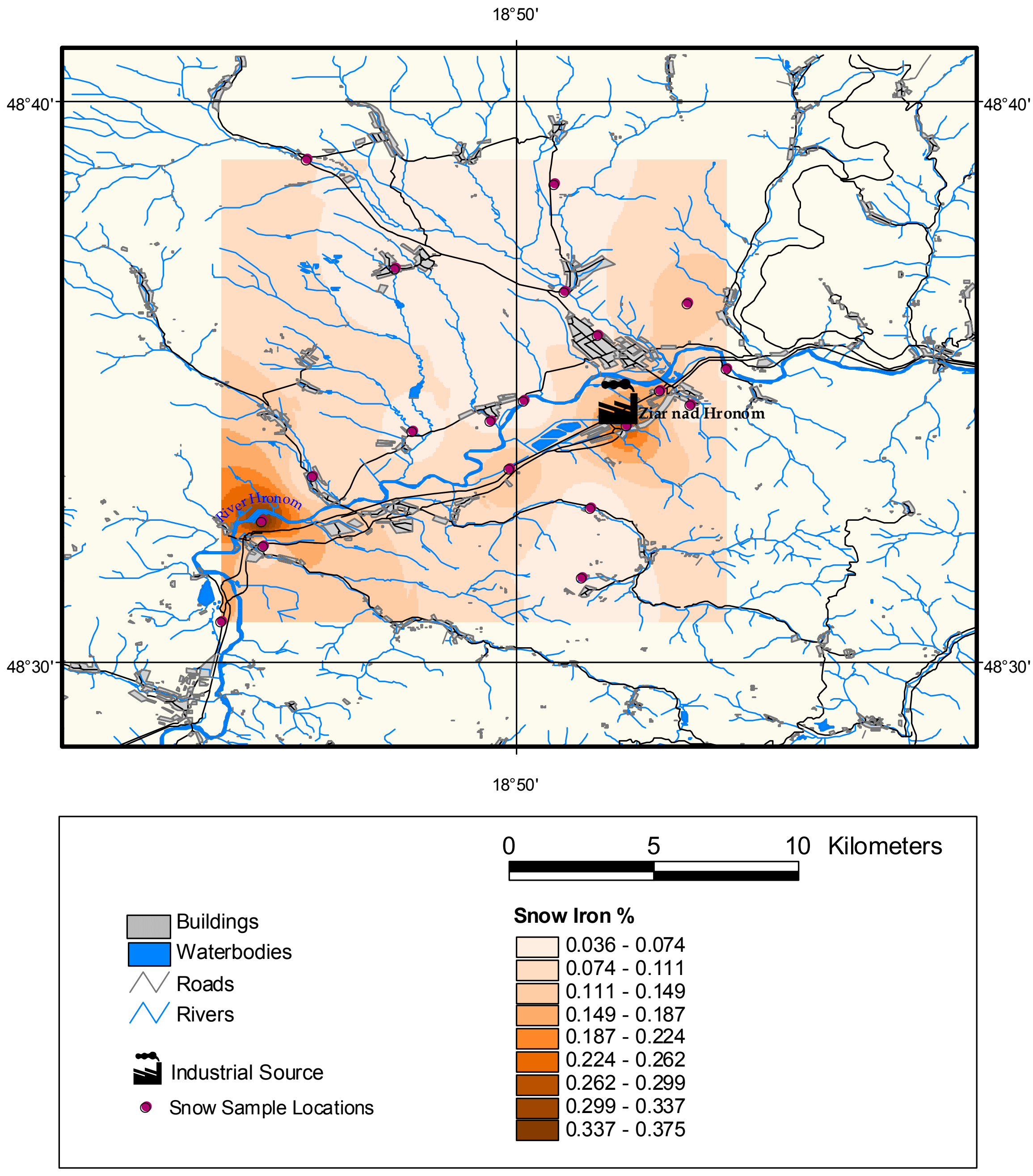


Figure 5.9 Interpolated surface map showing iron contents in snow around the Ziar nad Hronom aluminium factory in the Ziarska Kotlina Basin, Slovakia

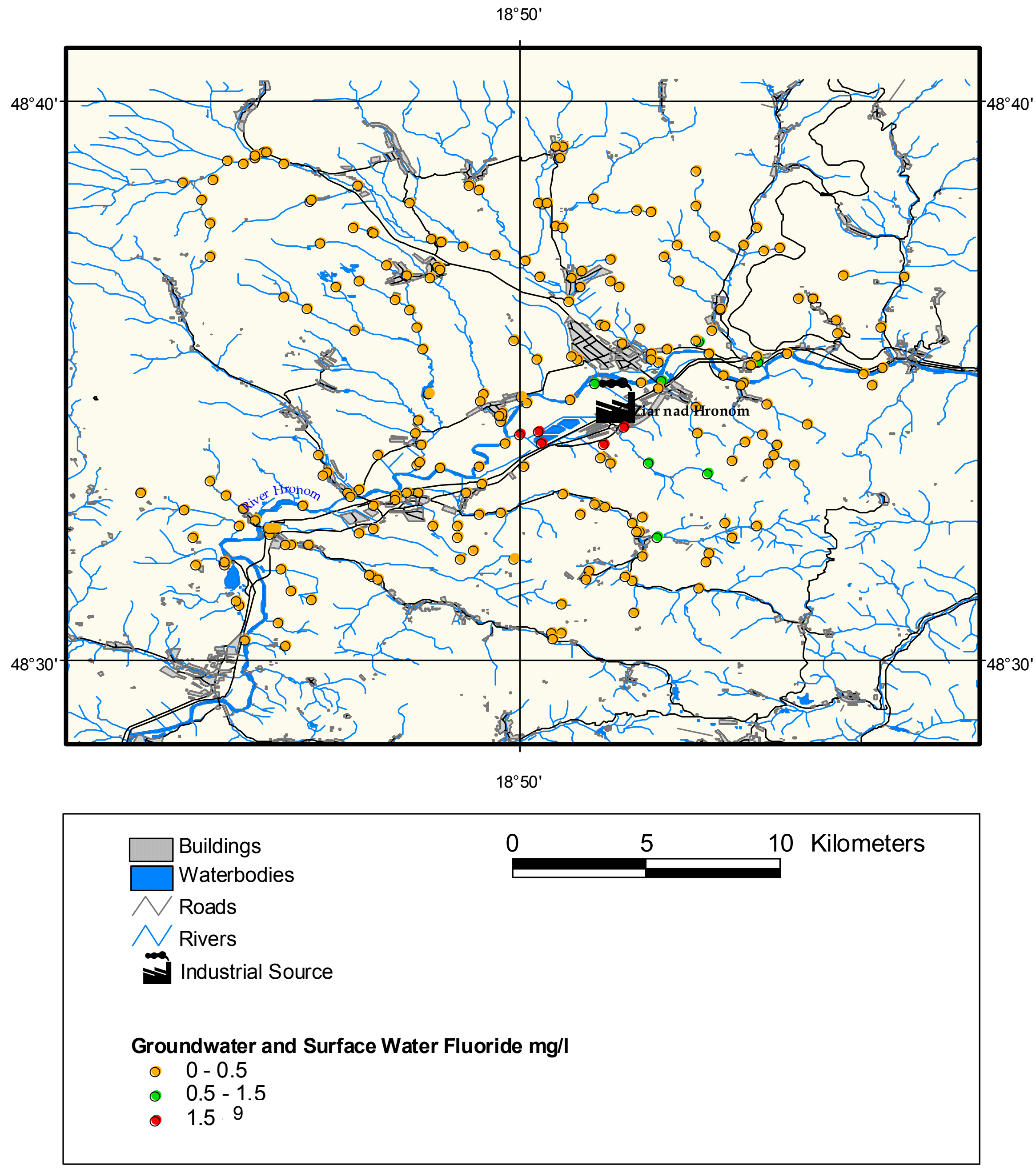


Figure 5.10 Ground and surface water fluoride concentrations in the Ziarska Kotlina Basin classified according to water quality guidelines (WHO, 1996b)

6 Fluoride Risk Assessment for Hungary

Gyorgy Toth, Fiona Fordyce and Bryony Hope

6.1 INTRODUCTION

Isolated cases of dental fluorosis have been reported previously in Hungary, associated with high-fluoride drinking waters. The mains drinking water supply in Hungary is derived from both cold (< 25^{o}C) and thermal (> 25^{o}C) groundwaters and the thermal waters generally contain higher fluoride contents than cold-well waters. However, the majority of drinking waters in Hungary contain low concentrations of fluoride and the risk of dental caries is more of a problem in this region. Industrial fluoride contamination has been reported around five industrial plants in the country, although the impacts of this contamination on surrounding ecosystems, including human health require further investigation. Information for Hungary as a whole and for a detailed study area in the Great Hungarian Plain where hydrogeological conditions result in high-fluoride thermal waters is presented in this chapter.

6.2 NATIONAL RISK ASSESSMENT

6.2.1 GIS Risk Scheme

The data incorporated into the Project Partner GIS (Country.apr) for Hungary are listed in Table 6.1. At the national level, the map of hydrogeological units (MAFI (Siposs and Toth, 1989)) (Figure 6.1), hydrogeology classified according to aquifer importance (Figure 6.2), recharge and discharge zones (Figure 6.3) geology (MAFI (Pecsi, 1989)) (Figure 6.4) the population of the main towns (Figure 6.5) and reported caries incidence data (Figure 6.6) were included in the GIS for background information only.

The national fluoride risk assessments for Hungary were carried out on the basis of the groundwater (cold and thermal wells) and drinking water chemistry databases for the whole country (MAFI (Toth, 1989)), water supply information, the location of industrial sources and fluorosis incidence (Tables 6.2 and 6.3).

Table 6.1 Data included in the Project Partner Country.apr risk assessment GIS for Hungary

		GIS Risk Assessment
Data	Cold Wells Water Chemistry Data for Hungary	Data categorised according to WHO fluoride water quality guidelines: < 0.5 mg/l Caries Risk, ≥ 1.5 mg/l Fluorosis Risk in risk assessment scheme
Data Source	From the database of the National Atlas of Hungary. Mineral and Thermal Wells. Hungarian Geological Survey (MAFI) (Toth, 1989)	
Data Type	532 analyses of groundwater from cold wells collected at a sample density of approximately 1 sample per 30 km^2 over the whole of Hungary. Data for: X, Y, Longitude, Latitude, Location, Welll Number, K, Na, NH_4, Ca, Mg, Fe, Mn, Cl, HCO_3, SO_4, NO_3, F, Temp	
Data	Thermal Wells Water Chemistry Data for Hungary	Data categorised according to WHO fluoride water quality guidelines: < 0.5 mg/l Caries Risk, ≥ 1.5 mg/l Fluorosis Risk in risk assessment scheme
Data Source	From the database of the National Atlas of Hungary. Mineral and Thermal Wells. Hungarian Geological Survey (MAFI) (Toth, 1989)	
Data Type	545 analyses of groundwater from thermal wells collected at a sample density of approximately 1 sample per 30 km^2 over the whole of Hungary. Data for: X, Y, Longitude, Latitude, Location, Welll Number, K, Na, NH_4, Ca, Mg, Fe, Mn, Cl, HCO_3, SO_4, NO_3, F, Temp	
Data	Drinking Water Chemistry Data for Hungary	Data categorised according to WHO fluoride water quality guidelines: < 0.5 mg/l Caries Risk, ≥ 1.5 mg/l Fluorosis Risk in risk assessment scheme
Data Source	From the database of the National Atlas of Hungary. Mineral and Thermal Wells. Hungarian Geological Survey (MAFI) (Toth, 1989)	
Data Type	3266 analyses of drinking water collected at each major settlement at a sample density of approximately 1 sample per 6 km^2 over the whole of Hungary. Data for: X, Y, Longitude, Latitude, Location, Welll Number, Ca, F	
Data	Hydrogeological Units for Hungary	Data categorised according to aqufer importance for drinking water and included as background information layer only
Data Source	From the National Atlas of Hungary. Hydrogeology. Hungarian Geological Survey (MAFI) (Siposs and Toth, 1989)	
Data Type	Digital map of the main hydrogeological units of the whole of Hungary.	
Data	Recharge and Discharge Zones for Hungary	Data included as background information layer only
Data Source	From the National Atlas of Hungary. Hydrogeology. Hungarian Geological Survey (MAFI) (Siposs and Toth, 1989)	
Data Type	Digital map of recharge and discharge zones of the whole of Hungary	
Data	Population of Hungary	Data included as background information layer only
Data Source	1991 Census of Hungary	
Data Type	Digital map of towns with population statistics	
Data	Industrial Sources	Data included in risk assessment scheme
Data Source	Previous Studies	
Data Type	Coordinates of the Mosonmagyarovar, Alumasfuzito, Ajka Redmud, Ajka Alufactory and Varpalota Alufactory Industrial Sources	
Data	Water Supply Information	Data included in risk assessment scheme
Data Source	Water Supply of Hungary	
Data Type	Knowledge of water fluoridation and use of water for drinking	
Data	Fluorosis Incidence	Data included in risk assessment scheme
Data Source	Previous Studies	
Data Type	Coordinates of towns Bar, Dunaszekcso and Herceghalom fluorosis incidences	
Data	Dental Caries Incidence	Data included as background information layer only
Data Source	Previous Studies	
Data Type	Coordinates of towns Herceghalom, Csepa, Szeleveny, Tiszakurt, Kaptalanfa caries prevalences	

Table 6.2 Dental caries risk assessment scheme for Hungary

Caries Risk						
Location	**Phase 1**		**Phase 2**		**Final Risk**	**Assessment Rationale**
	Well or drinking water F mg/l < 0.5	**Potential Risk**	**Water Fluoridated**	**Potential Risk**		
Hungary	No	Low	No	Low	Low	Fluoride content is sufficient
	Yes	High	No	High	High	Fluoride content is insufficient
	Yes and No	High/low			High/ low	Water has low fluoride content but higher fluoride water is available in the vicinity
	Unknown				Unknown	If the water fluoride content is unknown the risk is not assessed.

Table 6.3 High-fluoride risk assessment scheme for Hungary

High-Fluoride Risk						
Location	**Phase 1**		**Phase 2**		**Final Risk**	**Assessment Rationale**
	Well or drinking water F mg/l ≥ 1.5	**Potential Risk**	**Water used directly for drinking**	**Potential Risk**		
Hungary	No	Low	Yes	Low	Low	Fluoride content should not normally cause problems, but may do under certain circumstances in hot climates
	Yes	High	Yes	High	High	Water contains high fluoride which may cause health problems
	Yes and No	High/low			High/ low	Water has high fluoride content but lower fluoride water is available in the vicinity
	Unknown				Unknown	If the water fluoride content is unknown and there is no evidence of fluorosis incidence or industrial sources, the risk is not assessed.
	Fluorosis Incidence					
	Yes	High	No	Low	Moderate	There is a history of fluorosis in the region but the water is no longer used for drinking therefore the risk is moderate as the situation should be monitored in case high fluoride waters are used for drinking in the future
	Industrial Source					
	Yes	High	Yes	High	High	An industrial source of fluoride is present and the waters are used for drinking therefore high risk

6.2.2 Hydrogeology and Water Quality

Water from cold (< 25 ^{o}C) and thermal wells (> 25 ^{o}C) and surface waters are utilised in a complex mains water supply system in Hungary and water is commonly transferred between settlements. Although water supply network data for over 3000 settlements were made available to the project (Table 6.4), it was not possible to incorporate this detailed information into the risk assessment at the national scale. This information is available from the Hungarian Geological Survey (MAFI) and would be essential for any detailed follow-up studies to assess risks and epidemiological links between environmental fluoride and health.

Table 6.4 Examples of water supply network information for settlements in Hungary

County	Settlement	Population	Local Exploitation l	Imported Water l	Exported Water l	Water Consumption l	Source of Imported Water
F	ABA	17376	163.2	0	0	88.7	Aba
B	ABALIGET	12548	31.1	9.5	0	16	Abaliget
H	ABASAR	24554	130.4	0	0	102.9	Abasár
BAZ	ABAUJALPAR	15662	0	1.5	0	1.3	Boldogkováralja Regionális vízmu
BAZ	ABAUJKER	26718	0	15.2	0	10.4	Golop Regionális vízmu
BAZ	ABAUJLAK	02820	1.6	0	0	1.3	Abaújlak
BAZ	ABAUJSZANTO	03595	0	176.2	0	77.8	Golop Regionális vízmu
BAZ	ABAUJSZOLNOK	26338	2.1	0	0	2.1	Abaújszolnok
BAZ	ABAUJVAR	02273	6.4	0	0	4.4	Abaújvár
SZ	ABADSZALOK	12441	168.2	57.4	30.1	133.9	Abádszalók
GY	ABDA	11882	0	111.5	0	97.9	Gyor Városi Vízmu
BAZ	ABOD	10357	3.4	0	0	1.4	Abod
P	ABONY	27872	620.2	0	0	394.4	Abony
P	ACSA	18573	48.9	0	0	32.6	Acsa
GY	ACSALAG	33385	0	19.9	0	18.3	Bosárkány Ktvm
V	ACSAD	07214	59.9	0	22.4	13.4	Acsád
H	ADACS	23241	77.4	0	0	59.4	Adács
VE	ADASZTEVEL	07302	47.6	0	18.7	18.4	Adásztevel
F	ADONY	08925	0	133.2	0	88.1	Ercsi Kápolnásnyék Gárdony Bika-völgy
VE	ADORJANHAZA	31307	49.3	0	39.9	10.5	Csögle
B	ADORJAS	06868	0	5.2	0	3.5	Adorjás
BAZ	AGGTELEK	09362	0	20.8	0	11.6	Aggtelek forrás-vízmu
GY	AGYAGOSSZERGENY	29407	0	12.8	0	9.5	Fertomenti Reg. Vízmu
SZSZ	AJAK	08776	0	236.1	0	173.7	Kisvárda
VE	AJKA	06673	746.4	3007.1	0	1232.6	Ajka + Nyírádi Regionális Vízmu
BK	AKASZTO	21944	205	0	0	156	Akasztó
BAZ	ALACSKA	33093	0	18.2	0	16.4	ÉRV Lázbérc Reginális vízmu + ÉRV Kazin
F	ALAP	26824	18.2	0	0	13.9	Alap
SZ	ALATTYAN	25265	92	0	0	59	Alattyán
P	ALBERTIRSA	31653	347.3	0	0	206.1	Albertirsa
F	ALCSUTDOBOZ	15176	0	44.5	0	30.9	Tatabánya Bicske Csabdi Reg. rendszer
H	ALDEBRO	06345	99.8	0	69.8	21.8	Aldebro
Z	ALIBANFA	02644	0	11.5	0	11.1	Zalaszentiván
B	ALMAMELLEK	13329	12.5	0	0	7.9	Almamellék
K	ALMASFUZITO	32346	466.2	0	0	255.3	Almásfüzíto
Z	ALMASHAZA	23384	0	0.9	0	0.8	Zalaszentgrót
BE	ALMASKAMARAS	29595	0	37.2	0	23.1	Almáskamarás
B	ALMASKERESZTUR	20376	49.8	0	47	1.5	Almáskeresztúr
BAZ	ALSOBERECKI	20482	0	29.3	0.6	15.8	Ricse Regionális vízmu
S	ALSOBOGAT	34184	15.5	0	0	5.6	Alsóbogát
BAZ	ALSODOBSZA	19664	0	10.2	0	10.1	ÉRV Keleti csúcsvízmu
BAZ	ALSOGAGY	14429	1	0.2	0	0.8	Alsógagy
B	ALSOMOCSOLAD	17385	10.5	0	0	5.9	Alsómocsolád
T	ALSONANA	29665	15.1	0	0	8	Alsónána
Z	ALSONEMESAPATI	19512	0	13.7	0	13.3	Nemesapáti
P	ALSONEMEDI	23199	107	0	0	79.1	Alsónémedi
T	ALSONYEK	11563	121.8	0	80	18	Alsónyék
VE	ALSOORS	30526	50.9	120	0	93	Alsóörs
Z	ALSOPAHOK	32081	0	76.6	0	43.7	DRV Nyugat-Balatoni Regionális vízmu
N	ALSOPETENY	16425	0	14.2	0	7.2	Dunamenti Regionális Vízmu Vác
Z	ALSORAJK	18829	0	13.9	0	10.1	Felsorajk
BAZ	ALSOREGMEC	23223	0	45.2	32.5	5	Sátoraljaújhely Kistérségi Vízmu
Z	ALSOSZENTERZSEBET	08767	8.2	0	0.9	2.9	Alsószenterzsébet
F	ALSOSZENTIVAN	25283	9.1	0	0	6	Alsószentiván
B	ALSOSZENTMARTON	33279	0	20	0	18.9	Egyházasharaszti
V	ALSOSZOLNOK	22549	0	9.3	0	6.6	Szentgotthárd
BAZ	ALSOSZUHA	28839	0	1.9	0	1.9	ÉRV Borsodszirák
BAZ	ALSOTELEKES	08217	0	3.1	0	2.4	ÉRV Borsodszirák
H	ANDORNAKTALYA	17987	0	285	200	61.9	Andornaktálya D-i vm
V	ANDRASFA	12317	0	7.2	0	6.1	Gyorvár
SZSZ	APAGY	20303	0	76.3	0	61.6	Levelek
CS	APATFALVA	14252	232.9	0	0	132.5	Apátfalva

The 532 cold and 545 thermal well records in the national groundwater chemistry database (MAFI (Toth, 1989)) collected at a sample density of 1 per 30 km^2 and the 3266 records collected from drinking taps in the major settlements (at a sample density of 1 per 5 km^2)

provide a comprehensive overview of fluoride contents in Hungarian waters. During the initial phase of the risk assessment, these data were categorised by fluoride concentration according to the WHO guideline values of < 0.5 mg/l caries risk and ≥ 1.5 mg/l fluorosis risk (Figure 6.7). The range in temperatures in Hungarian groundwaters is relatively large (8 – 100 °C) and fluoride contents in thermal waters (1.4 – 6.2 mg/l) are generally higher than in cold waters (0.2 – 3.3 mg/l) (Figure 6.8). Despite the use of thermal waters for drinking, the concentrations in tap waters are generally low (0.2 – 1.8 mg/l) (Table 6.5). Fluoride contents in cold and thermal wells show a weak correlation with bicarbonate content across the country (Figure 6.9).

Table 6.5 Fluoride contents in cold and thermal waters and drinking waters in Hungary

Water Source	Minimum Fluoride mg/l	Maximum Fluoride mg/l	Average Fluoride mg/l	Number
Thermal Wells > 25°C	0.60	6.2	1.4	344
Cold Wells < 25°C	0.30	3.3	0.2	532
Drinking Water (Taps)	0.00	1.8	0.2	3266

Very few drinking water samples contain fluoride contents above 0.7 mg/l with the exception of waters from the centre of the Great Hungarian Plain. In Hungary, there are large subsurface water flow systems in both karstic and sedimentary basins. Using hydraulic potential-field data is it possible to delineate the main hydrodynamic regimes across the country (Figure 6.3). The location of an aquifer in relation to the hydrodynamic regime largely controls the geochemistry. For example, recharge zones are characterised by low TDS, Ca-Mg-bicarbonate-type waters whereas discharge zones are characterised by Na-bicarbonate-type waters. The high-fluoride drinking waters in the central Great Hungarian Plain lie in the discharge zone in an area where the groundwater flow direction is from northwest to southeast. The source of fluoride is assumed to be groundwaters at the north-western edge of the area around Tisakecske and Lakitelek. This area is a well-known geothermally active basin where a strong upward flow brings thermal waters from Miocene aquifers at depth into the shallow Quaternary drinking-water-bearing horizons ((Toth, 1989; Liebe et al., 1984). Waters in this high-fluoride region are characterised by low Ca-dominance and high F/Ca ratios (16 – 64%). This territory is key to understanding the migration of fluoride in the permeable aquifer system and has been studied in more detail as part of the present project. Geothermal waters also famously occur in the Budapest region where they are utilised for spa bathing. These waters also contain high fluoride concentrations (Figure 6.7).

6.2.3 Industrial Sources

In addition to natural sources, high environmental fluoride levels are associated with the five major aluminium and red mud production plants in Hungary (Table 6.6, Figure 6.6). To date, no detailed studies of the nature and extent of contamination and impacts on ecology and human health around these industrial sites has been carried out, however, no diseases caused by environmental exposure to fluoride have been reported in these localities. The industrial sources were included in the final risk assessment GIS as they represent areas that should be investigated in more detail in future studies (Table 6.1).

Table 6.6 Industrial sources of fluoride associated with aluminium production and red mud industries in Hungary.

Location of Industry
MOSONMAGYARÓVÁR
ALMÁSFÜZITŐ
AJKA REDMUD
AJKA ALUFACTORY
VÁRPALOTA ALUFACTORY

6.2.4 Fluoride Exposure and Health

Some dietary surveys relevant to the assessment of fluoride risks have been carried out in Hungary and are mentioned in this report for background information. Work by (Biro et al., 1996) demonstrated that, Mg intakes were just adequate, but Ca and Vitamin E intakes were generally deficient in Hungarian diets. In another dietary survey, Hungarian food and beverages were found to be more important sources of fluoride than water, especially in low-fluoride areas, accounting for 64 - 90 % of intake in 3 - 4 year-olds and 58 - 77 % in 14 year-olds. It should be noted, however, that beverages included all drinks made from tap water and only plain tap water was excluded from the study. Fluoride intakes from air as a percentage of total fluoride uptake were estimated at 0.01 - 0.06% for 3-4 year-olds and 0.03 - 0.17 % for 14 year-olds whereas fluoride ingested from dust represented 0.03 - 0.12% and 0.09 - 0.37% respectively for the same age groups (Schamschula et al., 1988a+b).

Schamschula et al. (1988c) suggested that the bioavailability of fluoride in Hungarian foods was lower than in water possibly due to the presence of Al, Ca and Mg. It was also demonstrated that fluoride could be lost to Al-complexes from cooking pots during food preparation. Parsley and celery leaves were high in Ca, Mg and F whereas potatoes were low in these elements. Ca intake was lowest in high-fluoride water areas, however, in the general population, levels of Ca were just adequate but Mg intakes were marginal.

In a further study of foods from three areas of Hungary with differing water fluoride contents, Schamschula et al. (1988d) demonstrated that maize flour and leafy vegetables had the highest fluoride contents. The highest food contents were not necessarily coincident with high-fluoride water areas, however, high-fluoride waters used in cooking did have an effect especially on boiled foods such as rice, potatoes and soups. Toth and Sugar (1978) concluded that the daily dietary intake of fluoride in Hungary from foodstuffs including the effect of cooking water was 0.096 - 0.567 µg/g/ day.

Information on dental fluorosis incidence in Hungary is limited. Schamschula et al., (1985) measured caries and dental fluorosis prevalence in 3 groups of Hungarian children aged 14 who were exposed to contrasting fluoride concentrations in drinking water (Table 6.7). Although community fluorosis index assessments showed that prevalence increased with water fluoride concentrations, index values below 0.6 were not considered a public health problem (Dean et al., 1942). However, dental fluorosis related to environmental exposure has been reported historically in three regions of Hungary, Herceghalom to the west of

Budapest and the towns of Bar and Dunaszekcso in the south near the Ukrainian border (Table 6.8 and Figure 6.6). As a consequence, the water supplies in these towns were changed and the population no longer drink high-fluoride water.

Table 6.7 Concentrations of water fluoride and community fluorosis index results, Hungary (Schamschula et al., 1985)

	Low	Intermediate	High
	n = 45	n = 53	n = 41
Water Fluoride mg/l	0.06 – 0.11	0.5 – 1.1	1.6 – 3.1
Community Index of Fluorosis	0.00	0.04	0.20

Farkas et al. (1999) examined morning spot-urine samples of 27 – 59 children from 22 settlements across the country to determine fluoride status relating to uptake from drinking water with a view to fluoridating water supplies in Hungary. Five settlements with high-fluoride water contents of 1.3 – 2.0 mg/l were deliberately included in the study, Csepa, Szeleveny, Tisakurt from the Central Hungarian Plain and Kaptalanfa and Herceghalom in Transnubia (Figure 6.6). Results demonstrated a strong correlation between the fluoride content of drinking water and urinary fluoride excretions. As part of the study, the dental status of 6 – 12 year old children in four settlements was assessed. The proportion of healthy teeth in areas with 2 mg/l fluoride in water (38 – 60%) was significantly higher than in areas with low-fluoride waters (20 – 37%) and the amount of dental caries was higher in the low-fluoride areas (DMF-T values 2.0 in villages with 2 mg/l fluoride in water and 2.82 – 3.52 in villages with low-fluoride in water) (Table 6.8). Studies into the possible benefits of fluoridation are ongoing and at the present time, water supplies are not fluoridated in Hungary.

Table 6.8 Dental fluorosis and caries incidence in some Hungarian settlements.

Location	Water F mg/l	Fluorosis Prevalence Rate %	Dental Caries Rate %	Healthy Teeth %
Bar^	>4^	Unknown	-	-
Dunaszekcso^	2.2-2.4^	Unknown	-	-
Herceghalom^	2.0-2.2^	Unknown	DMF-T = 2.0 at 1.3 - 2 mg/ F in water DMF-T = 2.82 - 3.52 at low F in water#	38 - 60% at 1.3 - 2 mg/l F in water 20 - 37% at low F in water#
Kaptalanfa	1.3 - 2.0#	None	DMF-T = 2.0 at 1.3 - 2 mg/ F in water DMF-T = 2.82 - 3.52 at low F in water#	38 - 60% at 1.3 - 2 mg/l F in water 20 - 37% at low F in water#
Csepa	1.3 - 2.0#	None	DMF-T = 2.0 at 1.3 - 2 mg/ F in water DMF-T = 2.82 - 3.52 at low F in water#	38 - 60% at 1.3 - 2 mg/l F in water 20 - 37% at low F in water#
Szeleveny	1.3 - 2.0#	None	DMF-T = 2.0 at 1.3 - 2 mg/ F in water DMF-T = 2.82 - 3.52 at low F in water#	38 - 60% at 1.3 - 2 mg/l F in water 20 - 37% at low F in water#
Tiszakurt	1.3 - 2.0#	None	DMF-T = 2.0 at 1.3 - 2 mg/ F in water DMF-T = 2.82 - 3.52 at low F in water#	38 - 60% at 1.3 - 2 mg/l F in water 20 - 37% at low F in water#

^ Historical fluorosis incidence # (Farkas et al., 1999) DMF-T = Decayed, missing and filled teeth index

Although, information on dental caries incidence is provided by the above study, this was not included in the final risk assessment scheme as dental caries prevalence across Hungary is likely to be more widespread and caused by a variety of factors whereas the study refers to individual settlements. The locations of historical fluorosis incidences were included in the risk assessment, however, as these are important indicators of high-fluoride risk associated with drinking water exposure.

6.2.5 Risk Avoidance Maps

Due to the nature of the water chemistry data available for Hungary, it was not possible to relate drinking water data to cold or thermal well sources. Therefore these data were combined in the GIS so that problem waters from any possible source (cold or thermal wells or drinking water taps) would be highlighted. The risk avoidance maps for Hungary are based on a grid size of 3 km^2 commensurate with the sample density of the combined cold, thermal and drinking water data sets. In each grid square, the water fluoride content, industrial source and fluorosis incidence data were combined with water supply information to produce the final risk maps (Annex 5 and 6).

Across most of Hungary, the risk of dental caries is high since the water supply is not fluoridated and the majority of Hungarian waters contain low fluoride (< 0.5 mg/l) concentrations. In isolated locations around the country, the risk of dental caries is high but higher fluoride waters are available in the vicinity (Annex 5). In contrast to the high-risk classification over most of the country, three regions are classified as low risk on the basis of the water fluoride contents (≥ 0.5 mg/l). The central Great Hungarian Plain between Sozlnok and Bekescsaba, examined in more detail as part of the present study where high-fluoride waters result in lower prevalences of dental caries, the Budapest region and the region around the town of Bar close to the Ukrainian border where dental fluorosis has been reported historically and (Annex 5). However, it should be noted that the communities of Bar and Dunaszekcso are not supplied with high-fluoride water in this area.

With the exception of the central Great Hungarian Plain, high-fluoride risks occur in very few isolated localities and in many cases low-fluoride waters are available in the vicinity (Annex 6). The locations of all industrial sources have been categorised as high risk because the extent of environmental impact requires further study around these sites. The three localities of Herceghalom, Bar and Dunaszekcso where fluorosis incidence occurred in the past are categorised as moderate risk in the scheme as the population of these towns no longer drink high-fluoride water. The moderate classification indicates that the situation should continue to be monitored in the future to ensure high-fluoride waters are not used for drinking. The geothermal regions of the central Great Hungarian Plain and Budapest are categorised as high risk as fluoride contents in water exceed 1.5 mg/l in these areas. However, due to the complex mixing of different waters in the public supply network, drinking water received at tap generally has a lower fluoride content than source well waters and no evidence of dental fluorosis has been reported in these regions. The special geological characteristics of the central Great Hungarian Plain area are well known to hydrogeologists in Hungary and this area is highlighted as high risk to indicate that the region is the focus of on-going study.

6.3 CENTRAL GREAT HUNGARIAN PLAIN STUDY AREA

As a result of the national risk assessment carried out for Hungary, data from the hydrogeology, cold well, thermal well and drinking water databases for Hungary (MAFI: Pecsi, 1989; Toth, 1989) were examined in more detail in the central Great Hungarian Plain but this study has not been included in the risk assessment GIS as there was no further detailed locational information to add to the system. The detailed study area lies in the central part of the Great Hungarian Plain between the River Tisza and the River Harmas-Koros. The meandering River Tisza is the second largest river in the Carpathian-Basin and the River Harmas-Koros; a tributary of the River Tisza also originates in the East Carpathians (in Romania). The area is relatively flat: the lowest-lying section along the River Harmas-Koros lies approximately 83-85 m above sea level (asl). The topography rises to 120-130 m asl within 40 km to the west, marking the regional watershed between the River Danube and River Tisza.

6.3.1 Geology and Hydrogeology

The regional geology of the area comprises Upper Miocene, Pliocene and Quaternary fluvio-lacustrine sediments, which form a multi-layered aquifer system. Two distinct hydro-stratigraphic units can be distinguished in the area. The lower unit is the Upper Miocene and Pliocene multiple sand reservoir system between 500-1500 m depth representing the main thermal water-bearing formation. The underlying Upper Miocene Lower Pannonian clay formation forms an impervious barrier between the basement Mesozoic hard rocks and the thermal water bearing horizon. The porous formations within these sequences are sheet-like sand bodies, which are often multi-layered, laterally coalescent and pinching and wedging-out forming sand lenses and sandy patches of limited lateral dimension. The upper hydro-stratigraphic unit is the Quaternary multi-layered aquifer system ranging from the surface to 500-m depth.

Due to the depositional development of the entire aquifer system, the hydro-stratigraphic units are defined on the basis of geology only as the two units are inter-connected hydrogeologically. The western part of the aquifer complex is exposed to the surface via aeolian sands at the top of the sedimentary column. This is the main recharge zone of the complex. The main discharge zone lies near the River Harmas-Koros. Despite the simple geological and boundary conditions, the hydrodynamics of the area based on geothermal and hydrogeochemical evidence is complex. Along the eastern bank of the River Tisza a positive geothermal anomaly was discovered in 1964. In this region at a depth of 200 m the water temperature is 42 °C compared to the regional average of 20 °C. This anomaly is caused by a strong upward movement of groundwater from the lower thermal water-bearing horizon to the main Quaternary aquifer. The water then flows eastwards to the Harmas–Koros Region, which is characterised by the lowest hydro-potential of the central Great Hungarian Plain.

6.3.2 Hydrogeochemistry

The hydrodynamic regime in various parts of the aquifer largely controls the geochemistry. For example, the recharge zone is characterised by low TDS, Ca-Mg-bicarbonate-type waters, whereas the deeper aquifer units and the discharge zones are characterised by Na-bicarbonate-type waters. These chemical differences are not only a result of simple ion exchange on clays along flow lines in addition, the higher TDS caused by higher bicarbonate and Na contents indicate a (possible bacterially) decomposed organic component of the 500 - 1000 m deep aquifer units.

Higher (>1-2 mg/l) fluoride values are generally found in the deeper and warmer groundwater. The upper zone (Quaternary) of the aquifer usually contains less than 0.3-0.4 mg/l fluoride. However, this is not the case to the east of the geothermal anomaly region, where the upper aquifer complex also contains high (1 – 2 mg/l) fluoride waters forming a large plume in the east of the territory. This fluoride anomaly is examined in more detail as follows.

6.3.3 Anomalous Fluoride Region

On the basis of existing hydrogeological and hydrogeochemical (cold wells, thermal wells and drinking water data, MAFI: Toth, 1989), the study region is defined as an area of 60 x 60 km (3600 km^2), with anomalous fluoride concentrations (> 0.5 mg/l) in an area of 20 x 20 km (400 km^2) (Figure 6.10). The horizontal gradient of the groundwater table in the western part of the region is up to 2-3 m per km, whilst in the eastern part is very small or zero. According to piezometric head measurements in deeper boreholes, the vertical hydraulic gradient is 2-5 m per 100 m downward in the western region and 3-6 m per 100 m upward in the eastern area (Figure 6.11). Groundwater movement is controlled by the piezometric heads of the main rivers and groundwater evaporation. The Quaternary aquifer complex is the main source of drinking water in the Great Hungarian Plain. The majority of cold water wells are drilled into this multi-layered aquifer system. The basement of these layers dips to the southeast and in regional groundwater models, the anisotropic direction has to be taken into account (Figure 6.12).

The 3.3 million-year-old Upper Pliocene aquifer complex plays an important role in determining the regional groundwater flow paths (Figure 6.13). Around the cities of Kecskemet, Tiszakecske, Csongrad and Szentes, this complex consists of gravely sand layers with excellent permeability (west from the River Tisza). In the eastern part of the territory there are no gravelly layers and the sand layers have lower permeability acting as a barrier to the W-E regional flow system forcing water to the upper horizons. The lower aquifer horizons of the Upper Pannonian (Upper Miocene) complex form the main thermal water-bearing system in the Carpathian Basin. The sandstone strata of the Upper Pannonian are of lacustrine delta slope origin. This 5.5-8 million-year-old old deposit has good permeability and uniformity extending throughout the basin (Figure 6.14).

In terms of hydrochemistry, the spatial distribution of Ca is determined by the main recharge-discharge zones of the area and clearly demonstrates the role of the ion exchange processes. Groundwater in the anomalous fluoride area has very low Ca contents (Figure 6.15). The Na distribution is similar to that of Ca but the amount of Na is much greater than expected from the Ca content in the recharge zone and groundwater in the anomalous fluoride area has very high Na contents (Figure 6.16). The chloride content also varies according to the regional flow system, but the amount of this constituent is relatively low compared to the Na content and there is little spatial correlation between Cl and fluoride (Figure 6.17). The bicarbonate content of the groundwaters reflects the regional flow system, however, concentrations in the eastern high-fluoride area are relatively high (Figure 6.18). The greater amounts of bicarbonate (HCO_3) and Na in this area indicate the presence of (possible bacterially) decomposed organic material. Bicarbonate concentrations of more than 500 mg/l usually occur in the Great Hungarian Plain at depths of 600-700 m except in areas where the upward movement of groundwater from depths of over 600 m is dominant. Ammonia (NH_4) concentrations in the groundwater system are also dependant on the flow regime and the decomposition of organic matter in the aquifer units. The high concentrations of ammonia in the recharge zone indicate that the source of ammonia is more persistent than Na and HCO_3 sources (Figure 6.19).

In summary, the area of the central Great Hungarian Plain between the River Tisza and River Harmas-Koros contains anomalous fluoride concentrations in drinking water derived from groundwater sources. Investigations carried out for the present study demonstrate that that the anomaly is caused by the upward movement of the groundwater from the thermal water-bearing horizon to the main Quaternary aquifer. These upward-moving waters then flow eastwards to the Harmas –Koros Region. Hydrochemically, these waters favour high fluoride contents having low CaF_2 precipitation potential – low Ca, high Na and temperature and aquifer units containing fluoride-bearing minerals.

6.3.4 Health Data

As outlined in section 6.2.4 above, studies by Farkas et al. (1999) demonstrated that children consume high fluoride waters in this region and as a consequence have better dental status in terms of caries than the rest of the country but are at potential risk of fluorosis especially if fluoride is consumed from other sources such as toothpaste and dental products and mineral water containing high fluoride concentrations.

6.4 CONCLUSIONS

More then 90% of the drinking water resources in Hungary originate from groundwater but in general these waters contain very low (< 0.3 mg/l) concentrations of fluoride. In some regions the fluoride content of the drinking water ranges between 0.7 - 2.2 mg/l, however, although dental fluorosis has been reported historically in Hungary, it is not a major public health problem. With the exception of the geothermally active, central Great Hungarian Basin, there are very few locations where water fluoride contents exceed 1.5 mg/l and in several of these cases, lower fluoride waters are available in the vicinity. In the locations of Herceghalom, Bar and Dunaszekcso where fluorosis incidence was reported in the past, the population no longer drink high-fluoride waters and the risk of dental fluorosis has been significantly reduced. Five industrial locations associated with aluminium and red mud production require further investigation to assess the environmental impact of these industries in terms of fluoride. Geothermal waters of the central Great Hungarian Plain do contain high fluoride waters, but these are mixed with other waters before supply to the public and no incidences of dental fluorosis have been reported. However, children could be at risk of fluorosis in this region if fluoride is also consumed from other sources such as dental products and it is recommended that monitoring and studies of these waters and health effects should continue in this region.

The majority of Hungarian waters contain less fluoride than the recommended minimum contents for dental caries prevention (< 0.5 mg/l) and the water supply is not fluoridated, therefore, the risks of dental caries are classified according to the present scheme as high over most of the country.

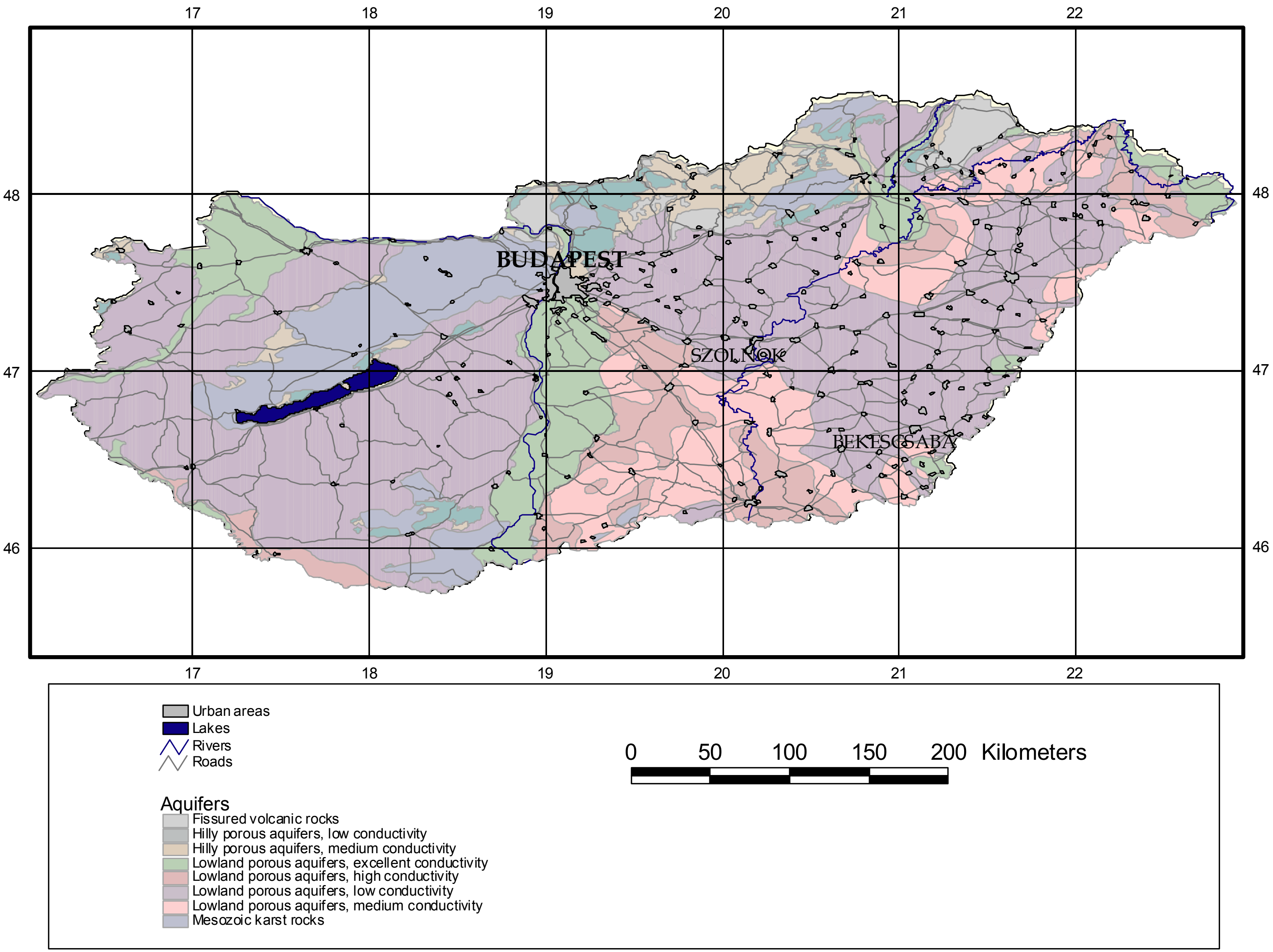


Figure 6.1 Main hydrogeological units of Hungary (MAFI (Siposs and Toth, 1989))

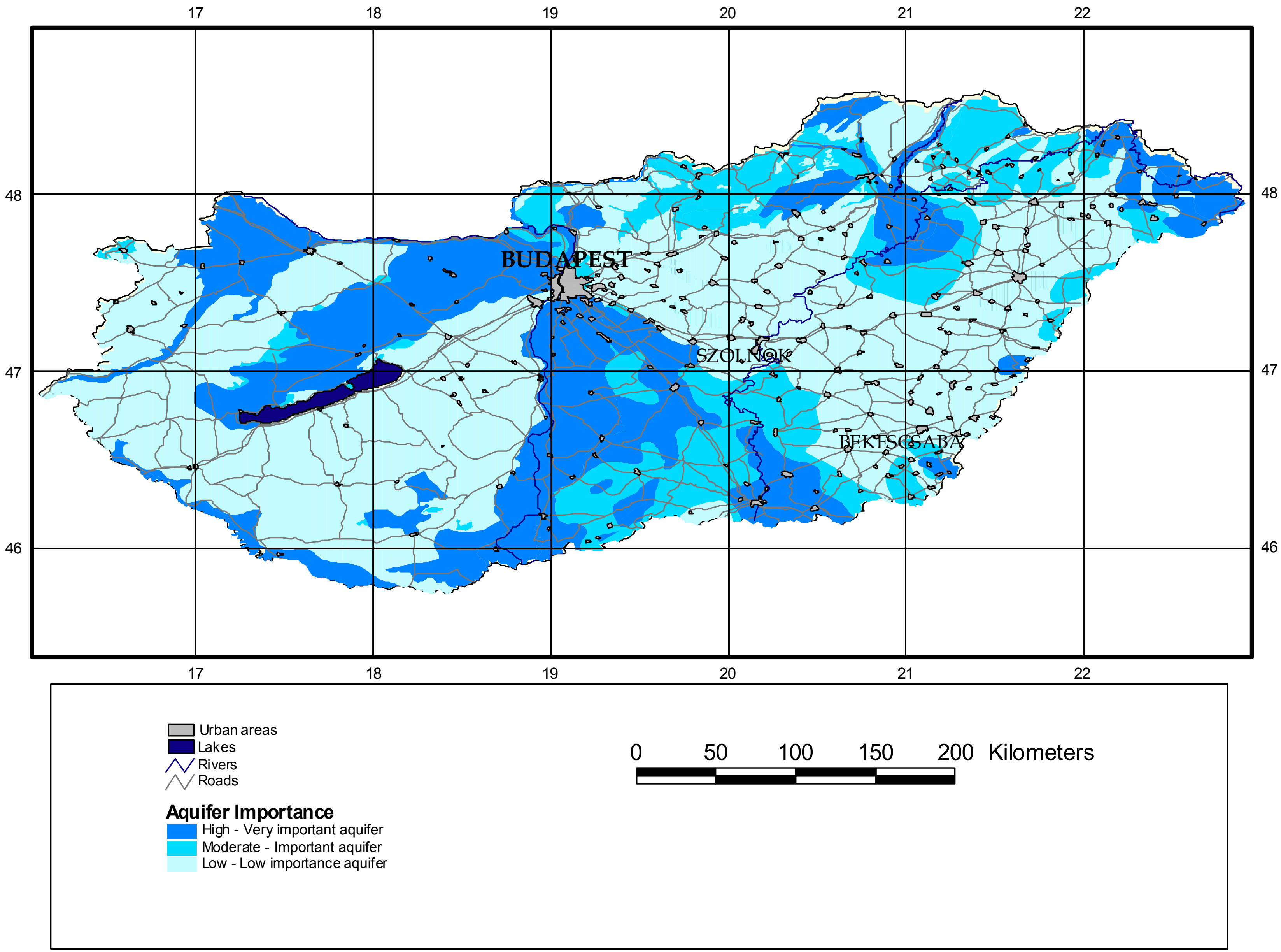


Figure 6.2 Main hydrogeological units of Hungary classified according to aquifer importance

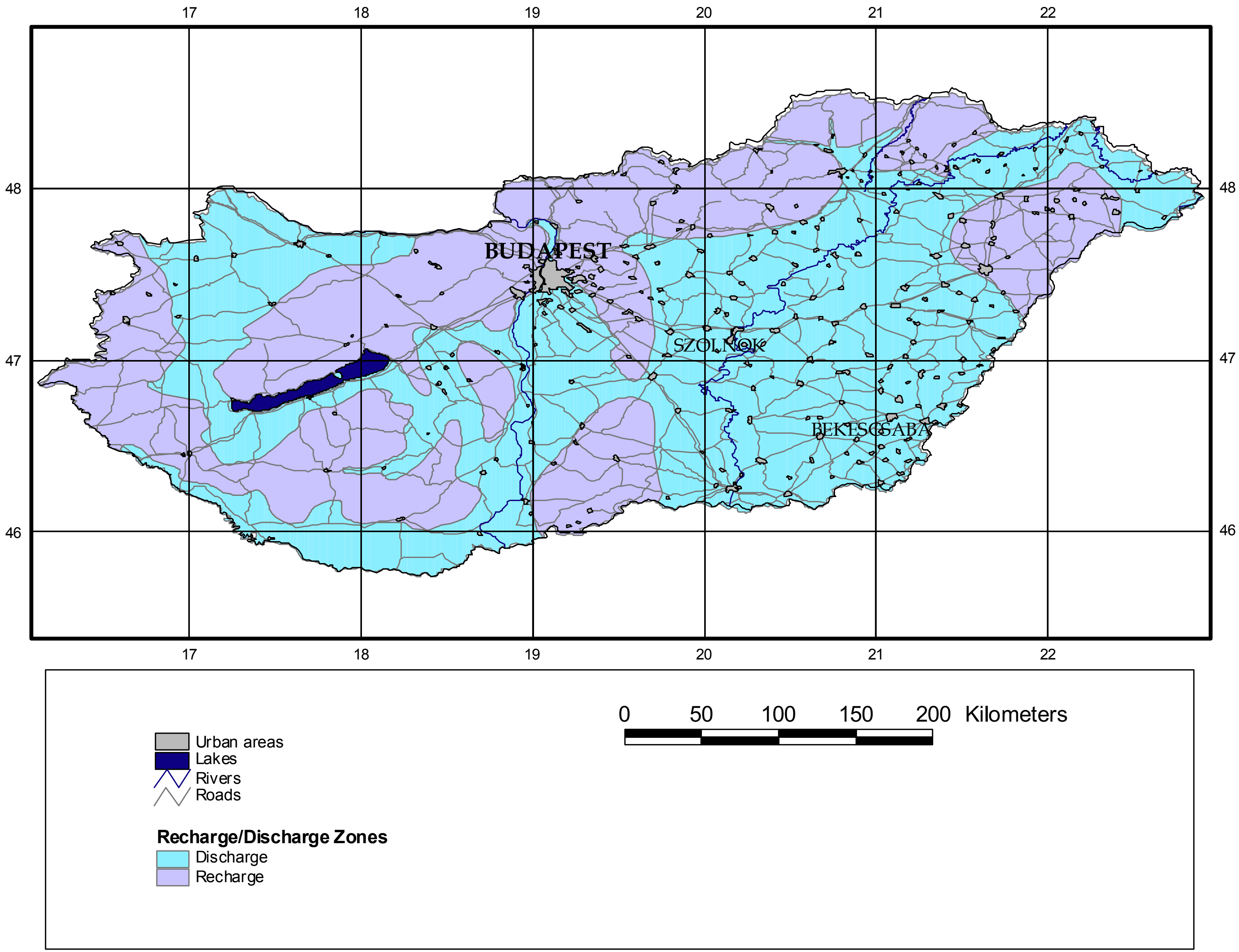


Figure 6.3 Major recharge and discharge zones of Hungary (MAFI (Siposs and Toth, 1989))

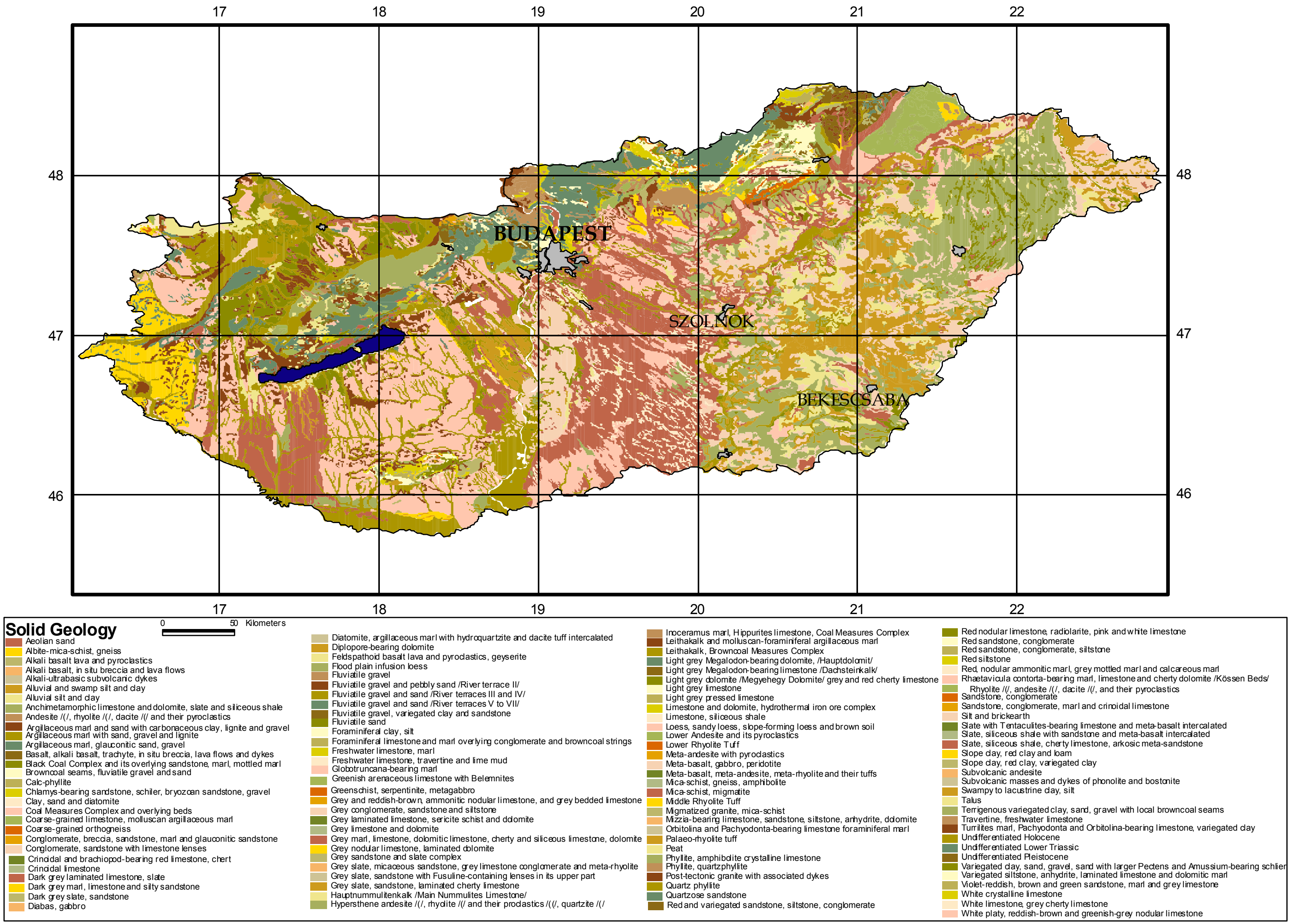


Figure 6.4 Main geological units of Hungary (MAFI (Pecsi, 1989))

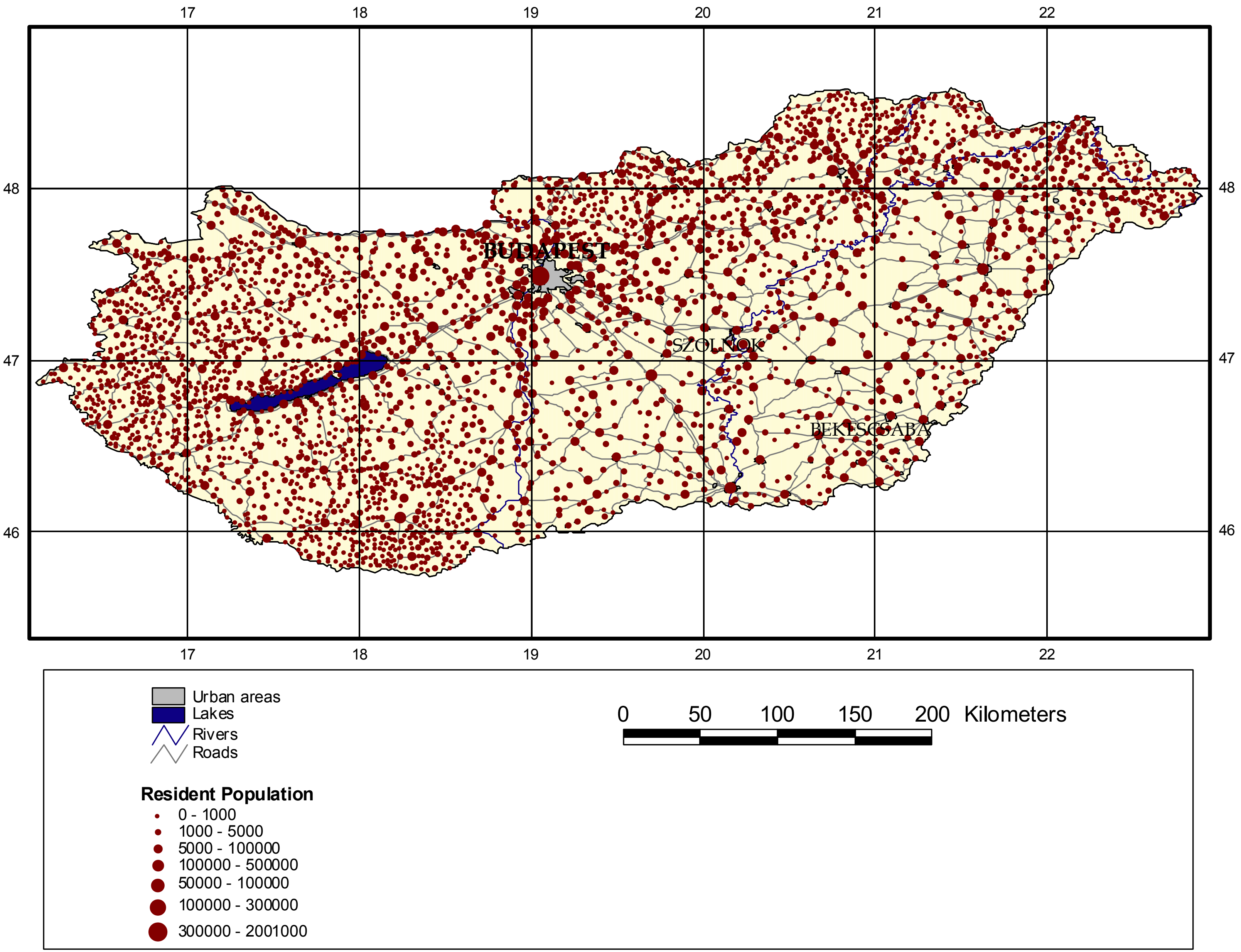


Figure 6.5 Population of the main settlements in Hungary (1991 Census)

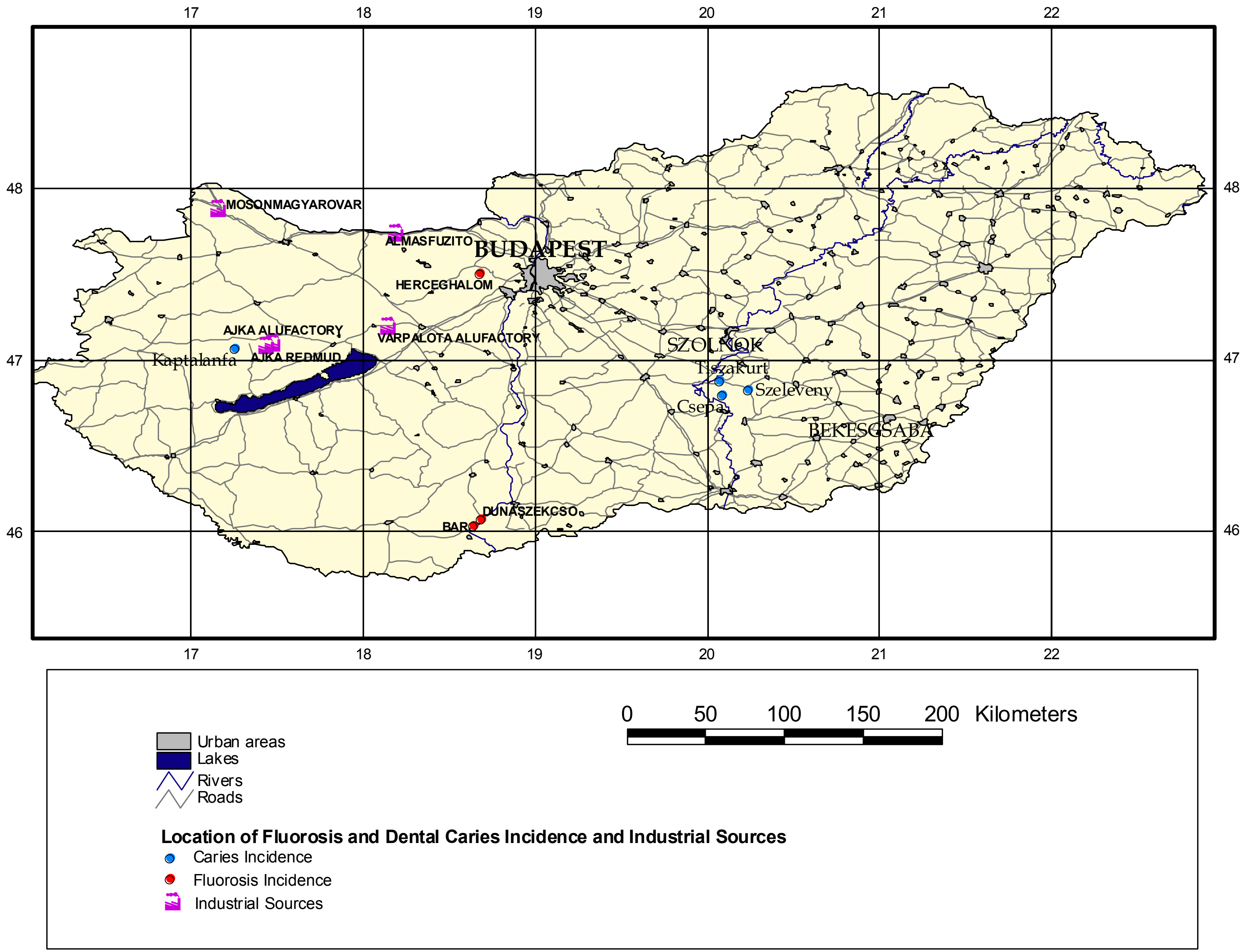


Figure 6.6 Locations of historic fluorosis prevalence, industrial sources of fluoride and dental caries incidence studies in Hungary

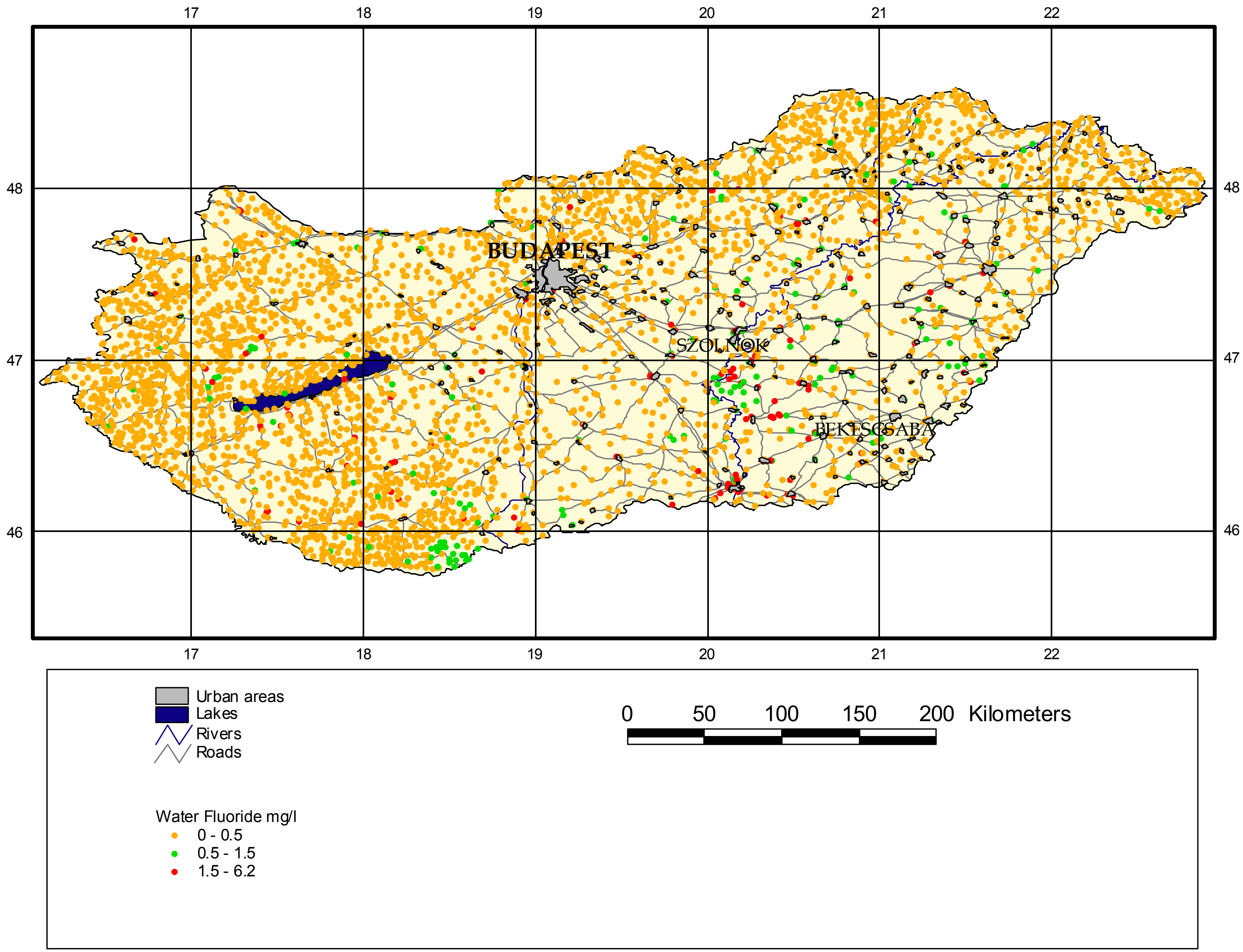


Figure 6.7 Groundwater and drinking water fluoride concentrations in Hungary (MAFI, Toth, 1989) classified according to water quality guidelines (WHO, 1996b)

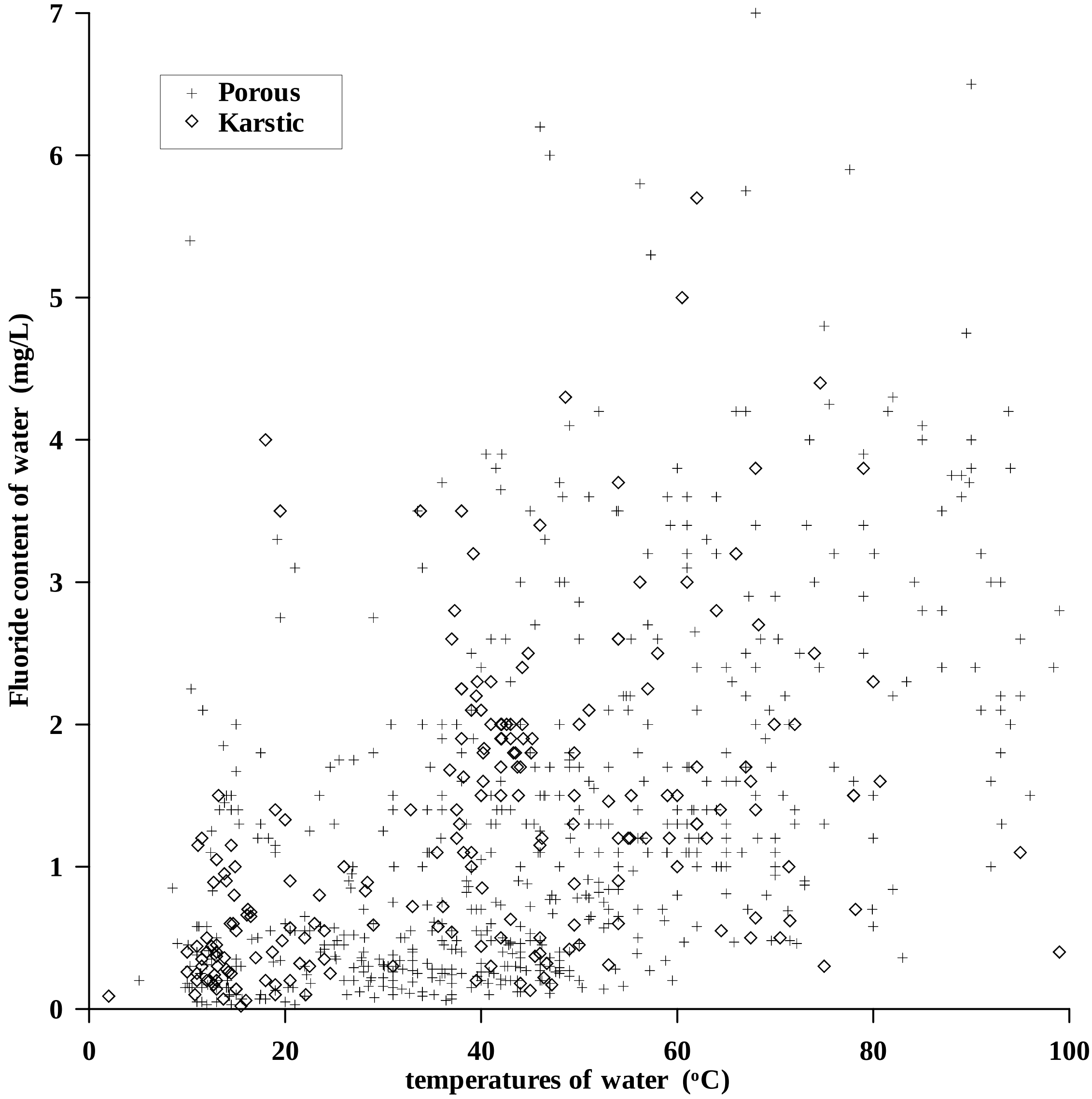


Figure 6.8 Plot of temperature against fluoride content of Hungarian cold and thermal groundwater (MAFI (Toth, 1989))

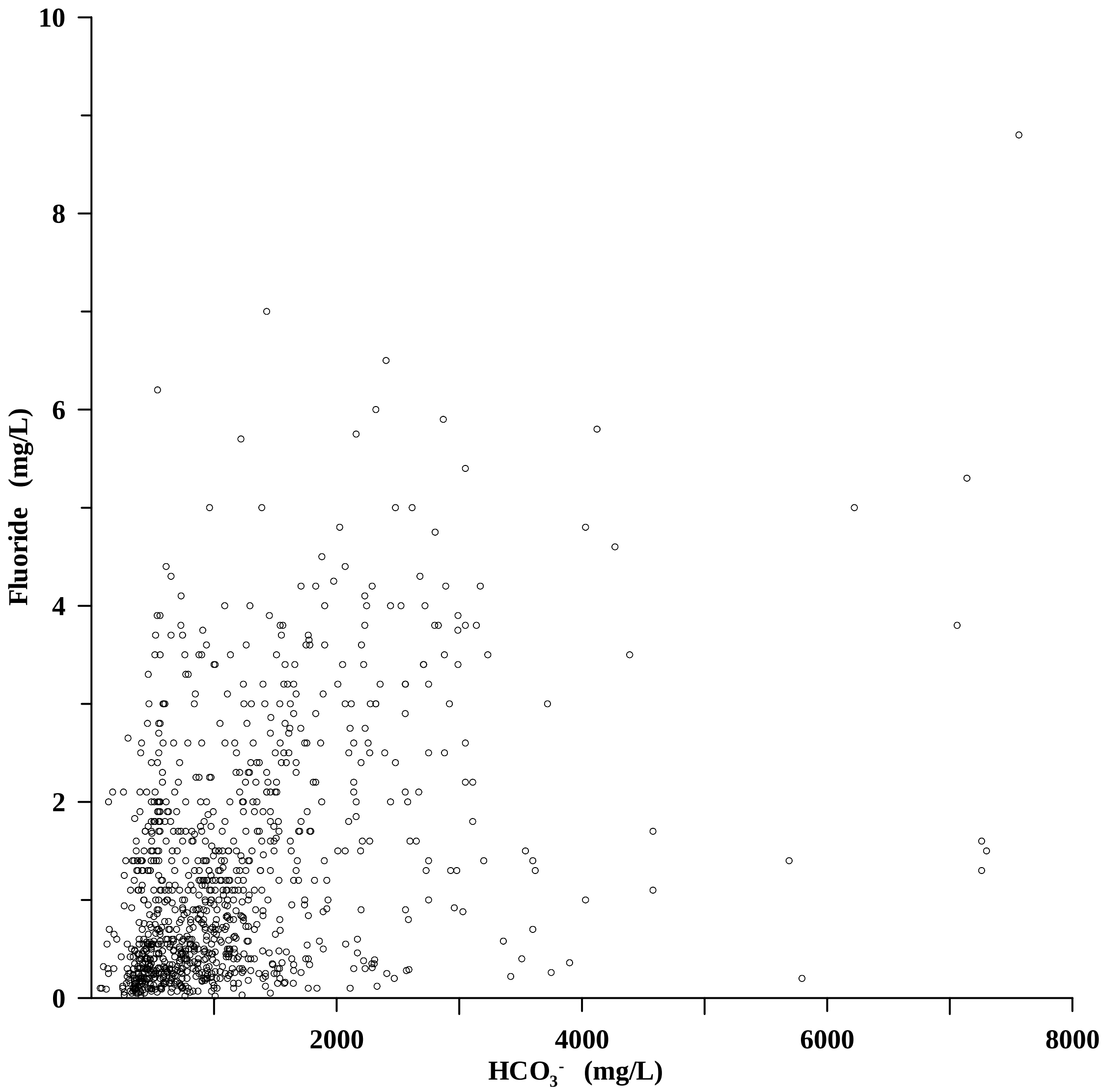


Figure 6.9 Plot of bicarbonate (HCO_3^-) against fluoride content of Hungarian cold and thermal groundwater (MAFI (Toth, 1989))

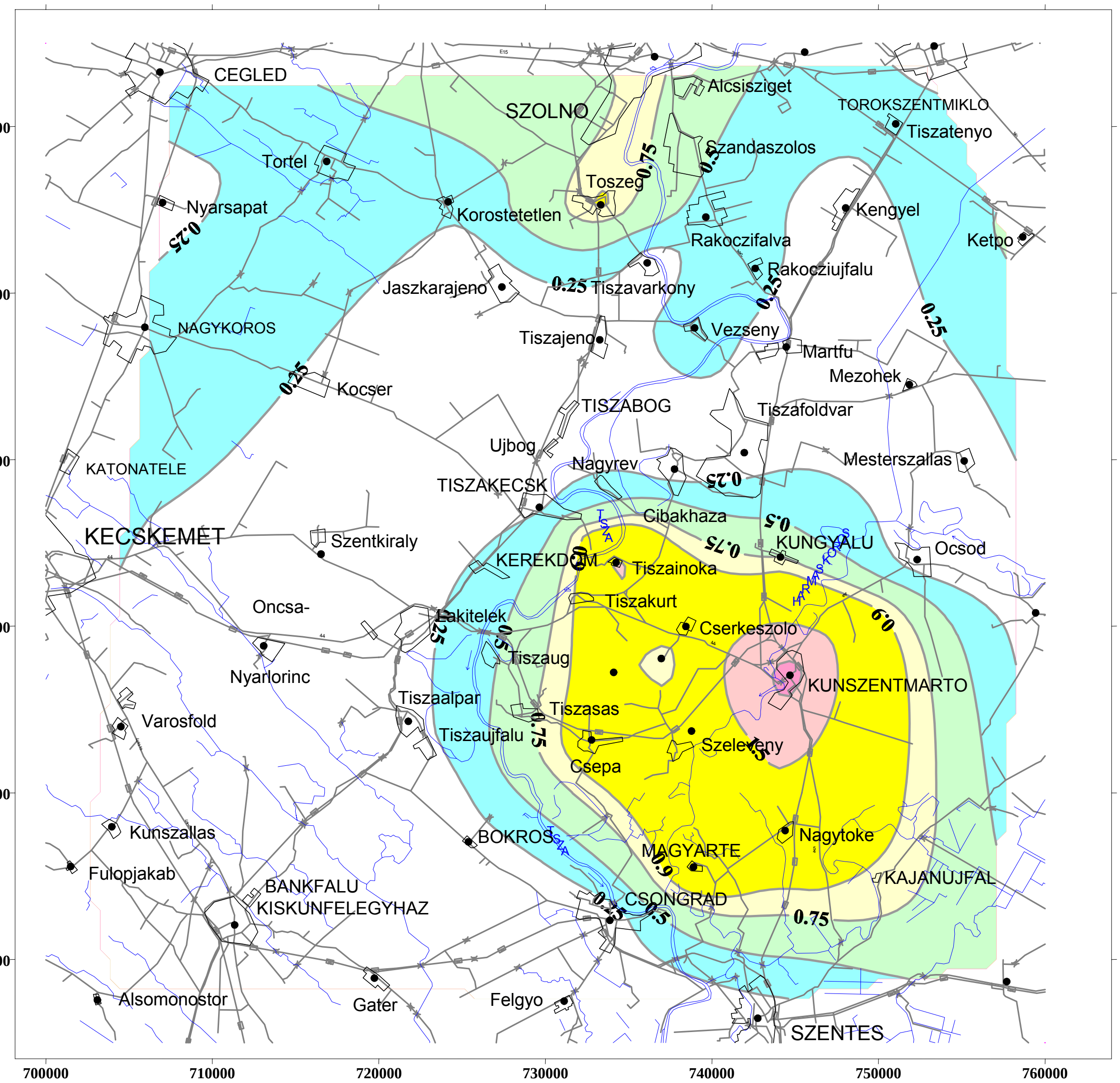


Figure 6.10 Contour surface map of the central Great Hungarian Plain study area showing anomalous fluoride contents (mg/l) in the drinking water supply system. Public water wells extracting water from 100 – 300 m depth are indicated as dots. Hungarian Grid Coordinates

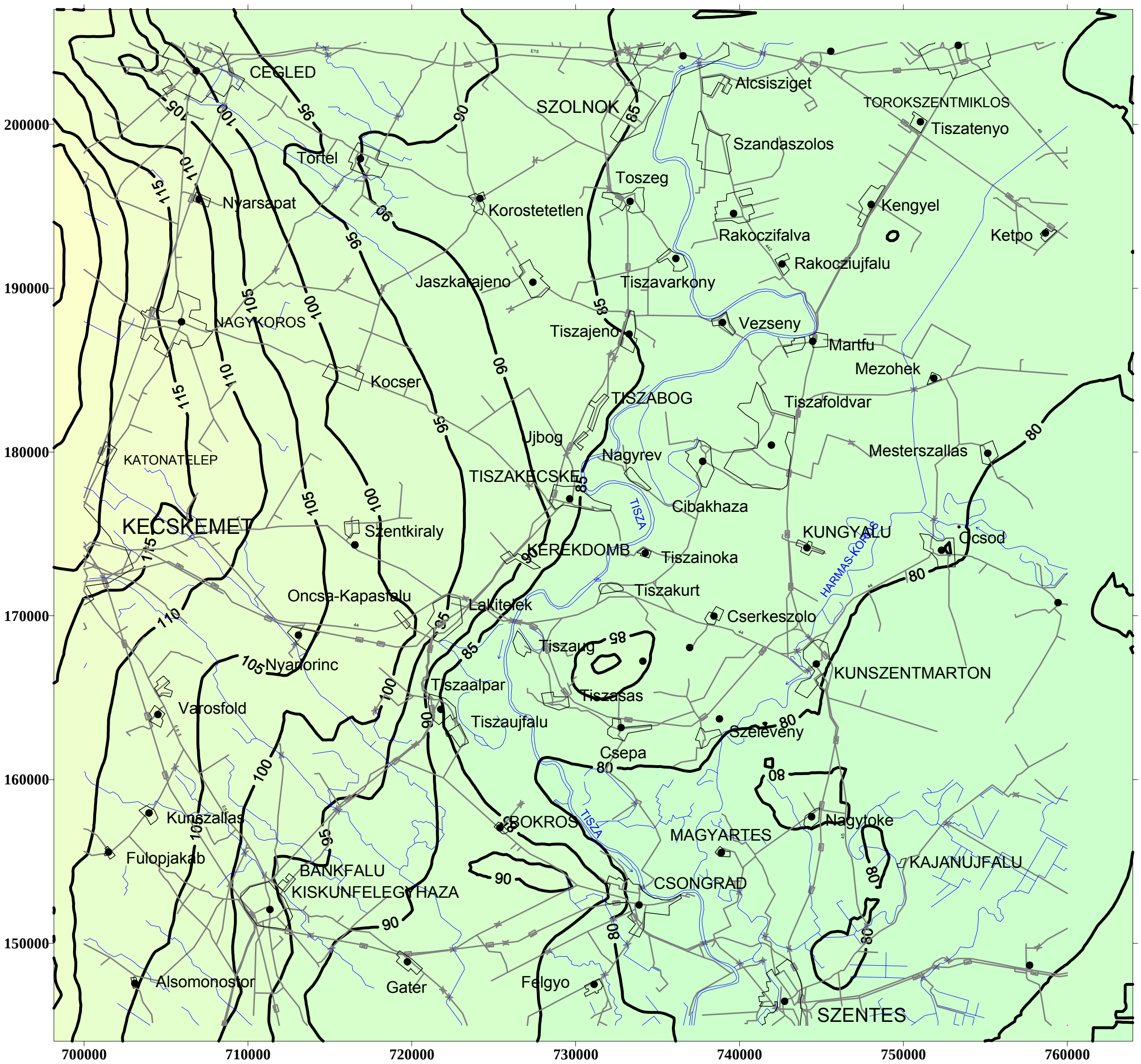


Figure 6.11 Contours (m) showing the groundwater table of the central Great Hungarian Plain study area. Hungarian Grid Coordinates

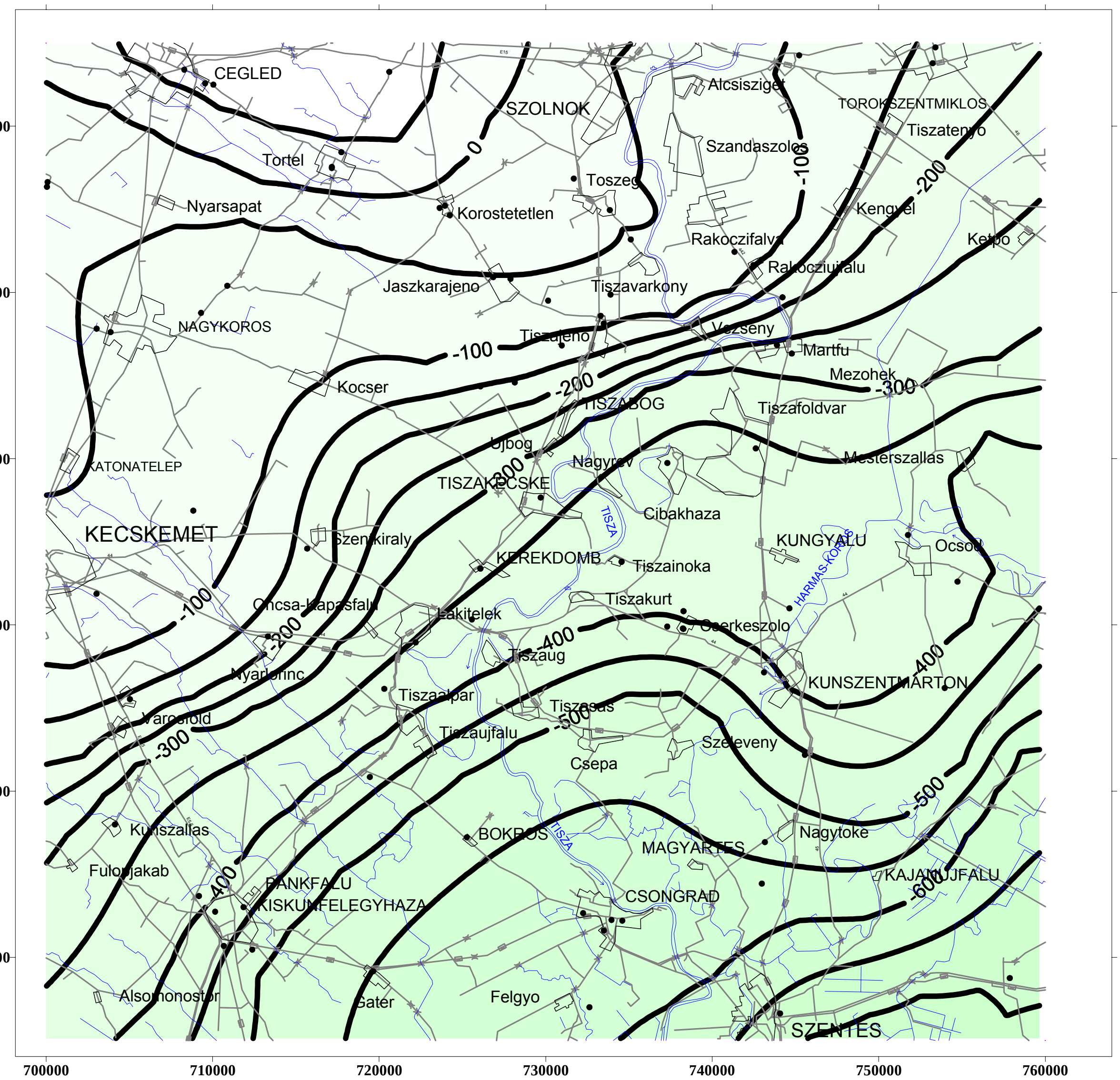


Figure 6.12 Contours (m asl) showing the basement of the Lower Quaternary fluvial sand aquifer complex in the central Great Hungarian Plain study area. Hungarian Grid Coordinates.

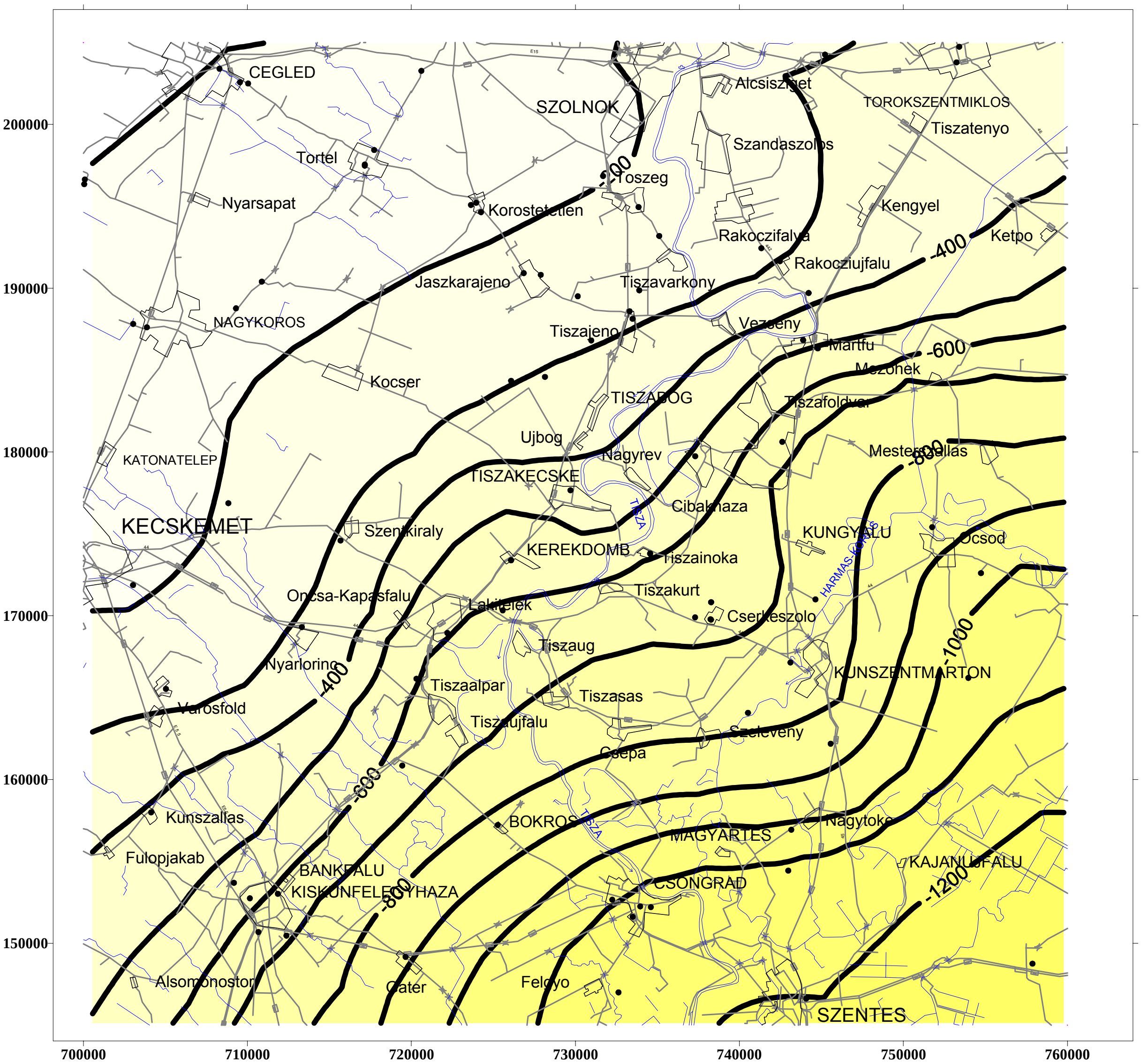


Figure 6.13 Contours (m asl) showing the basement of the Upper Pliocene fluvial sand aquifer complex in the central Great Hungarian Plain study area. Hungarian Grid Coordinates

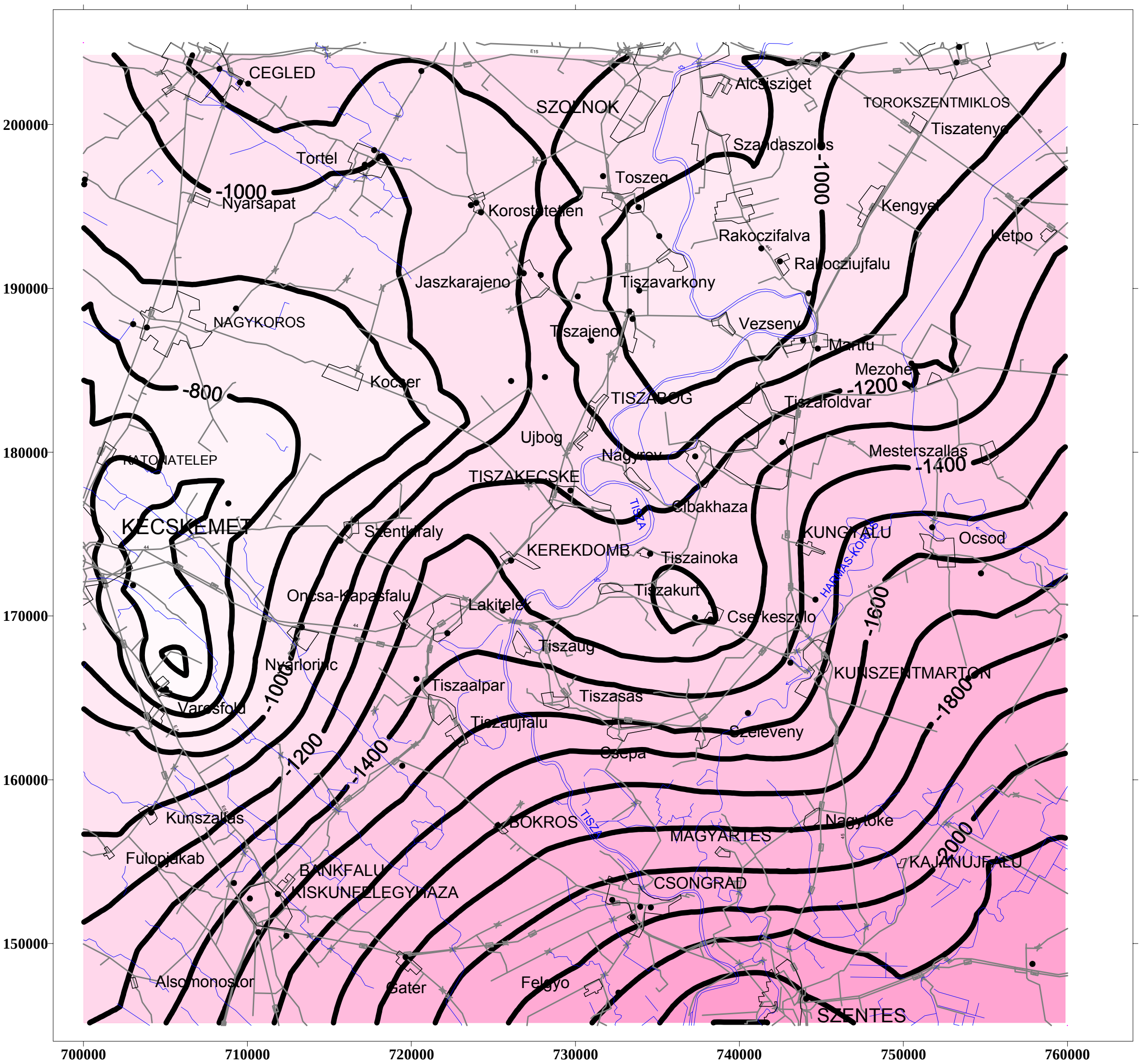


Figure 6.14 **Contours (m asl) showing the basement of the Upper Pannonian sand aquifer complex in the central Great Hungarian Plain study area.** Hungarian Grid Coordinates

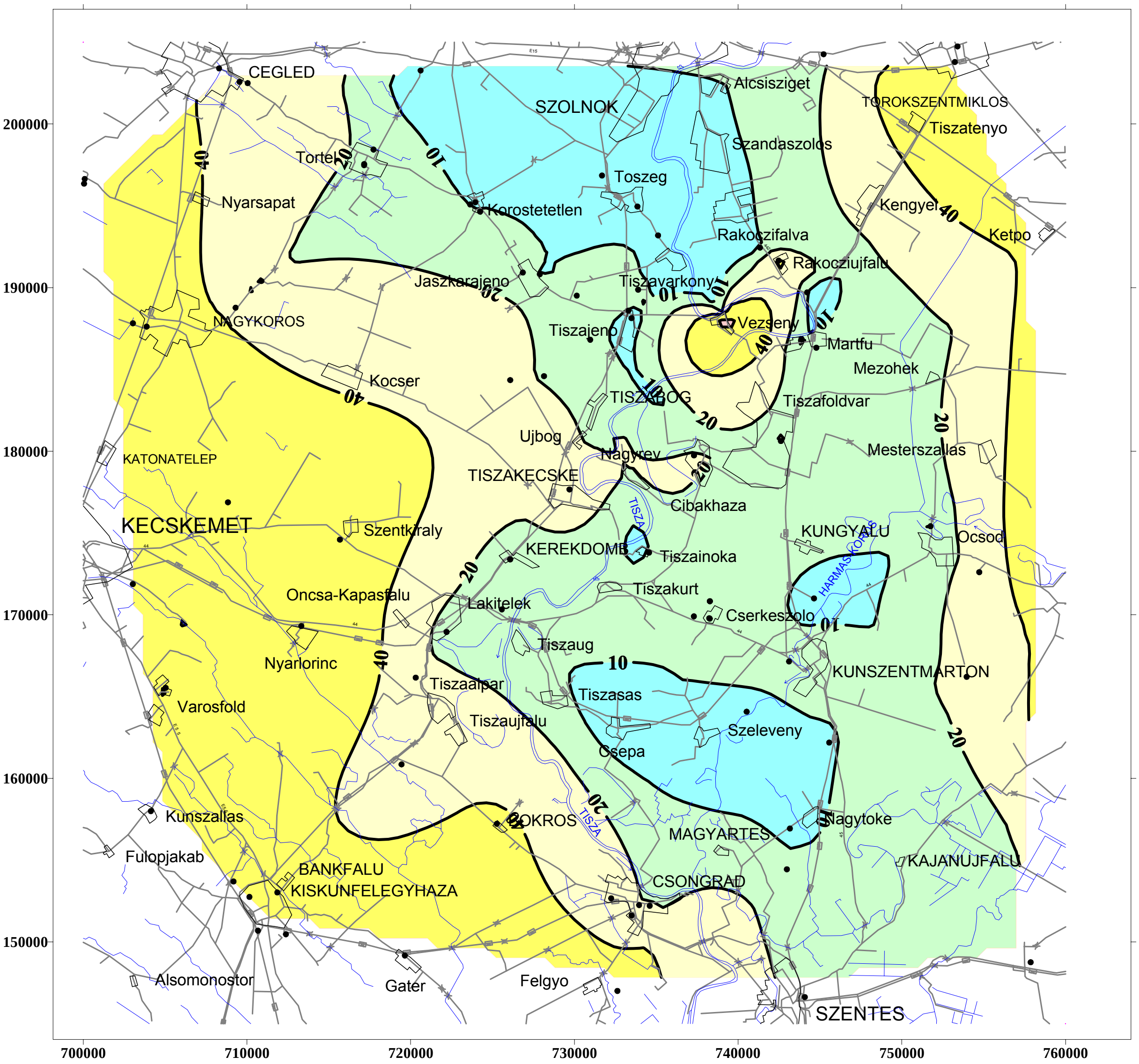


Figure 6.15 Contour map of the Ca content (mg/l) of the main drinking-water-bearing aquifer complex in the central Great Hungarian Plain study area. Depth of aquifers between 100 and 300 m. Hungarian Grid Coordinates

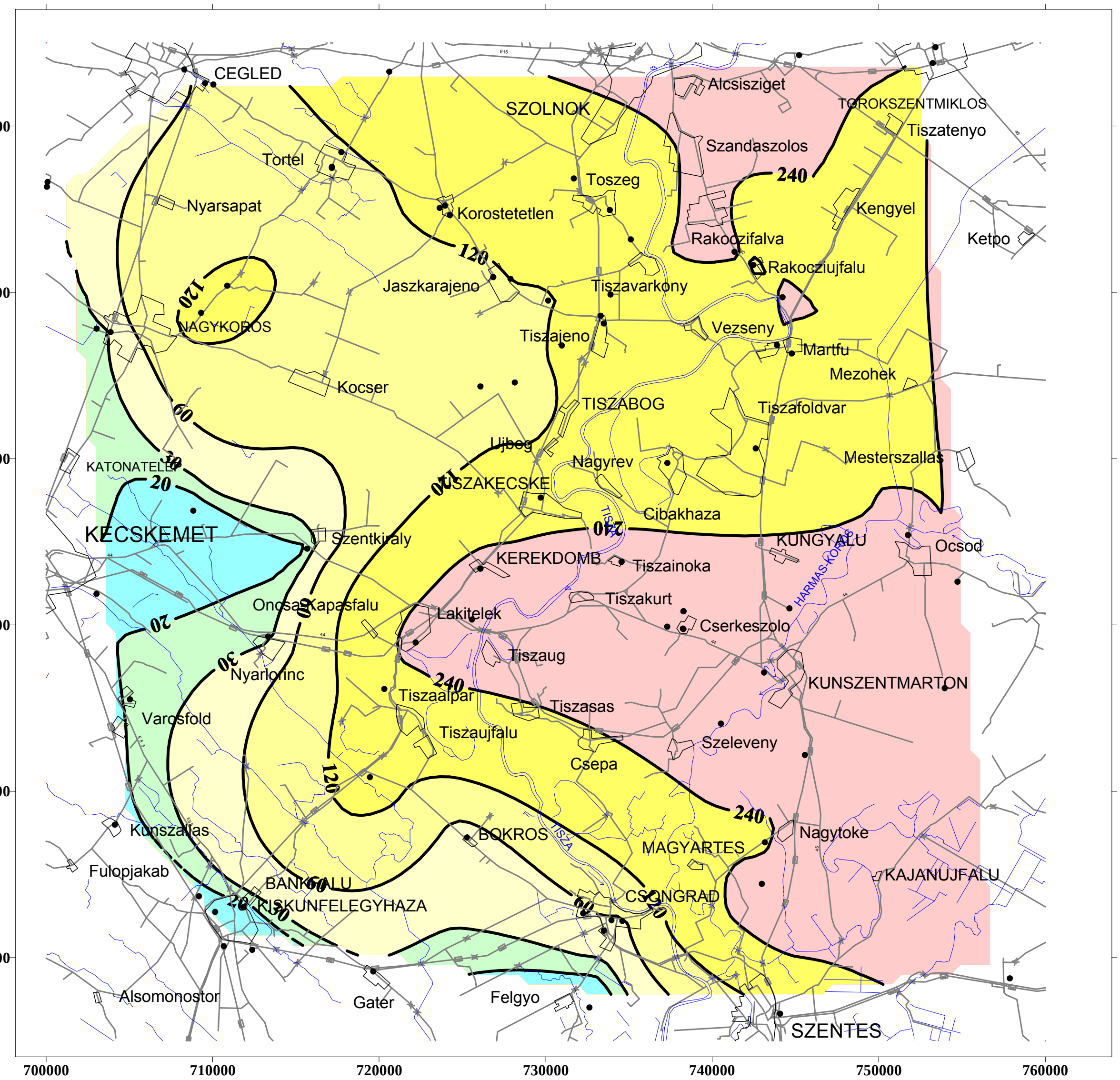


Figure 6.16 Contour map of the Na content (mg/l) of the main drinking-water-bearing aquifer complex in the central Great Hungarian Plain study area. Depth of aquifers between 100 and 300 m. Hungarian Grid Coordinates

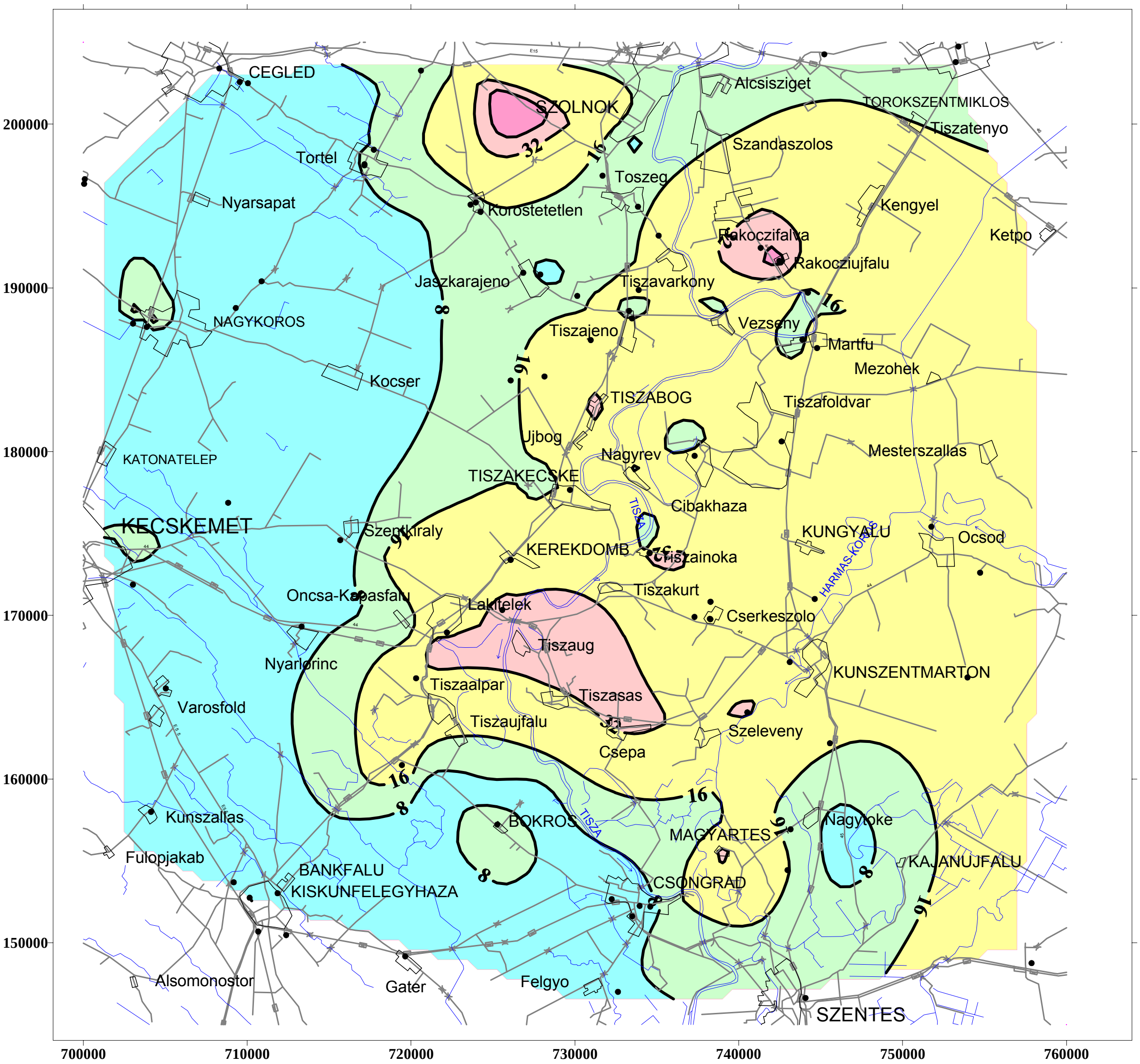


Figure 6.17 Contour map of the Cl content (mg/l) of the main drinking-water-bearing aquifer complex in the central Great Hungarian Plain study area. Depth of aquifers between 100 and 300 m. Hungarian Grid Coordinates

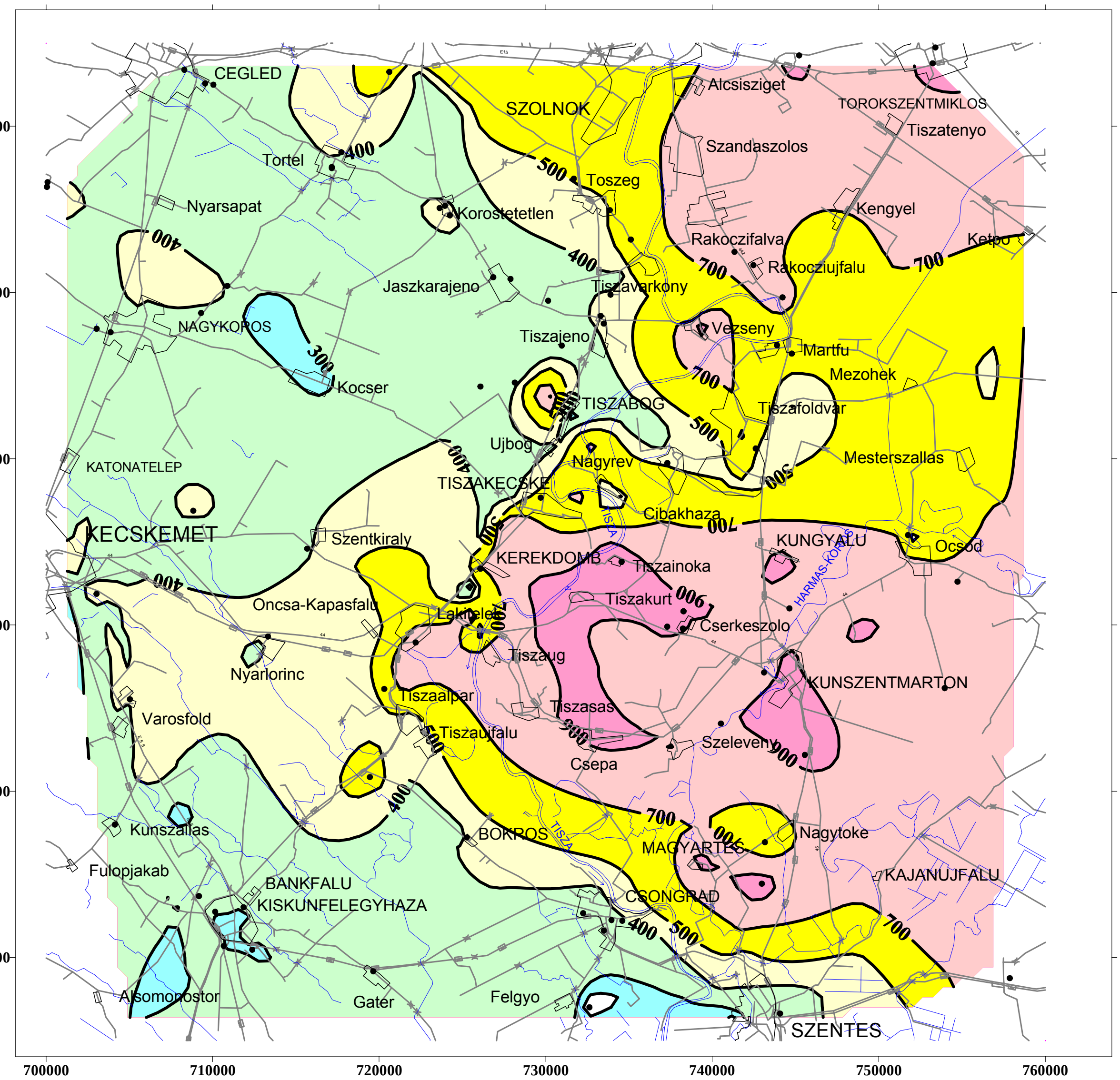


Figure 6.18 Contour map of the HCO_3 content (mg/l) of the main-drinking-water bearing aquifer complex in the central Great Hungarian Plain study area. Depth of aquifers between 100 and 300 m. Hungarian Grid Coordinates

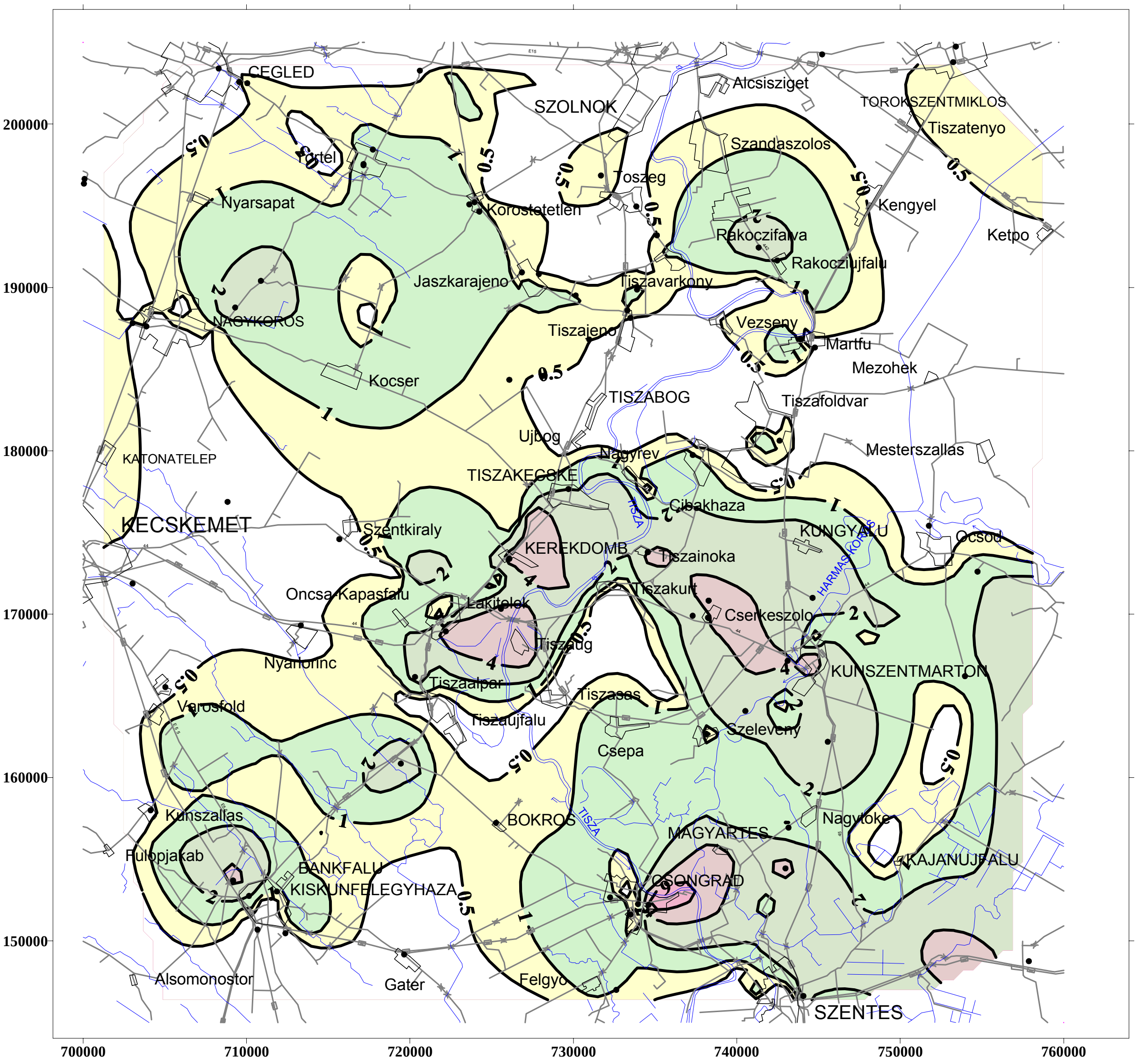


Figure 6.19 Contour map of the NH_4 content (mg/l) of the main drinking-water-bearing aquifer complex in the central Great Hungarian Plain study area. Depth of aquifers between 100 and 300 m. Hungarian Grid Coordinates

7 Fluoride Risk Assessment for Moldova

Uri Iljinsky, Vladislav Povorosnuk, Fiona Fordyce and Bryony Hope

7.1 INTRODUCTION

Several drinking-water-bearing horizons are exploited in Moldova, and as a general rule, deep water-bearing horizons contain more fluoride than shallow water-bearing horizons therefore the fluoride risk at any locality is very dependant upon which aquifer source is exploited. In the centre of the country, public water supplies extract deep water using electric pumps, as despite the high fluoride contents, this source is free from bacterial and agricultural pollution. However, since 1990, crises in the electricity supply in Moldova have limited the use of these pumps and as an alternative, the population have sunk over 150 000 shallow wells. Water quality in the shallow wells is extremely poor and in addition to bacterial and agricultural pollution, many of the shallow water-bearing horizons also contain elevated fluoride contents. It is desirable that the population return to drinking deeper uncontaminated waters, however, an assessment of fluoride risks and fluoride treatment technologies are essential as dental fluorosis related to drinking water consumption is endemic in central and western Moldova.

Despite these factors, no national fluorosis survey has been carried out in Moldova and prior to the present study, the relationships between fluoride in water and fluorosis severity had not been examined in detail. This chapter presents a national overview of fluoride and fluorosis in Moldova and the results of the first detailed geochemistry and health case study in the country, which was carried out in the Falesti Region.

7.2 NATIONAL RISK ASSESSMENT

7.2.1 GIS Risk Scheme

The data incorporated into the Project Partner GIS (Country.apr) for Moldova are listed in Table 7.1. At the national level, the map of hydrogeological units (ASG) (Figure 7.1), hydrogeology classified according to aquifer importance (Figure 7.2) and main population centres (Figure 7.3) were included in the GIS for background information only.

The national fluoride risk assessments for Moldova were carried out on the basis of the groundwater chemistry database for the whole country (ASG) water supply information and fluorosis incidences (Tables 7.2 and 7.3).

Table 7.1 Data included in the Project Partner Country.apr risk assessment GIS for Moldova

		GIS Risk Assessment
Data	Groundwater Chemistry Data for Moldova	Data categorised according to WHO fluoride water quality guidelines: < 0.5 mg/l Caries Risk, ≥ 1.5 mg/l Fluorosis Risk in risk assessment scheme
Data Source	From the database of the Association of State Geologists (ASG)	
Data Type	327 analyses of groundwater from recent sediments, Mid Sarmatian, Baden Sarmatian and Cretaceous-Silurian aquifers collected at a sample density of approximately 1 sample per 5 km^2 over most of Moldova. Data for: X, Y, Longitude, Latitude, Location, Sample Number, Aquifer, F, Na+K, Ca, Mg, Cl, HCO_3, CO_3, SO_4, Sr, Se, pH, Eh, TDS	
Data	Tap and Well Water Chemistry for Falesti Region	Data categorised according to WHO fluoride water quality guidelines: < 0.5 mg/l Caries Risk, ≥ 1.5 mg/l Fluorosis Risk in risk assessment scheme
Data Source	Present Study	
Data Type	27 analyses of tap and well water collected in Falesti, Cornesti and Kalarash. Data for: Location, Sample Number, F, Ca	
Data	Hydrogeological Units of Moldova	Data categorised according to aquifer importance for drinking water and included as background information layer only
Data Source	From the database of the Association of State Geologists (ASG)	
Data Type	Digital map of the main younger hydrogeological units of the whole of Moldova.	
Data	Main Population Centres of Moldova	Data included as background information layer only
Data Source	www.esri.com	
Data Type	Digital map of main settlements	
Data	Water Supply Information	Data included in risk assessment scheme
Data Source	Water Supply of Moldova	
Data Type	Knowledge of water fluoridation and use of water for drinking	
Data	'General' Fluorosis Prevalence	Data included in risk assessment scheme
Data Source	Previous Studies	
Data Type	Coordinates of towns with fluorosis incidence	
Data	Fluorosis Prevalence Girls and Boys Falesti Region	Data included in risk assessment scheme
Data Source	Present Study	
Data Type	Fluorosis prevalence statistics for Falesti, Cornesti and Kalarash	
Data	Dietary Fluoride and Ca Intake Girls and Boys Falesti Region	Data included as background information layer only
Data Source	Present Study	
Data Type	Dietary fluoride statistics for Falesti, Cornesti and Kalarash	

Table 7.2 Dental caries risk assessment scheme for Moldova

Caries Risk						
Location	Phase 1		Phase 2		Final Risk	Assessment Rationale
	Ground water F mg/l < 0.5	Potential Risk	Water Fluoridated	Potential Risk		
Moldova	No	Low	No	Low	Low	Fluoride content is sufficient
	Yes	High	No	High	High	Fluoride content is insufficient
	Yes and No	High/low			High/ low	Water has low fluoride content but higher fluoride water is available in the vicinity
	Unknown				Unknown	If the water fluoride content is unknown the risk is not assessed.

Table 7.3 High-fluoride risk assessment scheme for Moldova

High-Fluoride Risk						
Location	**Phase 1**		**Phase 2**		**Final Risk**	**Assessment Rationale**
	Ground water F mg/l ≥ 1.5	**Potential Risk**	**Water used directly for drinking**	**Potential Risk**		
Moldova	No	Low	Yes	Low	Low	Fluoride content should not normally cause problems, but may do under certain circumstances in hot climates
	Yes	High	Yes	High	High	Water contains high fluoride which may cause health problems
	Yes and No	High/low			High/ low	Water has high fluoride content but lower fluoride water is available in the vicinity
	Unknown				Unknown	If the water fluoride content is unknown and there is no evidence of fluorosis incidence, the risk is not assessed
	Fluorosis Incidence					
	Yes	High	Yes	High	High	There is evidence of fluorosis in the region and the waters are still used for drinking therefore high risk

7.2.2 Population

In 1999 the population of Moldova was estimated at 4.3 million (population density of 129 per km^2), residing in 1681 settlements, including 65 cities and urban areas, which account for 47% of the population. The largest cities of Moldova are the capital Kishinev (Chishinau), Tiraspol, Beltsy, Bendery, Ribnitsa and Kahul. A map of the main population centres in Moldova was included in the Project Partner GIS (Country.apr) for background information (Figure 7.3).

7.2.3 Geology and Tectonic Structure of Moldova

The territory of Moldova occupies 33 000 km^2 located in southeast Europe forming the southwest margin of the Ukrainian shield. The geology of Moldova comprises two main structures, the south-eastern part of the Russian platform, which dictates the geological structure over most of the territory and the northern margin of the Dobruja Depression in the south. The main geological structure is outlined in Table 7.4.

The tectonic structure of Moldova has a major influence on the hydrogeochemistry of groundwaters including the content of fluoride in water and has been and continues to be the focus of research. The basic geotectonic elements of the Moldovan territory are the Russian platform (Epi-Baikal) and the Scythian Plate. The Moldovan Plate is a continuation of the Volino-Pedolsk Plate in the north and centre of the country and the Dobruja Depression is contiguous to the Scythian Plate in the south of Moldova. The most noticeable differences in the development of these plates occurred in the latter part of the Palaeozoic era during the formation of the Depression in the Jurassic period when this region underwent intensive subsidence. The Precambrian basement of the Russian platform comprises a complex sequence of metamorphic and volcanic formations. The top of this sequence is found at great depths southwest of Soroky City and is buried to 3000 m in the Tsyganeno-Chadyr-Lunga region and 5000 – 6000 m in the central part of the Dobruja Depression.

The Scythian plate comprises metamorphic Palaeozoic rocks, which are highly folded and cut by igneous intrusions. These lithologies represent the denuded Dobruja mountain structure, which is buried in the northeast dipping from zero metres in the Danube river valley to 500 – 600 m below surface in the lower sections of the River Prut basin. Friction between the two plates occurs in a zone marked by deep faulting between Kahul and Vulkanesti. The Moldovan Plate, like the Ukrainian plate as a whole, is characterized by a series of tectonic breaks and comprises a faulted block structure. During the latter parts of the Cretaceous period, the Black Sea basin developed resulting in folding and faulting of the strata, which continued into the late Cretaceous and Palaeogene periods. The older Moldovan plate and Dobruja Depression restrain the western limits of the basin.

Between the River Prut in the west and the centre of the country around Beltsy-Kalarash-Kahul, younger Neogene strata of the Carpathian basin are overlain on the Moldovan plate, Dobruja Depression and Scythian plate. The Neogene deposits reach a thickness of 600 m in the Prut region. Underlying ‘stratigraphic highs’ related to coral reefs in the Moldovan plate influence the form of Neogene Lower Sarmatian Torton sediments around Bolotino-Ungheny and Middle Sarmatian deposits around Kamenka-Kishinev-Komrat-Kahul, which outcrop in linear ridges. These ridges have been folded and faulted by regional Carpathian deflections. In Upper Pliocene and Quaternary times, Moldova experienced multi-directional movements of various intensity on different tectonic blocks. These have influenced the accumulation of sediments across the country resulting in different thickness and lithological characteristics.

Geological information has not been included in the risk assessment scheme for Moldova but is presented in this report for background information.

Table 7.4 Main geological units of Moldova

<table>
<tr><td colspan="6">Quaternary</td></tr>
<tr><td colspan="6">Continental deposits of loams, sandy soils and clays up to 5 m in depth cover most of the country. In the south sandy loams and large alluvial terraces with gravel and pebble beds associated with river floods. Alluvial deposits vary from metres to several tens of metres thick.</td></tr>
<tr><td>Neogene</td><td>Pliocene</td><td colspan="4">Middle and Upper Pliocene</td></tr>
<tr><td rowspan="9">Neogene deposits are found across the whole territory with the exception of the Dnister River valley south to Kamenka City and the Prut River valley south to Edinsti City. The sequence youngs from north to south comprising Miocene and Pliocene deposits.</td><td rowspan="3">Pliocene deposits were laid down transgressively on Miocene beds and are developed mainly in the south of the country where they are exposed in ravines and river valleys.</td><td colspan="4">Sands, clays and gravelly pebble beds are developed across the whole country</td></tr>
<tr><td>Lower Pliocene - Pontian Beds</td><td colspan="2">Pontian Beds Western Facies</td><td>Pontian Beds Eastern Facies</td></tr>
<tr><td>Pontian Deposits are found in the south of the country and are split into two distinct facies on the basis of conditions of formation.</td><td colspan="2">The base of the Western Facies is characterized by greenish-grey clays overlain by shallow-water deposits of clays and fine-grained quartz sands interbedded with limestones. The deposits reach a thickness of 120 m in the Prut region.</td><td>Sands, sandstones, siltstones, clays and limestones not more than 15 m thick characterize the Eastern Facies.</td></tr>
<tr><td>Miocene</td><td>Upper Miocene - Meotian Beds</td><td colspan="3">Meotian Beds</td></tr>
<tr><td rowspan="5"></td><td></td><td colspan="3">These deposits are transgressively developed over the Upper Sarmatian in the centre and south of the country. The beds comprise continental (delta, lake-lagoon) and brackish water deposits of clay interlayered with fine-grained sands and sandstones up to 200 m thick in the Prut region.</td></tr>
<tr><td>Upper Miocene - Sarmatian Beds</td><td colspan="3">Upper Sarmatian</td></tr>
<tr><td rowspan="3"></td><td colspan="3">These deposits are found in the central and southern regions of the country and comprise shallow marine, continental-alluvial, lagoonal and lake facies of clays, siltstones, and sandstones interlayered with oolitic limestones. Thickness increases from the northeast to 200 m in the southwest.</td></tr>
<tr><td>Middle Sarmatian</td><td>Middle Sarmatian Deep Water Facies (West)</td><td>Middle Sarmatian Shallow Water Facies (East)</td></tr>
<tr><td>These deposits occupy the whole territory except areas where Neogene Strata are entirely absent (Dnister and Prut River valleys). They are exposed in central and northern regions and south of Bendery City are overlain by younger formations. Thickness increases from east to west to 300 m in the Prut region. Two lithological facies are defined in the Middle Sarmatian on the basis of conditions of formation. In the west a deep-water facies is developed whereas in the east shallow-water lithologies predominate. Separating these is an early Mid-Sarmatian reef facies 4 – 12 km wide around Kamenk-Orgheev-Kishinev-Chimishlia-Kahul. In the Kishinev region, the reef facies outcrops at surface forming hilly relief.</td><td>In the deep-water facies in the west, the lower part of the sequence comprises 10 - 20 m thickness of marls interbedded with numerous layers of volcanic tuff. These beds are overlain by carbonates, silty-clays with fine-grained sandy lenses, sands, marls and limestones which range from 15 – 20 m thick in the north of the country to 35 – 100 m thick in the south. 170 m thick grey siltstones and fine-grained sands characterize the top of the deep-water lithofacies with silty-clay lenses in the north between the Dnister and Prut rivers and in the south with thin layers of clays with fine-grained sands. These give way to 80 m thickness of Conherian layers comprising clays siltstones and fine-grained sands. Shallower marine sands, sandstones with clay layers and limestones of 15 – 30 m thickness, mark the western boundary of this facies.</td><td>In the east, shallow-water deposits comprise 5 – 40 m thick limestones (mainly marly and foraminiferic) overlain by cherty-limestone (limestone, alternated with diatom-spicule clays and marls). In the south of the territory, silty clays interlayered with sands and limestones predominate whereas over the rest of the country limestones form the base of this sequence. 30 m thick beds of clays and sands with thin layers of oolitic limestone form the upper beds of the shallow-water facies.</td></tr>
</table>

			Lower Sarmatian These limestone, marl, clay and sand deposits outcrop in the Dnister and Prut River valleys and in erosional river cuts to the south of Orgheev City. In general thickness ranges from 20 to 50 m, increasing under Middle Sarmatian reef deposits to 80 - 100 m.
		Middle Miocene – Baden Beds These extensive deposits cover the whole country with the exception of the north-east, south-east and extreme south-west	**Upper Baden Beds** These beds are found mainly in the west of the country as far east as Oknitsa-Beltsy-Kamenka-Rybnitsa-Dubossary-Orgeev-Kotovsk-Chimishlia-Komrat and as far south as Kahul City. Upper Baden deposits comprising limestones, sands, sandstones and clays outcrop in north, on the east bank of the Prut River and dip to the south around Falesti City. These deposits are developed on a basement of Cretaceous strata to the north of Falesti and on the Podolsk Suite over the rest of the country
			Lower Baden Beds Overlying the Upper Cretaceous formations in the extreme northwest of the country, these beds comprise pebbly limestones, greenish-grey clays and quartz sandstone up to 15 m thick and quartz sandstones interbedded with gypsum up to 27 m thick. Over the rest of the territory, the Lower Baden Beds comprise the 'Podolsk Suite' of rocks ranging in thickness from 3 – 200 m. In the north of the country these overlie the eroded surface of Cretaceous flint rocks and in the centre and south of the country overlie Palaeogene deposits In the Dnister River region, the Podolsk Suite comprises clay-sands and clays interlayered with pebble beds. Over the rest of the country, clays and clay-sands interlayered with marls are developed.
		Lower Miocene Thin (< 20 m) Lower Miocene continental eluviul-diluviul deposits consisting of flints in an unstructured mixed clay-silica matrix are found in the north of the territory.	
Palaeogene Palaeogene deposits are distributed over much of the territory from Dubossary City in the north to Kahul City in the southwest and comprise quartz sandstones, siltstones, claystones, shales and marls. These range from a few 10 of metres thick in the north to over 200 m thick in the south.			

Cretaceous	**Upper Cretaceous**	**Shallow Water Facies (West)**	**Deep Water Facies (East)**
Cretaceous deposits underlie most of Moldova except the extreme southwest of the county.	Sequences of Upper Cretaceous deposits extend from depth in the Leovo-Chadyr-Lunga region in the south to outcrop at surface in the Dnister and Prut river valleys in the north around Floresti City. The sequence increases in thickness from the northwest to 100 m in the southeast. The Upper Cretaceous is split into two lithofacies based on differing conditions of formation.	The upper sections of both the shallow and deep-water facies comprise quartz-glauconite sands with flints overlain by flint rocks in the north and white chalky limestone and chalk in the south.	The upper sections of both the shallow and deep-water facies comprise quartz-glauconite sands with flints overlain by flint rocks in the north and white chalky limestone and chalk in the south.
		The shallow water facies contains terrigenous deposits. At the base of this facies, quartz-glauconite sands, sandstones, spongolites and cherty-chalks predominate to the north of Ungheny City whereas to the south, quartz-glauconite sands and sandstones are developed	The lower part of the deep-water sequence comprises carbonate rocks.
	Lower Cretaceous		
	Sandstones clays, siltstones and mixed sand and claystones are found in the south of the country only, where they overlie the eroded surface of Jurassic formations. The northern extent of these deposits is between Leovo and Komrat.		
Devonian, Carboniferous, Permian, Triassic, Jurassic			
These deposits are developed in the south-west of Moldova in the Ante-Dobruja Depression where they form very thick beds of over 1000 m. Permian deposits are over 1000 m and Jurassic deposits over 2000 m thick and comprise sequences of mudstones, siltstones, sandstones, limestone dolomites and clays.			
Silurian			
Silurian deposits underlie nearly the whole Moldovan territory. The lower part of this system is dominated by carbonate limestone and dolomite rocks whereas the upper section comprises argillaceous sediments and siltstones. The thickness of these deposits ranges from 150m in the north of the country to over 200 m in the southwest.			
Ordovician			
The only deposits to survive erosion are hard quartz sandstones in the northwest of Moldova.			
Cambrian			
Cambrian formations comprise gravelly sandstones, siltstones and argillaceous rocks.			
Precambrian Basement			
The basement rocks of the Russian platform comprise crystalline Achaean and Proterozoic gneisses, gabbros and plagiogranites which outcrop in the S.Kosoutsy region, in the Dnister River valley in the north of the country only. These beds dip to the south-west to a depth of 600 m in Beltsy City region, 100 m in Kishinev, 2000 m in Komrat reaching a depth of over 4000 m in the Ante-Dobruja Depression in the south of Moldova where the basement comprises Palaeozoic reef formations. The basement has few major fault structures and is overlain by a thick sequence of gently dipping Palaeozoic reef formations and Mesozoic and Cainozoic strata.			

7.2.4 Hydrogeology

Hydrogeologically, Moldova forms the western part of the Black Sea artesian basin, which is hydrodynamically constrained by the Rivers Dnister and Prut. The characteristic features of the basin are a lack of regional-scale impermeable layers between the water-bearing horizons therefore the basin structure is that of an interconnected hydrodynamic system with water moment of varying degrees through weakly permeable deposits.

The territory is divided into three hydrogeological regions, the Dnister and Prut river valleys and the area between them. The region between the two rivers is further sub-divided into the northern territory (north of Orgheev City) which is characterised by Baden-Sarmatian and Cretaceous-Silurian aquifer complexes; the central territory characterised by Baden-Sarmatian aquifers and the southern territory (south of Hynchesti) characterised by Baden-Sarmatian and Conherian sand aquifers.

Approximately 90% of the groundwaters used for drinking are extracted from three main aquifers, the Baden-Sarmatian (66% of drinking water use), the Cretaceous-Silurian (16.5% of drinking water use) and the Middle Sarmatian Conherian (16.5% of drinking water use). Other aquifers are also exploited locally such as river alluvium in the Dnister and Prut valleys, Palaeozoic Reefs in the Dnister region and Upper Sarmatian and Pontian aquifers in the south of the country but these water resources are small compared to the main aquifer horizons. Shallow aquifers in recent Quaternary deposits are found across the whole country and are also used for drinking water.

In general, the water-bearing horizons dip from north to south and changes in groundwater chemistry with horizon depth are noted accordingly. This general pattern is interrupted in anomalous zones. The chemical characteristics of waters in each of the hydrogeological regions are determined by differences in the temporal development and form of the main tectonic structures in Moldova. Characteristic groundwater chemistry features are most evident for the Moldovan plate, which forms part of the Russian plate and the eastern limb of the Carpathian fold. The main water-bearing horizons are discussed in detail below.

Recent Quaternary Deposits – These water-bearing horizons comprise the uppermost lithological strata in Moldova and depending on the permeability, waters are found in a variety of different Quaternary formations. In the area between the Rivers Prut and Dnister, shallow groundwater resources are found in localized sandy lenses in loamy-sand deposits. In the Prut and Dnister river valleys, shallow groundwaters are found in fine- and coarse-grained quartz sands, which are often clayey with layers of gravel and pebbles. These aquifers are rarely over a few metres thick. Often these waters drain to the surface water network and their distribution is sporadic. The thickness of water-bearing alluvial deposits in the Prut and Dnister river valleys ranges from 1 to 20-30 m. Infiltration rates in the Rivers Prut and Dnister vary from 0.1-0.4m/24h, in floodplains to 90m/24h in the Dnister river valley. Infiltration factors are generally constant in the region. Well-flow-rates are generally low, normally 0.01-0.25l/sec and rarely 0.5-0.7l/sec. In the floodplains of the Prut and Dnister rivers, flow-rates increase to 20-30l/sec. The depth of Quaternary water-bearing horizons depends on topographic relief. In the north and central region of Moldova, depths are generally 5 – 10 m on watersheds and hilltops. In the south of the country, water deposits can be at 20 m depth but are found at shallower depths (1 – 5 m) at the base of slopes, in river valleys and floodplains. The degree of mineralisation of these waters ranges from 0.5 to 5 g/l. Fresh waters with mineralisation of 1 g/l are found in the north. Over most of the country, waters with 1-2 g/l mineralisation are found on watersheds, valley slopes and floodplains. In the bases of ravines and in the alluvium of small rivers, especial in the south of country, mineralisation increases to over 5 g/l. The chemical composition of these waters varies with increasing mineralisation in the following order:

$$HCO_3 \rightarrow HCO_3{+}SO_4 \rightarrow SO_4{+}HCO_3 \rightarrow SO_4{+}Cl \rightarrow Cl{+}SO_4.$$

Predominant cation combinations include Mg-Na-Ca, Na-Mg-Ca and Mg-Na. The cation dominance of waters changes from north to south. Ca-Mg-Na waters are found only in the Dnister river valley in the north. The majority of waters are Mg-dominated.

Pontian Deposits - Groundwaters are found in layers of sand and limestone interbedded with clays in the south of the country. These layers vary in depth from 7m in the north to 190 m in the Prut region. In the southeast of the country, these waters are sporadically distributed at depths of 50 – 80 m. These waters have a piezometric head of 0 – 170 m (high at Kahul 125 m and Jurjulesti 145 m) in the south. The piezometric surface is complex and varies from 90 – 100 m in the east and northeast to 10 m in the Prut region and 7 m in the south of Moldova. These waters are moderately abundant, with flow rates of 1-3 l/sec (80-260 m^3/24h) at 10-15 m depths. Water temperatures in summer are generally 12 - 19.5 °C and waters are fresh and saline, saline intrusion is a problem in this horizon. Fresh waters with mineralisation levels of 0.5-1 g/l are developed in a narrow strip (2-3 km) along the Prut River valley and are found in the south of Moldova around Kahul City. Over the rest of the territory saline waters with mineralisation levels of 2-3 g/l predominate. These waters are generally SO_4-HCO_3-Cl-dominated. In the Prut region and in the south of Moldova, waters are HCO_3-SO_4-dominated, but in the narrow strip along the Prut valley, waters are HCO_3-dominated. In terms of cation composition, waters are generally Na-dominated. Strongly Na-dominated waters occur in the east but round Vulkanesti waters become Na-Ca-Mg- and Ca-Mg-Na dominated. Fluoride concentrations in these waters also fall to 1.6 mg/l and Fe contents to 3 mg/l.

Upper Sarmatian-Meotian Deposits – These deposits contain abundant clays and are heavily weathered. The aquifer depth ranges from 40–50 to over 200 m with a piezometric head of over 100 m. In the Prut region, the piezometric head exceeds 150 m. The top of this horizon is at 105 m depth in the north of the country, 8 – 10 m in the Prut region and 5 m in the south. Water resources are relatively poor with flow rates of 1-3 l/sec (80-250 m^3/24h) at a depth of 10 m. Infiltration rates vary from 0.1 to 1-2 m/24h . Water temperatures are generally 14 - 7 °C. Waters of the Upper Sarmatian-Meotian Deposits are both fresh and saline with mineralised contents of 0.4 to 3.0 g/l. Fresh waters with mineralisation levels of 0.5-1.5 g/l are found in a 20 km-wide strip along the Prut valley. Over the majority of the territory, the waters are saline with mineralisation levels of 1.5-3.0 g/l. Water anion composition is consistent across the country and is HCO_3-dominated. SO_4-dominance is secondary to bicarbonate and rarely SO_4-HCO_3-Cl -dominance is also reported. HCO_3-dominance is associated with low mineralised waters (0.5 – 1.5 g/l) whereas SO_4-HCO_3-Cl-dominated waters are generally mineralised (1.5-3.0 g/l). These waters are generally Na-dominated (contents of Na range between 64 to 99 meq) and Na-Ca- and Na-Mg- dominance only occurs in the southeast of the country. The waters meet the Moldovan drinking water quality standards (2874-82) for all constituents except fluoride (3 mg/l).

Middle Sarmatian-Conherian Deposits – These deposits are developed in the south of the country between Hynchesti and Kahul. Water resources are found in fine-grained sands 5 – 10 m thick interbedded with clays at depths of 50 – 100 and 200 – 50 m.. The Piezometric surface falls from 80 m in the north to 10 m in the southeast. Piezometric head is 20 – 30 m in the north and 330 m in the south at Kahul. Due to the extensive exploitation of this horizon, the piezometric surface is complex. Flow rates across the horizon are generally consistent, commonly 0.7-1.6 l/sec. (60-140 m^3/24 h). In Komrat City flows of 3.3 l/sec (285 m^3/24 h) are achieved. Flow rates can vary from 0.01 to 0.6 l/sec locally. The infiltration rate of sands ranges from 0.45 to 5 m/24 h, and is generally 1 to 2m/24 h . These waters are fresh and poorly mineralised with dissolved salt quantities of 0.6 to 5.7 g/l. Mineralisation levels greater than 1.5 g/l are only reported along the Prut river. The anion composition of these waters varies across the country. In the north and centre, most waters are HCO_3-SO_4- or HCO_3 –dominated. In the north-west SO_4-HCO_3 waters predominate whereas to the south and southwest increased burial-depth and mineralisation result in HCO_3-Cl, Cl-HCO_3 and Cl- dominated waters. The majority of waters are Na-dominated and only in the northwest of the country are Na-Mg-dominated waters found. These waters do not meet Moldovan water quality standards for colourlessness (70^o), mineralisation (to 5.7g/l), iron (3mg/l) and fluoride (generally concentrations are at the Moldovan water quality standard of 1.2 mg/l). The strong colour of these waters is due to the presence of organic acids.

Baden-Sarmatian Deposits - This water-bearing horizon is present across the whole territory of Moldova with the exception of the Dnister and Prut river valleys. Hydraulically, this unit is connected to the Upper Sarmatian in the north of the country and the Upper and Middle Sarmatian in the centre and south of the country. Water is held in limestones with interbedded marls and sand lenses of 30 – 50 m and 100 – 150 m thickness. The limestone beds outcrop in the north of the country but are buried to 400 – 500 m in the south. The Baden Sarmatian deposits have piezometric heads ranging from 2 – 40 m in the north to over 300 m in the south. The piezometric surface is complex due to connectivity with rivers and the intensive exploitation of this aquifer. The piezometric surface varies from 200 m in the north to 7 – 10 m in the southeast. Flow rates vary greatly across the horizon, highest flows (over 500-1000 m^2/24h) are found in limestones of the Dnister valley. Fissure-flow in this region reaches 50 l/sec and well-flow 5-8 l/sec. Flow rates are lowest (0.01 to 0.5 l/sec) in the west (Prut region). In general, flow rates vary from 0.1 to 2.0 l/sec. Water temperatures are commonly between 10 and 24.5°C. The hydrochemistry of these waters is influenced by the degree of connectivity to surface waters. For example, mineralisation levels vary between 0.5 – 68 g/l, however, most waters contain dissolved salt contents of up to 3 g/l. Saline waters are found in the Ungheny region and the southwest of Moldova. Waters with 0.5 – 1.0 g/l mineralisation extend from the north to Orgeev City in the east, and to Chadyr-Lunga in the south exploiting permeable reefy limestone formations. Waters with mineralisation contents of 1.0 – 1.5 g/l are found in all territories and with 2 – 3 g/l in the Prut region. Highest mineralisation values (> 3 g/l) are found between Ungheny and Kahul. The majority of waters are HCO_3-SO_4-dominated but SO_4-HCO_3-dominated waters occur around Beltsy, Floresti and Ungheny. In the southwest, water compositions range from HCO_3-Cl-dominance to Cl-SO_4-waters and finally Cl-dominated waters in the very south of Moldova. Most waters are Na-dominated with the exception of the northern territories where Na-Mg-Ca-waters are found. These waters fail the Moldovan drinking water quality guidelines for mineralisation (10 g/l), hardness (16 mg/ecv-l), fluoride (> 3 mg/l), H_2S and several other parameters. Fluoride contents in the Prut region and southeast of the country are generally > 1.2 mg/l. High fluoride concentrations correlate with mineralised waters containing 1.5 g/l dissolved salts north of Orgheev and with waters containing 1.0 g/l dissolved salts over the rest of the country.

Cretaceous-Silurian Deposits – These strata underlie the whole country but are only used for drinking-water supply north of Beltsy. Over the rest of the territory, these waters are of poor quality. Water is contained within sands, sandstones, limestones, and spongolites of 50-100 m thickness, which outcrop in the north in the Dnister and Prut river valleys. In the south these strata are buried to over 500 m. Piezometric head values for these waters vary from 10 – 20 m in the north to 80 – 85 m in the Beltsy region. The piezometric surface drops from 240 m in the north to 60 m in the Beltsy-Glodeany region. In general, exploitation does not affect the piezometric surface except in the very north of the country where abstraction is greatest. Flow rates are irregular, in river valleys lying in tectonic fault zones (Reut, Kubolta, Kainar) rates up to 200 –300 m^3/24 h can be achieved. Flow rates are reduced (0.01 m/sec) in the south and east due to the presence of carbonate rather than terrigenous rock types. Water mineralisation varies from 0.5 to 2.8g/l and increases from north to south. In the very north of the country, waters containing 1.0 g/l dissolved salts are HCO_3-Ca-Mg – dominated. Waters with 1 – 1.5g/l dissolved salts are generally HCO_3-SO_4-Na-dominated. In the Prut region, groundwaters with mineralisation levels of > 1.5 g/l are SO_4-HCO_3-Na- and HCO_3-SO_4-Na-dominated. Water fluoride contents below 1.2 mg/l occur to the north of Ryshkany-Floresti, however, over the rest of the country Cretaceous-Silurian waters contain high fluoride contents (1.5 – 17 mg/l) generally exceeding 10 mg/l in the Prut region.

Palaeozoic Reef Deposits – These deposits are only exploited for drinking water in the Dnister river floodplain as far south as Kamenka and comprise sandstones of 20 – 30 m thickness. Piezometric head values are seasonally variable and flow rates are generally 1.5-7.0m^3/24h although greater flows are possible around faults. These waters are generally Cl-HCO_3-Na-Ca-dominated and fail the Moldovan water quality standards for dry residues (2.0 g/) and fluoride (9 mg/l).

Although hydrogeological conditions do not form part of the final risk assessment, the hydrogeological map of Moldova (ASG) (Figure 7.1) and a map of hydrogeological units classified according to aquifer importance (Figure 7.2) were included in the Project Partner GIS (Country.apr) for background information.

7.2.5 Fluoride Lithogeochemistry

The majority of previous investigations into fluoride in groundwaters of Moldova conclude that high concentrations are a result of rock-water and soil-water interactions (Gusleakov, 1978; Kozlov and Samarin, 1969; Krainov and Petrov, 1976). The fluoride contents of several lithologies exceed average crustal abundances (300 µg/g; Tebbutt (1983)) and the distribution of fluoride in over 5000 samples of different rock types has been most extensively studied in the works of Zhovinsky (1976a+b) and Zhovinsky (1981a) as follows.

Mineralogical, petrographical and chemical investigations demonstrate that the principal fluoride-bearing minerals are fluorite, phosphates, micas and clays. Fluoride mineralisation is restricted to the Proterozoic sandstones of northern Moldova whereas phosphates, micas and clay minerals are more importance sources over the rest of the territory.

Fluoride contents in recent Quaternary deposits vary from 43 µg/g in clay-rich horizons to 35 µg/g (average) in sandy deposits. Fluoride contents in sandy deposits range from 5 – 740 µg/g depending on the mineral composition. Terrigenous minerals such as micas, phosphates, glauconite, fluorite, fluorapatite and others are the main fluoride sources .

Poorly consolidated gravel and pebble deposits of the Lower Sarmatian and Upper Proterozoic breccias generally contain 23 – 150 µg/g fluoride held in micas, hydrated-micas apatite and occasionally fluorite.

Average fluoride concentrations in sandstones and siltstones are 32 µg/g whereas in clay-rich rocks concentrations are 40 µg/g. Low fluoride contents (5 – 50 µg/g) are characteristic of the quartz-rich Upper Proterozoic Kosoutsy sandstones. Fluoride contents increase to 124 –200 µg/g in polymictic sandstones of the Upper Proterozoic and high values of 560 µg/g are associated with authigenic phosphate cements in Jurassic sandstones. Highest fluoride contents are found in Cretaceous glauconitic sands (740 µg/g) and sandstones (590 µg/g) enriched with phosphates.

Sandstones and sands of Neogene age contain 12 – 77 µg/g fluoride (average 45 µg/g) whereas siltstones contain 3 – 9 µg/g fluoride and only in fluorapatite-bearing Jurassic horizons are contents elevated to 121 – 163 µg/g.

Clay-rich strata in Moldova principally comprise kaolinite, montmorillonite, dicckite, gallousite, chlorite, and hydrated-micas. Argillites of Jurassic age and Cretaceous clays are dominated by hydrated-micas and contain 8-80 µg/g fluoride whereas clay-rich strata of Silurian age containing hydrated-micas and montmorillonite contain 48 µg/g fluoride. Clay-rich deposits of Neogene age generally comprise carbonates containing montmorillonite with fluoride contents of 5 – 1104 µg/g. Clays containing more than 70 – 75 % montmorillonite generally have the highest fluoride contents.

Carbonate rocks are common in Silurian, Cretaceous and Neogene systems and are less prevalent in the Jurassic and Proterozoic sequences. Carbonates comprise limestones, chalk, dolomites and marls and constitute the main water bearing horizons in Moldova. Average fluoride contents are 56 µg/g in limestones, 44 µg/g in chalk, 78 µg/g in dolomites and 103 µg/g in marl. Investigations have revealed that the fluoride content of carbonates is inversely related to the degree of calcification and is correlated with the percentage clay content. The amount of fluoride was found to increase with clay content in the following succession: kaolinite > chlorite > hydrated-mica > montmorillonite. Hydrothermally altered Neogene limestones with insignificant clay contents have low fluoride concentrations (6 – 147 µg/g, average 5 – 8 µg/g) and similar limestones of Jurassic age contain 9 – 30 µg/g fluoride. In Neogene and Cretaceous pelitic limestones, average fluoride contents are 180 µg/g, and in clayey–glauconite limestones 37 µg/g. In Neogene and Cretaceous carbonaceous limestones, fluoride is associated with organic residues ranging from 26 – 100 µg/g. Silurian dolomites generally contain 25 – 223 µg/g fluoride (average 88 µg/g).

Phosphatic rocks occur in Cretaceous and Upper Proterozoic deposits and commonly contain spherical concretions of apatite-calcium composition containing high quantities of fluoride (2400-2700 and 3000 – 3200 µg/g). Siliceous rocks include cherts and spongolites of the Cretaceous system, which generally contain 7 – 54 µg/g fluoride.

Studies of the fluoride contents in Moldovan strata revealed that concentrations are generally elevated in the basal units of each stratigraphic sub-division namely, the lower layers in each deposit contain more fluoride than overlying layers (Zhovinsky, 1976a+b).

The average fluoride compositions of Moldovan rock strata have not been included in the final risk assessment as contents vary markedly within individual rock units and water chemistry rather than lithogeochemistry is a more important indicator of risk. However, these data are included in this report for background information (Table 7.5).

Table 7.5 Fluoride contents in different rock types of Moldova.

Geological Age	Rock Type	Fluoride µg/g		
		Minimum	Maximum	Average
Unconsolidated Rocks				
Neogene	Sand	12	77	45
Neogene	Sandstone	11	80	37
Palaeogene	Sand	-	341	341
Cretaceous	Sand	-	740	740
	Sandstone	90	590	340
Jurassic	Sandstone	14	60	30
	Siltstone	20	90	40
Permo-Trias	Siltstone	-	-	48
Proterozoic	Sandstone	7	560	75
	Siltstone	17	123	60
Argillaceous Rocks				
Neogene	Clay	5	1104	80
Palaeogene	Clay	-	-	38
Cretaceous	Clay	-	-	70
Jurassic	Argillite	8	80	52
Permo-Trias	Argillite	40	120	82
Silurian	Clay	-	480	480
	Argillite	70	150	140
Proterozoic	Argillite	17	120	82
Carbonate Rocks				
Neogene	Limestone	7	179	48
Palaeogene	Limestone	20	80	49
Cretaceous	Limestone	30	370	74
	Chalk	12	90	39
Jurassic	Limestone	9	30	17
Silurian	Limestone	6	230	62
	Marl	30	135	95
Siliceous Rocks				
Cretaceous	Chert	20	70	54
	Spongolites	40	100	70
Granitoides				
Achaean + Proterozoic	Granites	30	65	46

7.2.6 Fluoride in Soils and Agricultural Impacts

Zhovinsky (1976a) reports that fluoride contents in Moldovan soils vary from 15 –198 µg/g depending on the clay (montmorillonite-illite) and organic matter content. Terrigenous minerals and groundwaters enriched with fluoride are the main sources in soils. Vedina and Kreidman (1999) found fluoride concentrations of 64 – 307 µg/g in loamy and 260 - 500 µg/g in clay burnozems (brown steppe soils) from central Moldova. Fluoride contents were related to textural composition and were highest in clay mineral and humic layers. Fluoride mobility in these soils was controlled by the clay mineral content, Ca, Al, Fe and Si content and the soil pH.

Toma et al. (1999) also report that the fluoride content of Moldovan soils varies according to soil texture. Sandy soils contain 64 – 269 μg/g fluoride whereas sodic soils contain 542 – 794 μg/g fluoride and floodplain soils are characterized by high fluoride contents (500 – 1120 μg/g). These higher values are in excess of averages for world soils (200 μg/g, Zhovinsky (1979b)). Concentrations of water-soluble fluoride in Moldovan soils were reported to range between 0.2 – 14.6 μg/g, less than 1% of total fluoride. Fluoride contents in the different soil types are listed in Table 7.6.

Table 7.6 Total and water-soluble fluoride contents in Moldovan soils (depth 0 – 50 cm) (From Toma et al. , 1999)

Soil Type	Soil Texture	Total Fluoride μg/g		Water Soluble Fluoride μg/g	
		Minimum	Maximum	Minimum	Maximum
Forest Soils					
Burnozem	Sandy	64	247	0.6	2.3
(steppe brown)	Heavy loam	260	509	0.8	2.9
Light Grey	Sandy	90	220	0.8	2.3
	Light/ medium loam	161	558	0.2	5.8
Grey	Sandy	68	269	0.2	3.5
	Light/ medium loam	185	859	0.2	4.1
Dark Grey	Heavy loam	87	648	0.3	4.1
Chernozems (Steppe Soils)					
Podzolic	Heavy loam/ light medium clay	123	761	0.7	14.6
Leached	Light/medium loam	127	750	0.8	3.8
Calcareous	Loam	250	652	1.0	3.9
Sodic	Heavy clay	542	794	0.3	6.7
River Valley	Light clay	500	1120	0.6	4.3
	Heavy loam	285	1050	0.4	4.3

In studies of fluoride contents in different soils of Moldova, (Zhovinsky, 1979b; Zhovinsky and Kurayeva, 1987) found that top soils (from 0.1 m depth) developed over the Scythian Plate contained on average 37 μg/g fluoride and concentrations varied depending on the underlying bedrock composition. Elevated fluoride contents (70 – 80 μg/g) in top soils were found near fault zones and in areas where deep groundwaters rise to the surface (for example, Floresti Region, Skynyany, Chymyshliya, Bessarabaka, Gaydar and Kalarash). With the exception of fault zones and regions influenced by deep groundwater, fluoride concentrations in profile soils (0.2 – 0.3 m depth) varied between 10 - 50 μg/g to the north of Kaushany, and 80 – 90 μg/g in the south of the country. Highest fluoride contents were reported in the Danube depression near Valyeny and Suvorovo. Clay and loamy soils with 120 μg/g fluoride were found in southwest Moldova around Branesti (Prut River) and in central Moldova around Godeany, Kalarash, Lipoveny and Malayesti. Lowest fluoride contents were reported in the north of the country around Ryshkany and Ataky, to the south of Komrata and in the Prut River valley.

Toma et al. (1999) note that groundwaters used for irrigation from Cretaceous and mixed waters from Cretaceous-Lower Sarmatian Torton aquifers have high fluoride contents whereas waters from the Baden Sarmatian deposits have lower fluoride contents (< 0.5 mg/l) and water used for irrigation in the south of Moldova contains significant quantities of fluoride. The effects of high-fluoride irrigation waters on plant uptake were examined over a 5-year period and were found to increase the concentration of fluoride in wheat and in soils (Tale 7.7).

Table 7.7 Fluoride contents in wheat grown on irrigated and non-irrigated light calcareous chernozem soils (From Toma et al. ,1999)

Plant	Total Fluoride µg/g dry weight	
	No Irrigation	After Irrigation
Whole plant	12.2	28.2
Stems	4.7	13.8
Leaves	10.7	10.0

The effects of phosphate fertilizer application on plant uptake were also examined by Vedina and Kreidman (1999) and Toma et al. (1999). Moldova consumes approximately 46 000 tonnes/year phosphate fertilizer containing 600 – 2600 µg/g fluoride. Results showed that the fluoride content in wheat grown without fertilizer application was 6.13 µg/g (dry weight) whereas wheat grown in areas under superphosphate fertilizer for 23 years contained 10.38 µg/g. The concentrations of fluoride in the wheat leaves were greater than in the roots or grain. Long-term fertilizer application leads to retarded growth, chlorosis and reduction in the wheat yield as a result of fluoride toxicity. Dental fluorosis has also been reported in animals consuming high-fluoride water and grass grown on soils after long-term treatment with phosphatic fertilizer (40 – 50% of fluoride ingested in fodder is absorbed).

Melian et al. (1999) found increased fluoride concentrations in shallow groundwaters of Moldova as a result of agricultural pollution. The average fluoride pollution load per hectare per year assuming a 15% infiltration rate was estimated at 0.12 in 1987 and 0.0015 in 1995 in the Carpeineni Region and 0.16 in 1987 and 0.0015 in 1995 in the Balatina Region. Fluoride in shallow groundwaters ranged from 0.1 – 3.3 (average 0.6) mg/l in Carpeineni and 0.1 – 1.9 (average 0.9) mg/l in Balatina. High fluoride contents exceeding water quality standards were noted in both shallow and deeper groundwater resources in these regions.

Despite the lack of industrial fluoride sources in Moldova, anthropogenic activity does impact on the environment via the application of fluoride-bearing phosphate fertilisers in agriculture. However, agricultural fluoride contamination and uptake from soil sources were difficult to quantify in the final risk assessment therefore these data are included in this report to highlight the fact that groundwater is not the only source of fluoride in the Moldovan environment only.

7.2.7 Water Quality and Supply

A public supply network provides water for 59 of the main cities in Moldova and remaining settlements are fed by local systems. Water for the public supply is derived from groundwater resources and from the Rivers Dnister (border with Ukraine) in the east and Prut (border with Romania) in the west. The rivers are the two main water resources in the country and international agreements between Romania and Moldova cover the abstraction of water from the River Prut. Historically, the River Dnister was the drinking and irrigation water source in the Kishinev area. The Dnister water was mixed with groundwater for this purpose. Although there were records of an aquifer at Kishinev, this water was not used for drinking. Following economic progress and industrialisation, the River Dnister became polluted and the underground reserve around Kishinev was exploited.

It is estimated that the Moldovan groundwater reserves total 12.5 m^3. Before 1990, 1.5 million m^3 were abstracted but the level of abstraction differed across the country. In the central region, 700 000 m^3 were abstracted but in the River Prut region in the west of the country abstraction rates were much lower as there are only small towns in this area and the demand for water is less.

Prior to 1990, 6000 artesian wells to deeper fracture-flow-dominated water-bearing horizons were sunk in Moldova. Production from many of these wells was controlled by electric pumps. In recent years there have been serious crises in the electricity supply in Moldova and many of these pumps are currently non-operational. As a result, the population have dug over 150 000 shallow wells abstracting water from the first water-bearing horizon in recent sediments as an alternative source.

The economy of Moldova is predominantly based on agricultural and manufacturing industries and both sectors have suffered a dramatic down-turn since 1990 – 1991. As a result, anthropogenic contamination of the environment has abated in recent years. Data from groundwater quality monitoring demonstrate insignificant changes to the quality of deeper groundwaters whereas shallow unconsolidated aquifers, being more responsive to environmental impacts, show noticeable improvements. Despite these factors, there is currently a lack of provision of good quality drinking water over many areas of Moldova. In addition to problems caused by natural factors, both anthropogenic contamination and the failure of the public water supply system mean that waters are not treated correctly prior to distribution to the consumer and approximately 50% of the population use water which does not meet the Moldovan sanitary standards.

The principle problems in deeper groundwaters relate to high mineralisation, hardness, nitrate and sulphate contents, fluoride and heavy metals. 70% of the water being utilised in the country is not of good quality in terms of TDS, nitrate (500-600 mg/l in some cases) and sulphate. Much of the poor water quality is a result of agricultural pollution, especially in the south of the country, however, high-sulphate waters are related to water-rock interactions. In addition to these parameters, shallow groundwaters across the whole country are of unsatisfactory bacteriological status.

The consumption of poor quality water is a contributing factor along with other natural and social controls to high morbidity rates in the population, particularly among children and teenagers. The water quality standard for fluoride in Moldovan drinking waters is 1.2 mg/l and high-fluoride groundwaters exceeding this value are found over a significant proportion of the territory. With no alternative water sources available, the population have no choice but to consume this water. As a result, fluorosis is endemic in certain regions of the country. Previous attempts to develop effective and economic fluoride removal technologies have failed and the problem of defluoridation remains a prime concern in Moldova.

Water quality varies between regions, near the Dnister River, the alluvial aquifer is close to the quality standards, in the centre of Moldova, the groundwater is of poor quality and in the Prut River region, the alluvial aquifer fails the standards for nitrate, iron, hardness and fluoride. The fluoride problem in Moldova is most serious in this region.

In contrast to many of the groundwaters, fluoride concentrations in river waters are generally low. The River Prut water contains 0.2 – 0.5 mg/l and the River Dnister water 0.2 – 0.3 mg/l fluoride. Some fluoride contents in different Moldovan waters are presented in Table 7.8.

Table 7.8 Fluoride concentrations in Moldovan waters (Zhovinsky, 1979b)

Type of Water	Maximum Fluoride mg/l	Percentage of Sources Within Each Fluoride Concentration Range				
		< 0.5 mg/l	0.5 – 1.0 mg/l	1.0 – 1.5 mg/l	1.5 – 2.0 mg/l	> 2.0 mg/l
Surface	0.9	28	72	-	-	-
Well	7.0	42	33	15	4	6
Artesian Well	12.0	40	29	8	6	17

Hydrogeochemical investigations of fluoride in Moldovan groundwaters have been carried out by Kozlov and Samarin (1969), Krainov and Petrov (1976) and Zhovinsky (1979a). Fluoride hydrogeochemistry in the major water-bearing horizons used for centralized public water supply was studied more fully than waters used for local abstraction as data for local supplied were sparse. The studies focused on the Baden-Sarmatian and the Cretaceous-Silurian in the north and the Mid-Sarmatian – Conherian and Pliocene-Pontian horizons in the south as follows.

Cretaceous-Silurian Aquifer - The distribution of fluoride in waters from this aquifer corresponds to changing hydrodynamic conditions between the recharge zone in the north-northeast of the country to the deeply buried zone in the Prut region in the west. Chemical changes in this horizon are more regular than in the Baden-Sarmat horizon. In the north of the Dnister region in the recharge zone, HCO_3-Ca-Mg-waters correspond to the 1.0 g/l mineralisation isoline. Over the south of the country is a large hydrochemical zone with mineralisation values of 1.0 – 1.5 g/l and marked increases in SO_4 (25-35% mg/ecv) and Na (27% mg/ecv) contents. In the very south of the country waters contain 1.5 – 2.0 g/l dissolved salts of SO_4-HCO_3-Na and HCO_3-SO_4-Na composition and have a pH of 8.2. In the western Prut region around Ungheny, groundwaters of the Cretaceous-Silurian sequence are characterised by high mineralisation values (1.8 – 2.0 g/l), HCO_3-dominance and high alkalinity (pH 9.1). Redox conditions in the Cretaceous-Silurian aquifer vary from oxic (+ 100–200 mV) in the Dnister region to reducing (- 200– 270 mV) in the Ungheny region.

Groundwaters in the northern hydrochemical zone in the Dnister region and part of the middle zone where mineralisation levels are less than 1.52 g/l contain less than 1.2 mg/l fluoride. These waters extend southwards as far as Edinsti-Floresti and Rezina City. Over the rest of the country, the waters contain high fluoride contents increasing southwards from 1.2 mg/l to 10 mg/l in the southwest Prut region. Around Ungheny, fluoride concentrations reach 17 mg/l. These waters are used for drinking north of Ungheny and Kishinev, but in the south of the country the waters are not suitable for drinking due to high mineralisation and fluoride contents.

Water chemistry information for this horizon used for local water supplies is limited and is only available where geological investigations have been carried out. On the evidence of this type of data, fluoride concentrations in the Kishinev region are estimated at 8 – 9 mg/l.

Baden-Sarmatian Aquifer - The distribution of fluoride in groundwaters from this aquifer is dependant upon the hydrogeochemical zone and water type. Over the Moldovan platform in the north and centre of the country, low mineralised (2 g/l), HCO_3-Ca-Mg and HCO_3-SO_4-Cl-dominated oxic (Eh = 110 – 240 mV) waters have fluoride contents below 1.2 – 1.5 mg/l. Fluoride contents vary from 0.5 to 1.0 to 1.2 mg/l depending upon the degree of mineralisation of the water, the Eh and the depth of the water bearing horizons. As these strata dip westwards in the limb of the Carpathian fold, the groundwater chemistry alters to Na-Ca-dominated waters with high Na+K/Ca ratios and reducing conditions (Eh – 200 mV). Physio-chemical calculations of fluorite saturation (Krainov and Petrov, 1976) indicate that these waters are undersaturated with respect to fluorite. As a consequence, fluoride concentrations in Baden-Sarmatian groundwaters range from 1.2 mg/l over the Moldovan Platform in the north of the country to 5 – 10 mg/l in the Prut region to the west. Between these two regions, variations in groundwater geochemistry occur locally. Highly altered, high-fluoride waters are found around Kalarash-Beltsy and Kaushany- Bendery whereas low-fluoride SO_4-dominated waters are found around Floresti and low-fluoride, HCO_3-Ca-dominated waters occur in the Kishinev-Chimishlia region.

High-fluoride waters (> 1.5 mg/l) in the Kalarash-Beltsy region are thought to result from upward migration of deeper mineralised waters from the Cretaceous-Silurian aquifer via tectonically active fault zones in the area. In the Kaushany-Bendery region, waters contained in the Lower Sarmat Baden bed limestones are overlain by thick sequences of impermeable Mid-Sarmatian clays (150 – 200 m) and due to a lack of mixing with near-surface oxygenated waters these waters have high H_2S contents, are reducing (Eh < 0 mV) and undersaturated with respect to fluorite. In contrast, HCO_3-Ca-waters in the Kishinev-Chimishlia region are retained in limestone reefs extending from Kamenka to Chimishlia to Kahul with good infiltration of oxygenated near-surface waters.

Mid-Sarmatian-Conherian Aquifer – The fluoride content of waters from this water-bearing horizon, which is the principal source of centralised public supply in the south of Moldova, are generally lower than the Moldovan Drinking Water Standard of 1.2 mg/l. However, fluoride contents range up to 3.5 mg/l in the very south-east of Moldova close to the border with Ukraine. These waters are HCO_3-Na- and Cl-Na-dominated with poor colourlessness indices (> 35^o) due to organic acids and high Fe contents.

Recent Quaternary Aquifers - In general shallow groundwaters in Moldova have low concentrations of fluoride (< 1.5 mg/l) but concentrations of 8.5 – 10 mg/l have been reported in some localities. Over approximately two thirds of the country these waters contain < 0.5 mg/l fluoride but in the Dnister Hills, Codry and Baimaklia regions and the southern section of the Prut river valley, high-fluoride waters are associated with small river valleys where waters are highly mineralised (2 – 7 g/l). Areas with high-fluoride water in the north of the country include Orgheev, tributary valleys of the northern River Reut and the region between the Prut and Solonets rivers.

In summary, the distribution of fluoride in groundwaters of the different aquifer horizons is dependant on different hydrochemical regimes and tectonic influences. The presence of fault zones in the Moldovan plate results in anomalous fluoride concentrations due to the upward migration of deeper mineralised waters. High-fluoride waters are generally Na+K-dominated with high Na+K/Ca ratios and low fluorite saturation indices allowing fluoride to remain in solution. The hydrodynamic features of the aquifers also determine the fluoride concentration. Deeply buried altered waters contain higher fluoride concentrations than shallow waters and waters capped by impermeable layers with poor infiltration of near-surface oxic waters also contain high fluoride concentrations. In general terms, the fluoride content of Moldovan groundwaters increases with depth in the order Mid-Sarmatian (N1S2) < Baden Sarmatian (N1S1) < Cretaceous-Silurian (K2-S1). Beltsy City provides an example of these relationships whereby Baden-Sarmatian derived waters contain 0.4-0.9 mg/l, Upper Cretaceous limestone waters 1.5 - 2.6mg/l and Silurian limestone waters 3.8 – 6.5 mg/l fluoride.

The prolonged and intensive exploitation of groundwaters in Moldova has lead to falling groundwater levels in some water-bearing horizons and negative recharge balances altering the physio-chemical regime resulting in increased mineralisation and higher fluoride contents. For example in the public supply system of Kalarash, during 10 years of water exploitation from the Baden-Sarmatian horizon, fluoride contents increased from 1.5 – 5.25 mg/l. Similarly, at Falesti, fluoride concentrations in Cretaceous-Silurian aquifer waters rose from 5-5.5 mg/l to 7-8.4 mg/l over a 6-year period. At Chadyr-Lunga, an increase in fluoride content from 1.5-2.0 mg/l to 4.0-4.6 mg/l occurred over 5 years exploitation of waters from the Mid-Sarmatian aquifer.

Theoretical physio-chemical modelling of the speciation of fluoride in Moldovan waters carried out by Krainov and Petrov (1976) and Zhovinsky (1981a) indicated that the dominant forms of fluoride were free F^- ions, F-organic complexes, and MgF^-. CaF^- complexes were only important in Ca-rich waters where they account for up to 10% of the total fluoride content. Other complexes with Al, Fe and B account for insignificant proportions of the total fluoride content. In groundwaters of neural pH (6.5 – 7.5) 70 – 80% of fluoride is in free ionic form whereas in alkaline waters, 95 – 98% of fluoride is in free ionic form.

For the purposes of the present study, the 327 records in the groundwater chemistry database (ASG) collected at an average sample density of 1 per 5 km^2 over most of the Moldovan territory provide an overview of fluoride contents in the main drinking-water horizons (Recent Sediments (unconfined), Mid-Sarmatian, Baden-Sarmatian and Cretaceous-Silurian). During the initial phase of the risk assessment these data were categorized by fluoride concentration according to the WHO guideline values of < 0.5 mg/l caries risk and ≥ 1.5 mg/l fluorosis risk (Figure 7.4). Groundwaters from all four aquifers contain fluoride contents above the MAC of 1.5 mg/l but Mid-Sarmatian waters generally contain lower fluoride concentrations than water from the other horizons (Table 7.9).

High-fluoride (> 1.5 mg/l) groundwaters are distributed throughout Moldova but as indicated above, in general, waters in the west of the country contain more fluoride than in the east (Figure 7.4) and high-fluoride waters are widespread in the Beltsy-Falesti and Chadyr-Lunga regions.

Table 7.9 Fluoride contents in Moldovan groundwaters (ASG data)

Water Source	Minimum F mg/l	Maximum F mg/l	Average F mg/l	Number
Unconfined – Quaternary, Pliocene Pontic - Levantin Sediments	1.4	7.6	3.1	45
Mid Sarmatian – Conherian	0.20	3.5	1.0	35
Baden-Sarmat (Lower Sarmatian)	0.17	15.7	2.4	161
Silurian-Cretaceous	0.10	16.2	2.9	86

7.2.8 Fluorosis Prevalence and Exposure

Endemic dental fluorosis related to intakes of high-fluoride waters have been reported in Moldova previously (for the last 60 – 70 years) particularly in the River Prut region and in the south of the country. Several local medical investigations into the disease had been carried, however, until recently, no national surveys were completed. In December 1998 the government introduced a national child dental health programme, which will run until 2007 and as part of this programme, all cases of dental fluorosis will be registered and prophylactic treatments must be implemented. No cases of skeletal fluorosis have been reported in the country but it is likely that skeletal fluorosis does occur and is diagnosed incorrectly as other conditions.

As part of the present study, the Preventative Medicine Service of Moldova collated dental fluorosis information from previous investigations. These studies were carried out in selected settlements in Moldova and although they provide an indication of fluorosis prevalence, they do not give a comprehensive overview of the situation in Moldova. The data are based on investigations carried out during the 1960's and between 1997-1998 (Table 7.10). The locations of these fluorosis incidences were included in the final GIS scheme of the present project as these are important indicators of high-fluoride risk (Figure 7.5).

Table 7.10 Previously documented fluorosis prevalence information for Moldova (Preventative Medicine Service Data)

Settlement	Year of Study	Population	Number of Fluorosis Patients	Fluorosis Prevalence %
Naslavcha Oknits	1965	-	-	30-50
Edintsy	1965	-	-	72
Glodeany	1965	-	-	60
Beltsy	1965	-	-	66
Falesti	1965	-	-	62
Falesti	1998	13000	6500	50
Kalarash	1965	-	-	50
Ungheny	1965	-	-	10-30
Komrat	1965	-	-	10-30
Congas, Komrat	1965	-	-	10-30
Chadyr-Lunga	1965	-	-	80
Chadyr-Lunga	1998	25000	12500	50
Chadyr-Lunga Region				
Kazakliea	1998	8000	6400	80
Baurchi	1998	8000	4000	50
Gaydar	1998	3100	1000	32
Beshgioz	1998	3750	1500	40
Djoltay	1998	2670	1200	45
Hyncheshty	1965	-	-	30
Bulboka, Nov. Aneny	1965	-	-	40
Pyrlitsa, Ungheny	1965	-	-	74
Ishkalevo, Falesti	1965	-	-	50
Skuleany, Ungheny	1965	-	-	10
Kiseliea, Komrat	1965	-	-	40
Fegedeu, Falesti	1965	-	-	60

More comprehensive data collected from the Regional Preventative Medicine Centres over 14 years indicate that approximately 160 000 children in Moldova suffer dental fluorosis and prevalence rates in settlements with high-fluoride waters reach 80% (Bahnarel and Shelaru, 1999).

Although a connection between high-fluoride waters and fluorosis prevalence has been established, the relationship is complex. For example, dental fluorosis occurs in regions with only 0.6 – 1.0 mg/l fluoride in water (Kiseliea and Bulboka) and settlements with the same water fluoride contents can have very different prevalence rates (for example Skuleany 10% prevalence and Pyrlitsa 70% prevalence).

Further investigations revealed that the prevalence of fluorosis depends upon the age of the water-bearing horizon exploited for drinking, fluoride speciation and the relationship between Ca and fluoride in the water. On this basis, the risks of fluorosis from waters with the same fluoride content in the different aquifers of Moldova were estimated follows: Cretaceous-Silurian (K-S) > Baden-Sarmatian (N1S1) > Mid-Sarmatian (N1S2) > Pontian (N2P). In general terms, the deeper, more altered waters are most toxic because Mg- and Ca-dominance decrease whereas alkalinity, and Na+K-dominance increase leading to a greater proportion of the most bioavailable form of fluoride in water, the free F^- ion.

As outlined in previous sections of this report, the uptake of fluoride in humans is inhibited by the presence of Ca during ingestion and the severity of fluorosis is enhanced when dietary Ca intakes are low. The relationships between fluoride and Ca content in water and fluorosis prevalence in Moldova were examined in more detail in previous studies. Comparison of the ratio:

$$\frac{\text{F mg/l}}{\text{Ca mg/l}} \times 100 \text{ (expressed as \%)}$$

in waters from different regions revealed that in general, the prevalence of fluorosis was greater in areas with high F/Ca ratios and that the F/Ca ratio in water is was important control on disease development when fluoride levels were close to the MAC. In general terms, when the F/Ca ratio was below 25% no dental fluorosis occurred in the local population, when the F/Ca ratio was between 25 and 80%, fluorosis prevalence rates were below 50% and when F/Ca ratios were greater than 100%, fluorosis prevalence rates reached 60 – 70%.

However, not all areas affected by fluorosis followed this pattern, in the Chadyr-Lunga region of southern Moldova, the population is supplied with HCO_3-SO_4- or SO_4-HCO_3– dominated and Na- Mg- dominated water containing 1.2 – 7.6 mg/l fluoride with F/Ca ratios of only 1 to 4%. Despite the low F/Ca ratios, fluorosis prevalence in some settlements in this region was 30 – 50% and reached 80% in Kazakliea. In this case, the total fluoride content and other factors such as the high mineralisation (1.5 – 6 g/l) of these waters were thought to affect the prevalence of fluorosis.

Although some general relationships between fluoride speciation and Ca content in waters and fluorosis prevalence have been established by the present and by previous studies, these factors have not been included in the final risk assessment scheme as they require further investigation to determine the true nature of the health impacts and relationships to disease.

7.2.9 Risk Avoidance Maps

The groundwater chemistry data for the four main drinking water horizons of Moldova were combined in the GIS so that problem waters from any possible source would be highlighted. The risk avoidance maps are based on a grid size of 5 km^2 commensurate with the sample density of the combined groundwater data sets. In each grid square, the water fluoride content and fluorosis incidence data were combined with water supply information to produce the final risk maps (Annex 7 and 8). However, it should be noted that over large areas of the country, the density of water chemistry and fluoride incidence information was insufficient to assess fluoride risk.

The maps show that on the basis of water fluoride contents, the risks of dental caries are low over most of the south of the country and are highest in the north-east. Although the water supply is not fluoridated in Moldova, most waters contain enough fluoride (> 0.5 mg/l) to prevent dental caries. Isolated high-risk areas occur in the Kishinev region and in the north-west of the country. Although the area around Beltsy is at risk of dental caries, higher-fluoride waters are available in the vicinity (Annex 7).

High-fluoride risks areas are widespread across Moldova, the locations of fluorosis incidence noted from previous studies are all categorised as high risk as it is assumed that people in these settlements continue to drink high-fluoride water. Two main problem areas are identified, the Chadyr-Lunga region in the south of the country and the Falesti-Beltsy region in the north-west, however, high risk areas are also found in the west and centre of the country between the River Prut and Kishinev (Annex 8). The Falesti region was the focus of more detailed geochemistry and health investigations carried out during the present study as follows.

7.3 FALESTI REGION DETAILED STUDY AREA

7.3.1 Study Methods

During the present investigation, the links between high-fluoride contents in drinking water and human fluorosis were examined in more detail in the towns of Kalarash, Cornesti and Falesti in Moldova (Annex 8), which lie in a known fluorosis hotspot region. The aim of the study was to examine dental and skeletal status based on the structural-functional state of bone tissue, the maxillodental system, physical development, nutritional data, anthropometric characteristics, and the distribution and degree of somatic diseases among the residents of regions with elevated fluoride contents in drinking water.

In total, medical examinations of 103 adolescents aged from 10 to 15 years (48 boys and 55 girls) were carried out (Table 7.11). 34 women (residents of Falesti) were also examined to establish time-series differences in the dental and bone status of "mother-daughter" pairs in the population (Table 7.12).

Table 7.11 Number of adolescents examined in the three study towns

Locality	N (total)	Boys		Girls	
		N	Average Age	N	Average Age
Kalarash	20	13	13.15±1.07	8	12.5±0.57
Falesti	58	30	12.57±1.36	33	12.0±0.26
Cornesti	21	5	13.0±1.0	14	12.8±0.42

N = number

Table 7.12 Characteristics of women examined in Falesti

Index	N	Age	Height	Body Mass
I Group	14	36.7±0.97	160.75±1.56	60.5±2.2
II Group	20	37.8±0.8	163.05±1.56	72.06±3.68

I Group = women with diagnosed osteoporosis according to ultrasound densitometry data
II Group = women with normal indices of bone mineral density N = number

General clinical, anamnestic, objective examination and orthopaedic examination methods were used during the study as follows:

- Anamnestic data - included the presence of concomitant pathology and the character of menstrual cycle formation in girls, etc. While interrogating adolescents' mothers, special attention was given to the character of pregnancy, labour and diseases present in the first year of life and feeding characteristics etc.

- Anthropometric examination - (V.V. Bunak method modified by P.F. Shaparenko) included the determination of body mass, linear (longitudinal and transversal), enveloping and angular dimensions. In addition, the so-called "anthropometric spots" were used - bone segments that can be felt through the skin and in particular cases even typical peculiarities of the muscles. The following criteria were measured:

    - Body mass
    - Body length
    - Hand length
    - Forearm length
    - Shoulder length
    - Shoulder blade length
    - Pelvis length
    - Thigh length
    - Shin length
    - Foot length (anthropometric)
    - General foot length
    - General arm length
    - Leg length
    - Head height
    - Neck length
    - Morphological face height
    - Head length
    - Head width
    - Humeral diameter
    - Pelvic diameter
    - Shoulder width
    - Forearm width
    - Shin diameter
    - Head girth
    - Neck girth
    - Chest girth
    - Hand girth
    - Buttocks girth
    - Shoulder girth
    - Girth of forearm's wide part
    - Girth of forearm's narrow part
    - Thigh girth
    - Girth of shin's wide part
    - Girth of shin's narrow part
    - Foot girth
    - Stomach girth
    - Thickness of back skin-fold
    - Thickness of shoulder skin-fold
    - Thickness of shin skin-fold
    - Thickness of stomach skin-fold
    - Thickness of thigh skin-fold

- Nutritional Status - was estimated by means of a questionnaire-weighing method and included the determination of proteins, fats, carbohydrates, amino acids, macroand microelements and vitamins in the food ration. The following indices of daily nutritional status were determined:

- Calorie content
- Vegetable proteins
- Animal proteins
- Irreplaceable amino acids:
- Tryptophan
- Leucine
- Isoleucine
- Valine
- Threonine
- Lysine
- Methionine
- Phenylalanine
- Replaceable amino acids:
- Histidine
- Arginine
- Cystine
- Tyrosine
- Alanine
- Serine
- Asparagine
- Proline
- Glycine
- Glutamic acid
- Carbohydrates
- Starch
- Cellulose
- Lactose
- Hemicellulose
- Mono-/disaccharides
- Vegetable fats
- Animal fats
- Linoleic acid
- Linolenic acid
- Cholesterol
- Triglycerides
- Phospholipids
- UFA Sum
- MUFA Sum
- PUFA Sum
- MSFA/PSFA Sum
- Mineral elements: K, Na, Ca, Mg, P, S, Cl, Fe, I, Mn, Cu, F, Zn, Se, Ca/Mg, Ca/P
- Vitamins and vitamin-like substances: A, B1, B6, B12, C, D, E, H, PP
- β- carotin, choline

- The structural-functional state of bone - was examined by an ultrasound densitometry method, using the "Achilles+" densitometer (Lunar Corp., Medison, WI) on heel bones consisting of trabecular (spongy) bone tissue. The following measurements were carried out:

  - The speed of the ultrasound signal through the bone (SOS, m/s), which is controlled by the bone density and flexibility.

  - The broadband ultrasound attenuation (BUA, dB/MHz), which reflects bone density, the number of bone trabeculae and the dimensions and spatial orientation of the bone trabeculae.

  - Bone stiffness index (STF, %), which is calculated according to the formula (STF = 0.5 × ((nBUA + n SOS), where nBUA = (BUA – 50) : 0.75 and nSOS = (SOS - 1380) : 1.8). This index shows the state of spongy bone tissue compared to normal standards for 20-year-old adluts.

The advantages of this method are the high precision, use of non-ionising radiation, portability and speed of examination. Unlike photon and X-ray densitometry this method gives qualitative estimations of spongy bone tissue and its architecture (orientation and thickness of the trabeculae). Numerous researches have shown the benefits of this method in forecasting the risk of osteoporotic vertebrae and femoral fractures and the considerable possibilities of its application to estimate the effectiveness of osteoprotective methods in prophylaxis and treatment of osteoporosis.

- Examination of the maxillodental system – the dental condition was determined according to CFM (sum of caries, filled and missing permanent teeth), cfm (the same with respect to temporary teeth) indices. Clinical forms of dental fluorosis were determined by means of Patrikyeyev (1958) classifications (Table 2.10) distinguishing between lines, mottling, chalk-like-spots, erosive and destructive forms of injury. The degree of dental fluorosis was estimated according to the four Gabovych and Ovrutsky (1969) categories of severity (Table 2.9).

Parametric (Student's t-test, one way analysis of variance (ANOVA)) and non-parametric (Vandervarden, Wilcoxon-Mann-Whitney and Spearman Rank correlation) statistical tests were carried out on the data using the "MS Excel-97 Statistics and Statgraphics 5.0" programmes.

7.3.2 Water Supply and Nutritional Status

According to data from the Republic of Moldova Water and Sanitation Service, the population of Falesti uses approximately equal quantities of tap water and water from shaft wells. In the past, 98% of water usage in the town was provided by the central public water supply system, the source of which is underground waters (21 artesian wells). Of these, 13 boreholes of 160-180 m depth are currently active. In recent years, power-cuts and electricity shortages in Moldova have meant a reduction in the availability of water from these wells and today, the town also exploits approximately 70 shallow wells, of 10 to 25 m depth.

A similar situation exists in Kalarash where, in the past, the population were supplied by water from a combination of deep wells (central public supply) and shallow wells. There is currently a lack of electricity to run the central public supply system and residents are entirely dependant on water from shallow wells.

Analysis of water samples collected from drinking water taps in Kalarash, Falesti and Cornesti indicate that the highest fluoride contents are found in Falesti (5.31 mg/l) (Table 7.13). According to international studies, this concentration of fluoride in water is high enough to contribute to the development of dental fluorosis without any marked changes in the structural-functional state of bone tissue. Conversely, fluoride concentrations in samples from well waters in Falesti do not exceed 2.43 mg/l.

The results also demonstrate that the fluoride concentrations in well waters within each town are highly variable. In Kalarash, well-water fluoride contents range from 0.19 to 3.65 mg/l and in Falesti from 0.39 to 2.43 mg/l. The incidence of fluorosis in these towns is not broadly distributed throughout the population but forms clusters around high-fluoride water sources.

In Cornesti the fluoride content in drinking water from shallow wells does not exceed 0.88 mg/l (Table 7.13). These concentrations are within the "beneficial fluoride window" (0.5 to

1.5 mg/l) and do not exert a negative influence on functional state of dental and bone systems.

The concentration of Ca in Cornesti well waters is generally higher than in Kalarash and Falesti waters. The low Ca concentrations in Kalarash and Falesti are likely to produce a negative influence on the calcium-phosphorus metabolism in the population of these towns and enhance the aggressive effects of fluoride.

No significant difference in water hardness between the three towns was identified.

Table 7.13 Analysis of water samples from different water supply sources

Town	Element	Tap Water		Well Water							
		1	2	3	4	5	6	7	8	9	10
Kalarash	Ca mg/l	1.60	4.85	34.00	3.25	1.60	105.30	24.30	187.90	192.80	131.20
	F mg/l	3.38	3.25	0.19	2.39	3.65	0.51	1.90	0.19	0.39	0.23
	pH	9.10	9.17	8.62	7.90	8.95	8.10	8.71	8.05	7.97	7.93
Falesti	Ca mg/l	6.50	-	22.70	35.65	45.30	14.6	27.50	53.45	34.00	24.30
	F mg/l	5.31	-	2.43	1.16	0.39	1.90	1.61	0.97	1.31	1.01
	pH	8.87	-	8.10	8.20	7.97	8.20	8.25	6.70	8.73	9.00
Cornesti	Ca mg/l	-	-	243.00	166.85	150.65	128.00	118.25	66.40	113.3	37.25
	F mg/l	-	-	0.26	0.41	0.37	0.32	0.49	0.33	0.25	0.88
	pH	-	-	7.80	7.12	7.45	8.02	7.68	8.47	8.15	8.33

A questionnaire-weighing method was used to determine nutritional status. For three days the daily ration was estimated in terms of the main macro- and micronutrients. To determine the adequacy of nutritional intake, results were compared to the “Norms of Physiological Needs of Ukrainian Population in Main Food Nutrients”. These were approved by Health Protection Ministry of Ukraine, Decree No272, 18.11.1999 (Table 7.14)

Table 7.14 Recommended daily nutritional intakes for Ukrainian adolescents (Health Protection Ministry, 1999).

Nutrient	Age: 11-13 years		Age: 14-15 years	
	Boys	Girls	Boys	Girls
Energy, kcal	2800	2550	3200	2650
Proteins, g	91	83	104	86
Animal in particular	46	42	52	43
Fats, g	82	75	94	77
Carbohydrates, g	425	386	485	403
Ca, mg	1200	1200	1200	1200
P, mg	1200	1200	1200	1200
Mg, mg	280	270	400	300
Fe, mg	12	15	12	15
Se, µg	40	45	50	50
Cu, mg	2.0	1.5	2.5	2.0
Zn, mg	15	12	15	13
I, µg	150	150	200	200
Vitamin A, µg	1000	800	1000	1000
Vitamin D, µg	2.5	2.5	2.5	2.5
Vitamin E, mg	13	10	15	13
Vitamin K, µg	45	45	65	55
Vitamin B1, mg	1.3	1.1	1.5	1.2
Vitamin B2, mg	1.5	1.3	1.8	1.5
Vitamin B6, mg	1.7	1.4	2.0	1.5
Vitamin B12, mg	2.0	2.0	2.0	2.0
Folate, µg	160	150	200	180
PP, mg	17	15	20	17
C, mg	75	70	80	75

Analysis of the nutrition data for adolescents during the present study revealed an imbalance in the consumption of the main nutrients, especially prominent in Kalarash (Tables 7.15, 7.16, 7.17 and 7.18). The dietary calorie content was considerably lower than recommended values. The calorie intake and content of vegetable proteins in the diet of Kalarash girls differed significantly from results in other towns ($p<0.05$) (Table 7.15). The content of vegetable and animal proteins and the main amino acids was considerably lower than recommended values in all the three towns.

Insufficient protein consumption, especially irreplaceable amino acids, may negatively affect the general physical development of adolescents in the study towns and the structural-functional state of bone tissue in particular, because proteins serve as the main plastic material for organic bone components.

This study also demonstrates that the dietary carbohydrate intake for boys and girls residing in all three towns is considerably lower than recommended values. Significant differences in carbohydrate intake between the three towns were noted (Tables 7.17 and 7.18).

Table 7.15 Estimated daily dietary protein intake of girls from the three study towns

Dietary Component	Cornesti	Kalarash	Falesti	P
Calorie content	1918.46±147.98	1518.08±98.103	1 953.12±740.45	1-2 <0.05
Vegetable proteins	32.53±3.34	23.20±2.34	32.42±15.8	1-2 <0.05
Animal proteins	25.65±2.28	23.24±2.87	18.13±6.7	>0.05
Irreplaceable amino acids:	18673.29±1524.4	15620.47±1227.98	15 130.61±5679.38	>0.05
Tryptophan	682.73±56.22	603.17±49.6	564.15±185.85	>0.05
Leucine	4109.41±354.64	3379.78±256.61	3 352.19±1288.66	>0.05
Isoleucine	2456.81±205.75	1989.37±144.16	2 066.84±787.21	>0.05
Valine	2819.4±225.496	2353.66±174.92	2 379.28±966.77	>0.05
Threonine	2052.86±161.13	1739.6±144.10	1 611.73±582.32	>0.05
Lysine	2910.62±241.48	2501.51±242.93	2 114.61±787.54	>0.05
Methionine	1085.75±85.59	956.53±82.204	881.77±278.43	>0.05
Phenylalanine	2555.45±228.54	2093.02±157.86	2 158.64±789.59	>0.05
Replaceable amino acids:	32101.5±2664.23	26626.7±2031.55	27110.0±10358.81	>0.05
Histidine	1362.86±114.94	1113.52±83.79984	1 145.57±500.405	>0.05
Arginine	2783.17±231.31	2597.72±289.5042	2 724.16±1225.34	>0.05
Cystine	810.67±61.94	674.74±57.541	785.77±232.325	>0.05
Tyrosine	1905.61±183.8	1621.60±132.3125	1 487.61±563.895	>0.05
Alanine	2151.10±162.48	1845.74±180.8834	1 755.36±595.43	>0.05
Serine	2560.51±209.55	2189.33±177.0559	2 096.54±663.42	>0.05
Asparagine	3642.80±301.9183	3176.64±261.5688	2 855.80±933.055	>0.05
Proline	3732.33±430.7868	2829.91±208.8167	3 001.51±1218.59	>0.05
Glycine	1982.72±164.8876	1815.29±202.1563	1 797.75±813.785	>0.05
Glutamic acid	11015.8±1026.43	8653.03±577.63	9 339.34±3521.21	>0.05

For units see Table 7.14

Table 7.16 Estimated daily dietary protein intake of boys from the three study towns

Dietary Component	Cornesti	Kalarash	Falesti	P
Calorie content	1998.66±264.39	2206.32±196.11	2144.67±300.10	>0.05
Vegetable proteins	36.79±5.96	38.81±5.33	33.91±8.93	>0.05
Animal proteins	16.71±5.08	25.13±5.67	28.87±7.44	>0.05
Irreplaceable amino acids:	16476.56±3166.18	21194.05±2397.73	20048.64±2316.22	>0.05
Tryptophan	608.41±105.69	794.28±86.73	750.57±95.29	>0.05
Leucine	3650.0±716.90	4714.1±549.84	4483.81±535.12	>0.05
Isoleucine	2207.11±397.37	2809.97±331.59	2651.42±344.64	>0.05
Valine	2466.61±443.20	3174.17±356.06	3028.51±342.43	>0.05
Threonine	1807.34±342.19	2325.46±261.614	2149.85±233.92	>0.05
Lysine	2522.80±589.15	3210.86±395.52	2963.69±331.9928	>0.05
Methionine	866.60±159.95	1209.72±150.71	1192.52±151.1453	>0.05
Phenylalanine	2336.87±433.59	2955.65±339.81	2821.70±386.0751	>0.05
Replaceable amino acids:	29521.2±5057.85	36484.7±4012.61	34666.1±4904.621	>0.05
Histidine	1178.68±241.68	1432.41±165.52	1478.69±171.94	>0.05
Arginine	2478.75±429.01	3371.19±427.72	2979.40±426.96	>0.05
Cystine	752.14±99.29	925.57±117.32	942.30±183.11	>0.05
Tyrosine	1637.68±305.59	2188.41±274.61	2155.32±248.21	>0.05
Alanine	1987.80±355.36	2432.68±249.85	2345.28±277.6105	>0.05
Serine	2329.92±447.34	2952.05±322.84	2838.21±354.38	>0.05
Asparagine	3458.99±742.68	4222.24±439.88	3769.38±427.37	>0.05
Proline	3499.55±645.82	4150.05±528.43	4111.08±604.15	>0.05
Glycine	1875.04±304.89	2313.99±243.66	2046.64±292.78	>0.05
Glutamic acid	10207.9±1589.70	12408.5±1516.43	11871.8±2164.597	>0.05

For units see Table 7.14

Table 7.17 Estimated daily dietary carbohydrate and fat intake of girls in the three study towns

Dietary Component	Cornesti	Kalarash	Falesti	P
Carbohydrates	267.01±24.29	188.54±13.05	285.11±93.51	1-2 <0.05
Starch	155.87±17.78	100.89±10.31	160.16±73.82	1-2 <0.05
Cellulose	9.04±1.71	5.15±0.795	3.13±1.49	1-3 <0.05
Lactose	4.49±1.34	7.35±1.71	4.41±1.74	>0.05
Hemicellulose	9.50±1.29	5.69±0.43	8.17±3.34	>0.05
Pectine	3.31±0.56	1.97±0.21	1.08±0.48	>0.05
Sitosterol	0.05±0.01	0.05±0.007	0.03±0.005	>0.05
Mono-/disaccharides	101.99±12.59	80.55±8.06	115.82±17.73	>0.05
Organic acids	7.66±1.39	4.68±0.698	1.89±1.035	1-3 <0.05
Vegetable fats	28.76±5.19	30.55±7.48	36.42±34.12	>0.05
Animal fats	46.08±7.74	39.49±4.058	42.41±0.02	>0.05
Linoleic acid	16.66±2.51	17.95±3.94	17.07±12.24	>0.05
Linolenic acid	0.75±0.469	1.55±0.79	1.92±1.76	>0.05
Cholesterol	0.26±0.03	0.28±0.05	0.29±0.09	1-2 <0.05 1-3 <0.05
Triglycerides	63.28±5.17	63.63±6.66	53.45±15.89	>0.05
Phospholipids	2.52±0.31	2.43±0.35	2.83±0.16	>0.05
UFA Sum	22.37±2.37	21.18±2.16	13.95±0.03	1-3 <0.01
MUFA Sum	23.46±2.29	22.46±1.83	20.72±1.21	>0.05
PUFA Sum	17.95±2.82	19.96±4.64	19.39±14.22	>0.05
MSFA/PSFA Sum	1.50±0.22	1.63±0.36	1.56±1.14	>0.05

For units see Table 7.14

Table 7.18 Estimated daily dietary carbohydrate and fat intake of boys in the three study towns

Dietary Component	Cornesti	Kalarash	Falesti	P
Carbohydrates	304.60±43.35	312.08±32.77	326.83±65.19	>0.05
Starch	172.24±21.06	191.22±28.87	175.96±48.97	>0.05
Cellulose	7.33±1.11	6.76±1.119	6.72±1.73	>0.05
Lactose	1.77±0.75	9.27±4.297	7.80±2.99	1-3±0.05
Hemicellulose	10.87±1.74	10.49±2.23	10.17±2.95	>0.05
Pectine	3.93±0.92	3.37±0.64	1.98±0.61	>0.05
Sitosterol	0.07±0.02	0.08±0.009	0.06±0.022	>0.05
Mono-/disaccharides	121.52±33.49	107.52±11.36	137.43±41.71	>0.05
Organic acids	5.86±1.58	6.35±1.57	6.21±0.99	>0.05
Vegetable fats	32.79±6.17	42.90±9.359	25.45±6.83	>0.05
Animal fats	40.02±10.64	46.22±7.09	51.82±11.04	>0.05
Linoleic acid	16.03±3.79	22.47±4.70	12.52±3.79	>0.05
Linolenic acid	0.25±0.0668	1.84±0.898211	0.62±0.417152	>0.05
Cholesterol	0.13±0.038	0.32±0.057	0.38±0.115	>0.05
Triglycerides	50.80±7.33	74.22±10.49	64.97±10.45	>0.05
Phospholipids	2.39±0.36	3.18±0.43	3.33±0.63	>0.05
UFA Sum	16.61±2.28	24.89±3.81	28.20±4.78	>0.05
MUFA Sum	18.49±3.03	25.36±3.12	23.88±3.62	>0.05
PUFA Sum	16.59±3.79	24.74±5.46	13.78±3.99	>0.05
MSFA/PSFA Sum	1.90±0.69	1.59±0.38	2.69±0.74	>0.05

For units see Table 7.14

The content of pectine, hemicellulose, cellulose and organic acids in Falesti girls diet was significantly lower than in the other towns. Similarly the content of pectine in Kalarash girls diet was significantly lower than Cornesti values. The lactose content in Cornesti boys diet was lower than in the other towns.

The dietary fat content showed little variation between the different towns and is within the bounds of recommended norms (Tables 7.17 and 7.18). However, further analysis of the fat component showed that the content of linolenic acid in Cornesti boys and girls diet is significantly lower than values in the other towns. The content of cholesterol in Cornesti girls diet is noticeably lower than Kalarash and Falesti values. An imbalance in fat consumption can be detrimental to the human skeletal structure as fats are known to play an active part in Ca absorption in the body and to be sources of some liposoluble vitamins, notably Vitamin D necessary for bone remodelling.

Dietary estimates of mineral elements that greatly influence the metabolism of bone tissue showed insufficient Ca and P consumption. In an area of increased fluoride and adequate Mg consumption the low Ca and P intake can contribute to the formation of aggressive fluoride compounds (Tables 7.19 and 7.20). It should also be noted that not only deficiencies of Ca and P but changes in the dietary ratios of Ca/Mg and Ca/P can enhance the uptake of fluoride in the human digestive system.

Table 7.19 Estimated daily dietary mineral element intake of girls in the three study towns

Element	Cornesti	Kalarash	Falesti	P
Ca mg	520.18±48.89	490.2029±48.97	352.88±157.16	>0.05
P	960.41±71.36	834.96±72.16	900.45±438.53	>0.05
Mg	319.00±28.36	276.79±30.43	259.06±110.56	>0.05
Ca / Mg	1.73±0.18	1.98±0.23	1.35±0.031	2-3 <0.05
Ca / P	0.55±0.039	0.61±0.054	0.40±0.02	1-3 <0.05 2-3 <0.05
F µg	538.51±60.6	874.1±222.86	2528.9±176.0	>0.05
Na	1451.59±160.35	1099.44±143.24	1 599.87±794.78	>0.05
K	2845.81±320.89	2127.02±146.99	1 924.53±972.27	>0.05
S	442.85±30.84	369.95±35.67	398.56±112.04	>0.05
Cl	1852.57±236.79	1264.62±122.78	2 170.27±933.63	1-2 <0.05
Fe	13323.1±1321.54	9633.50±689.46	12338.5±5180.72	1-2 <0.05
I	43.80±9.24	36.53±3.81	28.47±4.42	>0.05
Mn	3263.91±293.34	2584.86±299.906	3 165.79±1344.86	>0.05
Cu	1776.51±348.47	1182.26±118.63	1 815.23±1281.07	>0.05
Zn	6993.39±691.3523	6210.21±511.4786	6 672.01±3516.24	>0.05
Se	118.06±10.71	80.18±7.55	102.71±43.04	1-2 <0.05

For units see Table 7.14

Table 7.20 Estimated daily dietary mineral element intake of boys in the three study towns

Element	Cornesti	Kalarash	Falesti	P
Ca mg	419.04±77.51	620.38±127.06	547.02±152.49	>0.05
P	920.97±157.52	1143.13±150.11	1083.53±157.46	>0.05
Mg	314.70±38.59	372.79±48.70	323.74±65.005	>0.05
Ca / Mg	1.28±0.12	1.74±0.26	2.06±0.64	>0.05
Ca / P	0.46±0.04	0.53±0.057	0.53±0.09	>0.05
F µg	463.82±41.05	1304.26±201.3	2362.45±686.7	>0.05
Na	1446.04±180.43	1581.86±310.10	1622.70±350.22	>0.05
K	3179.64±379.64	3247.44±454.53	2474.61±398.16	>0.05
S	452.53±62.05	536.05±57.17	444.77±67.35	>0.05
Cl	2067.40±271.94	2310.52±516.46	2333.68±673.05	>0.05
Fe	13751.0±1908.34	14329.8±1428.58	14622.3±2722.02	>0.05
I	32.13±3.91	50.99±8.23	38.25±6.24	>0.05
Mn	3379.68±461.08	4014.71±596.61	3956.17±1568.17	>0.05
Cu	1427.72±201.96	1601.92±173.68	2090.65±553.2789	>0.05
Zn	6670.56±1011.77	7792.18±772.41	7236.01±1019.17	>0.05
Se	131.23±15.16	133.34±15.40	121.96±24.05	>0.05

For units see Table 7.14

The content of vitamins and vitamin-like substances in the daily diet are given in Tables 7.21 and 7.22.

Table 7.21 Estimated daily dietary vitamin and vitamin-like substance intake of girls in the three study towns

Dietary Component	Cornesti	Kalarash	Falesti	P
Vitamin A	0.48±0.31	0.21±0.037	1.41±1.19	>0.05
Vitamin B1	1.11±0.08	0.82±0.06	1.07±0.55	1-2 <0.05
Vitamin B6	1.61±0.16	1.44±0.11	1.46±0.8	>0.05
Vitamin B12	5.20±3.78	1.40±0.20	15.58±15.02	>0.05
Vitamin C	174.64±36.53	144.94±32.43	49.26±24.74	1-2 <0.05 2-3 <0.05
Vitamin D	0.58±0.13	0.74±0.21	0.73±0.72	>0.05
Vitamin E	18.37±1.97	16.88±2.91	18.37±7.47	>0.05
Biotin (Vitamin H)	25.45±7.17	18.26±2.52	39.50±22.22	>0.05
PP	1.08±0.56	0.87±0.21	1.28±2.13	>0.05
β-carotin	2.43±0.35	2.44±0.23	1.72±0.62	>0.05
Choline	295.19±47	244.03±28.7	412.14±145.4	>0.05
Folacine	172.41±23.91	115.88±9.387	177.34±109.8	1-2 <0.05

For units see Table 7.14

Table 7.22 Estimated daily dietary vitamin and vitamin-like substance intake of boys in the three study towns

Dietary Component	Cornesti	Kalarash	Falesti	P
Vitamin A	0.12±0.02	0.26±0.05	1.14±0.55	1-2 <0.05
Vitamin B1	1.22±0.14	1.26±0.14	1.10±0.19	>0.05
Vitamin B6	1.85±0.26	1.99±0.23	1.54±0.25	>0.05
Vitamin B12	0.57±0.24	1.69±0.49	12.57±6.79	>0.05
Vitamin C	141.02±18.67	142.14±29.82	107.78±34.44	>0.05
Vitamin D	0.28±0.06	0.92±0.19	1.17±0.47	1-2 <0.01 1-3 <0.05
Vitamin E	17.10±2.89	23.18±3.52	16.94±3.55	>0.05
Biotin (Vitamin H)	10.96±2.38	24.00±4.20	41.27±10.92	1-2 <0.01 1-3 <0.05
PP	0.82±0.39	1.14±0.51	1.48±0.84	1-3 <0.05
β-carotin	3.08±0.51	2.13±0.22	1.70±0.39	>0.05
Choline	210.11±33.80	324.27±59.67	446.68±71.37	1-3 <0.05
Folacine	156.71±27.21	172.58±21.14	193.87±30.23	>0.05

For units see Table 7.14

7.3.3 Dental Status in Kalarash, Cornesti and Falesti

The current study is an advance on previous investigations into high-fluoride waters and fluorosis in Moldova as it is the first time that the structural-functional state of bone tissue and the maxillodental system have been studied in relation to the fluoride concentration of the water and the nutritional status of the population.

The results of the maxillodental examinations indicate that water containing between 1.5 to 5 mg/l provokes dental fluorosis development without any significant change in the structural-functional state of bone tissue confirming results of previous investigations elsewhere into fluorosis. The higher fluoride content in Falesti water (up to 5.31 mg/l) compared with Kalarash (up to 3.65 mg/l) resulted in a greater prevalence of dental fluorosis and higher degree of dental injury (Figures 7.6 and 7.7) in adolescents from Falesti.

During the examinations, lines, mottling, chalk-like-spots and erosive forms of dental fluorosis (Patrikyeyev (1958) classification) were observed. The destructive form of fluorosis was not present in adolescents from the study towns. In terms of the severity of dental fluorosis, I and II degrees were most prevalent. However, a considerable percentage of the adolescents examined had III degree fluorosis (Gabovych and Ovrutsky (1969) classification).

No dental fluorosis was observed in Cornesti adolescents. However, the extraordinarily low prevalence and intensity of caries in adolescents of this town is probably due to the prophylactic action of the fluoride content in the water, which is within the WHO recommended limits (0.5 – 1.5 mg/l). The population of this town no longer consume high-fluoride waters therefore the prevalence of dental fluorosis has fallen.

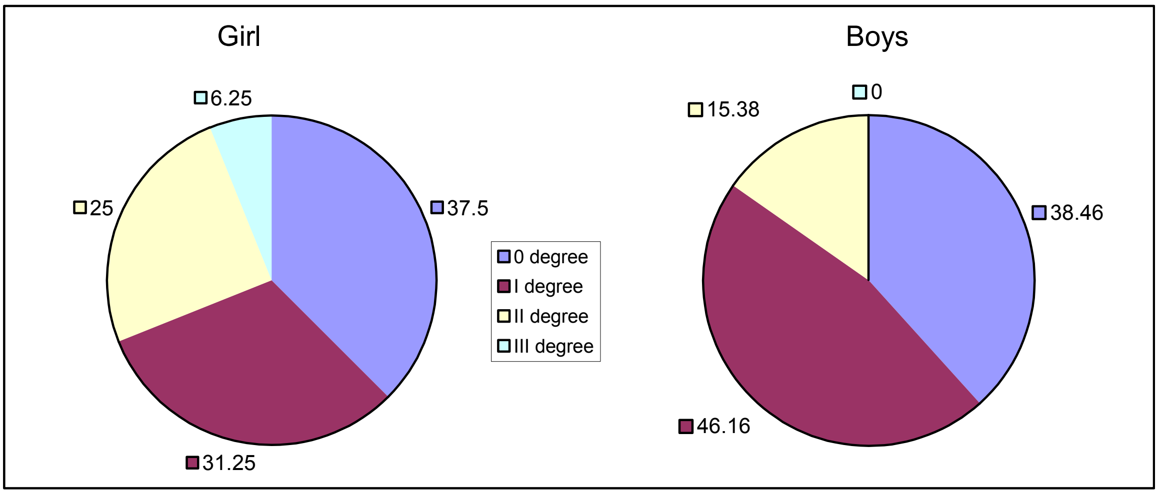


Figure 7.6 Percentage of Kalarash adolescents with I, II and III degree fluorosis (Gabovych and Ovrutsky (1969) classification)

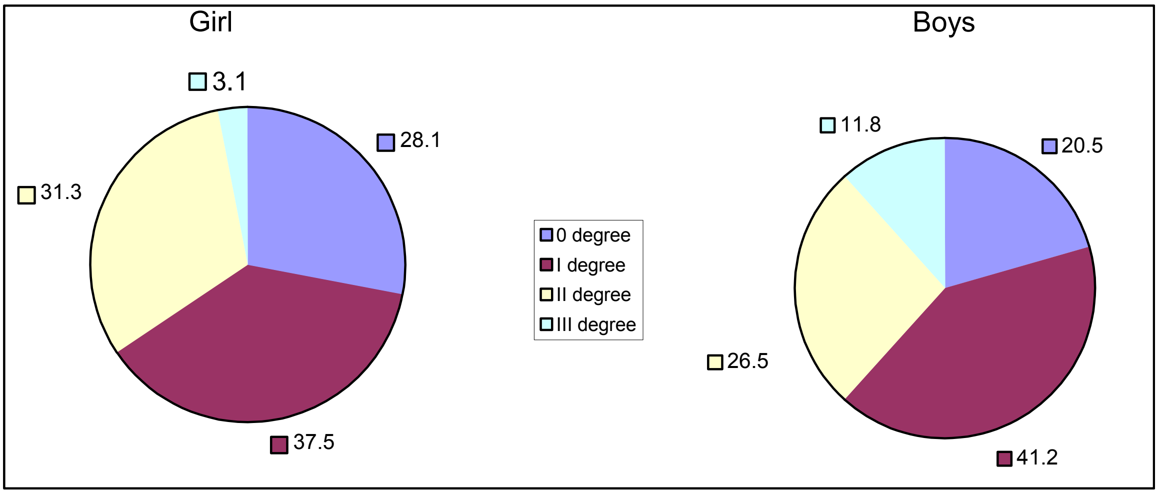


Figure 7.7 Percentage of Falesti adolescents with I, II and III degree fluorosis (Gabovych and Ovrutsky (1969) classification).

The fluoride concentration in well waters from within each of these towns is highly variable therefore the incidence of dental fluorosis is not distributed throughout the towns but forms clusters associated with high-fluoride water sources. In adolescents using water from shallow wells containing less than 1.5 mg/l fluoride, only 0-I degrees of fluorosis were observed whereas more severe forms of dental fluorosis were reported in adolescents using tap water derived from deeper artesian wells.

Tables 7.23, 7.24, 7.25 and 7.26 and Plates 7.1 and 7.2 show the severity of dental fluorosis in incisor teeth (which erupt and change at different stages during the first year of life) and pre- and secondary molars which begin to form during the second year of a child's life. These results show that in adolescents residing in towns with high fluoride concentrations in the water (Kalarash and Falesti), there is little variation in the severity of dental injuries to different types of teeth. In contrast, the different types of teeth show varying degrees of injury in Cornesti adolescents.

Results for 'mother-daughter pairs' show that mothers who received water from the deeper electric pumped wells in the past have well developed dental fluorosis whereas their daughters who now only have access to the shallow well water show lesser effects of the disease. However, it is desirable that the population return to drinking the deeper water as soon as possible due to the very poor bacterial quality of the shallow water wells. There is therefore a need to remove fluoride from the deeper water.

Table 7.23 Degree of dental fluorosis in different teeth types among Kalarash girls (n=16)

Dental Fluorosis Degree	Lower incisors		Upper incisors		Premolars and second molars	
	n	%	n	%	n	%
0	10	62.5	6	37.5	7	43.75
I	4	25	5	31.25	4	25
II	1	6.25	4	25	5	31.25
III	1	6.25	1	6.25	0	0

Table 7.24 Degree of dental fluorosis in different teeth types among Kalarash boys (n=13)

Dental Fluorosis Degree	Lower incisors		Upper incisors		Premolars and second molars	
	n	%	n	%	n	%
0	11	84.62	9	69.2	5	38.46
I	1	7.69	2	15.4	6	46.16
II	1	7.69	2	15.4	2	15.38
III	0	0	0	0	0	0

Table 7.25 Degree of dental fluorosis in different teeth types among Falesti girls (n=32)

Dental Fluorosis Degree	Lower incisors		Upper incisors		Premolars and second molars	
	n	%	n	%	n	%
0	12	40.6	13	40.6	13	40.6
0	10	31.3	8	25	8	25
I	8	25	9	28.1	10	31.3
II	1	3.1	2	6.3	1	3.1
III	1	3.1	2	6.3	1	3.1

Table 7.26 Degree of dental fluorosis in different teeth types among Falesti boys (n=34)

Dental Fluorosis Degree	Lower incisors		Upper incisors		Premolars and second molars	
	n	%	n	%	n	%
0	9	26.5	9	26.5	12	35.3
I	13	38.2	11	32.3	13	38.2
II	8	23.5	5	26.5	6	17.7
III	4	11.8	5	14.7	3	8.8

Plate 7.1 Dental fluorosis (II degree (Gabovych and Ovrutsky (1969) classification)

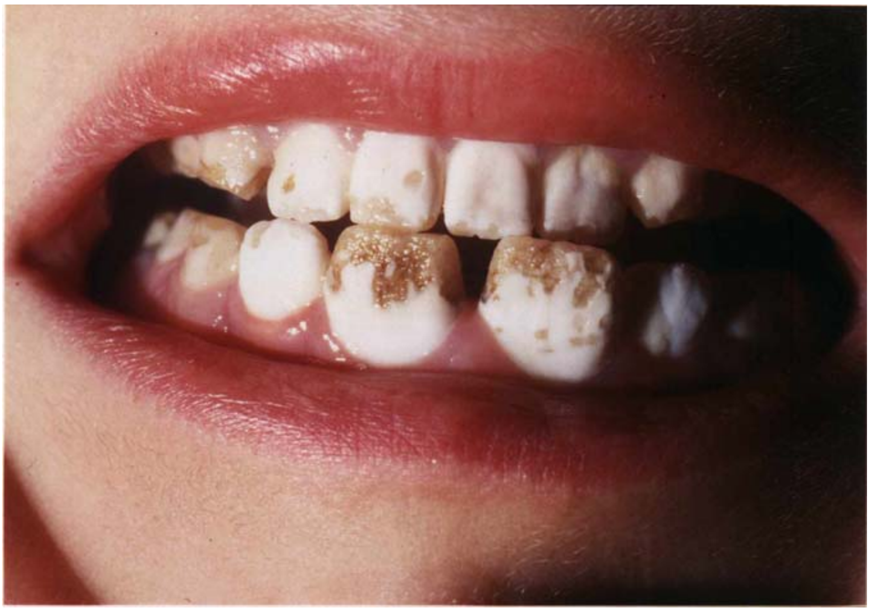


Plate 7.2 Dental fluorosis (III degree Gabovych and Ovrutsky (1969) classification)

7.3.4 Skeletal Status in Kalarash, Cornesti and Falesti

This is the first study to investigate the structural-functional state of bone tissue using ultrasound in areas of high fluoride in drinking water in Moldova. Results demonstrate that the speed of sound (SOS) index (which indicates bone density and elasticity), the broadband ultrasound attenuation (BUA) index (which reflects bone density and the amount, dimensions and spatial orientation of the trabeculae) and the STF (bone stiffness index) (which reflects the state of spongy bone tissue) showed no variation compared with normal standards for 20 year old adults (Table 7.27).

These results are in agreement with previous investigations into skeletal fluorosis and show that fluoride concentrations in drinking water up to 5 mg/l cause dental fluorosis without significant changes in the structural-functional state of bone tissue.

Table 7.27 Indices of bone tissue structural-functional state in adolescents from Cornesti, Kalarash and Falesti

Index	Cornesti		Kalarash		Falesti	
	Girls	Boys	Girls	Boys	Girls	Boys
SOS	1555.4± 22.0	1588.8±38.4	1569.8± 13.4	1563.5±14.8	1562.2± 14.3	1574.1±20.4
BUA	102.9± 10.85	114.2± 20.1	108.6± 6.7	106.0± 7.0	102.9± 7.5	105.0± 8.47
SI	83.9± 12.4	101.0± 22.9	91.9± 7.0	88.15±7.76	85.91± 6.7	90.6± 10.5

The structural-functional state of bone tissue in 34 women residents of Falesti was also determined at the same time as the examination of their adolescent daughters to establish hereditary and temporal relationships between mother and daughter pairs. The women were divided into two groups - one with normal indices of mineral density and another with diagnosed osteoporosis.

Results showed that women with osteoporosis had lower ultrasound densitometry and body mass indices than the group of healthy women (Table 7.28). The subjects were standardized for age, height, state of menstrual function and place of residence (nutritional and water supply status) and results showed that low body mass is evidently a risk factor for osteoporosis in women. This may be because fatty tissue is known to act as a base for androgen oesterification into oestrogens. Girls born from osteoporotic mothers had lower indices of structural-functional state of bone tissue than girls born from mothers who had normal bone tissue, however, differences between the two groups were not statistically significant. These results demonstrate the importance of hereditary factors in osteoporotic development.

Table 7.28 Indices of structural-functional state of bone tissue in "mother-daughter" pairs

Index	n	Age	Height	Body Mass	SOS	BUA	SI
Ia Group	14	36.7±0.97	160.75±1.56	60.5±2.2	1534±3.7	107.2±1.36	80.9±1.4
Ib Group	14	11.6±1.21	152.9±5.11	38.4±4.3	1551.4±6.7	99.6±3.32	80.6±3.8
IIa Group	20	37.8± 0.8	163.05±1.56	72.06±3.7	1570.6±5.2	120.45±1.2	99.9±1.9
IIb Group	20	12.0±0.38	151.54±4.42	38.45±3.2	1561.8±4.6	103.45±2.4	86.2±2.6

Ia Group - women diagnosed with osteoporosis according to ultrasound densitometry data
IIa Group - women with normal indices of bone tissue mineral density
Ib Group - daughters of women diagnosed with osteoporosis according to ultrasound densitometry data
IIb Group - daughters of women with normal indices of bone tissue mineral density

7.3.5 Physical Development and Anthropometric Parameters in Cornesti, Kalarash and Falesti

Anthropometric data is given in Table 7.29. Indices of physical development and anthropometric parameters (height, body mass, chest girth etc.) in Kalarash boys are significantly lower than boys in Cornesti. This is evidence of delayed physical development (linear bone growth and augmentation of transversal dimensions) in boys from Kalarash. No significant difference in physical development was observed between girls from Kalarash and Cornesti. In girls, shoulder blade length is greater in Kalarash than Cornesti but transversal chest diameter, thigh width, back thickness and stomach thickness were greater in Cornesti than Kalarash. This indicates poor nutritional status and imbalanced physical development in girls from Kalarash.

Table 7.29 Anthropometric indexes in adolescents from the three study towns

Index	Cornesti		Kalarash		Falesti	
	Girls	Boys	Girls	Boys	Girls	Boys
Height	153.2±1.46	161.7±4.1	152.2±2.49	158.7±3.1	151.7±2.11	152.9±2.19
Weight	42.7±2.28	51.2±3.74	40.4±2.6	45.9±2.7	40.3±1.85	39.9±1.62
Anthropometric hand length	16.2±0.27	17.5±0.29	15.5±0.29	16.6±0.44	15.8±0.3	16.07±0.25
Forearm length	23.4±0.35	24.7±0.88	22.7±0.63	24.2±0.63	23.3±0.32	23.52±0.46
Shoulder length	27.8±0.59	30.4±2.4	27.6±0.65	30.1±0.85	29.5±0.57	29.1±0.65
Shoulder blade length	15.07±0.46	16±0.6	12.7±0.48	14.1±0.47	14±0.28	14.2±0.32
Pelvis length	14±0.42	14.7 ±0.4	13.3±0.58	14.01±0.32	14.5±0.32	14.3±0.32
Thigh length	37.4±0.81	38.7±1.76	37.6±1.14	38.2±1.87	36.1±0.72	36±0.59
Shin length	38.5±0.45	40±1.53	38.4±0.77	41.5±1.02	38.7±0.68	39.1±0.71
Kinematic foot length	17.6±0.28	19±0.58	16.4±0.28	17.6±0.32	16.8±0.32	17.5±0.34
General foot length	24.4±0.29	25.7±0.88	23.2±0.54	24.4±0.37	23.4±0.41	24.3±0.39
General arm length	63.3±1.0.2	68.2±2.46	62.3±1.83	68.4±1.88	63.42±1.07	63.19±1.25
Anthropometric leg length	73.1±0.94	78.7±3.2	72.94±1.45	76.55±2.48	70.94±1.20	72.39±1.35
Head height	20.1±0.31	22.4±0.17	21.06±0.45	21.08±0.61	20.19±0.19	20.66±0.19
Morphological face height	10.2±0.47	11.5±0.28	9.33±1.14	10.39±0.32	9.61±0.14	10.05±0.24
Neck length	6.35±0.23	6.84±0.6	7.28±0.49	6.94±0.34	6.65±0.19	6.76±0.23
Head length	17.7±0.16	18.4±0.44	17.07±0.53	16.95±0.21	16.86±0.38	17.48±0.12
Head width	14.6±0.09	15±0	14.09±0.24	14.76±0.19	14.4±0.11	14.75±0.11
Trunk length	41.1±1.15	44.7±1.67	42.4±0.75	43.19±1.25	40.31±0.89	41.3±0.82
Humeral diameter	33.1±0.58	34.84±1.09	32.7±0.76	35.06±0.64	31.12±0.62	32.5±0.47
Pelvic diameter	25±0.46	25.4±0.38	25.25±0.52	25.48±0.70	24.36±0.48	23.5±0.51
Transversal diameter of chest	22.2±0.56	24.17±0.44	23.44±0.87	24.09±0.66	20.95±0.31	21.92±0.39
Sagittal diameter of chest	15.6±0.37	16.84±0.44	15.12±0.47	15.62±0.44	14.39±0.3	15.03±0.33
Shoulder width	5.03±0.2	5.64±0.53	4.86±0.26	5.73±0.85	4.42±0.13	4.42±0.12
Forearm width	6.22±0.16	7.1±0.71	5.88±0.21	6.53±0.24	5.71±0.15	6.22±0.12
Hand width	6.93±0.14	7.84±0.32	6.57±0.14	7.17±0.28	6.85±0.15	7.05±1.15
Thigh width	9.55±0.28	10.7±0.49	9.34±0.39	9.16±0.26	8.38±0.18	8.44±0.17
Shin width	8.81±0.27	9.34±0.49	8.48±0.37	8.83±0.26	7.87±0.14	7.93±0.13
Foot width	8.93±0.22	9.5±0.15	8.52±0.21	8.98±0.22	8.72±0.15	8.95±0.13
Head girth	54.15±0.38	55.5±0.76	54±0.45	53.8±0.54	53.5±0.33	53.34±0.22
Neck girth	29.15±0.42	32.84±1.30	28.28±0.48	28.07±2.38	28.48±0.36	29.09±0.38
Chest girth	72.75±1.96	77.5±3.32	72.54±2.46	73.7±1.58	70.58±1.58	69.65±1.22
Stomach girth	59.15±1.33	68.67±3.53	62.55±2.86	63.63±1.09	58.52±1.05	59.48±0.88
Buttocks girth	80.93±2.42	84.34±4.67	80.82±2.99	79.99±2.05	74.73±1.36	72.63±1.45
Shoulder girth	21.81±0.72	24.04±1.73	21.37±0.93	21.97±0.59	19.73±0.44	20.12±0.37
Girth of forearm's wide part	21.15±0.56	24.67±1.31	20.42±0.67	21.7±0.49	19.37±0.32	20.57±0.41
Girth of forearm's narrow part	14.69±0.26	16.5±0.5	13.95±0.35	15.14±0.42	13.89±0.24	15.41±0.94
Hand girth	17.31±0.31	19.17±0.88	16.85±0.43	18.75±0.43	16.85±0.24	18.34±0.44
Thigh girth	51.38±0.76	53±2.31	48.25±2.45	47.99±1.35	46.09±1.03	42.96±1.38
Girth of shin's wide part	28.93±1.28	27.5±3.04	30.12±1.02	31.07±1.22	29.23±0.48	28.56±0.65
Girth of shin's narrow part	19.23±0.77	18.17±1.48	20.92±1.34	21.61±0.55	19.74±0.32	19.79±0.43
Foot girth	20.88±0.61	20±1.33	20.4±0.48	21.93±0.48	21.45±0.31	21.96±0.42
Thickness of back skin- fold	8.62±0.64	10.67±2.18	9.5±0.78	6.5±0.32	7.96±0.45	7±0.33
Thickness of shoulder skin-fold	8.62±0.58	9.34±1.86	8.63±0.94	7.67±0.54	8.18±0.41	7.63±0.37
Thickness of stomach skin-fold	8.46±0.67	12.67±2.91	11.37±1.18	8.75±0.69	8.71±0.45	8.41±0.51
Thickness of shin skin-fold	13.38±1.05	15.67±1.86	12.63±0.73	12.58±1.51	11.78±0.56	11.52±0.38
Thickness of thigh skin-fold	16.46±1.45	20.34±1.21	15.87±0.52	14±1.36	12.82±0.47	12.93±0.57

7.3.6 Summary of Geochemistry and Health Investigations

In summary, the analysis of drinking water samples related to measurements of nutritional status, dental and skeletal examinations of adolescents from Kalarash, Cornesti and Falesti and women from Falesti revealed considerable differences between the three study towns as follows:

- The fluoride concentration in the Kalarash (3.65 mg/l) and Falesti (5.31 mg/l) water supply system exceeds the WHO threshold (1.5 mg/l) by 2-5 times leading to the development of dental fluorosis in the population of these towns.

- The fluoride concentration in well waters from within each of these towns is highly variable therefore the incidence of dental fluorosis is not distributed throughout the towns but forms clusters associated with high-fluoride water sources. Deep artesian waters, in general contain higher fluoride concentrations than shallow wells.

- In Kalarash and Falesti, the prevalence and degree of severity of dental fluorosis is dependant on the fluoride concentration in drinking water.

- In contrast, the fluoride content of well waters in Cornesti is within the WHO optimum level of (0.5 – 1.5 mg/l) and dental fluorosis was not evident among Cornesti adolescents

- The daily nutritional status of adolescents in all three towns does not accord with recommended normal intakes to meet adolescent physiological needs.

- The dietary fluoride intakes are high for girls, in Cornesti 538.51±60.6 µg/day, in Kalarash 874.1± 222.86 µg/day and in Falesti 2528.9±176.0 µg/day.

- The dietary fluoride intakes are high for boys in Cornesti 463.82±41 µg/day, in Kalarash 1304.26±201.3 µg/day and Falesti 2362.45±686.7 µg/day.

- Daily dietary intakes are characterized by insufficient irreplaceable amino acids and proteins and by imbalances in carbohydrate, fat and vitamin consumption.

- Deficiencies in the amount of dietary Ca and P necessary for peak bone mass formation in adolescents and for adequate mineralisation of the skeleton were also identified. These may exacerbate the detrimental affects of fluoride on dental and skeletal mineralisation.

- Although dental fluorosis is prevalent in Kalarash and Falesti, comparisons between mother and daughter pairs demonstrated that in subjects with normal bone mineral status, concentrations of up to 5 mg/l fluoride in drinking water do not cause essential changes to the structural-functional status of bone tissue.

- However, the results demonstrate that fluoride concentrations of up to 5 mg/l in drinking water can have a negative impact on peak bone mass formation and structural-functional state when there are other risk factors such as a hereditary disposition to osteoporosis. These relationships require further investigation as the subject group examined during the present study is small.

- In all three towns, adolescents suffered from a delay in physical development (boys) and disharmonious physical development (girls).

- These results demonstrate the need for primary and secondary prophylaxis for osteoporosis and fluorosis in the study area.

7.3.7 Risk Avoidance Maps

The information presented in the previous section of this report demonstrates that high-fluoride groundwaters have a serious negative impact on human health in the Falesti region. In order to carry out the current project risk assessment, data for dietary fluoride and Ca intake, drinking water chemistry and fluorosis prevalence were included in the GIS (Table 7.1). It was not possible to adopt a grid square approach for the preparation of the final risk avoidance maps in this case due to the limited spatial distribution of the data and the final risk assessment maps present the data as point locations representing each of the study towns. Dietary Ca and fluoride intakes are included in the GIS for background information only (Figures 7.8, 7.9, 7.10 and 7.11).

Results show that the risks of dental caries in the region are low due to the high fluoride concentrations in the water and low prevalence of dental caries were noted in the region during the present study. The detailed risk assessment for Falesti therefore focuses on high-fluoride risk on the basis of the drinking water chemistry (Figure 7.12), water supply information and fluorosis prevalence (Figures 7.13 and 7.14) according to the scheme detailed in Table 7.30.

The final risk avoidance map (Annex 9) shows that high-fluoride risks occur in Falesti and Kalarash. Although Cornesti lies within the high-fluoride region defined on the basis of national water chemistry data, the present study has demonstrated that water fluoride contents are below the MAC of 1.5 mg/l in this town and there is no incidence of dental fluorosis therefore high-fluoride risks are low (Annex 9).

Table 7.30 High-fluoride risk assessment scheme for the Falesti region

High-Fluoride Risk						
Location	**Phase 1**		**Phase 2**		**Final Risk**	**Assessment Rationale**
	Drinking water F mg/l ≥ 1.5	**Potential Risk**	**Water used directly for drinking**	**Potential Risk**		
Cornesti	No	Low	Yes	Low	Low	Fluoride content should not normally cause problems, but may do under certain circumstances in hot climates
Falesti, Kalarash	Yes	High	Yes	High	High	Water contains high fluoride which causes health problems
	Fluorosis Incidence					
Falesti, Kalarash	Yes	High	Yes	High	High	There is evidence of fluorosis in the area and high fluoride waters are still used for drinking therefore high risk
Cornesti	No	Low	Yes	Low	Low	There is no evidence of fluorosis in the area and waters contain low fluoride contents

7.4 CONCLUSIONS

Several of the natural groundwater resources used for drinking in Moldova are Na+K-dominant and contain high concentrations of fluoride and dental fluorosis is a significant problem in this country. The main areas of concern are the Falesti-Beltsy region in the north and the Chadyr-Lunga region in the south. Detailed studies of the Falesti region demonstrate high high-fluoride risks in the towns of Falesti and Kalarash but low risk in Cornesti.

Geochemistry and health studies carried out as part of the present project demonstrate that waters containing > 1.5 mg/l cause dental fluorosis in the population and prevalence rates of > 70% among adolescents are not uncommon in settlements consuming high-fluoride waters. Within settlements, fluorosis prevalence shows a strong spatial correlation with the location of high-fluoride water sources. Investigations into skeletal status carried out for the first time in Moldova, reveal that water contents below 5 mg/l fluoride do not adversely affect bone mineral formation except in individuals with a genetic predisposition to osteoporosis. However, these results require further investigation due to the small sample population of the current project. Nutritional studies indicate that diets are deficient in Ca, P, vitamins and proteins, which may exacerbate the negative health effects of fluoride in the region. Studies of 'mother-daughter pairs' highlighted some evidence that dental fluorosis severity has declined in recent years since the supply of high-fluoride water from deep pumped wells is now erratic in Moldova and the population abstract lower-fluoride water from shallow wells as an alternative. However, water quality in the shallow wells is extremely poor and it is desirable that the population return to drinking the deeper water as soon as possible. This will require the removal of fluoride from these waters.

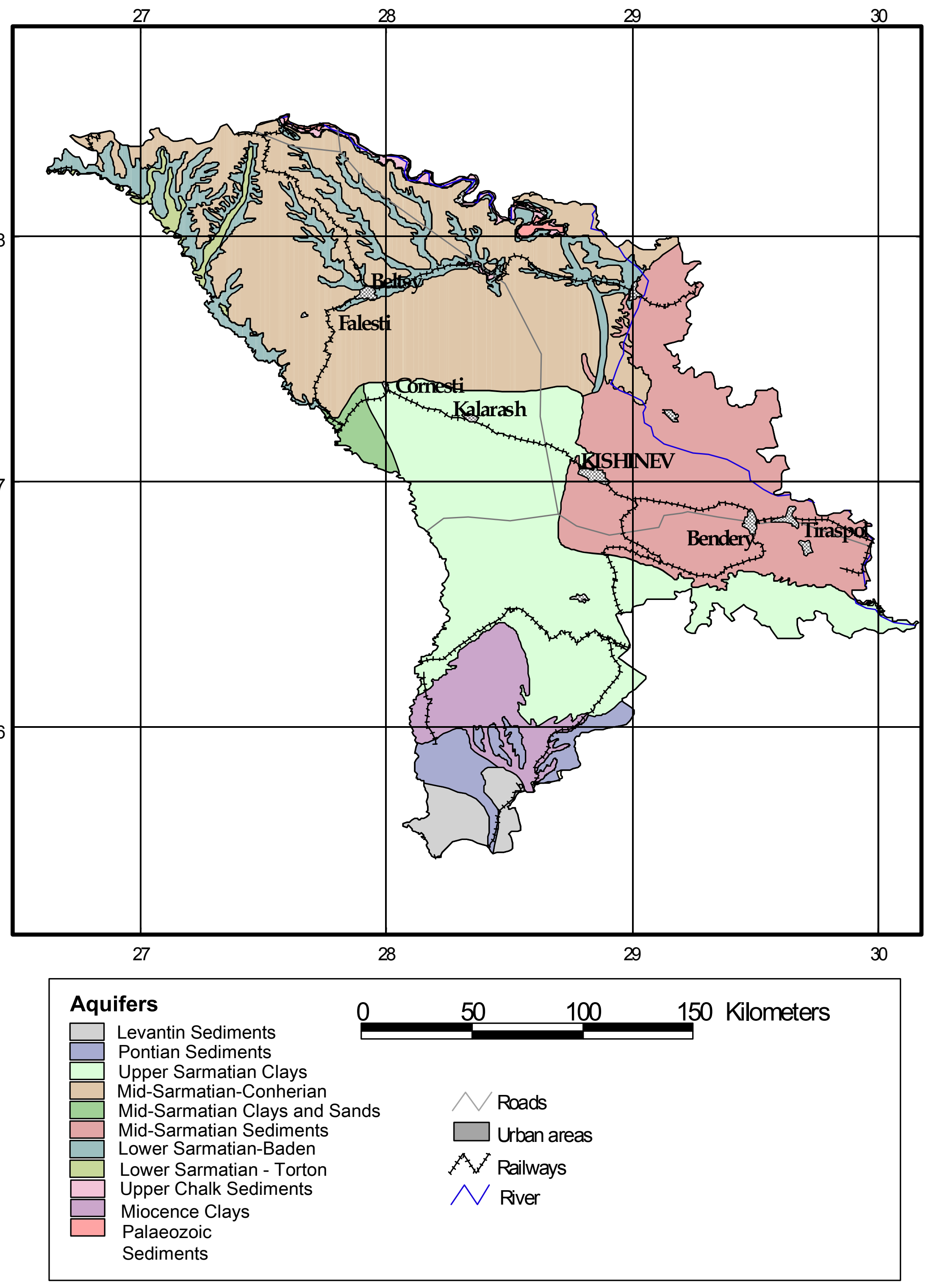


Figure 7.1 Main hydrogeological units of Moldova (ASG)

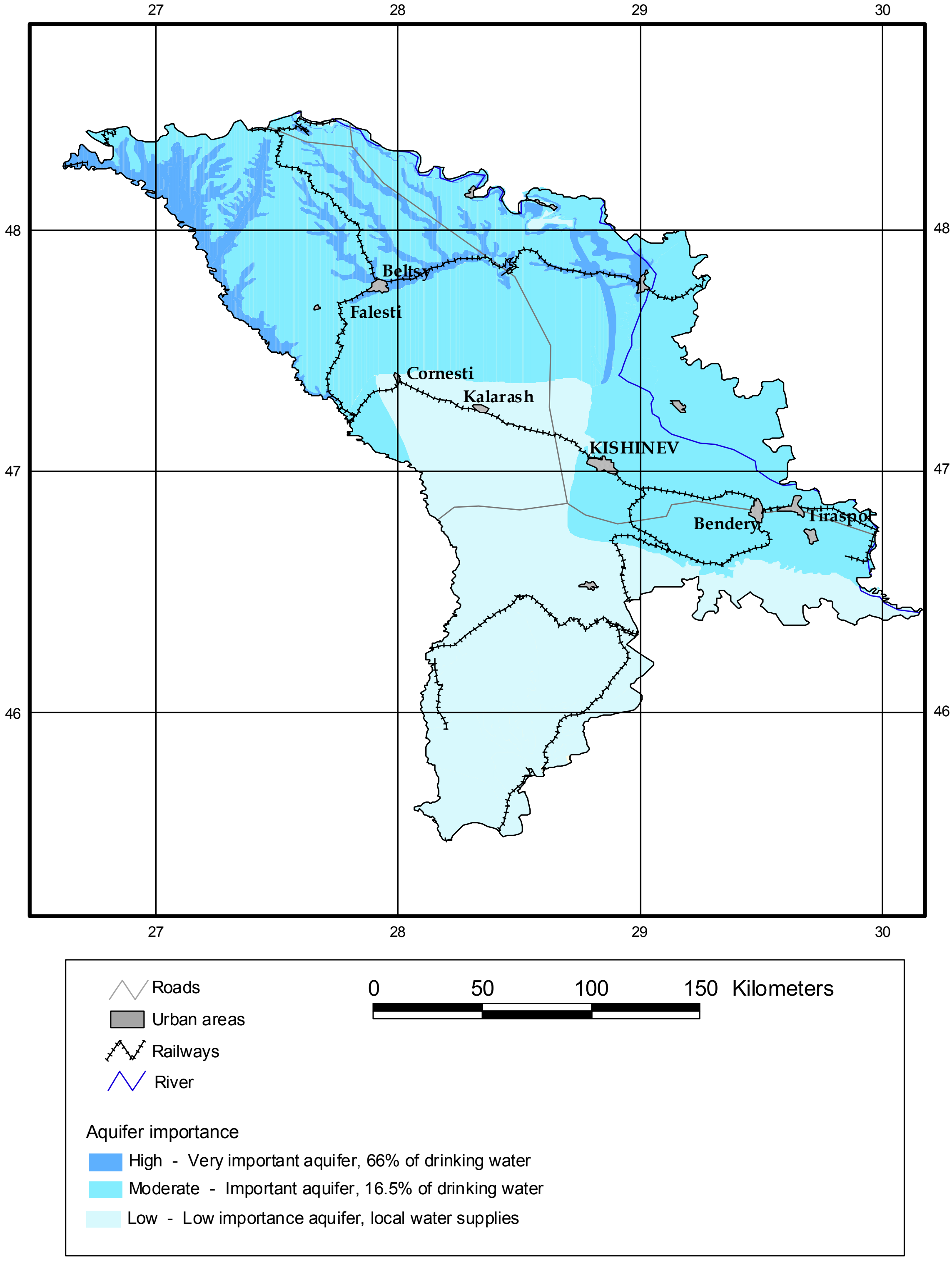


Figure 7.2 Main hydrogeological units of Moldova classified according to aquifer importance

Figure 7.3 Main population centres of Moldova

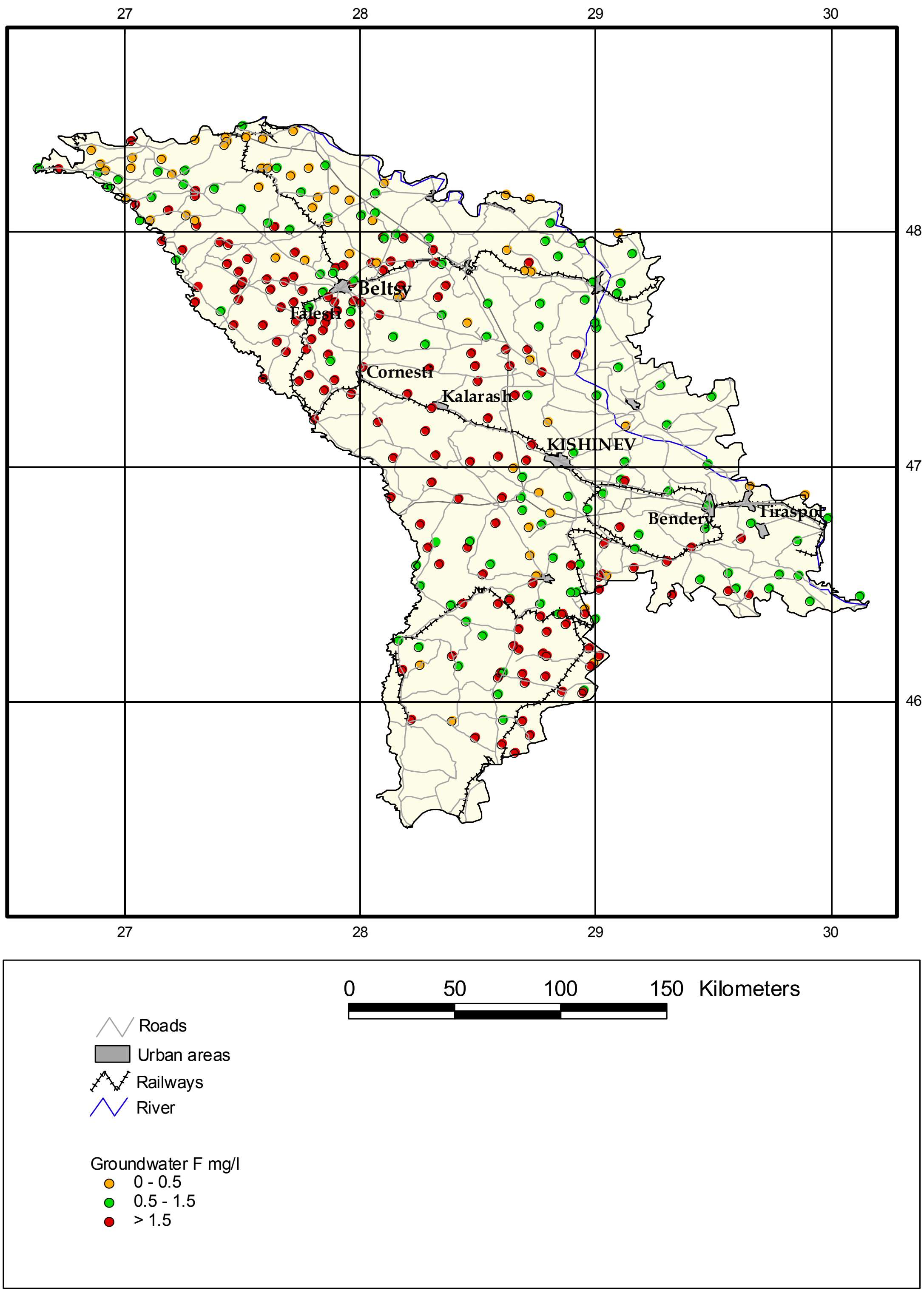


Figure 7.4 Groundwater fluoride concentrations in Moldova (ASG) classified according to water quality guidelines (WHO, 1996b)

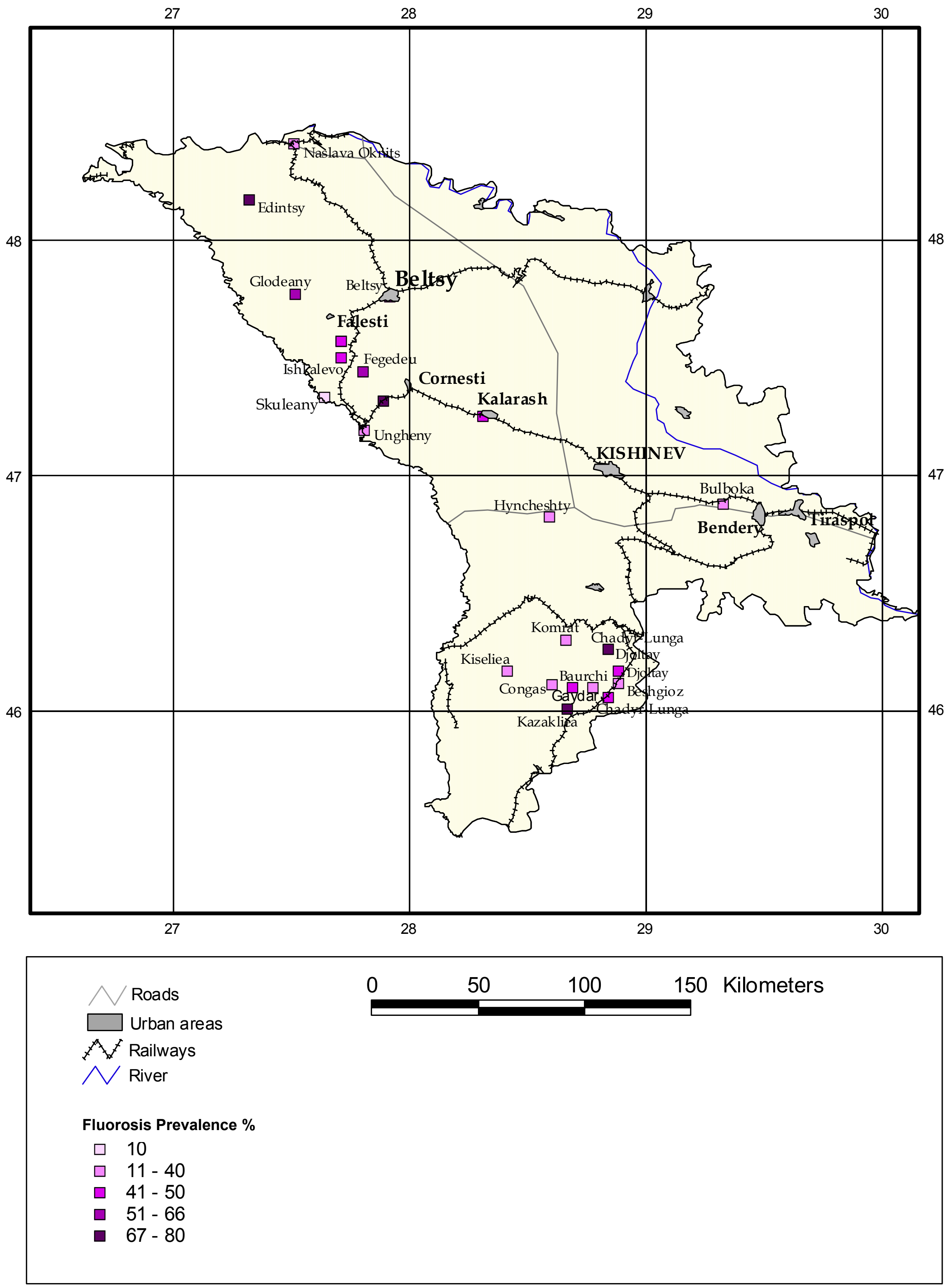


Figure 7.5 Locations of known fluorosis incidence in Moldova from Preventative Medicine Service data

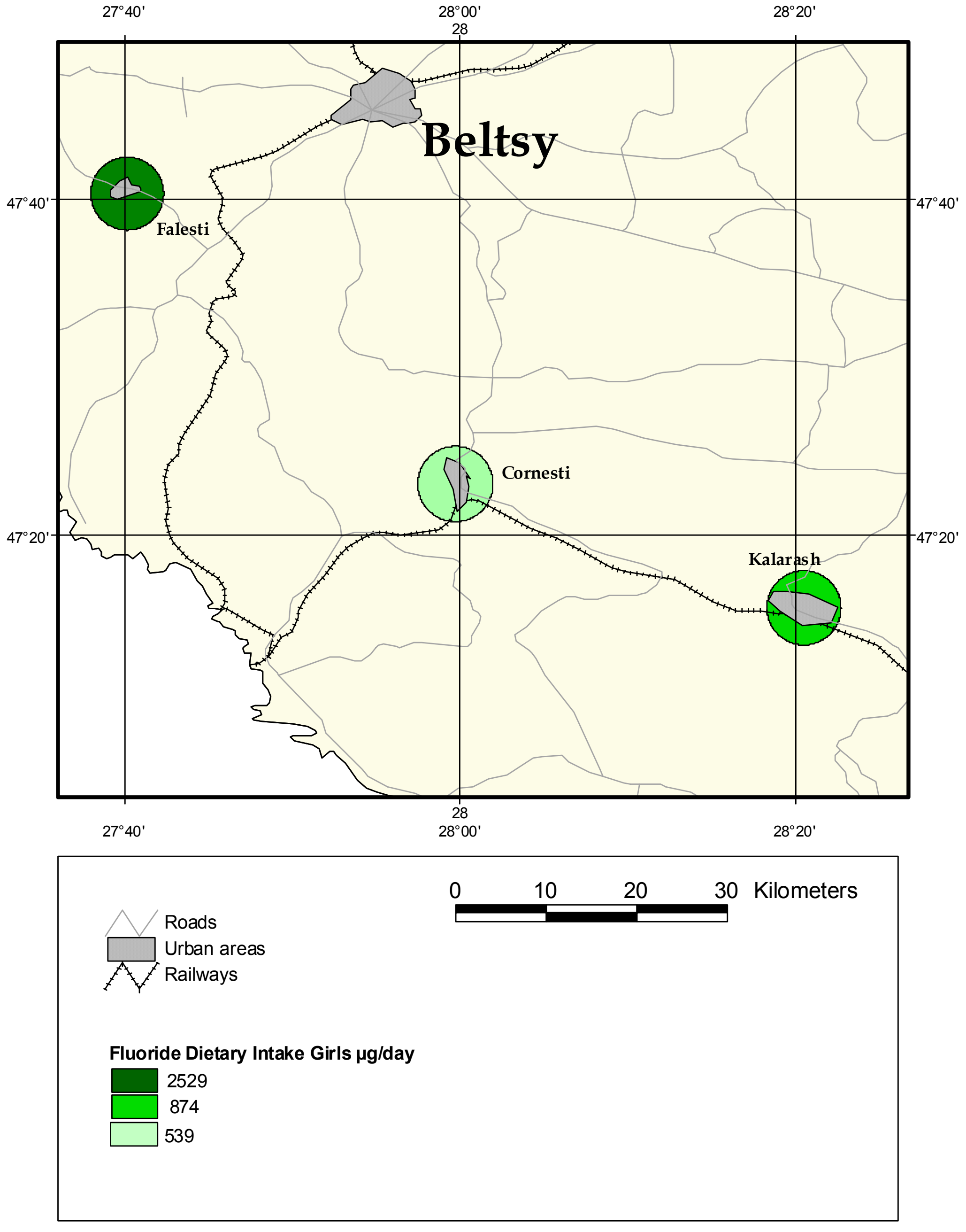


Figure 7.8 Fluoride daily dietary intakes in girls in Falesti Region, Moldova

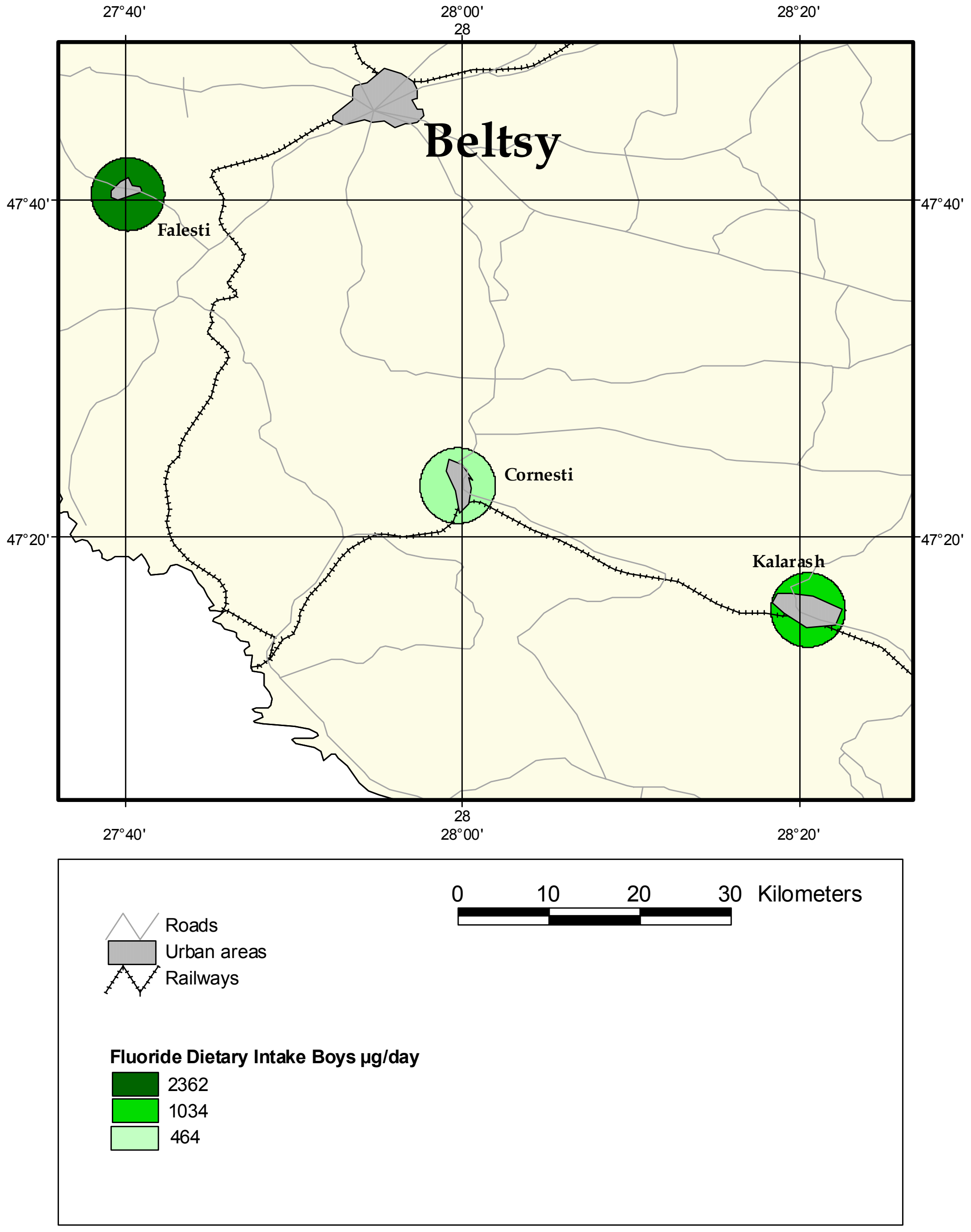


Figure 7.9 Fluoride daily dietary intakes in boys in Falesti Region, Moldova

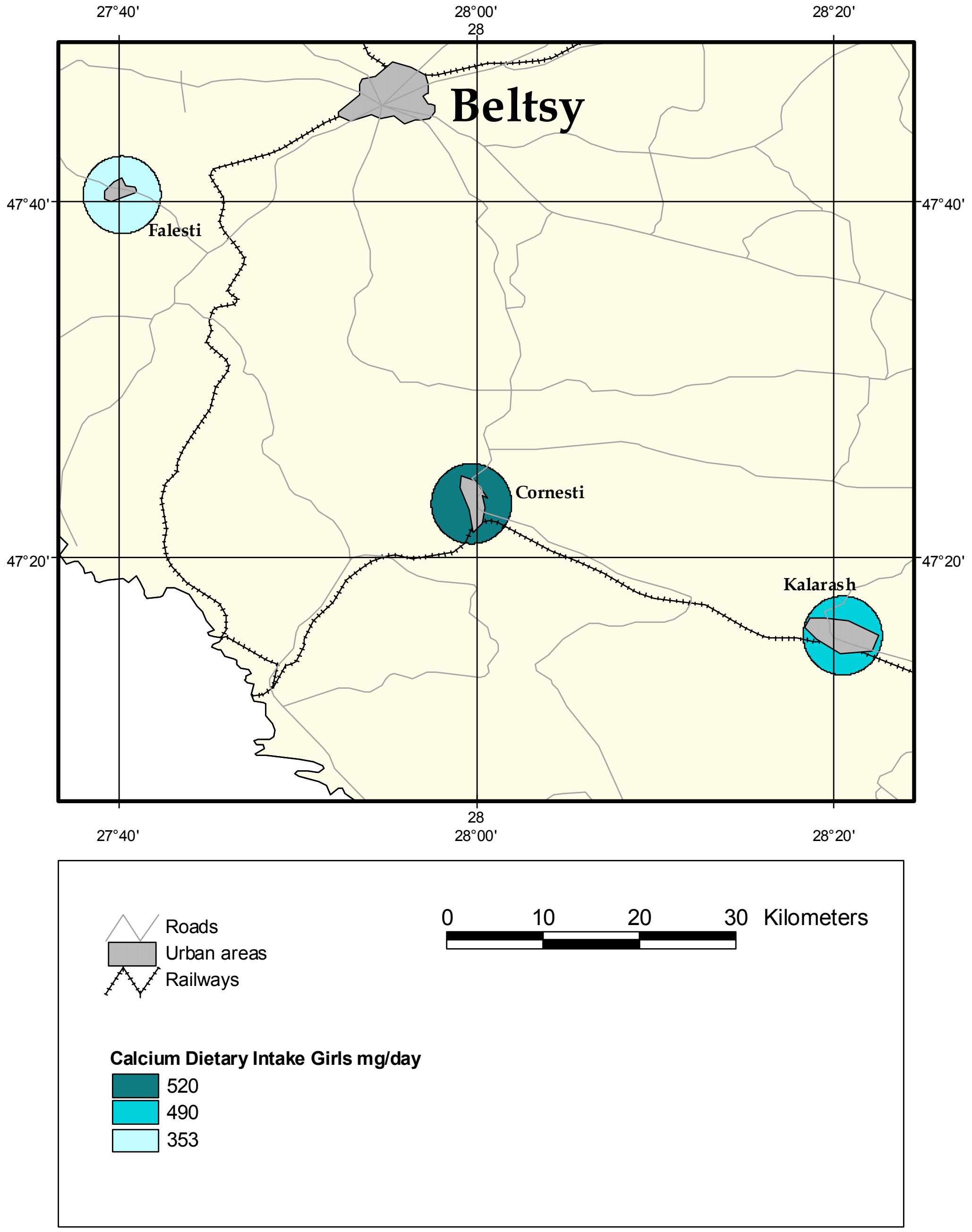


Figure 7.10 Calcium daily dietary intake in girls in Falesti Region, Moldova

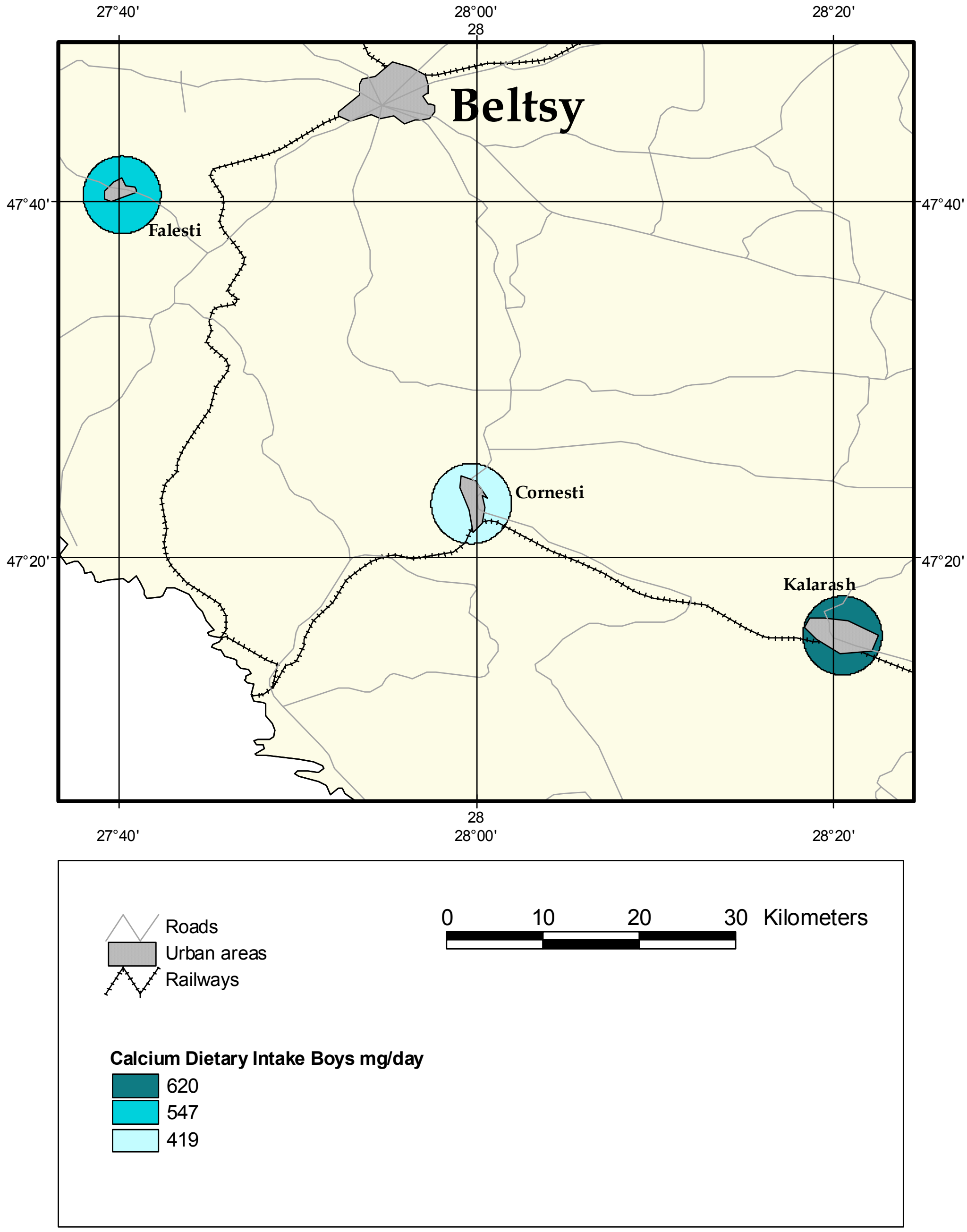


Figure 7.11 Calcium daily dietary intake in boys in Falesti Region, Moldova

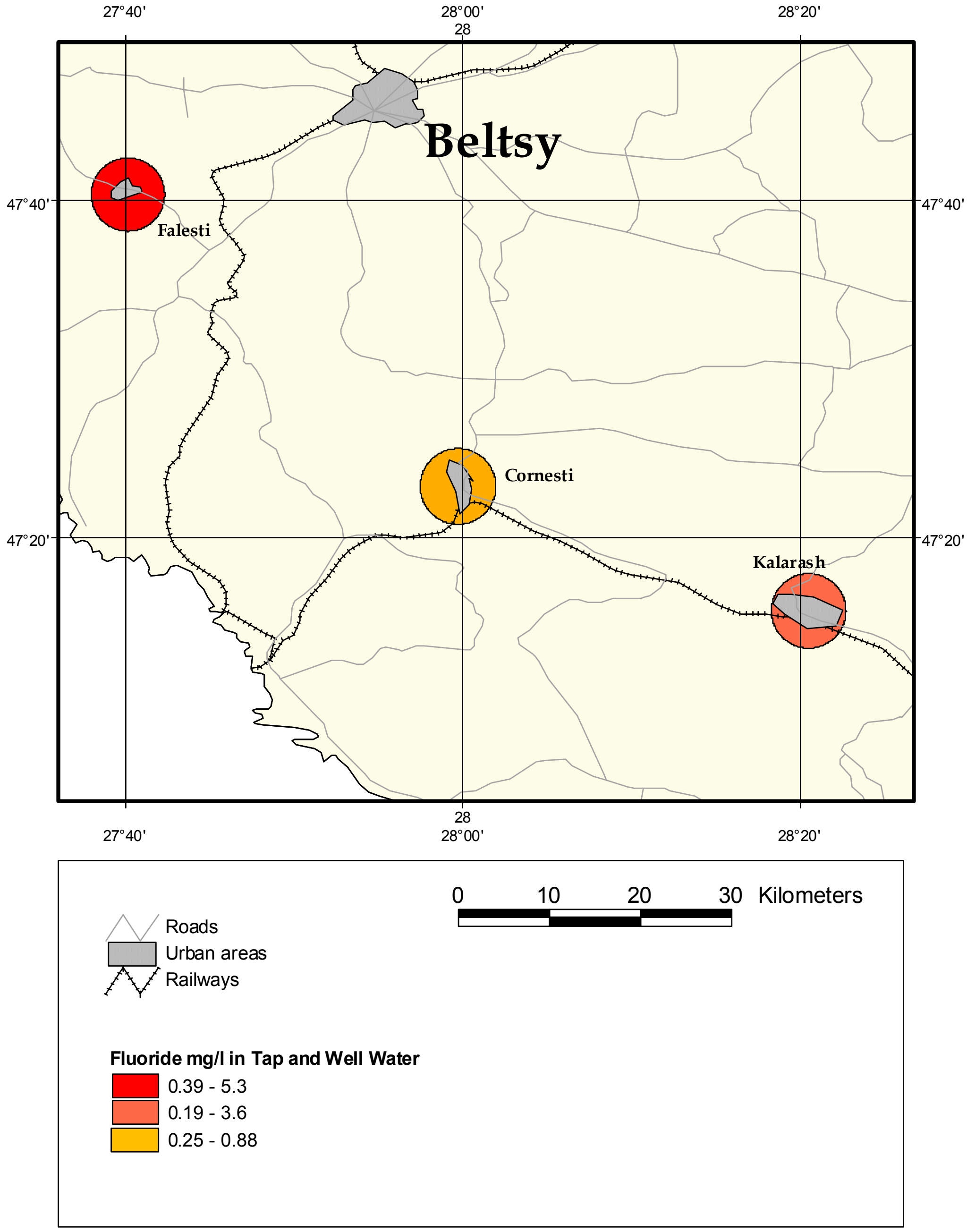


Figure 7.12 Fluoride concentrations in drinking water in Falesti Region, Moldova

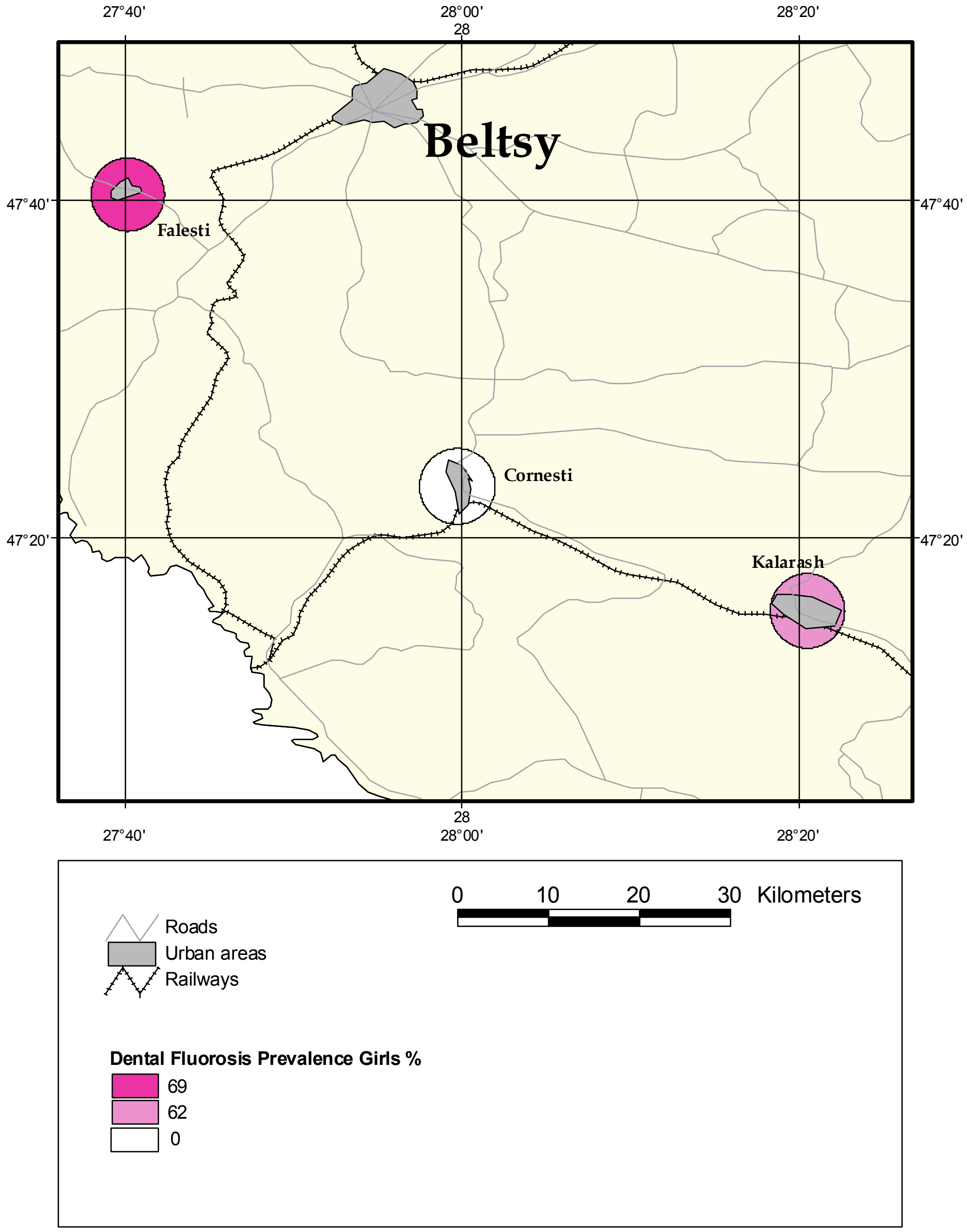


Figure 7.13 Dental fluorosis prevalence in girls in Falesti Region, Moldova

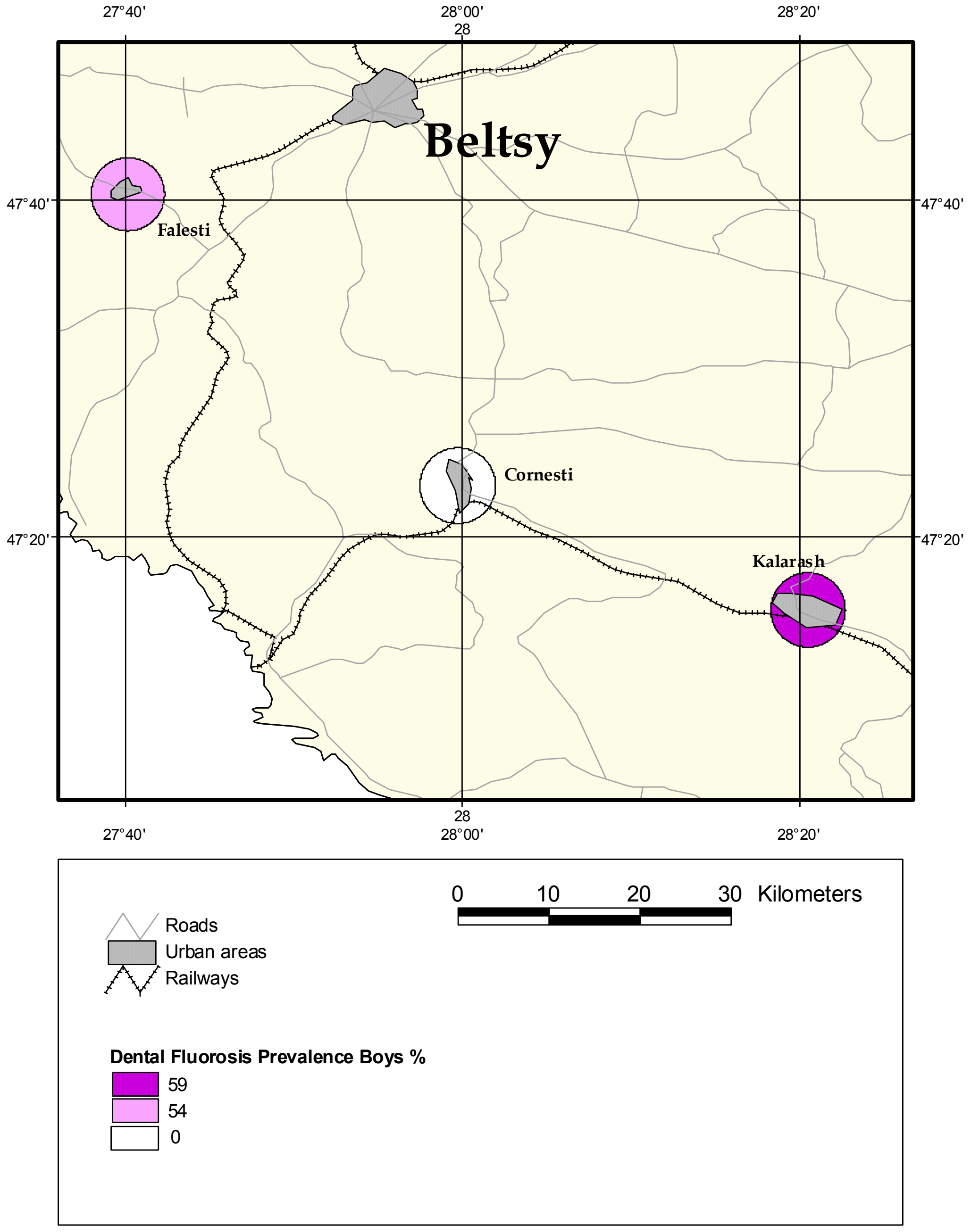


Figure 7.14 **Dental fluorosis prevalence in boys in Falesti Region, Moldova**

8 Fluoride Risk Assessment for Ukraine

Edward Zhovinsky, Vladislav Povorosnuk, Fiona Fordyce and Bryony Hope

8.1 INTRODUCTION

The full extent of high-fluoride waters in Ukraine is unknown as no national hydrgeochemical surveys have been carried out. However, several groundwater horizons exploited for drinking are known to contain high fluoride, many of which are associated with tectonically active fault zones. Dental fluorosis is endemic in the Poltava and Odessa regions of Ukraine and has been reported the coal-mining region of Lvov, however, no national fluorosis surveys have been completed and the full extent of fluorosis prevalence is unknown. This chapter presents a national overview of fluoride and fluorosis in Ukraine, the results of the first detailed geochemistry and health case studies in the country, which were carried out in Lvov and Odessa as part of the present project and examines the fluoride risks in Poltava, Odessa, Lvov and Kiev regions in more detail.

8.2 NATIONAL RISK ASSESSMENT

8.2.1 GIS Risk Scheme

The data incorporated into the Project Partner GIS (Country.apr) for Ukraine are listed in Table 8.1. At the national level, the maps of tectonic regions (IGMOF) (Figure 8.1), main population centres (IGMOF) (Figure 8.2), dental fluorosis and caries incidences (Figure 8.3) and water chemistry data derived from health investigations carried out during previous studies and the present project (Figure 8.4), were included in the GIS for background information only.

Due to the lack of national survey data for hydrogeochemistry and fluorosis, the national fluoride risk assessment for Ukraine was carried out on the basis of the likely water fluoride content and dietary intake of populations in the different regions of Ukraine estimated by biogeochemical experts. The scheme is outlined in Table 8.2 and is based on the following information.

Table 8.1 Data held in the Project Partner Country.apr risk assessment GIS for Ukraine

		GIS Risk Assessment
Data	Groundwater Chemistry Data for Kiev Region	Data categorised according to WHO fluoride water quality guidelines: < 0.5 mg/l Caries Risk, ≥ 1.5 mg/l Fluorosis Risk in risk assessment scheme for Kiev Region
Data Source	Data base of the Institute of Geochemistry and Ore Mineral Formation (IGMOF), Ukraine	
Data Type	93 analyses of groundwater from Quaternary, Palaeogene, Cretaceous, Jurassic and Proterozoic aquifers collected at a sample density of approximately 1 sample per 5 km^2 over most of the region. Data for: X, Y, Longitude, Latitude, Well Number, Aquifer, pH, F, Ca, Mg, Na+K, Fe^{2+}, Fe^{3+}, NH_4, NO_2, NO_3, Cl, SO_4, HCO_3, CO_3, CO_2, HBO_2, I, Br, Se, Zn, Pb, Mn , Mo, Be, B, Co, Ni I, As, U	
Data	Groundwater Chemistry for Lvov Region	Data categorised according to WHO fluoride water quality guidelines: < 0.5 mg/l Caries Risk, ≥ 1.5 mg/l Fluorosis Risk in risk assessment scheme for Lvov Region
Data Source	Data base of the Institute of Geochemistry and Ore Mineral Formation (IGMOF), Ukraine	
Data Type	59 analyses of groundwater from Quaternary and Cretaceous aquifers collected at a sample density of approximately 1 sample per 5 km^2 over most of the region. Data for: X, Y, Longitude, Latitude, Well Number, Aquifer, pH, F, Ca, Mg, Na+K, Fe^{2+}, Fe^{3+}, NH_4, NO_2, NO_3, Cl, SO_4, HCO_3, CO_3, CO_2, HBO_2, I, Br	
Data	Groundwater Chemistry for Odessa Region	Data categorised according to WHO fluoride water quality guidelines: < 0.5 mg/l Caries Risk, ≥ 1.5 mg/l Fluorosis Risk in risk assessment scheme for Odessa Region
Data Source	Data base of the Institute of Geochemistry and Ore Mineral Formation (IGMOF), Ukraine	
Data Type	58 analyses of groundwater from Neogene aquifers collected at a sample density of approximately 1 sample per 5 km^2 over most of the region. Data for: X, Y, Longitude, Latitude, Well Number, Aquifer, pH, F, Ca, Mg, Na+K, Fe^{2+}, Fe^{3+}, NH_4, NO_2, NO_3, Cl, SO_4, HCO_3, CO_3, Cu, Zn, Pb, Ni, U	
Data	Groundwater Chemistry for Poltava Region	Data categorised according to WHO fluoride water quality guidelines: < 0.5 mg/l Caries Risk, ≥ 1.5 mg/l Fluorosis Risk in risk assessment scheme for Poltava Region
Data Source	Data base of the Institute of Geochemistry and Ore Mineral Formation (IGMOF), Ukraine	
Data Type	111 analyses of groundwater from Quaternary and Palaeogene aquifers collected at a sample density of approximately 1 sample per 5 km^2 over most of the region. Data for: X, Y, Longitude, Latitude, Well Number, Aquifer, pH, F, Ca, Mg, Na+K, Fe^{2+}, Fe^{3+}, NH_4, NO_2, NO_3, Cl, SO_4, HCO_3, CO_3, CO_2, HBO_2, I, Br, Se, Zn, Pb, Mn , Mo, Be, B, Co, Ni I, As, U	
Data	Tap and Well Water Chemistry for Localities	Data included as background information layer only
Data Source	From the present and previous investigations	
Data Type	Fluoride contents in Arciz, Vilkovo, Izmail, Podgorny, Tarutino, Khar'kov, Dnepropetrovsk, Donetsk, Zaporozh'ye	
Data	Main Population Centres of Ukraine	Data included as background information layer only
Data Source	www.esri.com	
Data Type	Digital map of main settlements	
Data	Water Supply Information	Data included in risk assessment scheme for regions
Data Source	Water Supply of Ukraine	
Data Type	Knowledge of water fluoridation and use of water for drinking	
Data	'General' Fluorosis Prevalence	Data included in risk assessment scheme for regions
Data Source	Previous Studies	
Data Type	Coordinates of towns with fluorosis incidence	
Data	Fluorosis Prevalence Adolescents Odessa Region	Data included in risk assessment scheme for Odessa and Lvov regions
Data Source	Present Study	
Data Type	Fluorosis prevalence statistics for Arciz and Podgorny	
Data	Fluorosis Prevalence Adolescents Lvov Region	Data included in risk assessment scheme for regions
Data Source	Present Study	
Data Type	Fluorosis prevalence statistics for Sosnovka, Silyets, Zhovkva	
Data	Fluorosis Hotspots	Data included in risk assessment scheme for regions
Data Source	Previous Studies	
Data Type	Location of dental fluorosis incidences	
Data	Tectonic Features	Data included as background information layer only
Data Source	From the database of the Institute of Geochemistry and Ore Mineral Formation (IGMOF), Ukraine	
Data Type	Digital map of main tectonic features in each study region	
Data	Tectonic Regions	Data included as background information layer only
Data Source	From the database of IGMOF, Ukraine	
Data Type	Digital map of main tectonic regions of Ukraine	

Table 8.2 Fluoride risk assessment scheme for Ukraine

Fluoride Risk			
Location	**Groundwater F mg/l**	**Risk Category**	**Assessment Rationale**
Ukraine	0 – 0.3	Dental Caries Risk	Very low fluoride regions
	0.3 – 0.6	Possible Dental Caries Risk	Low fluoride regions
	0.6 – 0.8	Optimum Concentration	Fluoride contents should not normally cause health problems
	0.8 - 2	Possible High Fluoride Risk	Waters in Kiev Region associated with mining are of possible concern
	0.8 - 4	Possible High-Fluoride Risk	Waters in the regions of Dnepropetrovsk, Donetsk, Zaporozh'ye are of possible concern
	0.6 – 1	High Fluoride Risk	Waters in the coal-mining region of Lvov are of concern, fluorosis is reported in this area
	0.6 – 1.2	High Fluoride Risk	Waters in the southern region of Odessa where people drink greater quantities of water are of concern, fluorosis is reported in this area
	1.5 - 2	High Fluoride Risk	Waters in Poltava region are of concern, fluorosis is reported in this area
	2 - 3	High Fluoride Risk	Waters in Poltava region are of concern, fluorosis is reported in this area
	3 - 8	Very High Fluoride Risk	Waters in Poltava region are of concern, fluorosis is reported in this area

8.2.1.1 Fluoride Exposure and Health

The health of the population is a basic indicator of the environmental status of a region. Over hundreds of years, the quality of potable water supplies has determined the good or bad health of the population. The content of fluoride in potable water is one of the main components determining the suitability for use and is of increasing interest due to health effects on the population (Nekrasova, 1998). The main centres of endemic dental fluorosis occur in Poltava, Dnepropetrovsk, Khar'kov, Donetsk, Odessa and very locally in Vinnisza. The most studied high-fluoride area in Ukraine is the Buchak fluoride hydrogeological province comprising many localities with 2.5 – 8 mg/l fluoride in drinking water (Shylkina, 1997a). The province is thought to be the largest in the former Soviet Union encompassing 34 000 km^2 and 2 million people and is situated in eastern-central Ukraine extending from Chernigiv Region in the north to Zaporozh'ye Region in the south in the Dnepro-Donetsk basin. Poltava Region lies in the centre of the province and has the greatest incidence of dental fluorosis in people and animals.

The rural population of Ukraine mainly utilise water from shallow shaft wells exploiting aquifers in recent sediments with high fluoride concentrations. Fluoride concentrations in these wells can vary between 20 – 30 % of annual mean values between summer and winter. The general relationships between drinking water fluoride concentrations and disease prevalence in Ukraine were established by (Gabovych, 1951)(Table 8.3). It should be noted, however, that in the warm climatic conditions of the mid-latitudes of the former Soviet Union, mild forms of dental fluorosis have been reported when water contains only 0.5 – 0.7 mg/l fluoride (Groshikov, 1985) and it is well documented that high Ca contents in water reduce the development of dental fluorosis in otherwise high-fluoride regions.

Furthermore, within the same village, fluoride contents can vary markedly between different wells for example, Gabovych and Minkh (1979) report concentration ranges between 0.4 – 3.6 mg/l in one settlement. As a result, endemic fluorosis is not distributed evenly in villages but has a cluster pattern of prevalence associated with high-fluoride water sources resulting in widely varying dental status within the same locality.

Table 8.3 General classification of the fluoride content of drinking waters and disease prevalence in Ukraine (Gabovych, 1951).

Water Fluoride mg/l	Dental Caries Prevalence %	Dental Fluorosis Severity Total %	Disease Prevalence
< 0.7	100	-	100
0.7 - 1.0	Minimum	I degree	4
1.0 - 1.4	Minimum	II degree	20
1.4 - 2.0	Minimum	I - II degree	40
> 2.0	Minimum	III - IV degree	40 - 100

There are a number of regions in Ukraine with elevated fluoride contents in the environment and a resultant increased prevalence of osteoarthrosis among residents (Korzh et al., 1997; Shylkina, 1997a). Despite this fact, prior to the present study no comprehensive investigations into the structural functional state of bone tissue, maxillodental status, physiological status and diet had been carried out.

8.2.1.2 Industrial and Agricultural Sources

In Ukraine, fluoride-bearing minerals and deposits are utilised as raw materials in industry and agriculture. Fluoride is used in the fluorescence industry and the widespread application of phosphate fertilisers containing readily soluble fluoride results in environmental dispersion of the element. The processing of apatites and phosphates for fertilisers can result in 50% of the fluoride entering the atmosphere in gases and smoke. Atmospheric contamination by fluoride is detected around superphosphate, aluminium, beryllium, zircon, enamel, glass, brick, cement, metallurgical, chemical and nuclear industrial sites. Fluoride is also elevated in sewage, which can impact on the environment and local population if not treated correctly in disposal ponds.

In addition, coals in the region contain 50 – 400 μg/g fluoride, which enters the atmosphere on combustion of this fossil fuel. High fluoride concentrations in organic deposits such as coals and carbonaceous soils can be explained by the fact that plants accumulate fluoride (2 – 3.6 μg/g fluoride have been reported in tree trunks and plant stems). One of the worst affected coal mining regions is the Chervonograd area in the centre of the Lvov-Volynsk coal basin (Table 8.5 and Figures 8.2 and 8.3). The annul extraction of 4 - 5 million tons of coal causes marked changes in the geological environment, formation of anthropogenic landscapes and pollution of soils, groundwater, surface water and air. By the end of 1995 and beginning of 1996 this lead to the widespread distribution of dental diseases (fluorosis and hypoplasia) in children in the town of Sosnovka and on a smaller scale in the cities of Chervonograd and Gornjak. Elevated levels of fluoride in waters in certain districts of the

Kiev Region are also associated with lignite mining. In both Regions, the districts affected have been classified as high risk in the assessment scheme due to the effects of industrial contamination.

During the present study, the hydrochemistry of well waters in the proximity of industrial sites in Khar'kov (2 samples), Dnepropetrovsk (34 samples), Donetsk (36 samples) and Zaporozh'ye (36 samples) was examined (Table 8.5 and Section 8.5 Appendix 8.1). Results demonstrated that fluoride contents were not enhanced in these regions as a result of industrial activity, however, these regions are classified as high risk on the basis of natural fluoride groundwater concentrations.

8.2.1.3 Hydrogeology

Fluoride concentrations in Ukrainian waters are influenced by the concentrations in rocks, speciation of fluoride, climate, degree of mineralisation of waters, chemical composition of waters, temperature and pressure regimes, etc. (Zhovinsky and Kurayeva, 1987). The two most important natural sources of fluoride in Ukrainian waters include water-rock-biochemical interactions with minerals such as apatite, tourmaline and micas during the percolation of waters from surface through sedimentary strata and secondly, the upwelling of deep mineralised high-fluoride groundwaters in faulted regions. Increased concentrations of fluoride are also found in organic-rich waters in Ukraine as a result of accumulation by living organisms (Posokhov, 1965). In water-rock reactions, the concentrations of fluoride are largely controlled by the solubility of the main fluoride minerals as follows:

Mineral	*Soluble Concentration at 200 °C mg/l*
Fluorite (CaF_2)	*15*
Sellaite (MgF_2)	*87*
Villiaumite (NaF)	*41700*

Villiaumite is more soluble than fluorite or sellaite and dissolves in most waters. Fluorite solubility increases with temperature but decreases in waters with high Ca contents. However, the presence of other cations such as Na and K and highly mineralised waters increase the solubility of fluorite.

Groundwaters generally contain greater fluoride concentrations than surface waters and low concentrations of fluoride are observed in most surface waters in Ukraine (< 0.5 mg/l). The range in fluoride contents of surface waters is narrow, for example in the Dnepro River fluoride ranges from 0.11 – 0.20 mg/l, in the Dnister River from 0.09 – 0.31 mg/l and in the Yasna River from 0.07 – 0.32 mg/l. Fluoride contents in surface and groundwaters are seasonally variable. For example, seasonal ranges of 0.09 – 0.266 mg/l in the Dnepro River, 0.12 – 0.178 mg/l in the River Ros, 0.31 – 0.45 mg/l in the Sula River and 0.17 – 0.3 mg/l in the southern Bug have been reported (Zhovinsky, 1979a). Some fluoride contents in different Ukrainian waters are presented in Table 8.4.

Table 8.4 Fluoride concentrations in Ukrainian waters (Gabovych and Minkh, 1979; Zhovinsky, 1979a)

Type of Water	Maximum Fluoride mg/l	Percentage of Sources Within Each Fluoride Concentration Range				
		< 0.5 mg/l	0.5 – 1.0 mg/l	1.0 – 1.5 mg/l	1.5 – 2.0 mg/l	> 2.0 mg/l
Surface	0.8	94	6	-	-	-
Well	5.6	67	19.4	8	3	3
Artesian Well	13.0	60	22	7	4	7

The distribution of fluoride in potable groundwaters in Ukraine is governed by a number of factors, including the following three basic controls:

- *The character of the water bearing horizon and chemical composition of water*
- *Relationship between the source of potable water and tectonically active fault zones*
- *The influence of anthropogenic factors, including the influence of mining and, to a lesser degree, agro-industrial practices*

The distribution of fluoride in the main water-bearing horizons of Ukraine varies with age. In general, with increasing depth and from north to south, Ca^{2+} and HCO_3^- contents decrease whereas Mg^{2+}, Na^+, K^+, Cl^-, F^- contents increase. Exceptions to this rule occur in the Poltava Region where localised high contents in shallower water-bearing horizons are caused by the presence of phosphatic rocks containing up to 3000 µg/g fluoride (Table 8.5 and Figure 8.5).

The water bearing horizons of Neogene deposits in the Odessa Region are characterized by significant variations in the contents of fluoride dependant on the distance from tectonically active fault zones (Table 8.5 and Figure 8.6). Within this one Region, the fluoride contents of the Sarmatian (N1S2) aquifer waters can vary from 0.05 mg/l to 7 mg/l close to fault zones around the towns of Arciz, Tarutino and Podgorny.

Mineral waters (1 – 2 g/l mineralisation) found at depths of 650 m are used therapeutically in Ukraine. These waters are alkaline with high Na+K+Cl-dominance and low Ca, Mg and HCO_3 contents. The most widely used alkaline mineral waters in Ukraine are the Mirgorod (0.1 – 0.9 mg/l fluoride), Artemovsky (2.8 – 6.4 mg/l fluoride) and Lugansk (2.8 – 6.4 mg/l fluoride) waters from the west of the country, waters at the health resorts of Morshin and Truskavets in Lvov Region and waters from Feodoshyn in the Crimea (Figures 8.2, 8.3 and 8.4).

Iodine is present in small quantities in the Kiev area only (< 0.4 mg/l) whereas bromine is found in all waters and ranges from 0.001 to 0.2 mg/l compared to the average content in world waters of 0.42 mg/l.

Table 8.5 Fluoride contents in various types of waters in Ukraine

Location	Aquifer	Minimum F mg/l	Maximum F mg/l	Average F mg/l	Number
Odessa~	Neogene	0.05	0.8	0.4	58
Kiev~	Quaternary	0.00	0.3	0.2	28
	Palaeogene	0.00	1.15	0.3	26
	Cretaceous	0.18	0.6	0.2	15
	Jurassic	0.06	1.1	0.4	18
	Proterozoic	0.2	0.9	0.4	6
Poltava~	Quaternary	0.00	3.2	0.6	37
	Palaeogene	0.00	8.8	2.8	53
	Cretaceous	0.18	2	1.1	21
Lvov~	Quaternary	0.00	0.9	0.2	39
	Cretaceous	0.00	3.8	0.9	20
Khar'kov*	Well Water	0.4	1.8	1.1	2
Dnepropetrovsk*	Well Water	0.12	2.7	1.0	34
Donetsk*	Well Water	0.05	1.5	0.5	36
Zaporozh'ye*	Well Water	0.04	2.2	0.7	36
Podgorny*	Tap water	0.71	7.1	2.5	13
Arciz*	Tap water	-	-	2.54	1
Izmail~	Tap water	-	-	0.24	1
Tarutino*	Tap water	-	-	1.14	1
Sosnovka^	Tap water	0.1	3.5	-	-

~ IGMOF data * Data from the present study

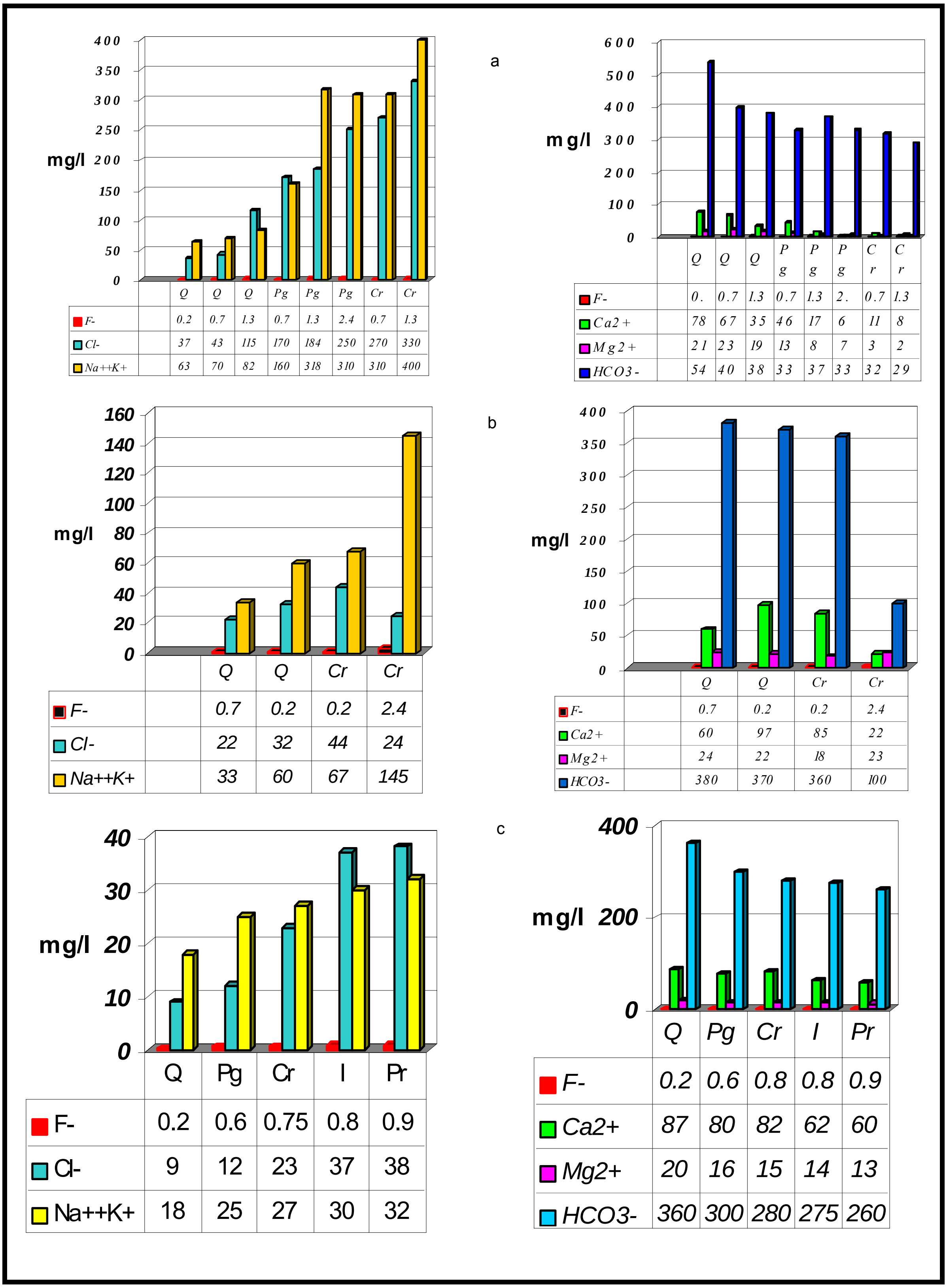
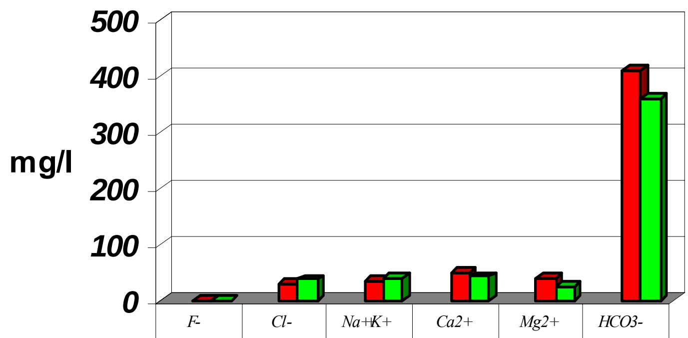


Figure 8.5 Average fluoride and major cation (Ca, Mg) and anion (Cl, Na+K, HCO_3) concentrations in groundwaters from Quaternary (Q), Palaeogene (Pg), Cretaceous (Cr), Jurassic (I) and Proterozoic (Pr) aquifers in a) Poltava b) Lvov and c) Kiev Regions (IGMOF data).



	F-	Cl-	Na+K+	Ca2+	Mg2+	HCO3-
N1S2	0.2	32	37	50	42	410
N1S2	0.7	38	40	43	25	360

Figure 8.6 Average fluoride and major cation (Ca, Mg) and anion (Cl, Na+K, HCO_3) concentrations in groundwaters from Neogene N1S2 aquifers in Odessa Region (IGMOF data).

As outlined in Chapter 3, geochemical speciation studies were applied to selected well water samples from the regional data sets in Poltava, Lvov, Kiev and Odessa using the PHREEQC (Parkhurst, 1995) modelling computer programme and thermodynamic constants from theWater4F database (Ball and Nordstrom, 1991). The results demonstrated that the dominant aqueous species (mobile forms) of elements in HCO_3-Na-Mg groundwater from Quaternary deposits of the Poltava Region were as follows (additional results are presented in Table 8.6):

calcium - Ca^{2+} , $CaSO_4$, $CaHCO_3$
sodium - Na^+
iron - Fe^{2+}, $FeCO_3$, $FeHCO_3$, $FeSO_4$
magnesium – Mg^{2+}, $MgSO_4$, $MgHCO_3^+$
potassium - K^+
fluoride - F^-, MgF^+
copper - $Cu(OH)_2$, $CuCO_3$, Cu (CO3)$_2$
zinc – $Zn(CO_3)_2$, $ZnCO_3$, Zn^{2+}, $ZnHCO_3$
lead - $PbCO_3$, $Pb(CO_3)_2$, $PbHCO_3$
nickel – $NiCO_3$, $Ni(CO_3)_2$

and the dominant mobile forms of elements in HCO_3-Na-Mg groundwater of Cretaceous deposits of the Poltava Region were:

calcium - Ca^{2+}, $CaSO_4$, $CaHCO_3$
sodium - Na^+
iron – Fe^{2+}, $FeHCO_3$, $FeCO_3$, $FeSO_4$
magnesium - Mg^{2+}, $MgHCO_3$ +, $MgSO_4$
potassium - K^+
fluoride - F^-, MgF^+, NaF^+
copper – CuCO3, $Cu(OH)_2$, $CuHCO_3$

zinc - $ZnCO_3$, Zn^{2+}, $Zn(CO_3)_2$, $ZnHCO_3$
lead – $PbCO_3$, $Pb(CO_3)_2$, $PbHCO_3$

In the Kiev Region, the mobile forms of chemical elements in HCO3-Ca-Na water from crystalline Proterozoic rocks were determined as follows:

calcium - Ca^{2+}, $CaHCO_3$, $CaCO_3$, $CaSO_4$
sodium - Na^+
iron - Fe^{2+}, $FeCO_3$, $FeHCO_3$, $FeSO_4$
magnesium - Mg^{2+}, $MgHCO_3^+$, $MgSO_4$
potassium - K^+
fluorine - F^-, MgF^+
copper - $Cu(OH)_2$, $CuCO_3$, $Cu(CO_3)_2$
zinc -$ZnCO_3$, $Zn(CO_3)_2$, Zn^{2+}, $ZnHCO_3$
lead - $PbCO_3$, $Pb(CO_3)_2$, $PbHCO_3$

In the Lvov Region, the mobile forms of elements in groundwater from Quaternary horizons were as follows:

calcium - Ca^{2+}, $CaSO_4$, $CaHCO_3$
sodium - Na^+
iron Fe (2) - Fe^{2+}, $FeHCO_3$, $FeCO_3$, $FeSO_4$
iron Fe (3) - $Fe(OH)_2$, $Fe(OH)_3$, $Fe(OH)_4$
magnesium - Mg^{2+}, $MgSO_4$, $MgHCO_3^+$
potassium - K^+

In the Odessa Region, water is abstracted from the Neogene aquifer horizon only and the dominant forms of mobile elements in HCO_3-Ca-Mg groundwater were:

calcium – Ca^{2+}, $CaHCO_3$, $CaSO_4$, $CaCO_3$
potassium - K^+
magnesium - Mg^{2+}, $MgHCO_3^+$, $MgSO_4$
fluoride - F^-, MgF^+, CaF^+
copper - $CuCO_3$, $Cu(OH)_2$, $CuHCO_3$, Cu^{2+}, $Cu(CO_3)_2$
zinc -$ZnCO_3$, Zn^{2+}, $Zn(CO_3)_2$, $ZnHCO_3$

whereas the dominant mobile forms of elements in HCO_3-Na groundwater were:

calcium - Ca^{2+}, $CaHCO_3$, $CaSO_4$, $CaCO_3$
potassium – K^+
magnesium - Mg^{2+}, $MgHCO_3^+$, $MgSO_4$
sodium - Na^+, $NaSO_4$
fluorine - F^-, MgF^+, NaF
copper – $CuCO_3$, $Cu(OH)_2$, $CuHCO_3$, Cu^{2+}

Table 8.6 Dominance of aqueous element species in selected waters in Ukraine calculated using the PHREEQC (Parkhurst, 1995) and Water4F (Ball and Nordstrom, 1991) programme and database

Proportion of Aqueous Element Species in Poltava (1), Lvov (2), Odessa (3) and Kiev (4) Regions, %									
Element Species	**1**	**2**	**3**	**4**	**Element Species**	**1**	**2**	**3**	**4**
Ca^{2+}	88.85	97.77	91.66	90.51	**F^{-}**	98.21	Not found	91.67	96.40
$CaSO_4$	6.23	1.41	2.10	1.53	MgF^{+}	1.18	Not found	7.56	2.35
$CaHCO_3^{+}$	3.80	0.67	5.11	5.09	CaF^{+}	0.04	Not found	0.72	1.16
$CaCO_3$	0.92	0.11	1.12	2.81	NaF	0.52	Not found	0.04	0.08
Na^{+}	99.49	99.89	99.60	99.56	**Cu^{2+}**	Not found	Not found	Not found	Not found
$NaSO_4^{-}$	0.27	0.05	2.50	0.06	$Cu(OH)_2$	41.29	Not found	33.15	55.99
$NaHCO_3$	0.23	0.03	0.30	0.30	$CuCO_3$	52.72	Not found	60.15	40.24
$NaCO_3^{-}$	0.02	0.002	0.02	0.05	$Cu(CO_3)_2^{2-}$	1.06	Not found	1.32	2.16
Fe^{2+}	64.31	91.49	Not found	52.30	$CuHCO_3^{+}$	2.65	Not found	3.36	0.89
$FeCO_3$	9.43	1.55	Not found	22.96	**Zn^{2+}**	31.24	Not found	27.90	11.47
$FeHCO_3^{+}$	21.22	4.87	Not found	22.73	$Zn(CO_3)_2^{2-}$	13.07	Not found	14.87	38.23
$FeSO_4$	3.95	1.16	Not found	0.78	$ZnCO_3$	38.10	Not found	40.04	41.91
$FeOH^{+}$	0.63	0.66	Not found	1.21	$ZnHCO_3^{+}$	12.97	Not found	15.14	6.28
Mg^{2+}	87.37	97.62	91.93	91.53	$ZnSO_4$	2.52	Not found	0.74	0.22
$MgSO_4$	7.25	1.67	2.50	1.83	$Zn(OH)_2$	0.48	Not found	0.36	0.95
$MgHCO_3^{+}$	3.46	0.62	4.74	4.75	**Pb**	Not found	Not found	Not found	Not found
$MgCO_3$	0.52	0.06	0.64	1.63	$PbCO_3$	92.33	Not found	Not found	88.82
K^{+}	Not found	99.91	99.88	99.90	$Pb(CO_3)_2^{2-}$	3.72	Not found	Not found	9.52
KSO_4^{-}	Not found	0.07	0.12	0.09	$PbHCO_3^{+}$	2.27	Not found	Not found	0.96
pH	7.65	7.10	7.60	8.00	pH	7.65	7.10	7.60	8.00
Types of waters: 1 — Cl-Na; 2 —HCO_3-Ca; 3 — HCO_3-Ca; 4 — HCO_3-Ca									

As indicated in Chapter 3, the biogeochemical activity of fluoride is not only dependent on the absolute concentrations of fluoride in solution but on the speciation and forms of fluoride present in the water. The speciation studies carried out in Ukraine, demonstrate that the concentration of the most biologically active form of fluoride, the free fluoride ion, decreases in waters with higher MgF^+ and CaF^+ contents. Speciation calculations indicate that the degree of ecological risk depends on the ratio

$$\text{Ratio K} = \frac{F^-}{MgF^+ + CaF^+} \quad \text{or more correctly} \quad \frac{F^-}{\sum \text{F-species}}$$

It should be noted, however, that these results are preliminary and further studies into the relationships between mobile element forms and disease outcomes are required before this information could be included in a risk assessment.

8.2.1.4 Dietary Information

Dietary surveys carried out by previous investigators have shown that the average content of fluoride in food varies from 0.54 to 1.6 mg across Ukraine. In Kiev the average is 0.78 mg, in Lvov 0.66 mg, in Odessa 0.74 mg and in Poltava 1.6 mg. Values in Poltava are higher because high-fluoride waters in the Region result in increased fluoride contents in bread.

Previous studies have also shown that in general, the average daily intake of fluoride from food is 0.5 – 1.1 mg and at concentrations of 0.4 mg/l, the average daily intake from water equals that of food whereas at 1 mg/l fluoride, the intake from water is 2 – 2.5 times that of food. Sea-food and foods grown in high-fluoride regions can contribute to the overall fluoride loading in the diet, however, in general, fluoride intake from water in Ukraine is 27% greater than that from food.

The daily requirement for water in Ukraine is approximately 3 l (45 ml per kg of body weight). Of this, 1 – 1.2 l (30 – 35%) is contained in foods, 1 – 1.5 l (33 – 50%) is digested in the form of liquids such as drinking water, tea, coffee, milk etc and 0.3 – 0.4 l (12%) is contained in fruit juices etc. In regions were fruit, vegetables, milk and dairy products (yoghurt etc) form a large component of the diet, the amount of water and other drinks consumed is generally less. In regions with high consumption of milk, fruit and vegetables, water intake is estimated at 1 l per day, in regions with limited vegetable, fruit and milk diets, water intake is estimated at 2 l per day and in hot regions water intake is estimated at 6 l per day. Based on these figures, at 1 mg/l water fluoride, daily dietary intake varies from 0.5 – 1.2 mg and increases markedly in hot climates with water contents between 1.6 and 6.6 mg/l to values above safe daily intakes. Intakes of between 0.1 and 0.15 mg per kg of body weight are thought to cause dental fluorosis.

Therefore, the severity and prevalence of the dental fluorosis are not only dependent on the fluoride concentrations in the water but on the climate and on general dietary intake. For example, in regions containing 4 mg/l fluoride in water, III and IV degree dental fluorosis rates were 25% lower in communities receiving adequate dairy products and vegetables than in other areas with poorer nutritional status. The favourable action of milk against the disease can be explained by the availability of proteins, Ca and vitamins and that less water and tea are drunk if more milk is consumed. Vegetables also have a protective effect as they contain water, and are a source of vitamins B1 and B2. Other investigators have shown that 2 – 46% of fluoride can precipitate out of boiling water during cooking, however, much of the fluoride is not lost and owing to evaporation, fluoride concentrations can rise during cooking. For example, raw carrots containing 0.22 mg/kg cooked in 1 mg/l and 4 mg/l fluoride waters had final fluoride contents of 0.83 mg/kg and 3.4 mg/kg respectively. The staple foods cabbage and potatoes show similar increases in fluoride content during cooking. Differences in the dietary and cooking habits of different regions explain, in part, different fluoride uptakes across Ukraine.

Based on dietary information, it is possible to approximate the daily amount of fluoride intake in different regions. Assuming an average daily food ration of 2 kg, a mean fluoride food content of 0.3 – 0.5 mg/kg and an average body weight of 70 kg, adult intakes of fluoride from food are estimated at 0.6 – 1 mg. In non-fluorosis-endemic areas, intakes of fluoride from food range from 0.7 – 1.2 mg. Total dietary intakes including water are estimated at 0.5 mg in fluoride-poor regions, 0.8 mg in fluoride-optimal regions and 1.2 mg in high-fluoride regions assuming water concentrations range from 0.1 – 10 mg/l.

There is also evidence to suggest that children fed formula milk made with water containing 1 mg/l fluoride obtain approximately 20 times more fluoride than breast-fed babies in regions with 0.1 mg/l fluoride in water assuming an average body weight of 1 kg.

Daily dietary intakes of Ca in Ukraine are low (400 – 500 mg) compared to recommended norms (1500 mg). This may, in part, explain the greater risk of fluorosis in areas where water fluoride concentrations are not excessively high. In a study of children in the Chernobyl region of Ukraine, (Zaichick et al., 1996) reported dietary Ca intakes of 259 - 1073 (mean 680) mg per day in subjects less than 7 years old whereas 7 - 18 year olds diets contained 420 - 427 (212) mg Ca per day. These ranges are much lower than comparable age groups in many developed countries 480 - 1210 (840) mg Ca per day and 692 - 1660 (1000) mg Ca per day respectively.

8.2.2 Risk Avoidance Maps

On the evidence above, biogeochemical experts in Ukraine have demonstrated that fluoride intake varies with climate (more in the south of the country due to greater water intakes in the hotter climate) and with the degree of physical activity of the person (Vanchanen, 1997). On the basis of the likely fluoride composition in drinking water and on daily intakes, four main biogeochemical fluoride provinces in Ukraine have been defined (Table 8.7). This scheme forms the basis for the final national risk avoidance map of Ukraine (Annex 10), however, it should be noted that these are general categorisations and there is much variability within regions as demonstrated for the results of the detailed study areas investigated during the present project. Where more detailed information for regions is available, this has been incorporated into the final risk avoidance map (Annex 10). It should also be noted that although the final map looks complete because it is based on regions rather than grid squares, over much of the territory of Ukraine the fluoride risks are unknown and the map presents the best estimates available at the current time. In general, risks of dental caries are highest in the north and west and far south of the country whereas optimal fluoride intakes are found in the centre-north, and south-east. High-fluoride risks occur in the centre-east in the regions of Poltava, Kirovograd, Dnepropetrovsk and Donetsk and locally in the Lvov, Odessa and Kiev regions.

Table 8.7 Daily fluoride intake from water and foodstuffs in the four fluoride biogeochemical provinces of Ukraine

Population Category	Normal Daily Intake of Fluoride in Ukraine mg	Daily Intake of Fluoride								Upper Safe Limit of Fluoride Intake mg
		First Province		Second Province		Third Province		Fourth Province		
Age of Children and Teenagers		mg	% of Normal Intake	mg	% of Normal Intake	mg	% of Normal Intake	mg	% of Normal Intake	
1 - 3 years	0.5	0.26	52	0.45	90	0.53	106	0.75	150	1.5
4 - 6 years	1	0.41	41	0.72	72	0.87	87	1.26	122	2.5
7 - 14 years	1.5	1.5	37	0.99	66	1.21	81	1.8	126	2.5
Adults Degree of Physical Activity/ Gravity of Work										
1	1.5	0.68	45	1.19	79	1.43	95	1.87	135	4
2	1.5	0.73	49	1.28	85	1.54	103	2.1	142	4
3	1.5	0.8	53	1.4	93	1.69	113	2.35	155	4
4	1.5	0.91	61	1.59	106	1.83	122	2.73	162	4
5	1.5	1.06	71	1.86	124	2.29	153	3.25	225	4

Province Category	Risk Category	Regions (Oblasts)
First Province	Very Low	Ivano-Frankovsk, Chernovszi , Lvov, Volyn, Rivno, Ternopol, Uzgorod
Second Province	Low	Zitomir, Chmelnisky, Vinnisza, Odessa, Nikolayev, Cherson, Crimea
Third Province	Normal	Lugansk, Khar'kov, Zaporozh'ye, Kiev, Cherkass, Chernigiv, Sumsky
Fourth Province	High + Very High	Poltava, Kirovograd, Dnepropetrovsk, Donetsk

Within these main provinces, four areas were selected for more detailed study as follows. The Lvov Region lies in the very-low fluoride biogeochemical province where daily fluoride intakes are generally below normal levels. However dental fluorosis occurs in this region associated with coal mining activities. The Odessa Region lies in the second province where fluoride intake is generally low, however, high-fluoride waters associated with tectonically active fault zones cause dental fluorosis in the population. In the third region around Kiev, water fluoride contents are generally within optimal levels but slight elevations in composition are associated with lignite mining. The fourth region of study is Poltava where high prevalence of dental fluorosis is associated with mineralised high-fluoride waters. Each of these regions is considered in detail as follows.

8.3 LVOV, ODESSA, KIEV AND POLTAVA STUDY REGIONS

8.3.1 Lvov Region

The Lvov Region in the very west of Ukraine lies in the first fluoride biogeochemical province with very low environmental fluoride as the contents in most waters in the Region range from 0 to 0.4 mg/l (Annex 10). The prevalence of dental caries in all ages of the population is 90% as a result of low fluoride contents in the water.

8.3.1.1 Hydrogeology

The water supply in the Region is derived from Cretaceous and Quaternary aquifers. Waters of the Cretaceous horizon are widely used for drinking and are found in a permeable marl, with ready infiltration of surface waters. These waters are HCO_3-Ca and SO_4-Ca dominated with mineralisation of 0.7 – 1.5 g/l. In the north, mineralisation is enhanced to 2.3 g/l due to increasing depth of the water bearing horizons. Good quality waters are found to a depth of 600 – 700 m in the north of the area, and to 300 – 400 m in the south. The contents of fluoride in waters of the Cretaceous horizon usually do not exceed 0.5 mg/l as these waters are HCO_3-Ca dominated, with low contents of Na and Cl. In only a few wells do the contents of fluoride reach 1 mg/l.

Some wells drilled into the Cretaceous horizon, have concentrations of 2 – 4 mg/l fluoride. These waters are Na-HCO_3-Cl-dominated with low Ca and Mg concentrations in a zone of rising mineralised waters associated with tectonically active faults in the Lvov-Volnysk coal basin. Quaternary deposits can be split into four main aquifer groups, sandy fluvio-glacial strata which contain the main drinking water resource, alluvial sediments in river basins, outwash plains and loess-loams, the latter contain very small water reserves. Quaternary horizons are mainly exploited in the north of the Region were fluvio-glacial sands and gravels contain low mineralised waters (0.4 g/l) at depths of 1 – 8 m. The concentration of fluoride in these HCO_3-Ca- and HCO_3-Na-dominated low Mg, Na and Cl waters does not exceed 0.3 mg/l. Data held by IGMOF (Table 8.5) indicate that in general the fluoride concentrations in waters from Quaternary horizons in the Region range from 0.0 – 0.9 mg/l and from Cretaceous horizons 0.0 – 3.8 mg/l.

There is a complex environmental situation in the centre of this Region. In the past, the mountains in this area were considered natural recreational sites, however, in recent years, adverse environmental impacts are associated with coal extraction in the Lvov-Volynsk basin. This basin is also tectonically active comprising a number of faulted blocks. The rocks and soils of the region are generally low in iodine and fluoride (0.12 – 0.20 µg/g) but are affected by the mining of sulphur and coal and contain increased contents of strontium (Sr), barium (Ba), Pb and Zn.

One of the most contaminated areas is the Chervonograd mining district in the centre of the basin. On an annual basis, 12 mines in this district produce 4 - 5 million tonnes of coal and

9.6 million tonnes of coal are dressed in the central processing plant in Chervonograd. The basic environmental problems associated with industrial activity in the basin are subsidence, formation of anthropogenic landscapes and the pollution of soils, groundwater, surface water and air. The settlements of Vilcina, Gorodishe, Mezhirechy, Chervonograd, Sosnovka and Sockal and the Rivers Western Bug, Solokia and Bolotny are the most polluted.

Within the district, human impacts on the hydrogeological environment result from coal mining activities and from the draining of land for agricultural use. Mining and subsidence have generated depressions of 500 – 700 m filled with lakes of 100 – 150 m diameter and flooding occurs in Sosnovka, Selca, Gornjak, Gorodishe, Mezhirechy, Volovin and Chervonograd. On average, subsidence over a 150km^2 area of the Lvov-Volynsk carboniferous basin ranges between 0.6 – 3.9 m.

Many substances pollute the environment in proximity to water abstraction sites. For example, in Sosnovka and Mezhirechy, heavy pollution of soils by As, Pb, Zn, Hg, Be, Co, Mo etc. is observed. Contamination by Co, Ni, Mo, V, Ba and Pb is worst in the vicinity of coal tips whereas contamination by As, Zn, Hg, P and Sb is dispersed between 1 – 3 km away and the maximum concentrations of mobile forms of Pb, Zn and Cr occur within 50 – 300 m of the dumps. The transfer ratio of pollutants from the coal tips to surrounding soils is highest for Pb (1.8), Ni (1.5) and Mn (1.3) whereas ratios for Zn, Cu and Cr are closer to 1.

Contamination is also associated with mine tailings-ponds and dressing-works and other industrial activities such as the Sockal synthetic fibres factory, the Novojavorsky sulphur plant and the Nikolaev cement factory. As a result of anthropogenic contamination, the contents of fluoride in potable water have risen from 0 – 0.4 mg/l (i.e. lower than normal standards) to up to 4 mg/l. For example, fluoride concentrations of up to 3.5 mg/l are found in the public drinking water supply mains of Sosnovka, Mezhirechy and Pravda and fluoride concentrations in Sosnovka have been increasing in recent years due to hydrogeochemical changes as a result of mining activity in the region (Table 8.8).

In addition to changes caused by mining activity, the contents of fluoride in water abstraction sites in the Chervonograd mining area are seasonally variable ranging from 0.1 to 2 – 2.5 mg/l and occasionally up to 3.8 mg/l. During the summer-autumn period the content of fluoride decreases to within normal ranges whereas contents of the major elements change insignificantly: Ca (16 - 34 mg/l), Na+K (212 - 310 mg/l).

Table 8.8 Examples of changes in element concentrations in Sosnovka groundwaters as a result of mining activity in the local environment

Element	Previous Concentrations mg/l	Recent Concentrations mgl	World Average in Water mg/l
Fluoride (F)	1	3.5	0.1
Barium (Ba)	0.129	1683	0.1
Manganese (Mn)	0.1	0.644	0.1
Cobalt (Co)	0.01	0.07	0.01
Phosphorous (P)	0.015	0.55	0.001
Cadmium (Cd)	0.003	0.007	0.001

Analysis of groundwaters carried out during previous studies from the mountainous regions of Sosnovka, located close to the Lvov-Volynsk carboniferous basin, demonstrate that waters in the area contain low Ca (35 mg/l) and very high Na (282 mg/l) Cl, K and Sr (5.95 mg/l). The minimum Ca contents were found in waters from the Cretaceous aquifer which contained 0 – 6 mg/l fluoride (Bezvushko, 1999).

The fact that deeper mineralised Na-fluoride waters occur below thin shallow aquifers containing good quality HCO_3-Ca-dominated waters was not taken into account during the construction of water abstraction wells in the Region. Wells penetrating the deeper mineralised waters were sunk and as a consequence dental fluorosis is now endemic in the area.

8.3.1.2 Exposure and Health

In 1994, 640 children were reported with dental fluorosis (prevalence rate 38 %) whereas in December 1995, the prevalence rate reached 68 %, the affected children all had extremely bad teeth and the number of cases in temporary teeth increased. By the end of 1995 and beginning of 1996 dental fluorosis and hypoplasia were widespread in children in Sosnovka and on a lesser scale in the cities of Chervonograd and Gornjak. The lined, mottled, chalk-like spots and erosive forms of dental fluorosis were reported in schoolboys living in Sosnovka but the destructive form of the disease was not evident. In 1996, 3203 children in Sosnovka, Chervonograd and Gornjak were suffering from fluorosis and of these, 271 had severe forms of the disease. The main areas affected are Sosnovka, Chervonograd, Lvov, Stryii and Drogobech (Figure 8.3).

The main cause of dental fluorosis in the Region is consumption of low-Ca, high-Na-K-Cl-Sr-fluoride drinking waters but is probably also influenced by the negative impact of the general environmental contamination in the Region on health. There is some evidence to suggest that dental fluorosis is exacerbated by atmospheric contamination around industrial plants, oil and gas wells and lead and zinc mines.

8.3.1.3 Geochemistry and Health Studies

During the present investigation, the links between high fluoride contents in drinking water and human fluorosis were examined in 138 children aged 11–15 years residing in the settlements of Sosnovka, Silyets, Zhovkva+Kulykiv and Peremyshlyany (Figures 8.3 and 8.7). These localities were chosen on the following grounds:

- Sosnovka town (SK) – fluorosis of varying degrees was revealed in children of this locality in 1994–1998. Analysis of samples taken at that time proved that the fluoride content in drinking water exceeded the recommended range (0.5 – 1.5 mg/l) by twice or three times (fluoride contents in water amounted to 4.5 – 6 mg/l). Previous research carried out in this town showed considerable deviations in the structural-functional state of bone tissue, dental enamel and periodontum. (Povorosnuk, 1998). People of Sosnovka use drinking water from a central supply.

- Silyets village (SL) – a locality 5 km from Sosnovka. People use drinking water from their own wells.

- Zhovkva town-Kulykiv village (ZK) – Zhovkva town is a regional centre and Kulykiv is an adjacent village. People use drinking water from their own wells.

- Peremyshlyany city (PR) – is a regional centre and people mainly use drinking water from their own wells.

To perform the analysis, 100 children (67 girls and 33 boys) were asked to collect water samples from their homes. The following numbers of water samples were collected in each location:

SK – 14 samples
SL – 39 samples
ZK – 31 samples
PR – 16 samples

Analysis of water samples was carried out at the Institute of Geochemistry, Ukraine by Prof E. Zhovinsky. The 100 children who provided water samples then underwent clinical, orthopaedic and stomatological examinations.

Epidemiological studies were executed using individual questionnaires based on the simplified evaluation scheme for stomatological status (WHO, 1986). This scheme is designed to record the condition of the dental enamel, the periodontum (gums), the mucous membrane of the oral cavity and any maxillofacial abnormalities. The questionnaires were also used to record the simplified index of oral cavity hygiene OHI-S (Green-Vermillion index), indices of gingivitis – PMA (papillary-marginal-alveolar), the Silness-Loe index of necessity of treatment (SPITN), and the Ramfiord periodontum index. The DMF-T index was also noted. The severity of fluorosis was determined according to the scheme of Gabovych and Ovrutsky (1969).

The structural-functional state of bone was examined by an ultrasound densitometry method, using the “Achilles+” densitometer (Lunar Corp., Medison, WI) on heel bones consisting of trabecular (spongy) bone tissue. The following measurements were carried out:

1. *The speed of the ultrasound signal through the bone (SOS, m/s), which is controlled by the bone density and flexibility*

2. *The broadband ultrasound attenuation (BUA, dB/MHz), which reflects bone density, the number of bone trabeculae and the dimensions and spatial orientation of the bone trabeculae.*

3. *Bone stiffness index (STF, %), which is calculated according to the formula (STF = 0.5 × ((nBUA + n SOS), where nBUA = (BUA – 50) : 0.75 and nSOS = (SOS - 1380) : 1.8). This index shows the state of spongy bone tissue compared to normal standards for 20-year-old adults.*

The advantages of this method are the high precision, use of non-ionising radiation, portability and speed of examination. Unlike photon and X-ray densitometry this method gives qualitative estimations of spongy bone tissue and its architecture (orientation and thickness of the trabeculae). Numerous researches have shown the benefits of this method in forecasting the risk of osteoporotic vertebrae and femoral fractures and the considerable possibilities of its application to estimate the effectiveness of osteoprotective methods in prophylaxis and treatment of osteoporosis.

Parametric (Student's t-test, one way analysis of variance (ANOVA)) statistical tests were carried out on the data using the "MS Excel-97 Statistics and Statgraphics 5.0" programmes.

Only one of the water samples collected and analysed during the present study contained fluoride which exceeded the WHO recommended upper limit of 1.5 mg/l. Fluoride contents in the remaining water samples were below this threshold (Table 8.9)

Table 8.9 Fluoride concentrations in waters related to disease prevalence in the four settlements under examination in the present study.

Water F mg/l	Dental Condition	Sosnovka n (%)	Silyets n (%)	Zhovkva + Kulykiv n (%)	Peremyshlyany n (%)
< 0.19	Caries	–	26 (66.7)	9 (29)	5(31.3)
0.20–0.50	Toothache	4 (28.6)	13 (33.3)	13 (33.3)	11(68.8)
0.51–0.99	Fluorosis I – II degree	9 (64.3)	–	–	–
1.0–1.5	–	–	–	–	–
> 1.5	Fluorosis I – II degree	1 (7.1)	–	–	–

n = number of children and water samples % = percentage of children and water samples
(only 22 of the Zhovkva+Kulykiv samples were included)

The majority of water samples from Sosnovka contain low fluoride reflecting the fact that in response to previous fluorosis problems, an alternative water source has been installed in the town in recent years. Two years ago, fluoride concentrations in water were 3 – 4 mg/l whereas currently drinking waters contain 1 – 2 mg/l fluoride. However, it is recommended that water fluoride contents should be monitored through time, during the February-March spring period in particular as some seasonal variations in high-fluoride contents have been reported during previous investigations.

During the present study, 4 (28.6%) children from Sosnovka had complaints of toothache in the basal third of their teeth whereas during examinations carried out in Sosnovka in 1997, 78% of children experienced this pain syndrome. Dental fluorosis (I–II degree) was revealed in 9 (64.3%) children of Sosnovka. The other localities did not show this pathology.

Indexes of the structural-functional state of bone tissue in children from each study area are given in Table 8.10. There were no significant differences between areas, except that body mass was considerably lower in children from Peremyshlyany.

Table 8.10 Structural-functional state of bone tissue in children from the four study areas.

Locality	Age years	Height m	Weight kg	SOS m/s	BUA dB/MHz	Stiffness %
Sosnovka	12.8±0.1	1.51±0.03	45.9±3.1	1565±6	104.8±2.1	87.9±2.7
Silyets	12.3±0.1	1.49±0.02	43.4±1.9	1574±4	104.8±1.4	90.4±1.6
Zhovkva	12.3±0.3	1.54±0.02	44.9±2.1	1569±6	104.1±2.0	88.7±2.8
Peremyshlyany	12.1±0.2	1.47±0.02	37.2±1.3	1582±6	97.9±1.7	87.9±2.0

Results of the stomatological examinations are given in Table 8.11. The DFM-T index is considerably increased in children of Zhovkva and Peremyshlyany indicating a higher prevalence of dental caries in these areas. In addition, changes in periodontum tissues were more pronounced in children residing in Sosnovka and Zhovkva.

Table 8.11 Dental indices for enamel and periodontum in children in each of the four study areas.

Locality	DMF-T absolute values	SPITN, grades	PMA %	OHI-S, grades	IR, conv. unities
Sosnovka	2.45±0.77	0.50±0.13	18.7±5.1	0.74±0.15	0.56±0.13
Silyets	2.63±0.32	0.33±0.07	13.3±3.2	0.63±0.15	0.38±0.09
Zhovkva	6.69±0.89	0.51±0.12	20.8±4.5	0.84±0.20	0.58±0.12
Peremyshlyany	5.06±0.87	0.33±0.16	10.5±5.4	0.43±0.21	0.24±0.14

DMF-T = sum of decayed, filled and missing teeth
SPITN = index of necessity of periodontum tissue treatment
PMA = index of gingivitis
OHI-S = index of oral cavity hygiene (index of Green-Vermillion)
IR =Ramfiord Index

In summary, despite the recent provision of waters with lower fluoride contents in Sosnovka, dental fluorosis (I and II degree) is still prevalent (64.3%) in this town. No evidence of dental fluorosis was found in Zhovkva-Kulykiv, Silyets and Peremyshlyany.

No evidence of changes in the structural functional state of bone tissue as a result of high fluoride exposure was evident from the present study.

8.3.2 Odessa Region

The Odessa Region in the very south of Ukraine lies in the second fluoride biogeochemical province with low environmental fluoride (Annex 10).

8.3.2.1 Hydrogeology

The main water-bearing horizon in this Region is the Neogene Sarmatian aquifer comprising inter-layered clays, sandstones, marls and limestones, which are horizontally and vertically inconsistent. The depth of this horizon ranges from 20 – 30 m in the north and 250 – 500 m in the south. These waters are generally HCO_3-Mg, HCO_3-Na, HCO_3-Ca, SO_4-Na dominated with mineralisation of 0.3 – 1.1 g/l. In the centre of the region, the water quality is good whereas close to the Black Sea coast (50 – 100 km) the mineral content of these waters increases due to saline intrusion. SO_4-Na waters with low Ca, Mg, HCO_3 and high Cl contents are indicative of saltwater ingression in the coastal zone. In Odessa district, mineralisation ranges from 0.5 – 0.9 to 1.4 g/l whereas on the coast, values of 1.4 – 1.9 g/l are reported in Cl-dominated waters. In Saratov district high mineralisation values of 1.7 – 2.3 g/l are found in SO_4-Na-Cl-dominated waters and waters with low mineral contents are also scarce in the Nikolayev district.

The contents of fluoride in waters of the Odessa Region generally do not exceed 0.5 mg/l. Wells abstracting Cl-Na-dominated waters on the Black Sea coast contain 0.1 mg/l fluoride. These waters also contain high SO_4 and HCO_3 contents and are not chemically characteristic of most natural waters. In the coastal zone, HCO_3-Mg and HCO_3-Ca dominated waters with low Na contents contain 0.45 mg/l fluoride.

In contrast to the generally low concentrations of fluoride in Sarmatian waters across the region, high fluoride waters containing up to 7 mg/l are associated with a tectonically active fault zone in the south of the region around Tatarbunary, Arciz and Tarutino. These waters are Na-Cl dominated with low Ca and Mg contents rising from depth in the fault zone.

8.3.2.2 Exposure and Health

As indicated above, the fluoride concentrations in waters from Quaternary Sarmatian aquifers generally range from 0.05 to 0.8 mg/l (Table 8.5). These low concentrations result in dental caries in the local population. Previous studies have shown that 35% of 7 year-olds, 65% of 10 year-olds and 85% of 15 year-olds suffer dental caries and disease prevalence is rising. The prevalence of caries in the Region is exacerbated by poor social and environmental conditions such that the propensity to disease is not only a function of exposure but is also determined by the ability of the individual to resist disease. Thus the general strength and protection of the enamel and dentin are important controls on the severity of dental caries. For example the use of fluoridated toothpaste reduces the risk of dental caries but is less likely to be applied in poor regions (Money and Ivanov, 1996).

Although the Region as a whole is classified as a low-fluoride area, endemic dental fluorosis occurs in the south of the Region and prevalence rates of 90% have been reported in Tatarbunary and Tarutino (Figures 8.3 and 8.8).

8.3.2.3 Geochemistry and Health Studies

During the present study, tap-water chemistry and human dental status in the high-fluoride fault zone of Odessa Region were examined in more detail. Analysis of fluoride concentrations in tap-water samples revealed 2.54 mg/l in Arciz, 1.14 mg/l in Viklovo-Tarutino, 0.24 mg/l in Izmail and 0.71 – 7.1 mg/l in the village of Podgorny (Figure 8.8 and Tables 8.12 and 8.13). High fluoride concentrations in Podgorny waters show a strong correlation with proximity to the fault zone.

Table 8.12 Chemistry of tap water samples (n = 1) in the towns of Arciz, Vilkovo-Tarutino and Izmail, Odessa Region

Element	Arciz	Vilkovo-Tarutino	Izmail
	mg/l		
Na	526.05	20.76	44.48
K	5.29	2.64	2.31
Ca	8	43.2	65.6
Mg	4.9	17.64	34.3
Fe	0.34	0.21	0.21
CO_3^{2-}	36	-	-
HCO_3^-	1037	158.6	271.45
SO_4^{2-}	216	57.6	108
Cl^-	3.55	6.75	8.17
Mn	0.29	0.0005	0.0008
Ni	0.0014	0.0004	-
V	0.0073	0.0007	0.0008
Cr	0.0145	0.0023	0.0008
Mo	0.0145	0.0012	0.0008
Zr	0.087	0.0092	0.0084
Cu	0.0073	0.0023	0.0004
Pb	0.0044	0.0014	0.0013
Ag	<0.0014	<0.0002	-
Bi	0.0029	0.0007	0.0013
Zn	-	0.069	-
F	2.54	1.14	0.24

Table 8.13 Fluoride contents, pH and proximity to fault zone of tap waters from Podgorny Village, Odessa Region

Sample Number	F mg/l	pH	Degree of Proximity to Tectonic Fault Zone
1	0.75	8.7	
2	3.45	8.89	++
3	1.9	8.28	+
4	1.49	7.92	+
5	1.16	8.92	
6	2.45	8	++
7	1.42	9.1	+
8	7.13	8.25	+++
9	2.16	8.04	++
10	0.87	8.85	
11	1.49	8.45	+
12	0.71	7.71	
13	7.13	7.31	+++

97 adolescents in the town of Arciz and 28 in the adjacent village of Podgorny underwent dental examinations using the same methods described in previous sections of this report.

Dental caries (in permanent teeth) prevalence in adolescents of Arciz town was 37.11% its severity (based on the DFM-T index) was 0.88±0.15. Corresponding values in Podgorny village were significantly lower, 14.29 % and 0.25±0.13, respectively.

Periodontal injuries, mainly gingivitis, were diagnosed in 40.21 % of the adolescents examined in Arciz and in 64.29 % of Podgorny subjects. The papillary-marginal alveolar index (PMA) showed a greater degree of periodontal injuries in Podgorny subjects than in Arciz (Table 8.14)

Table 8.14. Prevalence and degree of catarrhal gingivitis in adolescents from the Arciz and Podgorny study areas.

Catarrhal Gingivitis Index	Arciz % of Adolescents, n = 97	Podgorny % of Adolescents, n = 28
Minor	84.62	33.33
Medium	10.26	27.78
Severe	5.12	38.89

The average number of injured dental sections per child according to the SPITN index was 0.87±0.14 in Arciz and 2.00±0.41 in Podgorny. 62.89% of adolescents in Arciz and 35.71% in Podgorny showed no evidence of bleeding gingivae or tartar. However, 17.91 % of Arciz adolescents and 29.42 % in Podgorny presented with injuries to all 6 dental sections.

69.07 % of Arciz adolescents suffered from maxillodental anomalies, whereas in Podgorny the prevalence was somewhat lower (60.71%) (Table 8.15).

Table 8.15 Prevalence and degree of maxillodental anomalies in adolescents from Arciz and Podgorny study areas

Maxillodental Anomalies	Arciz	Podgorny
	% of Adolescents n = 97	% of Adolescents n = 28
Minor – incorrect location of teeth, extra teeth and adentia	56.72	35.29
Medium – high density, minor gingivae and occlusion	25.37	35.29
Severe – pronounced pathological occlusions	17.91	29.42

The prevalence of dental fluorosis in Arciz adolescents was 92.78 % and in Podgorny 85.71 %. During examinations, lines, mottling, chalk-like-spots and erosive forms of dental fluorosis were recorded ((Patrikyeyev (1958) classification). The destructive form of dental fluorosis was absent in the study area (Table 8.16).

Table 8.16 Prevalence of various dental fluorosis forms (Patrikyeyev (1958) classification) in adolescents from Arciz and Podgorny, Odessa Region.

Locality		Form of Dental Fluorosis				
		Lined	Mottling	Chalk-like-spots	Erosive	Destructive
Arciz	Number	30	41	13	6	0
	%	33.33	45.56	14.44	6.67	0
Podgorny	Number	4	13	5	2	0
	%	16.67	54.17	20.83	8.33	0

In terms of dental fluorosis severity, I and II degree fluorosis were the most prevalent. However, a significant proportion of adolescents in Podgorny suffered from III and IV degree dental fluorosis (Tables 8.17 and 8.18).

Table 8.17 Prevalence and severity of dental fluorosis (Gabovych and Ovrutsky (1969) classification) in Arciz adolescents

Degree of Dental Fluorosis		Dental Category				
		General	Upper Incisors	Lower Incisors	First Molars	Premolars and Other Molars
0	Number of subjects	7	17	29	25	14
	%	7.22	17.53	29.90	25.77	14.43
I	Number of subjects	55	44	46	49	46
	%	56.70	45.36	47.42	50.52	47.43
II	Number of subjects	24	26	17	17	30
	%	24.74	26.89	17.53	17.53	30.93
III	Number of subjects	7	7	4	3	4
	%	7.22	7.22	4.12	3.09	4.12
IV	Number of subjects	4	3	1	3	3
	%	4.12	3.09	1.03	3.09	3.09
Total	Number of subjects	97	97	97	97	97
	%	100	100	100	100	100

Table 8.18 Prevalence and severity of dental fluorosis (Gabovych and Ovrutsky (1969) classification) in Podgorny adolescents

Degree of Dental Fluorosis		Dental Category				
		General	Upper Incisors	Lower Incisors	First Molars	Premolars and Other Molars
0	Number of subjects	4	5	7	5	4
	%	14.28	17.86	25.00	17.86	14.29
I	Number of subjects	8	10	13	14	8
	%	28.57	35.72	46.43	50.00	28.57
II	Number of subjects	6	4	5	5	10
	%	21.43	14.28	17.86	17.86	35.71
III	Number of subjects	5	5	1	2	2
	%	17.86	17.86	3.57	7.14	7.14
IV	Number of subjects	5	4	2	2	4
	%	17.86	14.28	7.14	7.14	14.29
Total	Number of subjects	28	28	28	28	28
	%	100	100	100	100	100

Prevalence of injuries among premolars and other molars was 85.57 % in Arciz subjects and 85.71 % in Podgorny and the severest forms of injury also affected these teeth. The prevalence of fluorosis injury decreased in the following order:

upper incisors (Arciz 82.47 % and Podgorny 82.14 %) >
first molars (Arciz 74.23 % and Podgorny 82.14%) >
lower incisors (Arciz 70.10 % and Podgorny 75.00 %)

The groups of teeth most commonly affected by dental fluorosis injury were premolars and other molars, which are formed during the 2^{nd} and 3^{rd} year of life. This suggests that drinking waters with elevated fluoride contents influence the maxillodental system immediately after birth and breastfeeding.

In summary, although water fluoride contents in Odessa Region in general are low and the Region is classed as low-fluoride risk, high-fluoride waters associated with fault zones are a problem in the Arciz-Podgorny-Tarutino area in the south. This study has demonstrated that whereas dental caries prevalence rates are low in Arciz and Podgorny, (37.11 % and 14.29 % respectively) very high prevalence of dental fluorosis 85.71 - 92.78 % in adolescents result from the consumption of high-fluoride drinking water and this area is highlighted as high risk in the final assessment scheme (Annex 10).

8.3.3 Kiev Region

The Kiev Region in the north of Ukraine lies in the third fluoride biogeochemical province with optimal environmental fluoride (Annex 10).

8.3.3.1 Hydrogeology

Drinking water horizons are found in Quaternary, Cretaceous, Jurassic and Proterozoic strata and fracture-permeability waters of the Achaean Ukrainian crystalline basement. Waters from the fractured Achaean basement have low productivity, flow rates reach a maximum of 0.5 – 1 m^3/hour. These waters are HCO_3-Ca dominated with mineralisation of 0.5 – 1.0 g/l. Late Proterozoic sandstones and interbedded clays increase in thickness from south to north. Waters from these horizons are generally HCO_3-Ca dominated and contain 0.4 – 0.7 mg/l fluoride and mineral contents are generally low (20 – 80 mg/l), only HCO_3 contents reach a maximum of 460 mg/l. In the western and eastern margins of the Region, fluoride contents are lowest (0.25 mg/l) whereas in the south, highest fluoride contents of 0.7 mg/l are reported.

Jurassic sandy-gravel aquifers are capped by a layer of impermeable clays resulting in piezometric heads of 500 – 600 m in waters in this horizon, which forms the main drinking water supply for the cities of Kiev and Poltava etc. The waters are HCO_3–Ca dominated with 0.4 – 0.9 g/l mineralisation. Increased mineralisation is found in groundwaters in isolation in sandy layers influenced by saline waters associated with faults. The fluoride concentration in Jurassic aquifer waters ranges from 0.37 to 1.3 mg/l. Fluoride contents of 0.37 – 0.6 mg/l are found on the margins of the Region where the majority of water is abstracted and concentrations rise to 1 mg/l in the centre of the region. Hydrochemical studies have shown that the Ca content of the water controls the amount of fluoride in solution. At Ca concentrations of 100 mg/l, waters contain 0.48 mg/l fluoride, at 48 mg/l Ca, waters contain 1 mg/l fluoride. The Na composition also exerts a control on the fluoride content in solution. Higher fluoride contents are associated with increased mineralisation, alkalinity, Cl-Na contents and lower Ca and Mg contents in these waters.

The water bearing horizons of Cretaceous age lie unconformably over Jurassic clays and comprise clays, sandstones and fissured marls. Waters in Cretaceous horizons are HCO_3-dominated with mixed cation compositions and mineralisation levels of 0.3 – 0.8 g/l. Water-bearing horizons are constrained by impermeable Jurassic clays below and poorly permeable fractured Cretaceous marls above. The poor permeability of the Cretaceous marls inhibits the penetration of surface waters and most water resources are located close to the top of this unit and are most abundant in valleys and rivers were the unit is exposed

In areas of higher topography, where the unit is overlain by other deposits, water resources are limited. In general these waters contain low (0.18 – 0.4 mg/l) fluoride. Only in wells located in the centre of the Dnepropetrovsk-Donetsk basin, is there a marked rise in fluoride concentrations (2.0 – 2.5 mg/l) associated with Cretaceous phosphatic deposits. In general, Cretaceous waters contain less than 1 mg/l fluoride and are widely used for drinking.

Palaeogene sandstone, clay and kaolinite deposits overlie the Khar'kov clays and form two aquifer layers in the Kiev Region. HCO_3-Ca waters with low mineral contents and 0.2 – 1.0 mg/l fluoride predominate.

Quaternary alluvial deposits do not contain significant groundwater resources in this Region. However, fluvio-glacial deposits are exploited for drinking water. These waters are generally HCO_3-Ca or HCO_3-Mg dominated with low mineral contents (0.2 – 0.4 g/l) and high infiltration of meteoric waters. The concentrations of fluoride generally do not exceed 0.5 mg/l. However, increased concentrations can result from the agricultural use of fertilisers and land improvements (drainage).

In general terms, the contents of fluoride in groundwaters is consistent in the region and varies from 0 to 1.5 mg/l. Data held by IGMOF (Table 8.5) indicate that fluoride contents in the various aquifers range from 0.0 – 0.3 mg/l in Quaternary deposits, 0.0 – 1.15 mg/l in Palaeogene sediments, 0.18 – 0.6 mg/l in Cretaceous strata, 0.06 – 1.1 mg/l in Jurassic rocks and 0.2 – 0.9 mg/l in Proterozoic sediments. The lowest concentrations of fluoride in drinking water occur in Tarashansky and Volodarsky districts (average < 0.12 mg/l) whereas the highest concentrations (average 1 mg/l) are found in Stavishe, Dimer and Jagotinsky districts.

8.3.3.2 Exposure and Health

Approximately 35% of children and 25% of adults consume water with less than the recommended 0.5 mg/l fluoride for caries prevention. In areas where water concentrations are less than 0.7 mg/l fluoride, 90% of the population suffer dental caries whereas between 0.7 and 1 mg/l fluoride, dental caries is not present but I degree fluorosis (chalky-white patches) is found in 4% of the population.

As a result of the Chernobyl nuclear accident, 30 1000 hectares of northern Ukraine are polluted with radiogenic Caesium (Cs)-137 (average 1 curie per km^2). The prevalence of diseases (including dental caries and fluorosis) in children is enhanced in the Kiev Region as a result of the contamination. In Polesky district (Cs-137 0.2-91.3 curie per km^2) the prevalence of dental caries has increased 2.4 times, in Ivanovsky district (Cs-137 0.3-4.2 curie per km^2), 90 % of the population suffer dental caries. In Kiev district, (Cs-137 0.5-1.0 curie per km^2), the levels of dental caries are not a problem. In districts polluted with radioelements there is an augmentation of Cl and reduction of Si and Mg in dental enamel. Chlorine and K concentrate in the enamel surface, Ferri lactas and Al in the tooth-root and Na and Mg in the dentin.

Although the majority of water fluoride concentrations in Kiev Region are low, localised high concentrations (1 – 2 mg/l) associated with the lignite mining industry occur in Dimer and Stavishe districts. Fluoride ingested from potable water and inhaled in air in these regions causes mild forms of dental fluorosis. These districts have been highlighted as high risk in the final assessment scheme whereas the rest of Kiev Region is categorised as optimal or low fluoride intake (Annex 10).

8.3.4 Poltava Region

The Poltava Region in the east of Ukraine lies in the fourth fluoride biogeochemical province with high environmental fluoride (Annex 10).

8.3.4.1 Soils

The main soil types found in the region are forest-steppe, podzols (brown soils) and Azov back soils and arid-steppe (chestnut soils) comprising loams, sand, boulder clay, peat, sandy-clays, heavy-loams and clays. Previous studies have demonstrated that soil fluoride contents in south-west Ukraine range from 15 – 79 µg/g (average 36 µg/g) and that the content decreases with depth as organic-rich surface horizons contain highest fluoride contents (Zhovinsky, 1981b). The distribution of fluoride in organic-rich soils of the Poltava Region is outlined in Table 8.19. In general, fluoride is concentrated in the fine soil fractions but relationships with organic matter content are less clear.

Table 8.19 Distribution of fluoride in organic soils in Poltava Region

Soil Parent Material	F µg/g (Total Soil)	OM %	Mineral Composition	F µg/g in Size Fractions	
				0.01 - 0.001 mm	< 0.001 mm
Limestone	50	95	Quartz, zeolite, montmorillonite hydromica	235	400
Limestone	100	83	Quartz, hydromica	140	400
Dolomite	40	84	Hydromica, chlorite. quartz, feldspar, dioctaedron	120	280
Marl	90	66	Dioctaedron, hydromica, quartz, feldspar	180	317
Limestone	40	98	Quartz, feldspar, hydromica, chlorite, kaolinite, montmorillonite	60	140
Clay-Marl	150	34	Quartz, zeolite, montmorillonite, hydromica	100	262
Chalk	50	97	Quartz, adularia hydromica, quartz montmorillonite, kaolinite	70	275
Marl	90	68	Dioctaedron, hydromica, chlorite, quartz, feldspar	200	380

OM = organic matter

8.3.4.2 Hydrogeology

Poltava lies within the Dneprovsk-Donetsk artesian basin. In superficial sedimentary deposits (< 400 m depth) the water-bearing horizons occur in Cretaceous, Jurassic and Cainozoic (Palaeogene - Quaternary) strata. Good quality water is also derived from fractures in the underlying crystalline Ukrainian Achaean basement from granites and overlying sandy sediments. Exploitation of waters of this type is mainly confined to granites and gneisses of < 100 m depth.

The Cretaceous aquifer comprising interbedded clays and sandstones overlies Jurassic clays. Fluoride concentrations in waters from this horizon reach 2 mg/l reflecting mixing (caused by seepage via fractures in chalk deposits) with overlying high-fluoride waters in Palaeogene aquifers. These waters are generally HCO_3-Na and Cl-Na dominated.

The most important drinking water horizon in the region is the Palaeogene Buchak-Kaniv aquifer, which forms the Buchak hydrogeological fluoride province with groundwater concentrations ranging from 2.5 – 8 mg/l. The strata comprise glauconitic sands and clays overlying impermeable clays and marls. The thickness of the deposits ranges from 20 – 30 m to 80 – 100 m. The high concentrations of fluoride in relatively shallow groundwaters relate to the presence of fluoride-bearing phosphates in recent sediments and long residency times of water in this horizon. Fluoride concentrations vary from < 0.7 mg/l in the north increasing in the centre of the Dneprovsk-Donetsk basin to 5.6 – 9 mg/l. Fluoride concentrations decrease towards the southern margin of the basin and are directly related to the depth of burial of the aquifer horizon, which is greatest in the centre of the basin. Maximum fluoride concentrations in the centre of the basin correspond to highest fluoride contents in underlying Cretaceous (2.5 mg/l) and Jurassic (1.3 mg/l) strata as a result of water mixing between these horizons. In contrast to the Buchak, groundwater in horizons above and below this aquifer contain on average 0.8 mg/l fluoride The chemical composition of waters in this horizon varies but is characterised by low Ca and Mg and high Cl, Na and alkalinity, especially in the centre of the basin. Mineralisation levels increase from north to south, in the northwest of the Region, mineralisation levels of 0.5 – 0.9 g/l are reported in HCO_3-Na dominated waters and in the east and northwest of the territory, mineralisation levels rise to 2 g/l in Na-Cl dominated waters.

Due to the ready accessibility of these shallow deposits (120 – 180 m depth), and high production rates from this aquifer, the Buchak horizon is extensively exploited in the Region over an area of 34 000 km^2 containing 2 million people. Drilling of wells to deeper Cretaceous and Jurassic horizons is expensive in comparison. Although the maximum concentration of fluoride in well waters from this horizon is 8.8 mg/l, these waters are mixed with waters from other sources in the mains system before supply to the public resulting in maximum concentrations at tap of 4 mg/l

The Quaternary deposits comprise loess, loams, alluvial and fluvio-glacial sediments and reworked aeolian sands. Waters from these horizons generally contain low (< 1 mg/l) fluoride.

Water quality is generally good in upper water-bearing horizons but saline and mineral waters occur at depth and are used for industrial processing. The Volno-Podolsk artesian sub-basin is characterized by water-bearing horizons in Palaeozoic, Mesozoic and Cainozoic strata. Good quality waters occur up to depths of 600 – 700 m in the north of the basin and up to 300 – 400 m depth in the south. In the Prichernomorskij artesian sub-basin good quality waters are distributed in Cainozoic deposits, however, some salination of thin water-bearing horizons occurs in the south of the basin where the ground has been disturbed. In general, good quality drinking waters occur up to depths of 200 – 250 m in the north and 100 m in the south of the basin.

Data held by IGMOF (Table 8.5) indicate that fluoride concentrations in waters in Quaternary aquifers range from 0.0 – 3.2 mg/l, in Palaeogene sediments from 0.0 – 8.8 mg/l and in Cretaceous aquifers from 0.18 – 2 mg/l whereas in the Region as a whole, fluoride concentrations ranging from 0.5 – 18 mg/l have been reported in previous studies.

8.3.4.3 Industrial Sources

In addition to naturally elevated levels of fluoride in the Region, fluoride concentrations are enhanced by industrial pollution. The Region contains many mineral deposits including oil and gas, peat, coal, bulk minerals (basalt, diorite, andesite and amphibolite) and raw materials (salt, brick-clay fireclay, silica sand, limestone, chalk and bentonite clays) all of which are exploited. In Mirgorod and Karlovka the fluoride concentrations in the Buchak-Kaniv water-bearing horizon are 3.6 mg/l and 7 mg/l respectively associated with textile, manufacturing and engineering industries. In other localised areas the contents of fluoride increase up to 2 mg/l, for example in Ivanovsky district, associated with mining, chemical, textile, fur, shoe and wood industries.

8.3.4.4 Exposure and Health

Previous research in the Poltava Region has demonstrated the links between fluoride concentrations in the water and the prevalence of dental fluorosis (Table 8.20).

Table 8.20 Relationships between fluoride content in water and fluorosis prevalence in Poltava Region from previous studies

Water F mg/l	Dental Fluorosis Prevalence %	Severity (Gabovych, 1950)
1.4	20	I degree
1.8	30	I + II degree
3.4 – 3.5	100	III degree
2 – 5	100	III degree
> 5	100	III +IV degree in all teeth

The onset of dental fluorosis is thought to occur following exposure over a minimum of 9 – 12 months to water containing 4 mg/l fluoride or after 12 – 18 months to water containing 1.5 – 2.0 mg/l fluoride at estimated intakes of 0.075 mg per kg body weight (Nikolishyn, 1995).

Studies have also shown that 95% of fluoride retained in the body resides in the bones and teeth resulting in structural bone changes in the population of the Region. In populations consuming water with 2.2mg/l fluoride over 10 years, arthritis and osteoarthritus are widespread in several locations. Fluoride also interferes with the iodine metabolism causing inhibited thyroid function and gastro-intestinal, liver, endocrine and nervous system disorders have also been reported in the Region (Shylkina, 1997a+b).

High fluoride waters and endemic dental fluorosis occur throughout the region, which is categorised as high risk in the final assessment scheme (Annex 10). However, highest water fluoride concentrations and dental fluorosis hotspots are associated with fault zones between Mirgorod and Poltava and this area has been highlighted as very high risk in the final national risk assessment scheme (Annex 10).

8.3.5 Risk Avoidance Maps

The datasets incorporated into the final risk avoidance maps of the four detailed study regions are listed in Table 8.1. The locations of tectonically active fault zones were included in the Project Partner GIS (Country.apr) for background information only (Figures 8.7 – 8.10). The locations of known fluorosis hotspots in each region were included in the risk assessment (Figures 8.7-8.10). Dental fluorosis and dental caries prevalence information collected from previous studies and during the present geochemistry and health investigations (Table 8.21) were also incorporated into the GIS (Figures 8.7 – 8.10), however, only dental fluorosis prevalence information was included in the final risk assessment. Dental caries prevalence was included for information only.

Although localised water chemistry data were collected during previous and current health investigations (Table 8.21) this information is included in the GIS for information only. The final risk assessment is based on the systematic regional groundwater chemistry data sets for Lvov, Odessa, Kiev and Poltava held by IGMOF as outlined in Table 8.1. Groundwater chemistry data for the main drinking water horizons in each Region were combined in the GIS so that problem waters from any possible source would be highlighted (Figures 8.6 – 8.10).

At the Regional level the datasets were of sufficient sample density to adopt a grid-square approach to the presentation of the final risk avoidance maps according to the schemes outlined in Tables 8.22 and 8.23. A grid size of 5 km^2 commensurate with the sample density of the groundwater data sets was selected and in each grid square, the water fluoride content and fluorosis incidence/fluorosis hotspot data were combined with water supply information (water is not fluoridated in Ukraine) to produce the final risk maps (Annex 11 - 18). It should be noted, however, that over significant areas of the Regions, the distribution of water chemistry and fluoride incidence information was insufficient to assess fluoride risk.

Table 8.21 Water fluoride, dental fluorosis and dental caries information for Lvov, Odessa, Kiev and Poltava Regions collated from previous studies and the present project

Region	Location	Water F mg/l	Dental Fluorosis Prevalence %	Dental Caries Prevalence %
Lvov	Sosnovka	0.2 - 3.5*	71.4*	0
	Silyets	0 - 0.5*	0	66.7*
	Zhovkva + Kulykiv	0 - 0.5*	0	29*
	Peremyshlyany	0 - 0.5*	0	31.3*
	Chervonograd	3 - 3.8*	38 – 68^	-
	Lvov	3 - 3.8*	38 – 68^	-
	Stryii	3 - 3.8*	38 – 68^	-
	Drogobech	3 - 3.8*	38 – 68^	-
Odessa	Odessa	0.01 - 0.6*	-	35 – 85^
	Arciz	2.54*	92.78*	37.11*
	Tatarbunary	2 - 7*	90^	-
	Tarutino	1.14*	90^	-
	Podgorny	2.5 – 7.1*	85.71*	14.29*
	Izmail	0.24	-	-
Kiev	Kiev	0.7 - 1.0*	4	0^
	Kiev	< 0.7*	-	90^
	Dimer	0 - 3*	Unknown	-
	Dimer	1 – 2^	Unknown	-
	Dimer	0 – 1^	-	30^
	Ivanovsky	-	-	90^
	Polesky	-	-	90^
	Stavishe	1 – 2^	Unknown	-
	Stavishe	0 - 3*	Unknown	-
	Stavishe	0 - 0.12^	-	30^
	Tarashansky	0 - 0.12^	-	30^
	Volodarsky	0 - 0.12^	-	30^
	Jagotinsky	1 – 2^	Unknown	-
	Girnik	3 - 3.8^	38 – 68^	-
	Buchak	3.4 - 3.5^	100^	-
Poltava	Poltava	1.4^	20^	-
	Poltava	> 5^	100^	-
	Poltava	1.8^	30^	-

^ Data from previous studies * Data from the present study

Table 8.22 Dental caries risk assessment scheme for Lvov, Odessa, Kiev and Poltava Regions, Ukraine

Caries Risk						
Location	**Phase 1**		**Phase 2**		**Final Risk**	**Assessment Rationale**
	Ground water F mg/l < 0.5	**Potential Risk**	**Water Fluoridated**	**Potential Risk**		
Lvov Odessa Kiev Poltava	No	Low	No	Low	Low	Fluoride content is sufficient
	Yes	High	No	High	High	Fluoride content is insufficient
	Yes and No	High/low			High/ low	Water has low fluoride content but higher fluoride water is available in the vicinity
	Unknown				Unknown	If the water fluoride content is unknown the risk is not assessed.

Table 8.23 High-fluoride risk assessment scheme for Lvov, Odessa, Kiev and Poltava Regions, Ukraine

High-Fluoride Risk						
Location	**Phase 1**		**Phase 2**		**Final Risk**	**Assessment Rationale**
	Ground water F mg/l ≥ 1.5	**Potential Risk**	**Water used directly for drinking**	**Potential Risk**		
Lvov Odessa Kiev Poltava	No	Low	Yes	Low	Low	Fluoride content should not normally cause problems, but may do under certain circumstances in hot climates
	Yes	High	Yes	High	High	Water contains high fluoride which may cause health problems
	Yes and No	High/low			High/ low	Water has high fluoride content but lower fluoride water is available in the vicinity
	Unknown				Unknown	If the water fluoride content is unknown and there is no evidence of fluorosis incidence, the risk is not assessed
	Fluorosis Incidence					
	Yes	High	Yes	High	High	There is evidence of fluorosis in the region and the waters are still used for drinking therefore high risk

Results show that on the basis of water fluoride contents, the risks of dental caries are high over most of Lvov Region, however in the Chervonograd mining area, alternative high-fluoride water sources are available in the vicinity (Figure 8.6 and Annex 11). In Odessa Region, dental caries risks are generally high. In the north of the Region no alternative high-fluoride water sources are available but alternative sources occur in the south around Arciz (Figure 8.7 and Annex 12). Waters in Kiev Region generally contain 0.5 mg/l fluoride and dental caries risk is high in this Region (Figure 8.9 and Annex 13). Finally in Poltava Region there are very few high dental caries risk areas as most waters contain > 0.5 mg/l and in several cases alternative higher-fluoride waters are available in the vicinity (Figure 8.10 and Annex 14).

In the Lvov Region, high-fluoride waters (> 1.5 mg/l) and dental fluorosis hotspots are concentrated around the Chervonograd mining region although fluorosis incidence has been reported further south around Drogobech and Stryii (Figure 8.6 and Annex 15). Although alternative low-fluoride waters are available in the Chervonograd area, this mining region is the main focus of high-fluoride concern. Based on the evidence of the geochemistry and health studies carried out as part of the present project, Silyets, Peremyshlyany and Zhovkva are classified as low risk (no incidence of fluorosis was reported) whereas Sosnovka is classified as high risk (fluorosis is still a problem in this town). In Odessa Region, most waters in the north contain low fluoride contents (< 1.5 mg/l), however, clusters of dental fluorosis occur along the fault zone between Podgorny and Tatarbunary in the south of the region where fluoride contents are elevated in water and these areas are classified as high risk (Figure 8.7 and Annex 16). In Kiev Region, waters generally contain low concentrations of fluoride but isolated occurrences of dental fluorosis are associated with mining activities in the Dimer-Buchak, Girnik, Stavishe and Jagotinsky districts (Figure 8.9 and Annex 17), which are classified as high risk accordingly. Finally, in the Poltava Region, the majority of waters contain > 1.5 mg/l fluoride and high-fluoride waters are particularly concentrated along a fault zone between Poltava and Mirgorod and to occur the northwest of Mirgorod (Figure 8.10 and Annex 18). Alternative low-fluoride water sources are available in some localities to the southeast of Poltava but in general, the area is high risk in terms of elevated fluoride in water and adverse health outcomes.

8.4 CONCLUSIONS

Information on the prevalence of fluorosis and fluoride contents in water for Ukraine is limited, however, on the basis of available evidence, biogeochemical experts have demonstrated that in general, fluoride concentrations in potable groundwaters increase with depth and from north to south across the country. A strong correlation between high-fluoride and high- alkaline, Na+K-Cl and low-Mg-Ca waters is found in all regions. High-fluoride waters result from the dissolution of fluoride-bearing minerals such as phosphate in the case of Poltava Region and are associated with tectonically active fault zones where deeper mineralised waters rise to surface, in Lvov, Odessa and Poltava Regions. High-fluoride waters are also caused by mining activities in Lvov and Kiev Regions. Groundwaters with generally elevated fluoride contents are also found in the Dnepro-Donetsk artesian basin comprising Poltava, Dnepropetrovsk, Donetsk and Kirovograd Regions. Biogeochemical experts have established that dietary fluoride intakes increase from north to south in Ukraine as a result of greater water consumption in warmer climates. On the basis of this information four broad fluoride biogeochemical regions have been established, which indicate that risks of dental caries are highest in the west and south of the country, optimal fluoride intakes are found in the southwest and north –northwest of the country whereas high-fluoride risks are dominant in the Dnepro-Donetsk basin in the regions of Poltava, Dnepropetrovsk, Donetsk and Kirovograd. However, these classifications provide a generalised overview of the situation and within each Region of Ukraine, water fluoride contents and fluoride intake can vary markedly. For example, although the regions of Lvov and Odessa are generally classified as low-fluoride in certain districts of these Regions, high- fluoride waters and endemic dental fluorosis are of great concern.

Geochemistry and health investigations carried out for the present project indicate that water fluoride contents up to 3.5 mg/l in Lvov and 7 mg/l in Odessa Regions cause dental fluorosis in the local population. The structural functional skeletal state was also determined in Lvov and no evidence of detrimental changes to bone tissues were found. These results confirm the work of other international researches, which indicates that skeletal changes are not manifest at water fluoride concentrations of less than 5 mg/l. Based on the evidence of these studies and previous health and water chemistry information, the main areas of concern in terms of high-fluoride risks in Ukraine are the Chervonograd mining district of Lvov Region where dental fluorosis prevalence rates reach 64.3% associated with high-fluoride waters caused by natural sources related to tectonically active fault zones and anthropogenic mining activities; the Arciz area of southern Odessa Region where dental fluorosis prevalence rates reach 90% associated with upwelling deep mineralised waters in a tectonically active fault zone and the Poltava Region which lies in the Buchak high-fluoride province and contains the greatest number of known dental fluorosis incidences in Ukraine. High-fluoride waters and fluorosis also occur in the Dnepropetrovsk, Donetsk and Kirovograd Regions but these areas require further investigation before risks can be fully assessed. In general terms in Kiev Region, the risks of dental caries are greater than those of fluorosis, however, isolated incidences of minor forms of dental fluorosis do occur in this Region associated with mining contamination. High-fluoride risks in this Region are not a priority compared to other affected Regions of Ukraine.

Many studies around the world have shown that detrimental health outcomes associated with high-fluoride waters are not simply dependant on the total fluoride content in the water but on the chemical form or speciation of fluoride. Hydrochemical modelling studies carried out on selected Ukrainian waters indicates that the ratio of the F^- to MgF^+ and CaF^+ aqueous fluoride species may be an indicator of risk, however, these results are preliminary and require further investigation into the links with health.

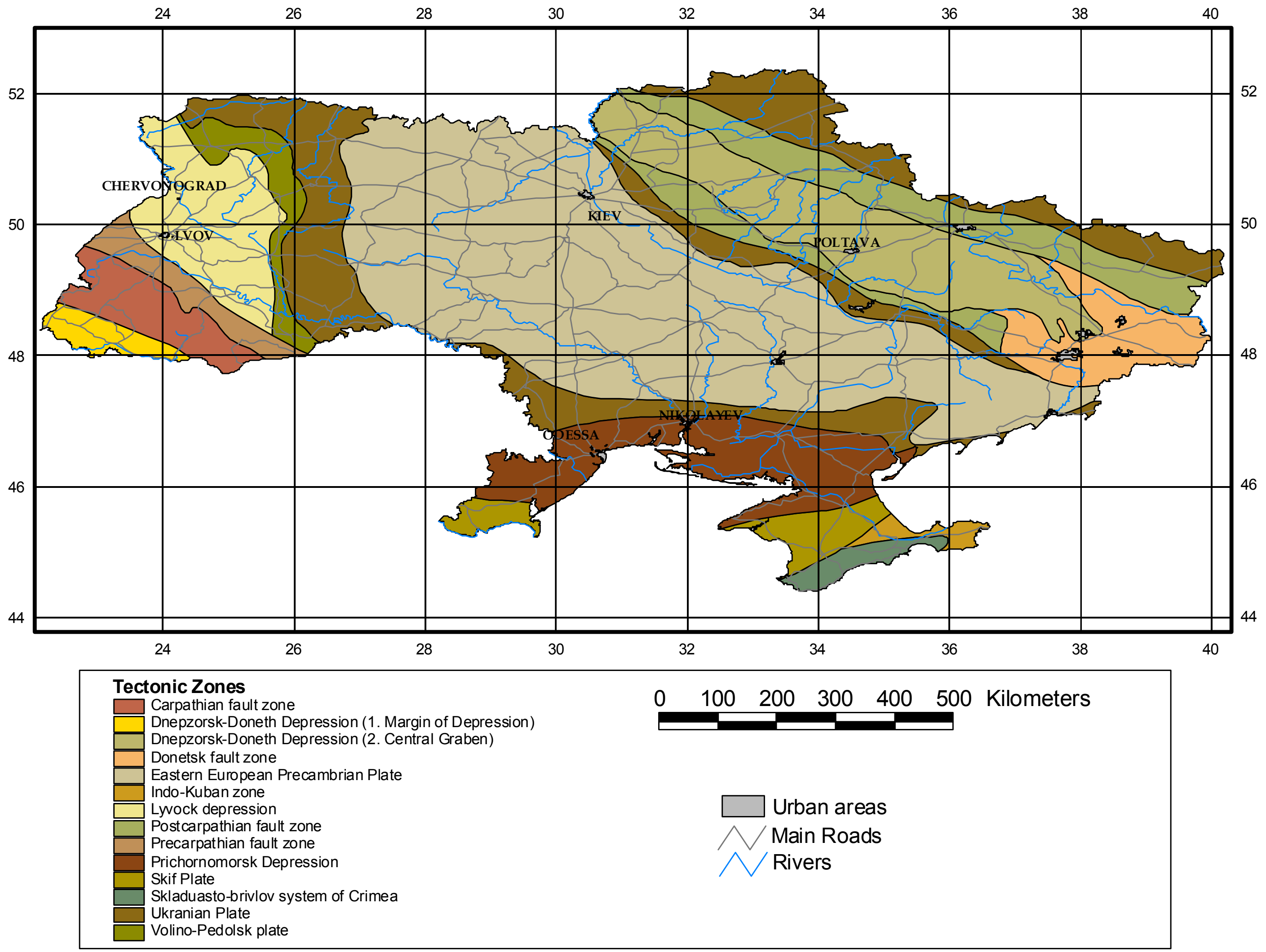


Figure 8.1 Main tectonic regions of Ukraine (IGMOF)

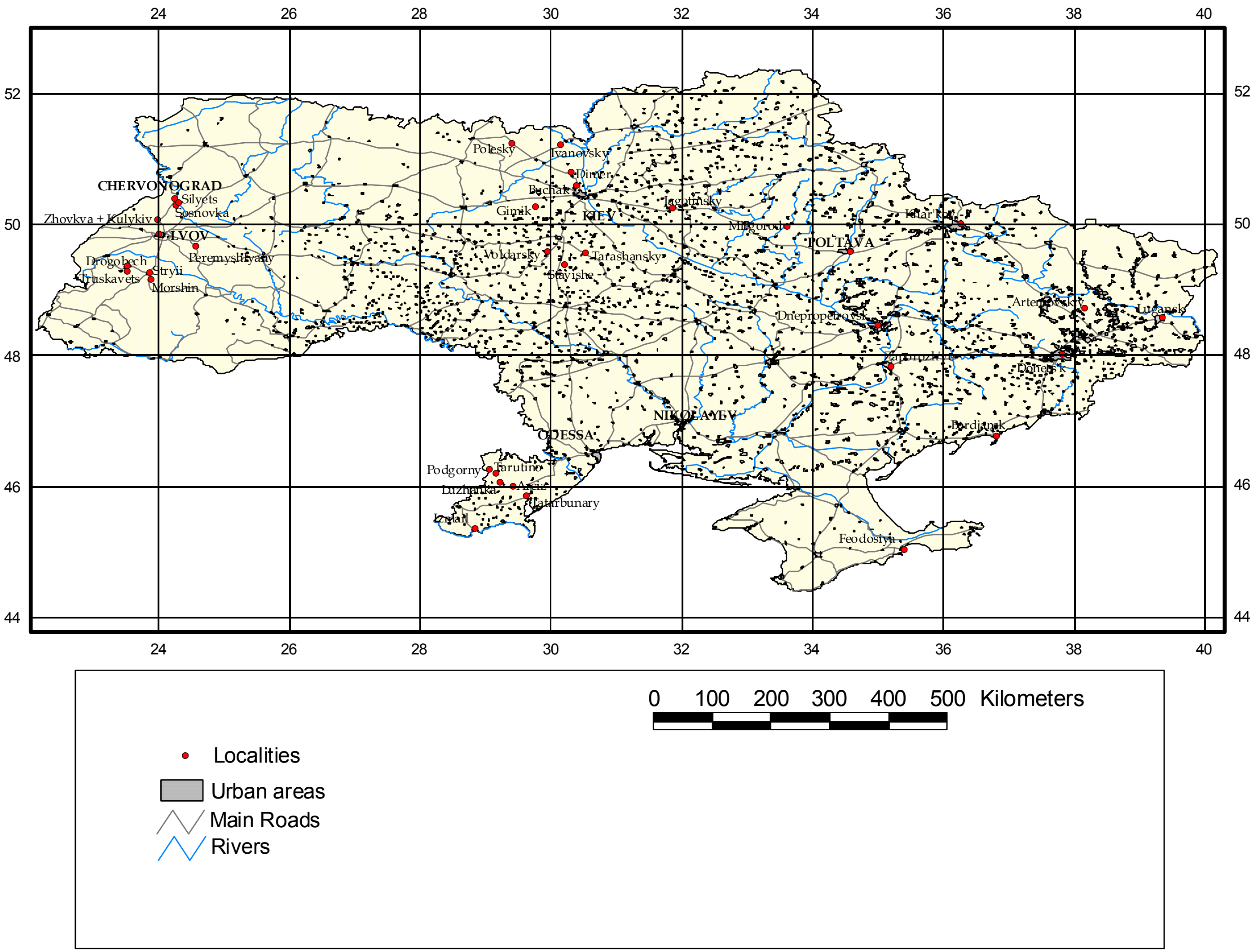


Figure 8.2 Main population centres and localities with water chemistry, dental fluorosis or caries information in Ukraine

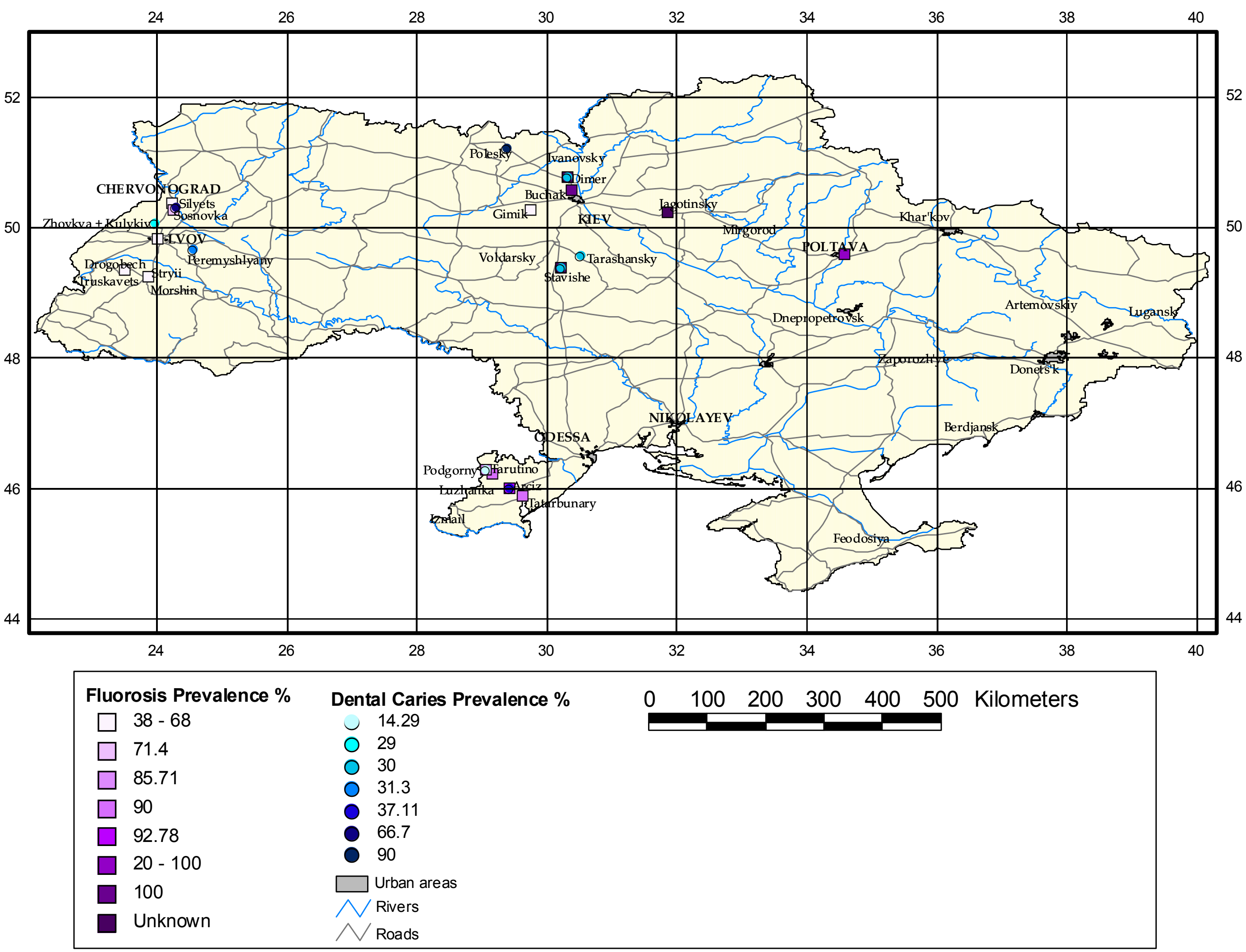


Figure 8.3 Dental fluorosis and caries prevalence locations in Ukraine (data derived from previous studies and the current project)

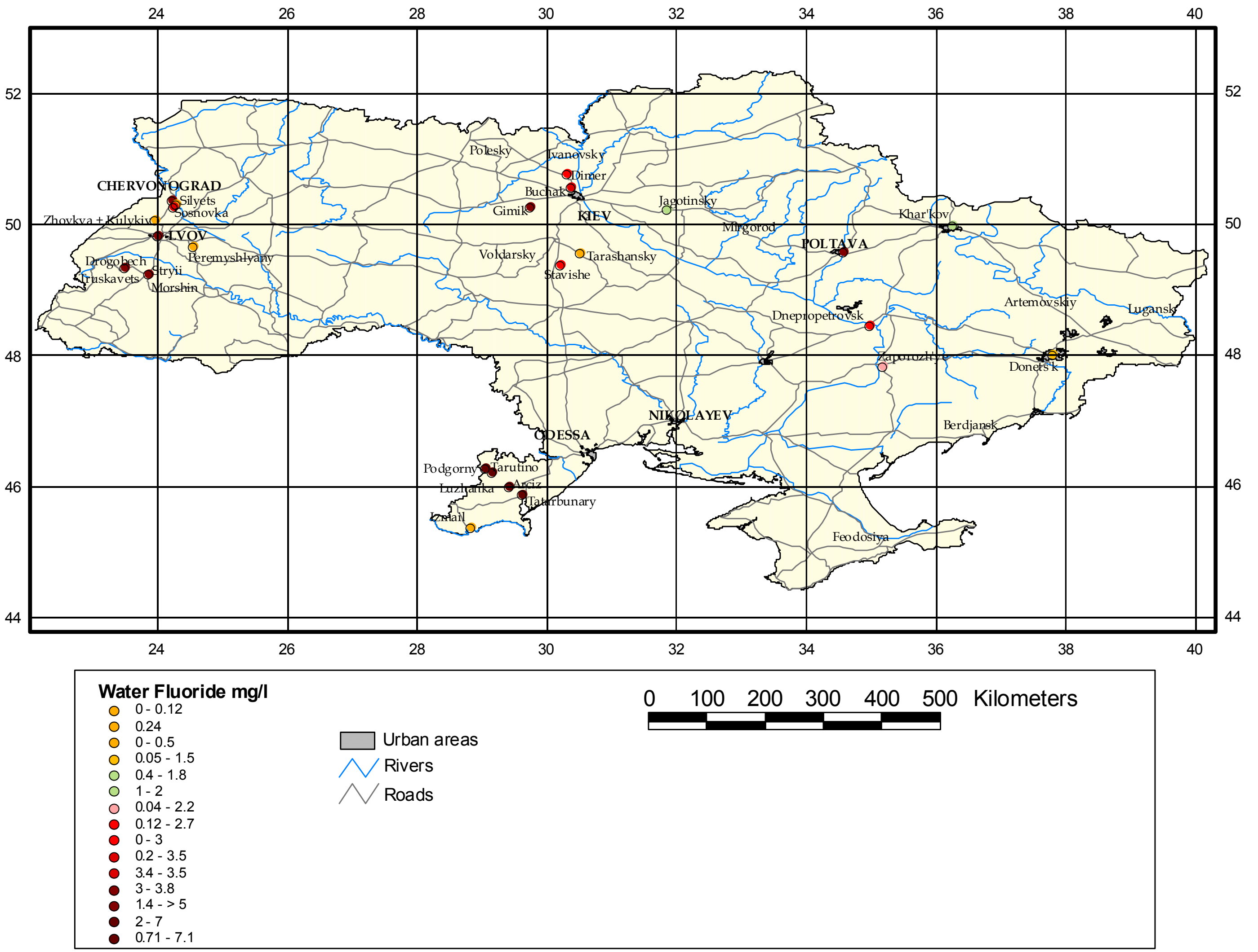


Figure 8.4 Fluoride concentrations in drinking water derived from health investigations carried out by previous workers and the current project

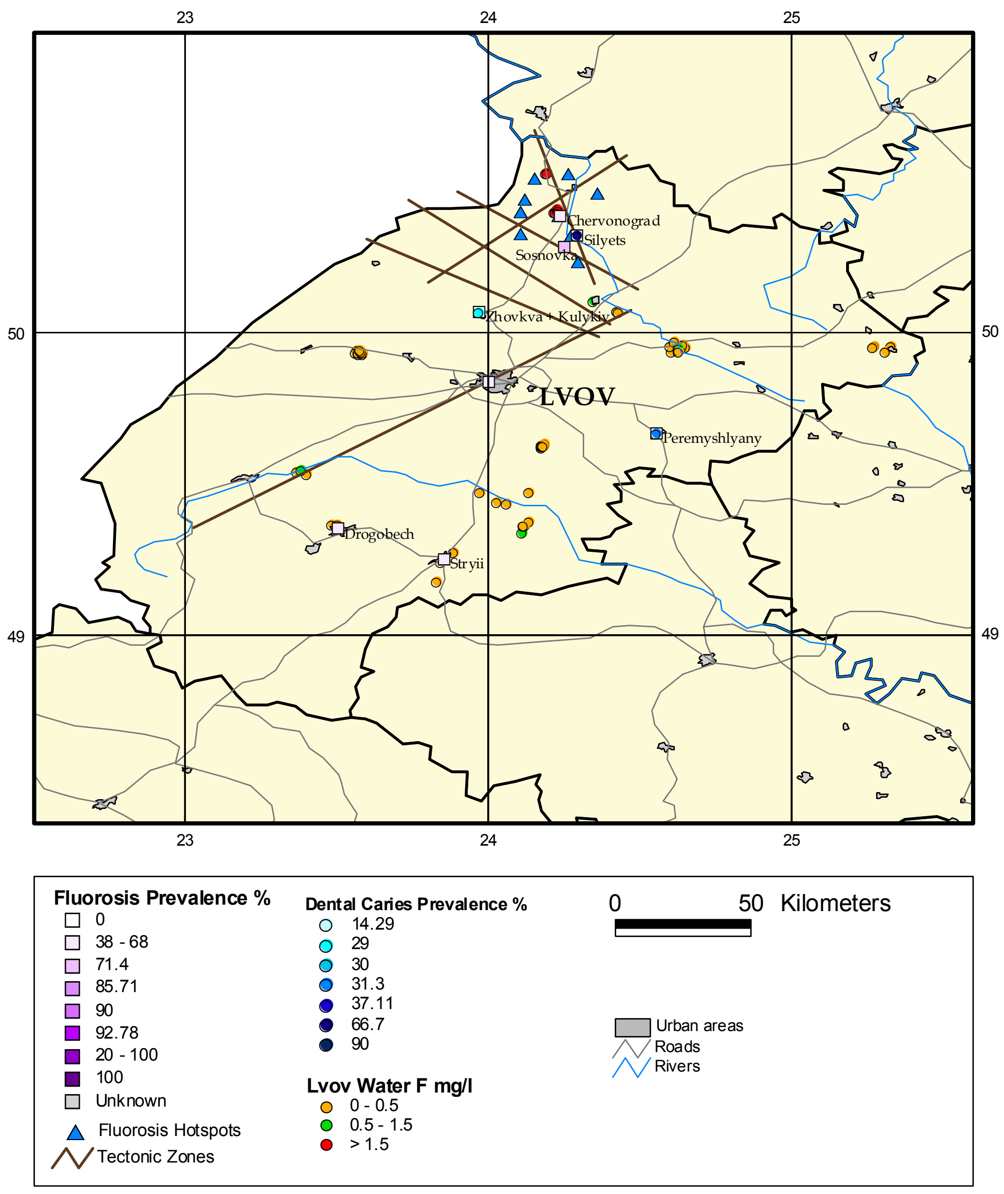


Figure 8.7 Dental fluorosis and caries prevalence data derived from previous studies and the present project and water fluoride contents in hydrogeochemical data (IGMOF) for Lvov Region

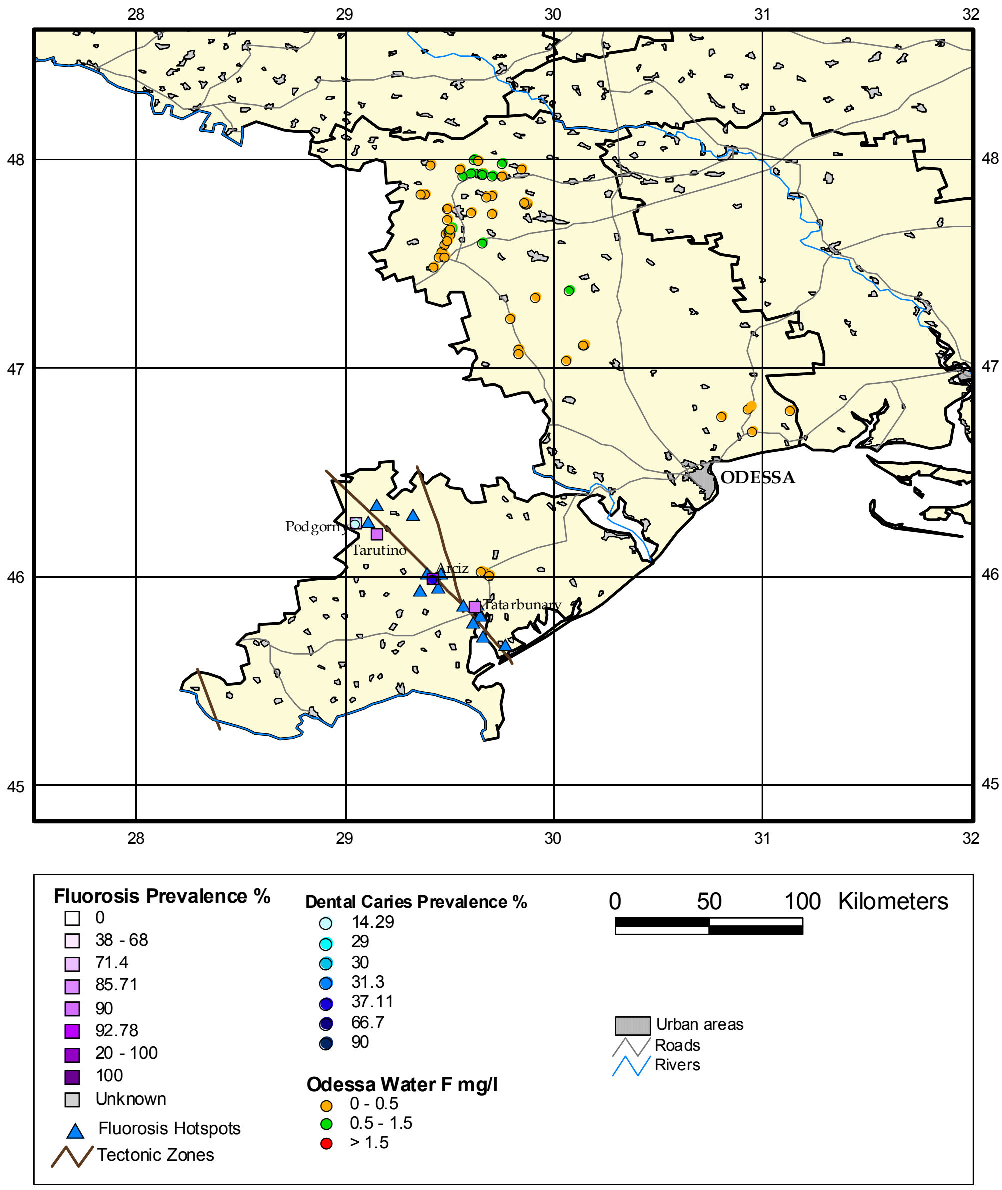


Figure 8.8 Dental fluorosis and caries prevalence data derived from previous studies and the present project and water fluoride contents in hydrogeochemical data (IGMOF) for Odessa Region

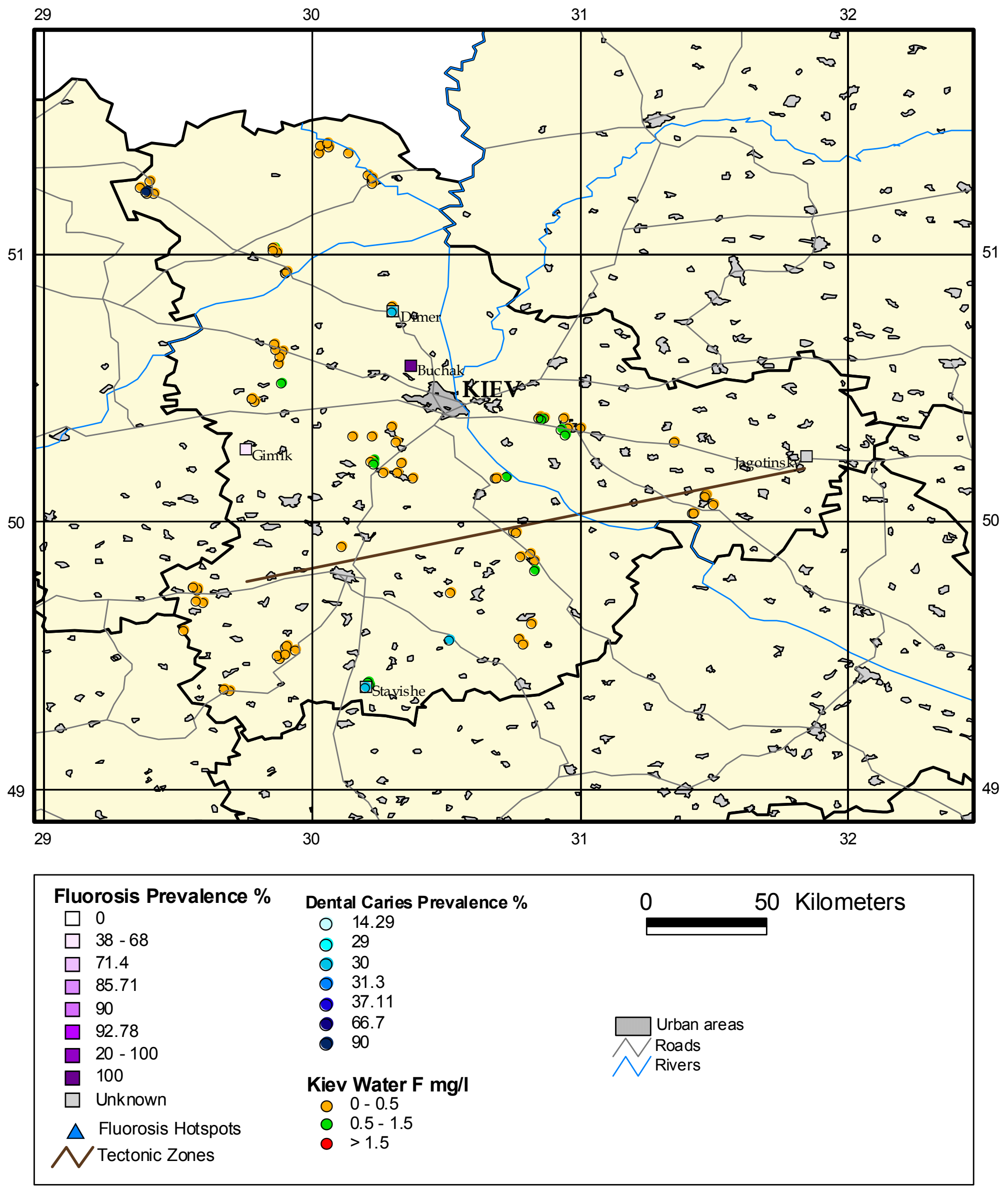


Figure 8.9 Dental fluorosis and caries prevalence data derived from previous studies and the present project and water fluoride contents in hydrogeochemical data (IGMOF) for Kiev Region

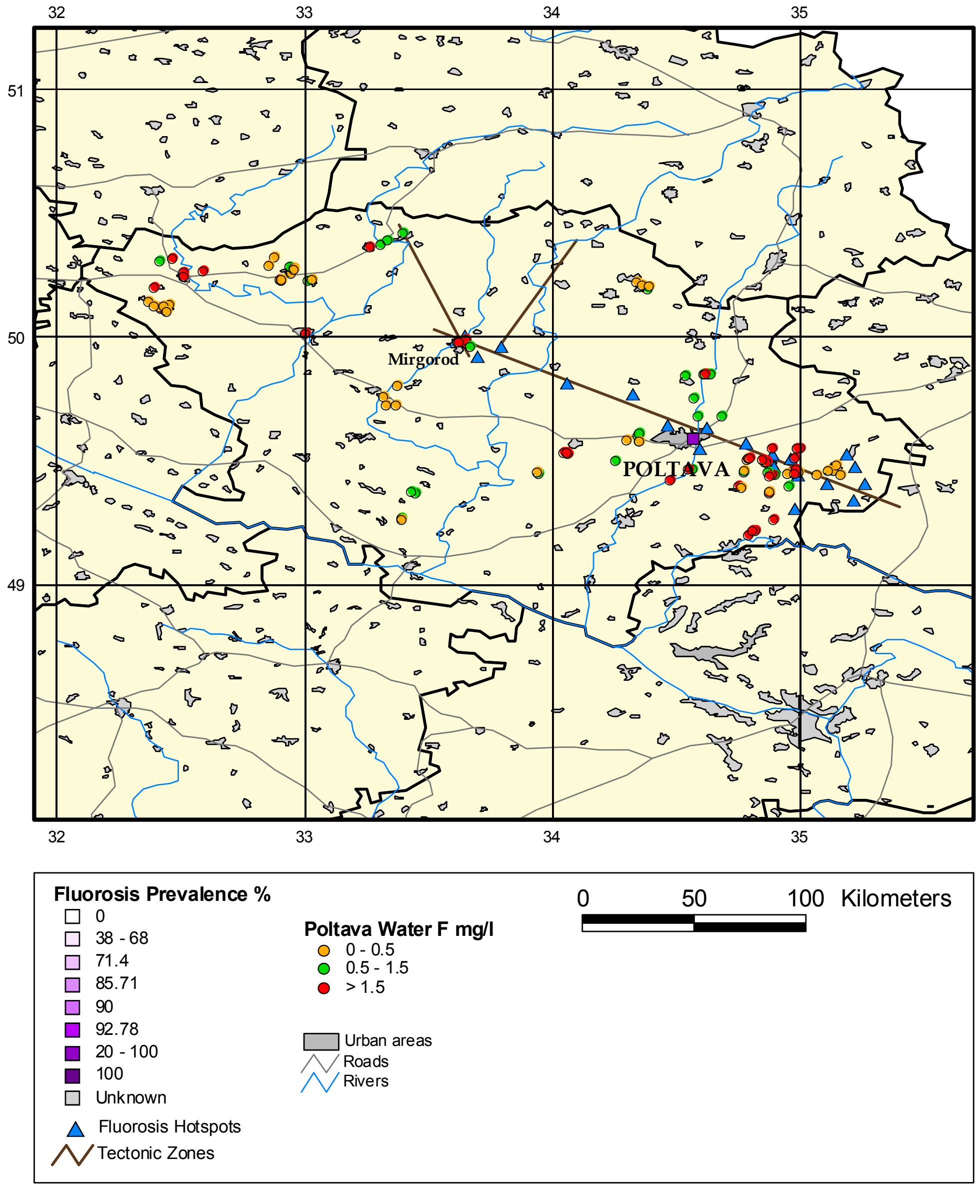


Figure 8.10 Dental fluorosis and caries prevalence data derived from previous studies and the present project and water fluoride contents in hydrogeochemical data (IGMOF) for Poltava Region

8.5 APPENDIX 8.1: HYDROGEOCHEMICAL DATA FROM INDUSTRIAL SITES IN ZAPOROZH'YE, DONETSK, DNEPROPETROVSK AND KHAR'KOV REGIONS OF UKRAINE

(Unless otherwise stated units are mg/l)

ZAPOROZH'YE

Cl – Na

№	№ drill	NO_3	NO_2	As	Pb	Zn	Se	U $nx10^{-3}$	Cd	Cu	V	Hg	Cr	Sr	Pa $nx10^{-9}$	F	Fenols	∑C
1.				0.070	0.0072	0.0078		<3.25	0.0004	0.0023	<0.0014	0.00007		1.36		0.30	<0.01	
2.	1/1K			<0.002	0.0078	0.0043	<0.010		0.0003	0.0036	0.0033	<0.001	0.0007	10.0		0.63	<0.001	
3.	7-K (N_1s_{1-2})	0.4	0.05	<0.002	0.0067	0.0040	<0.010		0.0005	0.0038	0.0068	<0.001	0.0011	10.0	5.0	0.57		
4.	8-K			<0.002	0.0124	0.0031			0.0003	0.0051	0.0068	<0.001	0.0004	11.0	5.0	0.60	<0.001	
5.	142																	
6.	695-B			0.001	<0.0015	0.01			0.00015	0.0047	<0.0014	0.0003	0.0012	3.07		1.15		
7.	1			<0.002	0.0093	0.0025	<0.01		0.0002	0.002	0.0090	<0.001	0.0004	1.8		0.22	<0.001	
8.																		
9.	289	11.2																
10.	829				0.25	0.006				0.01						1.63		

HCO_3-Cl. HCO_3-Cl-SO_4-Na

№	№ drill	NO_3	NO_2	As	Pb	Zn	Se	U $nx10^{-3}$	Cd	Cu	V	Hg	Cr	Sr	Pa $nx10^{-9}$	F	Fenols	∑C
1.	3(5212/17a)			<0.002	0.0066	0.0042	<0.01		0.0006	0.0049	0.0049	<0.001	0.002	0.46		1.02	<0.001	
2.				0.014	0.0053	0.0012				0.0017		0.00006	0.0003	1.9				
3.																0.27	<0.001	
4.		10.9															<0.001	
5.	882-B			<0.0005	0.004	0.005	0.04		0.0017	0.0057	0.005		0.0064	0.14		1.3		4.4
6.	10/1			<0.002	<0.001	0.02			<0.0001	0.04	<0.001	<0.001	0.0060	0.09		1.5		3.3

Anion+cation

№	№ drill	NO_3	NO_2	As	Pb	Zn	Se	U nx10^{-3}	Cd	Cu	V	Hg	Cr	Sr	Pa nx10^{-9}	F	Fenols	∑C
1.	3732																	
2.	1252	6.2																
3.	14/1				0.0026	0.0407			0.00016	0.0719	<0.0014	<0.001	0.0015	0.276		0.93	<0.001	
4.				0.015		0.0077			<0.00014	0.0011	0.0002	0.00005	0.001	13.8		0.30	<0.001	
5.	1629 (N_1s_2)			<0.0005	<0.001	0.0029	<0.01		<0.00005	0.0014	<0.005	<0.001	0.0028	5.0		0.17		
6.	5	15.6		<0.002	0.0021	0.28		<3.25	0.00015	0.0076	0.0001	0.0006	0.0013	1.76		0.1		4.3

Br. I-Br

1.	40-P																	
2.	1			<0.002	0.0105	0.0027	<0.010		0.0002	0.0016	0.029	<0.001	0.0004	17.5	3.4	0.30	<0.0001	
3.	2			<0.001	0.0089	0.0061	<0.010		0.0006	0.314	0.0678	<0.001	0.0009	33.0		0.04	<0.001	
4.	746Г			<0.002	0.007	0.0032	<0.010		0.0004	0.0024	0.0678	<0.001	0.0003	38.0		0.09	<0.001	
5.	748Г (N_2)									0.0117	0.29		0.117	23.44		2.0		
6.	749Г (N_2)									0.0117	0.23		0.1749	17.49		2.2		
7.	1602Г N_1s_2			<0.002	0.0129	0.0045			0.0003	0.0031	0.0339	<0.001	0.0004	24.0		0.09	<0.001	
8.	1605Г (N_1t-s_1)			<0.002	0.0107	<0.0054			0.0005	0.0022	0.0110	<0.001	0.0007	111.0	0.37	0.05	<0.001	
9.				<0.002	0.0105	0.0027	<0.010		0.0002	0.0016	0.029	<0.001	0.0004	17.5	3.4	0.30	<0.001	
10.	2			<0.001	0.0089	0.0061	<0.010		0.0006	0.314	0.0678	<0.001	0.0009	33.0		0.04	<0.001	
11.	13581 (N_1t-s_1)																	
12.	10-K Pg_3			<0.002	0.0065	0.0028	<0.010		0.0003	0.0046	0.102	<0.001	0.0002	56.0	15	0.04	<0.001	
13.	11-K Pg_3			<0.002	0.008	0.0024	<0.010	<3.25	0.0003	0.0014	0.0904	<0.001	0.0002	68.0	7.5		<0.001	
14.	2P																	

SO_3

№	№ drill	NO_3	NO_2	As	Pb	Zn	Se	U $nx10^{-3}$	Cd	Cu	V	Hg	Cr	Sr	Pa $nx10^{-9}$	F	Fenols	∑C
1.	15/9	10.3						<3.25										
2.	2																	

Organic

1.																0.41		7.2
2.	223-B	0.5		<0.0005	0.0016	0.0052	<0.01		0.00008	0.0014	<0.005	<0.001	0.0046			1.44-1.70	<0.001	6.5
3.			0.2														<0.001	7.2

Natural

1.	1			<0.002	0.0040	0.0038	<0.01		0.003	0.0011	0.0037	<0.001	0.0003	0.45		0.33		4.2
2.	5	11.0		<0.002	0.0024	0.0014	<0.010	<3.25	0.0006	0.0020	0.0033	<0.001	0.0059	0.36		1.14	<0.001	
3.	5			<0.002	0.011	0.0028	<0.01		0.0002	0.0009	0.0023	<0.001	0.0004	0.80		0.29	<0.001	4.1
4.	4			<0.002	0.0031	0.0041	<0.010		0.0003	0.0018	0.0034	<0.001	0.0002	0.28		0.26	<0.001	
5.	4				0.25					0.025						1.67		3.2
6.	878-B			<0.002	0.0084	0.0039	<0.01		0.0003	0.0015	0.0020	<0.001	0.0028	0.20		0.76	<0.001	4.2
7.	71-84			<0.002	0.0001	0.0049	<0.01	<3.25	0.0024	0.0011	<0.005	0.001	0.0017	0.01		0.43		3.0
8.	4237/3			0.0002	0.0023	0.0034	0.00005		0.0002	0.001	0.0014		0.0004	1.04		0.24	<0.001	6.0
9.	6-a			<0.0005	<0.0010	0.0041	<0.01		0.0004	0.0038	<0.005	<0.001	0.0038			1.38		
10.	1			<0.002	0.0026	0.041			0.00016	0.072	<0.0014	0.00007	0.0015	0.28		0.93	<0.001	

Donetsk

SO4

№	№ drill	NO_3	NO_2	As	Pb	Zn	Se	U nx10^{-3}	Cd	Cu	V	Hg	Cr	Sr	Pa nx10^{-9}	F	Fenols	∑C
1.	A-3345/1p (P_1)						<0.010	<3.25		0.0007	0.010			5.0.0051	<1	1.5	<0.1	
2.				<0.002	0.007	0.004	<0.010	65	0.003	0.003	0.009	<0.001	0.002	2.8	<1	0.2	<0.1	2.8
3.		25.0		<0.002	0.006	0.005	<0.010	160	0.0005	0.002	0.007	<0.001	0.0005	2.0	<1	0.4		

Cl-SO_4(SO_4-Cl). HCO_3-SO_4

1.	1	20.0		<0.002	0.009	0.003	<0.010	65	0.0002	0.002	0.005	<0.001	0.004	1.3	<1	0.8		
2.	447ГД			0.002	0.002	0.002	<0.010	160	<0.001	0.008	<0.001	<0.001	0.002	2.1	<1	0.9	0.001	
3.	482ГД	<10		0.002	0.002	0.002	<0.010	0.006	0.0001	0.008	0.001	<0.001	0.002	2.1	<1	0.7	<0.001	4.3
4.	A-10720эр (T_1)	3.5		<0.002	0.006	0.003	<0.010	650	0.0006	0.006	0.005	<0.001	0.002	2.7	<1	0.3	<0.1	3.2
5.	A-3337p Э (P_1)						<0.010	<3.25		0.008	0.01	<0.001	0.008	1.4	<1	1.5	<0.1	
6.	2316 (C_2)																	
7.	6044Д		0.6	<0.002	0.01	0.003	<0.010	65	0.0006	0.001	0.003	<0.001	0.0004	4.1	11	0.3	<0.001	
8.	6044 (C_1)																	
9.	1389			<0.002	0.008	0.004	<0.010	650	0.0005	0.002	0.008	<0.001	0.0004	4.6	4.6	0.7	<0.001	
10.	670гд			<0.002	0.004	0.004		65	0.0002	0.002	0.006	<0.001	0.0005	2.9	<1	0.2		

Anion+cation

1.	A-1546-p	2.5				0.001		65			0.04			0.7	<1	0.2	<0.001	4.2
2.	480 (C_3)	40-52		0.002	<0.001	0.005	<0.010	65	<0.0001	0.001	<0.005	<0.001	0.0007		<1	0.3	<0.001	

HCO_3-Cl-Na

1.	80-C			<0.001	0.002	0.005	<0.010	<3.25	0.0001	0.001	<0.005	<0.001	0.002	0.6	<1	0.5	<0.1	
2.	1400 (P_{1-2})			<0.002	0.006	0.004	<0.010	3.25	0.0003	0.001	0.001	<0.001	0.0002	1.4	<1	0.5	<0.001	

Cl-Na

№	№ drill	NO_3	NO_2	As	Pb	Zn	Se	U nx10^{-3}	Cd	Cu	V	Hg	Cr	Sr	Pa nx10^{-9}	F	Fenols	∑C
1.	A5529 (T)						<0.010	35		0.006	0.01		0.01	0.7	<1	1.0	<0.001	
2.	A5535 (T)					<0.01		650		0.002	0.01		0.003	0.30	<1	0.7		
3.	79-C			0.004	<0.001	0.02	<0.010	<3.25	<0.001	0.003	<0.001	0.0003	0.0005	1.1	<1		<0.001	
4.	452ГД		0.5	0.005	<0.001	0.06		<3.25	0.0002	0.004	<0.001	<0.001	0.001	7.9	<1	0.4		
5.	1102Г (N)					0.005		<3.25						0.02		0.3		
6.	A5527 (T)							<3.25		0.002	0.02		0.005	0.9	<1	0.2		

I. Br. I-Br

1.	1118Г (Pg)				0.01	0.04		<3.25		0.004		0.001		0.001		1.5	<0.001	
2.	5861							<3.25		0.06	0.11		0.07	8.5	<1	0.11		
3.	3605	3.0		<0.002	0.009	0.003	<0.010	65	0.0003	0.001	0.010	<0.001	0.006	17.0	<1	0.5	<0.1	
4.	83-C			0.002	0.001	0.02	<0.010	<3.25	<0.001	0.003	<0.001	<0.001	<0.001	21.2	<1			
5.	1120Г (K)				0.001			<3.25		0.006				0.01		0.4	<0.001	
6.	1123Г						<0.010	<3.25		0.02	0.17		0.08	10.5	<1	0.3		
7.	1104Г (K)							<3.25		0.006	0.06	<0.001	0.06	4.8	<1	0.3		
8.	1109Г (Pg)							<3.25		0.006	0.16		0.2	6.2	<1	0.1		

Fe

1.	7939д (T_3)			<0.002	0.02	0.004	<0.010	<3.25	0.0002	0.007	0.014	<0.001	0.0007	0.20	<1	0.05	<0.001	2.4

Rn

1.	44 (Pz)	34.0			0.01			2600		0.004			0.005	13.5	50	1.5		
2.	48 (Pz)	3.5		<0.002	0.007	0.007	<0.010	650	0.0005	0.003	0.005	<0.001	0.0005	1.6	<1	0.3	<0.001	

Natural

1.	3279		0.3	<0.002	0.010	0.004	<0.010	<3.25	0.0003	0.006	0.005	<0.001	0.0007	0.04	<1	0.2	<0.001	3.0
2.	51					0.014	<0.010	<3.25		0.001	0.002	<0.001	0.004	0.3	<1	0.08	<0.001	
3.	T_3	0.07		0.0005	0.02	0.01	<0.010	6.5	0.001	0.003	<0.003	<0.001	0.04	0.04	<1	0.4	<0.001	
4.	A-1047 (T_3)			<0.002	0.006	0.003	<0.010	<3.25	0.0005	0.002	0.01	<0.001	0.0004	0.6	<1	0.3	<0.001	3.4
5.	1			<0.002	0.008	0.003	<0.010	<3.25	0.0002	0.002	0.003	<0.001	0.0004	0.3	<1	0.4	<0.001	4.6
6.	1	1.6		0.003	<0.001	0.004	<0.010	<3.25	<0.001	0.02	<0.001	<0.0003	<0.001	0.8	<1	0.7	<0.01	4.4

Dnepropetrovsk

Cl. HCO_3-Cl-Na

№	№ drill	NO_3	NO_2	As	Pb	Zn	Se	U $nx10^{-3}$	Cd	Cu	V	Hg	Cr	Sr	Pa $nx10^{-9}$	F	Fenols	∑C
1.	1 (P_2bč)						<0.01	<3.25	<0.004	0.004	<0.008		<0.004	0.16	<1	1.38-1.51	<0.01	
2.	4456/г			<0.002	0.008	0.0066	<0.01	<3.25	0.0002	0.0056	<0.005	<0.001	0.0005	0.18	<1	1.8	<0.001	
3.	311 (P_2bč)		0.068	<0.002	0.0072	0.0033	<0.01	<3.25	0.0004	0.0013	0.0018	<0.001	0.0002	1.4	<1	2.75	<0.001	

Anion+cation

№	№ drill	NO_3	NO_2	As	Pb	Zn	Se	U $nx10^{-3}$	Cd	Cu	V	Hg	Cr	Sr	Pa $nx10^{-9}$	F	Fenols	∑C
1.	1e			0.001	0.0012	0.0062	<0.01	3.25	0.00011	0.0023	<0.005	<0.001	0.0006	1.8	<100	0.64	<0.001	
2.	20337(P_2bč)			<0.002	0.0025	0.0086	<0.011	32.5	0.0003	0.01333	0.0016	<0.001	0.0002	2.20	<1	0.12	<0.001	
3.	1			<0.002	0.001	0.0086	<0.01	<3.25	0.0006	0.0012	0.001	<0.001	0.014	0.43	<1	0.29	<0.001	
4.	15540	30	0.022		0.008			6.5		0.005			0.0006	7.72	<1	0.26	<0.001	
5.	1936г/н	0.1	0.002		0.007			65		0.007	0.006		0.003	0.37	<1	0.82		

Cl-Na

№	№ drill	NO_3	NO_2	As	Pb	Zn	Se	U $nx10^{-3}$	Cd	Cu	V	Hg	Cr	Sr	Pa $nx10^{-9}$	F	Fenols	∑C
1.	1 (P_2bč)			0.003	<0.001	0.0053	<0.01	<3.25	0.0005	0.0016	<0.035	<0.001	0.0021		<1	1.35		
2.	1375р				<0.002	0.06	<0.01	<3.25	0.0002	0.0074	<0.0014		0.0008	1.56	<1			
3.	100 (P_2bč)		0.05	0.0005	0.0088	0.004	<0.01	<3.25	<0.0001	0.003	<0.005	<0.001	<0.0001	3.9	<1	1.73	<0.001	
4.	МТФ			0.0025	0.0015	0.0052	<0.01	<3.25	<0.0001	0.0015	<0.005	<0.001	0.003		<1	1.99		
5.	142					0.0049		<3.25		0.0048				1.1	<1	1.9	<0.001	4.2
6.	53г	5.0	0.005	0.007	0.0017	0.01	<0.01	<3.25	<0.00015	0.009	<0.0014		<0.0005		<1	2.14		
7.	99111			0.014	<0.001	0.0008		<3.25	<0.00015	0.0003	<0.0014	<0.001	0.0003	1.49	<1	0.83	<0.001	
8.			0.02	0.0025	0.0013	0.0054	<0.01	<3.25	<0.0001	0.0015	<0.0005	<0.001	0.0021		<1	1.69		
9.	1374р			0.003	0.0016	0.006	<0.01	<3.25	<0.00022	0.0012	<0.005	<0.001	0.003		<1	0.35		
10.	2 (I)			0.002	0.0015	0.0052	<0.01	<3.25	0.00018	0.0017	<0.005	<0.001	0.0015		<1	0.44		
11.								32.5		0.004	0.07		0.028	2.79	74	0.36		
12.	21087									0.012	0.099		0.05	10.47				

Si

№	№ drill	NO_3	NO_2	As	Pb	Zn	Se	U nx10^{-3}	Cd	Cu	V	Hg	Cr	Sr	Pa nx10^{-9}	F	Fenols	∑C
1.	2			<0.0005	<0.001	0.0046	<0.01	<3.25	<0.00005	0.0017	<0.005	<0.001	0.0004	0.12	<1	0.79	<0.001	4.6

Br. I-Br

1.	15357							<3.25		0.074	0.126		0.075	12.6	<1	1.59		
2.	21426(P_2 bč+T)					0.063		<3.25			0.05		0.025	2.5	<1	1.4	<0.001	
3.	15538							<3.25					0.06	24.0	<1	1.84		
4.	2			0.001	<0.0015	0.029		0.6	<0.00015	0.014	<0.0014	0.0002	<0.0015	35.7	13	1.2		
5.	1360рж			0.002	<0.001	0.0073	<0.01	<3.25	<0.0005	0.0042	<0.005	<0.001	0.0023		130	1.31		
6.	1359р				0.002	0.043	<0.01	<3.25	0.0002	0.008	<0.0014		0.0007	93.8	50			
7.	990П			0.0015	<0.004	0.0084	<0.01	<3.25	0.00005	0.0076	<0.005	<0.001	0.0057	73.0	17	0.15		
8.	3 (C)			<0.0005	<0.001	0.0053	<0.01	3.25	0.00006	0.0018	<0.005	<0.001	0.0043	4.26	<1	1.07		
9.						0.05		<3.25		0.07	0.1		0.1	2.24	<1			

Ra

1.	14090 (PR)		0.4	0.004	0.0013	0.007	<0.01	650	0.002	0.002	<0.005	<0.001	0.0009		125	1.31		
2.	15924(PR)							32.5			0.0024		0.0041	0.211	120	0.20		
3.	15881(PR)							65					0.0042	0.164	100	0.28		
4.	23960(PR)			0.002	0.003	0.007	<0.01	65	0.0002	0.003	0.014	<0.001	0.0005	7.1	50	0.83		
5.	23956			0.003	0.001	0.01	<0.01	65	0.0001	0.005	0.014	<0.001	0.0008	3.3	40	0.81		

Natural

1.	1			0.001	<0.001	0.0028	<0.01	16	0.0005	0.0014	<0.005	<0.001	0.0008	0.8	<1	0.54	<0.001	
2.	2			<0.002	0.008	0.0041	0.01	<3.25	0.0003	0.003	0.0065	<0.001	0.0009	0.08	<1	0.26	<0.001	2.8
3.			0.1	0.002	0.0024	0.0095	<0.01	<3.25	0.0025	0.096	<0.03	<0.001	0.0023	0.55	<1	0.13	<0.001	
4.	23731		0.012	<0.002	0.0045	0.0038	<0.01	<3.25	0.0005	0.0064	0.0029	<0.001	0.0004	0.15	<1	0.19	<0.001	

Khar'kov

HCO_3-SO_4

№	№ drill	NO_3	NO_2	As	Pb	Zn	Se	U $nx10^{-3}$	Cd	Cu	V	Hg	Cr	Sr	Pa $nx10^{-9}$	F	Fenols	∑C
1.	2 (Pg_2)			0.002	0.002	0.3	<0.010	<3.25	<0.001	0.03	<0.001	<0.001	0.002	4.1	<1	1.8	<0.001	4.8
2.	(Pg_3)	9.4		<0.002	0.005	0.005	<0.010	160	0.0003	0.01	0.004	<0.001	0.0002	1.6	<1	0.4	<0.001	
3.																		
4.																		
5.																		
6.																		
7.																		
8.																		
9.																		

9 Risk Assessment for Central Europe, Conclusions and Recommendations

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9.1 OVERALL RISK ASSESSMENT FOR CENTRAL EUROPE

The final stage of the project risk assessment GIS was to combine the national risk assessment information into a risk avoidance map for the whole Central European study region. A high-fluoride risk map was prepared for the region as the focus of the project was on identifying areas where fluoride removal technology should be targeted. During the map preparation, the national risk avoidance maps based on grid squares for Slovakia, Hungary and Moldova were combined with the biogeochemical region map of Ukraine. The regions on the map of Ukraine were reclassified from the original dental caries – high fluoride scheme presented in Chapter 8 to the low-moderate-high risk scheme adopted for the national maps of the other countries. The overall risk avoidance map of the Central European study area is presented in Annex 19. It should be noted, however, that although information coverage for Ukraine appears complete, this area of the map is based on regional rather than grid-square risk classes. The regional classifications represent general estimates only as information about high-fluoride risks in Ukraine is limited.

On the basis of the evidence presented in this report, high-fluoride risks in the region can be prioritised as follows:

High Priority	Location
1.	**Arciz District, Odessa Region, Ukraine.**
	High fluoride contents associated with upwelling mineralised water in tectonically active fault zones result in dental fluorosis prevalence rates of 90% in the local population. In this Region, water is abstracted from the Neogene aquifer and fluoride concentrations of 2 – 7 mg/l fluoride are reported therefore fluoride removal technology would be beneficial.
2.	**Falesti, Prut and Chadyr-Lunga Regions, Moldova**
	Moldovan groundwaters abstracted from deep horizons generally contain high concentrations of fluoride (up to 16 mg/l) and fluorosis prevalence in these regions reaches 80 – 90%. Although shallow low-fluoride waters are available, these are heavily polluted with biological and other contaminants and it is desirable that the population is able to drink deeper waters, however, this requires fluoride removal.
3.	**Poltava Region, Ukraine**
	The main water bearing horizon in this region, the Buchak-Kaniv contains high (up to 18 mg/l) fluoride due to the presence of phosphatic deposits at shallow depths. The Buchak-Kaniv aquifer supplies 2 million people and Poltava Region contains the highest number of dental fluorosis hotspots in Ukraine. Although lower-fluoride waters are available in deeper Cretaceous and Jurassic aquifers, exploitation at depth is prohibitively expensive therefore defluoridation of shallower waters is desirable.
4.	**Chervonograd Mining District, Lvov, Ukraine**
	High-fluoride waters associated with tectonically active fault zones and mining contamination result in dental fluorosis in the local population (64% prevalence rate). Alternative lower-fluoride waters have been supplied to the public in recent years but the disease is still endemic in the region. Defluoridation technologies may be helpful in this area

High–moderate risk areas have been identified in the Dnepropetrovsk, Donetsk and Kirovograd Regions and some districts of the Kiev Region of Ukraine; in the central Great Hungarian Plain and in association with historic fluorosis incidence and industrial contamination in Hungary and industrial contamination in Slovakia. These areas are of lower risk priority than those listed above and can be categorised as follows:

Moderate-Low Priority	Location
1.	**Dnepropetrovsk, Donetsk and Kirovograd Regions, Ukraine.**
	These regions lie in the Dnepro-Donetsk artesian basin where upwelling deep mineralised waters contain high fluoride concentrations. Dental fluorosis has been reported in these regions but the extent of health problems requires further investigation. Fluoride removal technology may be beneficial in these regions.
2.	**Dimer, Stavishe and Jagotinsky Districts, Kiev Region, Ukraine**
	High-fluoride waters (2 mg/l) are associated with mining activities in this Region and isolated incidences of dental fluorosis have been reported. However, the majority of the waters in this region contain low fluoride contents and low-fluoride waters are available locally but de-fluoridation technology may be useful in some instances.
3.	**Central Great Hungarian Plain**
	Upwelling thermal mineralised groundwaters in the Great Hungarian Plain result in elevated fluoride concentrations in drinking waters (up to 4 mg/l). There is no evidence of dental fluorosis in this region, which is not a priority for fluoride removal technology, however it is recommended that the situation continue to be monitored.
4.	**Bar, Dunaszekcso, Herceghalom, Hungary**
	Dental fluorosis incidence has been reported in these towns in the past, however, alternative low -fluoride drinking water supplies have been provided and the disease is no longer prevalent. These areas are not a priority for fluoride removal technology, however it is recommended that the situation continues to be monitored
5.	**MOSONMAGYARÓVÁR, ALMÁSFÜZITŐ, AJKA REDMUD, AJKA ALUFACTORY, VÁRPALOTA ALUFACTORY Industrial Sites, Hungary**
	The extent of environmental fluoride contamination associated with these industrial activities is not known but no incidences of dental fluorosis have been reported in these regions. It is recommended that these areas be investigated more fully to establish the environmental fluoride status.
6.	**Ziar nad Hronom Aluminium Plant, Ziarska Kotlina, Slovakia**
	High fluoride concentrations (up to 9 mg/l) occur in ground and surface waters in the immediate vicinity of this factory, however, the waters are not used for drinking and no dental fluorosis has been reported in the area. There is no requirement for fluoride removal technology at the present time but it is recommended that the situation should continue to be monitored

Although health risks associated with low concentrations of fluoride in drinking water were not the main focus of this project, dental caries risks were considered for the four study countries and can be summarized as follows:

Priority	Location
1.	**Hungary**
	The majority of drinking waters in Hungary contain low (< 0.5 mg/l) fluoride and are not fluoridated therefore the population is at risk of dental caries
2.	**Ukraine**
	Drinking waters in the west, north and very south of the country generally contain low (< 0.5 mg/l) fluoride and are not fluoridated therefore the population is at risk of dental caries
3.	**Moldova**
	Drinking waters in the north of the country generally contain low (< 0.5 mg/l) fluoride and are not fluoridated therefore the population is at risk of dental caries
4.	**Slovakia**
	Practically all natural waters in Slovakia contain low (< 0.5 mg/l) fluoride but these waters are fluoridated before supply to the public therefore the risks of dental caries are reduced

9.2 CONCLUSIONS

The main conclusions from the project can be summarized as follows:

- Like many naturally occurring elements, health problems can occur in humans when fluoride concentrations are too low (deficiency) or too high (excess). Fluoride enters the human organism via inhalation of air and ingestion of food and water. In most circumstances, water is the most important exposure route as almost all fluoride ingested in this form is absorbed in the gastro-intestinal tract. Once in the body, fluoride accumulates in the skeletal structure, as it is a powerful Ca-seeking element. Fluoride enters dental enamel converting the bone mineral hydroxylapatite to the stronger, less soluble fluorapatite. Experts are still uncertain whether fluoride is an essential element for human health, however, concentrations of 0.5 mg/l in drinking water are recommended to prevent dental caries. Conversely, concentrations of above 1.5 mg/l in water can cause dental fluorosis a disease characterised by the incomplete calcification of teeth resulting in marking, spotting, brown stains, erosion and destruction of the enamel. At higher concentrations (> 3 – 5 mg/l) fluoride interferes with bone calcification leading to the crippling disorder skeletal fluorosis.

- Dental fluorosis associated with the intake of high-fluoride drinking waters has been reported in the countries of Ukraine, Moldova and Hungary in Central Europe and this project combined hydrogeological and health information into a GIS-based risk assessment scheme to produce risk avoidance maps for the Central Europe Region. The aim of these maps was to highlight areas where defluoridation technology could be most effectively deployed.

- Although Slovakia was not included in the original outline of the project, it was incorporated into the study due to the availability of excellent hydrogeological and environmental data sets, which broadened the scope of the investigation.

- Although the main emphasis of the risk assessment was on high-fluoride areas, risks associated with low fluoride concentrations in water and dental caries were also considered as part of the project.

- During the first phase of the project, an initial assessment framework was devised based on the results of an international literature review and geochemistry and health expertise. In the framework, the following important controls on fluoride risks were identified: geology and tectonics, hydrogeology, water supply, fluoride concentrations in water, water type, anthropogenic sources of fluoride, fluorosis prevalence and health criteria and population density.

- These controls were assessed in terms of the data available for Slovakia, Ukraine, Moldova and Hungary and the final risk assessment scheme derived as follows:

    - Population Density – Although an area of high population density constitutes an inherently great risk than an area of low population density, risks also depend upon the exposure to fluoride in water. For example, a high population density in a region with high-fluoride waters is not a high-risk area if the population are supplied with low-fluoride waters from elsewhere. Details of the water supply regime were not known and population information was not available in a consistent format for all four countries. Therefore population data were included in the scheme as background information only.

    - Geology-Tectonics – information was not available in a consistent format for all four countries and although the mineral composition of different rock types exerts a fundamental control on fluoride concentrations in water, fluoride concentrations in the same rock unit can vary considerably and it is difficult to generalise. Investigations carried out during the project revealed a strong association between high-fluoride waters and tectonically active fault zones in Ukraine, however, not all fault zones are characterised by high-fluoride waters. These controlling factors could give a broad indication of risk in situations were no water chemistry data were available but were included as background information only in the risk assessment scheme developed for the present project as water chemistry data were available in all countries.

    - Hydrogeology – information was not available in consistent format for all four countries and although fluoride contents in different aquifers in the same location can vary markedly, concentrations also differ within the same aquifer unit and it is difficult to generalise. Although major aquifers used for drinking water constitute an inherently greater risk than minor aquifers, the risk also depends upon the extent of the water supply network. Detailed water supply information was not known in all countries therefore maps of the main hydrogeological units classified by aquifer importance in Moldova, Slovakia and Hungary were included in the scheme for background information only. No data were available for Ukraine.

- Water Type Chemistry – Physio-chemical controls on fluoride in groundwater dictate that high-fluoride waters are generally associated with high alkalinity-Na-K-Cl, low Ca and Mg waters as a lack of Ca inhibits the precipitation of the main fluoride bearing mineral fluorite (CaF_2) hence more fluoride remains in solution. During the present study, a strong association between high fluoride contents and mineralised Na-K-Cl waters was established in Hungary, Moldova and Ukraine, however fluoride concentrations (> 1.5 mg/l) occur over a range of water types. Whereas the water chemistry could be used to give a broad indication of likely water fluoride contents in areas were they are unknown, water type was included in this report for background information only as fluoride water chemistry data were available for the 4 study countries.

- Water Type Uptake – Many studies have shown that the development of dental fluorosis is not only dependant on the total fluoride concentration in the water but is enhanced by low Ca contents and depends upon the speciation of fluoride in the water. Thermodynamic modelling studies of selected Ukrainian waters carried out during the present study suggest that the ratio of F^- to MgF^+ and CaF^+ may be an indicator of potential health risk, however, these results are preliminary and require further investigation to determine health outcomes associated with different water types.

- Fluoride Concentrations in Water – Fluoride concentrations in water exert a fundamental control on disease incidence in the study region and water chemistry data were available nationally for Slovakia, Hungary and Moldova and in the Lvov, Kiev, Odessa and Poltava Regions of Ukraine. These data were categorised according to WHO health risk limits for fluoride in water (< 0.5 mg/l dental caries risk; 0.5 – 1.5 mg/l no adverse affects; ≥ 1.5 mg/l fluorosis risk) and incorporated into the final risk assessment scheme.

- Industrial Sources – High environmental fluoride concentrations are associated with industrial activities in the region such as aluminium production, fertilizer use and coal mining and the locations of these industries were incorporated into the final risk assessment GIS as these sites present potential problem areas.

- Fluorosis Prevalence and Health Information – No national surveys of fluorosis prevalence have been carried out in Moldova or Ukraine, however prevalence data derived from a number of previous studies and the present project were collated. This information and fluorosis incidences in Hungary were incorporated into the final risk scheme, as the occurrence of dental fluorosis is a fundamental indicator of high-fluoride risk were water defluoridation methods might be needed. No dental fluorosis has been reported in Slovakia. The relationships between dietary factors and dental fluorosis were examined in detail in the Falesti Region of Moldova as part of the project and this information was included in the final risk assessment GIS for information. Average dietary fluoride intakes across Ukraine were considered as part of the project and biogeochemical experts demonstrated that in general, intake increases from the north to the south of the country due to increased water consumption in warmer climates. Regional variances in dietary composition were incorporated into the final national risk assessment scheme for Ukraine.

- Water Supply - Basic information on the water supply regime in the four study countries was incorporated into the risk assessment GIS. In terms of dental caries risk, waters in Hungary, Ukraine and Moldova are not fluoridated before supply to the pubic whereas waters in Slovakia are fluoridated. Information about whether or not high-fluoride waters were utilised for drinking in potential problem areas was taken into account in the high-fluoride risk assessment. For example, if historical incidences of fluorosis associated with high-fluoride waters are known in an area, the area is categorised as high risk in the scheme. However, if the population are now supplied with low-fluoride drinking water from elsewhere, the final risk categorisation is reduced to moderate indicating that although no immediate health problems are evident, the situation should continue to be monitored in the future.

- Data relating to controls on fluoride risk were incorporated into the project risk assessment GIS, which is based on the ArcView® software package as this is readily available in Central Europe. Due to data confidentiality and IPR issues, two GIS were developed during the project. A generic GIS designed for general distribution contains the final risk avoidance maps of each of the study countries (Central.apr). The second GIS contains the risk avoidance maps and all the background information layers and is for dissemination by the project partners (Country.apr). Due to the different detail of data available to the project, both the GIS contain two levels of information. National data provide an overview of risks in each of the study countries and more detailed data for regions of further investigation are also included. During the present study, industrial fluoride contamination and ecological impacts in the Ziar nad Hronom area of Slovakia, geochemistry and health relationships in the regions of Falesti, Moldova and Lvov and Odessa in Ukraine and the hydrochemistry of Lvov, Odessa, Kiev and Poltava regions in Ukraine were examined in more detail to elucidate fluoride-related risks.

- With the exception of the national maps of Ukraine, the final risk avoidance maps of dental caries and high-fluoride were based upon a grid-square scheme. In each case the territory of interest was divided into a series of grid squares, the size of which was determined by the sample density of water fluoride data available for the region. Utilizing the GIS, within each square, water fluoride content, fluorosis incidence and industrial sources data were combined with water supply information to determine the overall risk as follows:

  - Dental Caries Risk - Water F mg/l < 0.5 - High Risk
    - If water is fluoridated (as in the case of Slovakia) the risk is reduced to moderate
    - Water F mg/l ≥ 0.5 - Low Risk

  - High –fluoride Risk – Water F mg/l ≥ 1.5 – High Risk
    - Or Industrial Source is present
    - Or Fluorosis Incidence is present
    - If high fluoride water is no longer used for drinking, the risk is reduced to moderate
    - Water F mg/l < 1.5 - Low Risk

- The national risk avoidance maps for Ukraine were prepared by categorising each region of the country into likely fluoride contents in water and uptake in the population. Although these maps look complete, they are based on very limited information and provide a very generalised picture, as fluoride risks within regions can vary markedly. For example, detailed information for the regions of Lvov, Poltava, Odessa and Kiev was incorporated into the final map and demonstrates that although the majority of the territory in the cases of Lvov, Odessa and Kiev is classified as low-fluoride, dental fluorosis hotspots are associated with mining and/ or water movement in tectonically active faults zones in the Chervonograd, Lvov, parts of Kiev Region and in the Arciz area of southern Odessa Region. Poltava Region lies in the centre of the Buchak-Kaniv fluoride hydrogeochemical province of Ukraine in the Dnepro-Donetsk basin and high-fluoride waters (up to 18 mg/l) are associated with shallow deposits of fluoride-bearing phosphorites in this region. Although lower-fluoride waters are available at depth, drilling costs prevent exploitation of these waters. Fluoride concentrations in waters are generally high in the Dnepro-Donetsk basin affecting the regions of Dnepropetrovsk, Donetsk and Kirovograd in addition to Poltava. Dental fluorosis has been reported in all these regions of Ukraine and geochemistry and health studies carried out during the present project indicate prevalence rates of 64% in Chervonograd (water fluoride up to 3.8 mg/l) and 90% in Arciz (water fluoride 2 – 7 mg/l). Low fluoride regions where dental caries may be a problem are located in the west, northwest and south of the country.

- High fluoride risks are also identified in the Falesti, Prut and Chadyr-Lunga regions of Moldova associated with deeper mineralised Na-K dominated waters. Although shallower water resources generally contain much lower fluoride concentrations in these regions, it is desirable that the population use the deeper waters as the shallow waters are heavily bacterially contaminated. Dental fluorosis has been reported in all these regions of Moldova and geochemistry and health investigations carried out during the present project indicate prevalence rates of 60% in the Falesti Region. Low fluoride areas where dental caries may be a problem are located in the north of the country.

- High fluoride waters are a feature of the central Great Hungarian Plain region of Hungary due to migration of deeper thermal waters into shallow Quaternary aquifers. No fluorosis incidence has been reported in this region but it is recommended that the situation be monitored in the future. High-fluoride water are also associated with the Mosonmagyarovar, Almasfuzito, Ajka Redmud, Ajka Alufactory, Varpalota Alufactory red-mud and aluminium production plants but the extent of environmental contamination and effects on health have not been investigated. Dental fluorosis has been reported historically in the towns of Bar, Dunaszekcso and Herceghalom but alternative low-fluoride waters have been supplied to these localities in recent years and the disease is no longer prevalent. However, it is recommended that the situation be monitored in the future. The majority of drinking waters in Hungary contain low fluoride concentrations (< 0.5 mg/l) and dental caries risk is of concern over most of the territory.

- High fluoride concentrations in surface and groundwaters (up to 9 mg/l) occur in the immediate vicinity of the Ziar nad Hronom aluminium factory in the Ziarska Kotlina Basin of Slovakia. Previous investigators have carried out detailed environmental investigations in this region. No incidence of fluorosis have been reported in the region and the population is supplied with water from elsewhere. Therefore, the final risk assessment for this region is reduced to moderate indicating that the situation should continue to be monitored in the future. Over almost the whole territory of Slovakia, water contents are less than 0.5 mg/l dental caries would be of concern but water is fluoridated before supply to the public and risks are therefore reduced to moderate in the assessment scheme.

- Geochemistry and health investigations incorporating assessments of drinking water fluoride, dental status and the structural functional state of bone tissue were carried out for the first time in Moldova and Ukraine as part of the present project in Falesti Region and Lvov Region respectively. The results of these studies indicate that intakes of water containing 3 – 4 mg/l fluoride cause dental fluorosis in the population, however, no detrimental effects on bone tissue formation were observed. These results confirm international studies, which indicate that skeletal fluorosis does not manifest until fluoride concentrations of 5 mg/l in water are consumed. Results of dietary surveys carried out in Falesti Region also demonstrate that diets are Ca, protein and vitamin poor, which probably enhances the severity of fluorosis in the region.

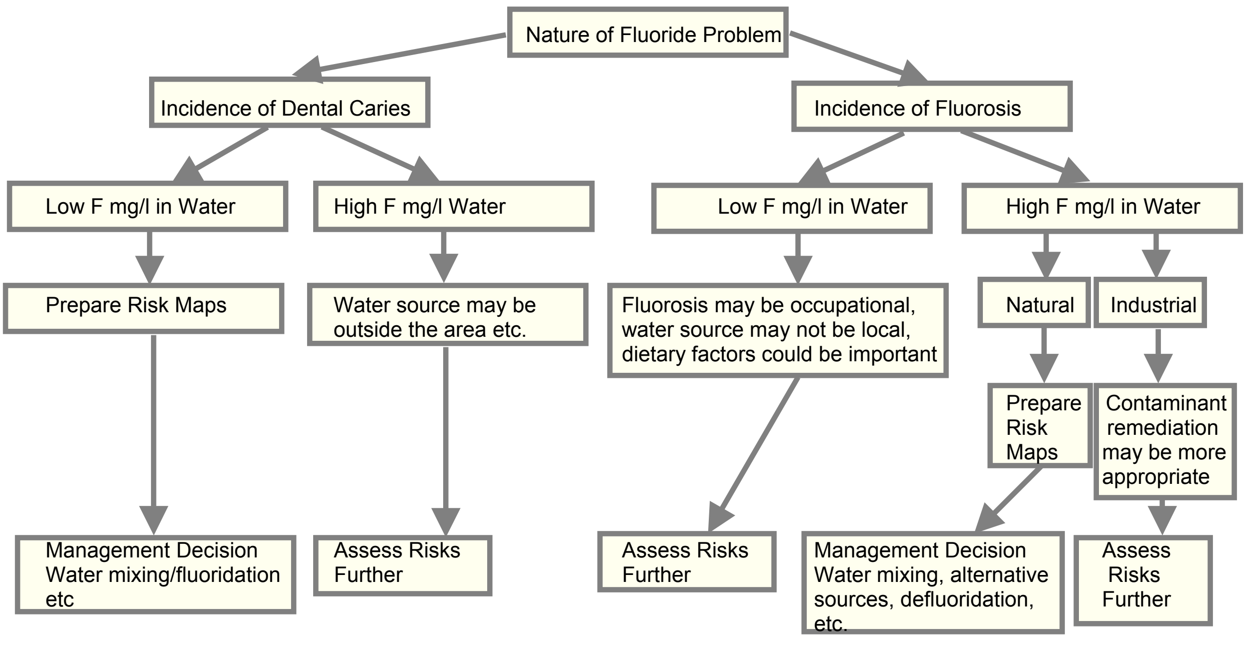
- On the basis of the high –fluoride risk assessment, the following areas are prioritised for defluoridation technology: 1. Arciz District, Odessa Region, Ukraine, 2. Falesti, Prut and Chadyr-Lunga Regions of Moldova, 3. Poltava Region, Ukraine, 4. Chervonograd Mining District, Lvov Region, Ukraine, 5. Dnepropetrovsk, Donetsk and Kirovograd Regions of Ukraine, however, further investigations are necessary to establish the extent of high-fluoride risks in these latter three regions.

9.3 RECOMMENDATIONS

The information presented in this report is based on generalized data and any follow-up implementation of defluoridation technologies should incorporate detailed localized assessments of environmental fluoride conditions and health effects in the local population. In particular, information on fluorosis incidence and water chemistry are sparse for Ukraine and Moldova and it is recommended that these areas should be the focus of future study.

Although detailed geochemistry and health studies were carried out for the first time in Ukraine and Moldova during this project, these data are preliminary and it is recommended that further investigations are carried out to elucidate the relationships between water type and fluoride content, diet, physiological status and fluoride – related diseases.

Based on the evidence of this study, the following generic risk assessment scheme is proposed for identifying water fluoride risks in other areas:



10 Fluoride Bibliography

1. **Akhmyedov, A and Gusyeynov, A. 1971**. The problem of maxillodental anomalies in adolescents residing in hotspots of endemic fluorosis. In: *Transactions of the Azerbyzhan State Medical Institute.* Vol. XXXII. Baku, 53-61.
2. **Andryeyev, I. 1981**. Influence of small-dose fluoride on development of maxillary bones in white rats. In: *Proceedings of the 60th Anniversary of Tartar Republic Stomatological Society.* Kazan, 85-86.
3. **Aoba, T. 1997**. The effect of fluoride on apatite structure and growth. *Critical Reviews of Oral Biological Medicine,* Vol. 8 (2), 136-153.
4. **Apambire, W B, Boyle, D R and Michel, F A. 1997**. Geochemistry, genesis, and health implications of fluoriferous groundwaters in the upper regions of Ghana. *Environmental Geology,* Vol. 33 (1), 13-24.
5. **Avtsyn, A and Zhavoronkov, A. 1981a**. Pathology of fluorosis. In: Avtsyn, A and Zhavoronkov, A.(ed.) *Pathology of Fluorosis.* (Novosibirsk: Nauka), 131-153.
6. **Avtsyn, A and Zhavoronkov, A. 1981b**. *Pathology of Fluorosis.* (Novosibirsk: Nauka).
7. **Avtsyn, A, Zhavoronkov, A, Rish, M and Strotchkova, L. 1991**. *Microelements of a Human Being.* (Meditsina: Moscow).
8. **Awad, M A, Hargreaves, J A and Thompson, G W. 1991**. Dental caries and fluorosis in 7-9 and 11-14 year old children who received fluoride supplements from birth. *Journal of the Canadian Dental Association,* Vol. 60 (4), 318-322.
9. **Awadia, A K and Bjorvatn, K. 1997**. Dental fluorosis: A review of literature with comments on its relationship with nutrition, nutritional status and cultural behaviour. *Journal of Dental Research,* Vol. 76 (5), 1151.
10. **AWWA. 1997**. *Water Quality Treatment, A Handbook of Public Water Supplies.* (USA: McGraw-Hill).
11. **Babyel, I, Granin, A and Zhavoronkov, A. 1968**. Changes in dental hard and periodontal tissues under experimental fluorosis. In: *Experimental and Clinical Stomatology*. Moscow, 144-148.
12. **Baelum, V, Manji, F and Fejerskov, O. 1986**. Posteruptive tooth age and severity of dental fluorosis in Kenya. *Scandinavian Journal of Dental Research,* Vol. 94 (5), 405-410.
13. **Bahnarel, I and Shelaru, I. 1999**. Health problems of population in Moldova bounded up with surrounding risk factors. In: *Conference Proceedings: Health and Surroundings*, Kishinev.
14. **Bailey, D, McKay, H, Mirwald, R, Crocker, P and Faulkner, R. 1999**. A six -year longitudinal study of the relationship of physical

activity to bone mineral accrual in growing adolescents: the University of Saskatchewan bone mineral accrual study. *Journal of Bone Mineral Research,* Vol. 14 (10), 1672-1679.
15. **Baker, J. 1998**. *Water Quality Improvement through Fluoride Reduction in Groundwater of Central Europe.* EC/6/A1 INCO-Copernicus Project Proposal.
16. **Baker J. (ed) 1999**. Water Quality Improvement Through Fluoride Reduction in Groundwater of Central Europe Technical Annex to First Annual Report, December 1999. Inco-Copernicus Programme Project (IC15-CT98-0139).
17. **Baker J. (ed) 2000**. Water Quality Improvement Through Fluoride Reduction in Groundwater of Central Europe Technical Annex to Second Annual Report, December 1999. Inco-Copernicus Programme Project (IC15-CT98-0139).
18. **Ball, J and Nordstrom, D. 1991**. *WATEQ4F- Users Manual.* (Reston: United States Geological Survey), 90-125.
19. **Banks, D, Reimann, C and Skarphagen, H. 1998**. The comparative hydrochemistry of two granitic island aquifers: The Isles of Scilly, UK and the Hvaler Islands, Norway. *The Science of the Total Environment,* Vol. 209, 169-183.
20. **Bardsen, A and Bjorvatn, K. 1998**. Risk periods in the development of dental fluorosis. *Clinical Oral Investigation,* Vol. 2, 155-160.
21. **Bartram, J and Balance, R. 1996**. *Water Quality Monitoring, a Practice Guide to the Design and Implementation of Freshwater Quality Studies and Monitoring Programmes.* (London: E&F Spon.).
22. **Berencsi, G. 1985**. The geopathological significance of drinking water on the Great Hungarian Plain. *Geographical Medicine,* Vol. 15, 141-150.
23. **Bezvushko, E V. 1999**. Factors in fluorosis in children. *Journal of Stomatology,* Vol. 3, 41-42.
24. **Bhagan, V U, Rajam, R and Renganathan, P S. 1996a**. Endemic fluorosis in Azhagappapuram village of Kanyakumari District of Tamil Nadu, India. *Asian Journal of Chemistry,* Vol. 8 (3), 536-538.
25. **Bhagan, V U, Santhi, D and Renganathan, P S. 1996b**. Study of fluorosis in Kavalkinaru village of Nellai Kattabomman District of Tamilnadu, India. *Asian Journal of Chemistry,* Vol. 8 (3), 553-556.
26. **Bidoli, E, Schinella, D and Franceschi, S. 1998**. Physical activity and bone mineral density in Italian middle-aged women. *European Journal of Epidemiology,* Vol. 14 (2), 153-157.
27. **Biro, G, Antal, M and Zajkas, G. 1996**. Nutrition survey of the Hungarian population in a randomized trial between 1992-1994. *European Journal of Clinical Nutrition,* Vol. 50, 201-208.
28. **Bowen, H. 1979**. *Environmental Chemistry of the Elements.* (London: Academic Press).
29. **Bradley, A D. 1991**. *A Preliminary Investigation of Alternative Buffers for the Determination of Fluoride in Natural Waters.* (Keyworth: British Geological Survey).

30. **Brown, D and Robertson, C. 1977**. Solubility of fluorite at 25°C. *US Geological Survey Journal of Research,* Vol. 5 (4), 506-517.
31. **Brown, W and Konig, K G. 1977**. Cariostatic mechanism of fluorides. *Caries Research,* Vol. 11 (Suppl 1), 1-327.
32. **Brusko, A and Tkatch, T. 1996**. Influence of static loading on epiphysical cartilage structure and longitudinal growth of long bones. *Orthorpaedics, Traumatology and Prosthetics,* Vol. 1, 55-59.
33. **Buiteman, J P. 1995**. *Water Treatment, Part 2 - Treatment Methods for Rural Areas.* (Delft: IHE).
34. **Bulsu, K R and Biswas, S K. 1993**. *Water Quality and Defluoridation Techniques. Prevention and Control of Fluorosis.* (New Delhi: Rajiv Ghandi National Drinking Water Mission).
35. **Burgstahler, A W. 1985**. Effects of Supplemental Vitamin-E on Dental Fluorosis in Rats - a Qualitative Preliminary-Study. *Fluoride,* Vol. 18 (4), 221-226.
36. **Burt, B A. 1994**. The case for eliminating the use of dietary fluoride supplements among young children. *Fluoride,* Vol. 27 (2), 121.
37. **Cauley, J, Murphy, P, Riley, T and Buhari, A. 1995**. Effects of fluoridated drinking water on bone mass and fractures: the study of osteoporotic fractures. *Journal of Bone Mineral Research,* Vol. 10 (7), 1076-1086.
38. **CEC. 1989**. *Scientific Assessment of EC Standards for Drinking Water Quality.* (Brussels: Commission of the European Communities).
39. **Chan, J T, Yip, T T and Jeske, A H. 1990**. The role of caffeinated beverages in dental fluorosis. *Med-Hypotheses,* Vol. 33 (1), 21-22.
40. **Chavassieux, P and Meunier, P. 1995**. Benefits and risk of fluoride supplements. *Archives of Paediatrics,* Vol. 2 (6), 568-572.
41. **Chen, Y C and Lin, M Q. 1997**. Nutrition survey in dental fluorosis afflicted areas. *Fluoride,* Vol. 30 (2).
42. **Chlebna-Sokol, D and Czerwinski, E. 1993**. Bone structure assessment on radiographs of distal radial metaphysics in children with dental fluorosis. *Fluoride,* Vol. 26 (1), 37-34.
43. **Cholak, J. 1959**. Fluorides: a critical review. *Journal of Occupational Medicine,* Vol. September, 501-511.
44. **Chyeryemnov, N, Kuznyetsov, P and Syeryebryennikov, O. 1984**. Influence of fluoride, calcium, phosphorous on mineralisation of mazillar and hard dental bone tissue. In: *New Methods of Treatment and Prophylaxis in Stomatology.* (Omsk: Collection of Scientific Works), 93-96.
45. **Ciullo, P A. 1996**. *Industrial Minerals and Their Uses, a Handbook and Formulary.* (Westwood, New Jersey: Noyes Publications).
46. **Clark, C. 1994**. Trends in prevalence of dental fluorosis in North America. *Community Dental Oral Epidemiology,* Vol. 22, 148-152.
47. **Dean, H. 1942**. The investigation of physiological effects by the

thidemiological method. *American Association of Education and Science,* Vol. 19, 23-31.
48. **Dean, H, Arnold, F and Elvove, E. 1942a**. Domestic water and dental caries. Part 2 - Study of 2832 white adolescents ages 12-14 years, of 8 suburban Chicago communities. *Public Health Report,* Vol. 56, 761-792.
49. **Dean, H, Arnold, F and Elvove, E. 1942b**. Domestic water and dental caries. Part 5 - Additional studies of the relation of fluoride in domestic waters and dental caries. *Public Health Report,* Vol. 57, 1155-1179.
50. **Den Besten, P K. 1999**. Mechanism and timing of fluoride effects on developing enamel. *Journal of Public Health Dentistry,* Vol. 59 (4), 247-251.
51. **Den Besten, P K, Heffernan, L, Featherstone, J and Shields, C. 1992**. Fluoride binding by matrix proteins in rat mineralising tissue. *Archives of Oral Biology,* Vol. 37 (6), 459-462.
52. **Dissanayake, C B. 1996**. Water quality and dental health in the Dry Zone of Sri Lanka. In: Appleton, J D, Fuge, R and McCall, G J H.(ed.) *Environmental Geochemistry and Health with specific reference to developing countries.* Vol. 113 (London: The Geological Society), 131-141.
53. **Dissanayake, C B and Chandrajith, R. 1999**. Medical geochemistry of tropical environments. *Earth-Science Reviews,* Vol. 47 (3-4), 219-258.
54. **Edmunds, W M. 1995**. *Groundwater, Geochemistry and Health.* (Keyworth: British Geological Survey).
55. **Edmunds, W M and Smedley, P M. 1996**. Groundwater geochemistry and health - an overview. In: Appleton, J D, Fuge, R and McCall, G J H.(ed.) *Environmental Geochemistry and Health with special reference to developing countries.* Vol. 113 (London: The Geological Society), 91-107.
56. **Eklund, S, Burt, B, Ismail, A I and Calderone, J. 1987**. High fluoride drinking water, fluorosis and dental caries in adults. *Journal of the American Dental Association,* Vol. 114 (3), 324-328.
57. **Eldarushyeva, Z. 1989**. Adolescents caries under different fluoride content in drinking water. *Kazan Medical Journal,* Vol. LXX (5), 358.
58. **Ericson, Y and Angamar-Mansson, B. 1983**. Fluoride concentration in rat and human teeth pulps and their possible interference with phosphatase activities. *Journal of Dental Research,* Vol. 62 (12).
59. **Fabiani, L, Leoni, V and Vitali, M. 1999**. Bone-fracture incidence rate in two Italian regions with different fluoride concentration levels in drinking water. *Journal of Trace Elements in Medical Biology,* Vol. 13 (4), 232-237.
60. **Farkas, I, Sajgo, M, Paldy, A, Pinter, A, Molnar, I, Rozsane, R, Heintz, A, Gyarmathine, D and Szoke, J. 1999**. Introductory research to implement systematic fluoridation. *Egeszegtudomany,* Vol. 43 (3), 253-261.

61. **Fedorov, Y, Sapogovskaya, T and Dmitriyev, I. 1972**. Interchange of fluoride and iodine under caries. *Therapeutic Stomatology,* Vol. 7, 6-9.
62. **Fejerskov, O, Larsen, M J, Richards, A and Baelum, V. 1994**. Dental tissue effects of fluoride. *Fluoride,* Vol. 27 (4), 15-31.
63. **Fejerskov, O, Manji, F and Baelum, V. 1990**. The nature and mechanisms of dental fluorosis in man. *Journal of Dental Research,* Vol. 69, 692-700.
64. **Fejerskov, O, Manji, F, Thylstrup, A and Larsen, M. 1977**. Clinical and structural features and possible pathogenic mechanisms of dental fluorosis. *Scandinavian Journal of Dental Research,* Vol. 85 (7), 510-534.
65. **Fleming, C M, Beal, J F and Levine, R S. 1989**. Photographic technique for the recording of children's teeth for signs of enamel mottling. *Journal of Audiovisual Media in Medicine,* Vol. 12 (1), 16-8.
66. **Fluoridation. 2000**. Posting Date. Fluoridation. http://www.fluoridation.com/
67. **Fordyce, F M and Vrana, K. (ed.) 2001**. *Development of a Fluoride Risk Assessment GIS for Central Europe. Final Report: Water Quality Improvements through Fluoride Reduction in Groundwater of Central Europe.* Inco - Copernicus 15-CT98-0139.
68. **Frant, M S and Ross, J W. 1968**. Use of total ionic strength adjustment buffer for electrode determination of fluoride in water supplies. *Analytical Chemistry,* Vol. 7, 1169-1171.
69. **Frencken, J E. 1990**. *Endemic Fluorosis in Developing Countries. Causes Effects and Possible Solutions.* (Delft: IHE).
70. **Frencken, J E, Truin, G J, Van't-Hof, M A, Konig, K G, Mabelya, L, Mulder, J and Ruiken, H M. 1990**. Prevalence of dental caries in 7-13-yr-old children in Morogoro District, Tanzania, in 1984, 1986, and 1988. *Community Dental Oral Epidemiology,* Vol. 18 (1), 2-8.
71. **Fuge, R. 1988**. Sources of halogens in the environment, influences on human and animal health. *Environmental Geochemistry and Health,* Vol. 10 (2), 51-61.
72. **Fuhong, R and Shuqin, J. 1988**. Distribution and formation of high fluoride groundwater in China. *Environmental Geology Water Science,* Vol. 12 (1), 3-10.
73. **Fukuda, Y, Igarashi, A, Takayama, T and Nakashima, S. 2000**. NMR-analysis on interaction between xylitol and fluoride or calcium. *Journal of Dental Research,* Vol. 79 (SISI), 3310.
74. **Gabovych, R. 1950**. Fluoride in drinking water and mottled dental enamel. *Hygiene and Sanitation,* Vol. 8, 13-15.
75. **Gabovych, R. 1951**. *Fluoride in Potable Waters of Ukraine.* (Kiev).
76. **Gabovych, R and Minkh, A. 1979**. *Hygienic Problems of Drinking Water Fluoridation.* (Moscow: Meditsina).
77. **Gabovych, R and Ovrutsky, G. 1969**. *Fluoride in Stomatology and Hygiene.* (Kazan: Tatpoligraph).

78. **Gerasimovskiy, V and Savinova, Y N. 1969**. Fluoride contents of volcanic rocks in the rift zone of East Africa. *Geokhimiya,* Vol. 12, 1466-1471.

79. **Gerlach, R, De Souza, A and Cury, J. 2000**. Fluoride effect on the activity of enamel matrix proteinases in vitro. *European Journal of Oral Science,* Vol. 108, 48-53.

80. **Giambro, N J, Prostak, K and Den Besten, P K. 1995**. Characterisation of fluorosed human enamel by colour reflectance, ultrastructure and elemental composition. *Fluoride,* Vol. 28 (4), 251-257.

81. **Gimblett, F G R. 1998**. *Adsorption Science and Technology.* (England: Multi-science Publishing Co Ltd).

82. **Gnatyuk, P. 1988**. Fluorosis and caries of temporal teeth. *Stomatology,* Vol. 67 (5), 67-68.

83. **Gnatyuk, P, Byezhan, L and Lazu, I. 1988**. Fluorosis prevalence in adolescents residing in regions with high fluoride content in drinking water. In: *Meeting of Moldovian Stomatologists.* Vol. 2 (Kishinev), 47-48.

84. **Gotjamanos, T. 1997**. Safety issues related to the use of silver fluoride in paediatric dentistry. *Australian Dental Journal,* Vol. 42 (3), 166-168.

85. **Grigorov, Y, Poverosnuk, V, Kozlovska, S and Sniper, L. 1992**. *Nutrition in Prophylaxis of Fluoride Intoxication.* (Kiev).

86. **Grigoryeva, L, Golovko, N, Nikolishiyn, A and Pavlyenko, L. 1993**. Fluoride influence on prevalence and intensity of stomatological disease in adolescents of Poltava Oblast. In: *Conference Proceedings - Fluoride Problems of Ecology, Biology, Medicine and Hygiene.* (Poltava), 25-26.

87. **Grimaldo, M, Borja-Aburto, V, Ramirez, A L, Ponce, M, Rosas, M and Diaz-Barriga, F. 1995**. Endemic fluorosis in San Luis Potosi, Mexico. *Environmental Research,* Vol. 68, 25-30.

88. **Groshikov, M. 1985**. *Non-caries Injuries of Dental Tissues.* (Moscow: Meditsina).

89. **Gusleakov, R. 1978**. *Material generalisation on the hydrochemistry of the Moldovian artesian basin and development of recommendations on the rational use of underground waters.* (Kishinev: Association of State Geologists).

90. **Hassan, M M. 2003**. The spatial pattern of risk from arsenic poisoning: a Bangladesh case study. *Journal of Environmental Science and Health Part A,* Vol. 38 (1), 1-24.

91. **Hawley, G M, Ellwood, R P and Davies, R M. 1996**. Dental caries, fluorosis and the cosmetic implications of different TF scores in 14-year-old adolescents. *Community Dental Health,* Vol. 13 (4), 189-92.

92. **Health Protection Ministry. 1999**. *Norms of Physiological Needs of Ukrainian Population in Main Food Nutrients.* Decree 272 (Kiev: Health Ministry of Ukraine).

93. **Heilman, J, Kiritsy, M, Levy, S and J., W. 1997**. Fluoride concentrations of infant foods. *Journal of the American Dental Association,* Vol. 128 (7), 857-863.

94. **Heller, K E, Eklund, S A and Burt, B A. 1997a**. Dental caries and fluorosis at various levels of fluoride in drinking water. *Journal of Dental Research,* Vol. 76 (SISI), 3038.
95. **Heller, K E, Eklund, S A and Burt, B A. 1997b**. Dental caries and dental fluorosis at varying water fluoride concentrations. *Journal of Public Health Dentistry,* Vol. 57 (3), 136-43.
96. **Helmer, R. 1998**. *Water Quality and Health.* (Delft: IHE).
97. **Helmer, R and Hesanhol, I. 1997**. *Water Pollution Control.* (London: E&FN Spon.).
98. **Hem, J. 1992**. *Study and Interpretation of the Chemical Characteristics of Natural Water.* (Reston: US Geological Survey).
99. **Hillier, S, Inskip, H, Coggon, D and Cooper, C. 1996**. Water fluoridation and osteoporotic fracture. *Community Dental Health,* Vol. 13 (Suppl 2), 63-68.
100. **Holland, R. 1980**. Cytotoxicity of fluoride. *Acta Odontologica Scandinavia,* Vol. 38 (2), 68-79.
101. **Horowitz, H S. 1992**. The need for toothpastes with lower than conventional fluoride concentrations for preschool-aged children. *Journal of Public Health Dentistry,* Vol. 52 (4), 216-21.
102. **Iljinsky, U and Kornaya, T. 1983**. *Drawing up a map of hydrogeological division into districts of Moldovian territory on condition of agricultural water-supply.* (Kishinev: Association of State Geologists).
103. **Ismail, A I. 1994**. Fluoride supplements: current effectiveness, side effects, and recommendations. *Community Dental Oral Epidemiology,* Vol. 22 (3), 164-72.
104. **Jacks, G, Rajagopalan, K, Alveteg, T and Jonsson, M. 1993**. Genesis of high-F groundwaters, southern India. *Applied Geochemistry,* Vol. Supplementary Issue (2), 241-244.
105. **Jackson, C, Kelly, S, Katz, B P, Hull, J and Stookey, G K. 1995**. Dental fluorosis and caries prevalence in adolescents residing in communities with different levels of fluoride in water. *Journal Public Health Dentistry,* Vol. 55 (2), 79-84.
106. **Jackson, R, Kelly, S, Katz, B P, Brizendine, E J and Stookey, G K. 1999**. Dental fluorosis in adolescents residing in communities with different water fluoride levels: 33-month follow-up. *Paediatric Dentistry,* Vol. 21 (4), 248-254.
107. **Jarup, L. 2004**. Health and environmental information systems for exposure and disease mapping and risk assessment. *Environmental Health Perspectives,* Vol. 112 (9), 995-997.
108. **Jedrychowski, W, Maugeri, U and Bianchi, I. 1997**. Environmental pollution in central and eastern European countries: a basis for cancer epidemiology. *Reviews of Environment and Health,* Vol. 12 (1), 1-23.
109. **Jenkins, G. 1967**. The mechanism of action of fluoride in reducing caries incidence. *International Dental Health,* Vol. 17, 385-390.
110. **Jimenez, L E, Spinks, T J, Bowley, N B and Joplin, G F. 1983**. Total-Body Calcium in Skeletal Fluorosis. *Lancet,* Vol. 1 (8339), 1443.

111. **Jowsey, J and Riggs, B. 1978**. Effects of concurrent calcium ingestion in intestinal absorption of fluoride. *Metabolism,* Vol. 27 (971-974).

112. **Kajaba, I and Bucko, A. 1968**. Health and nutritional status of children in an industrialised and agricultural area of Eastern Slovakia. 3. Investigations of the lipid metabolism. *Reviews of Czech Medicine,* Vol. 14 (3), 180-91.

113. **Karthikeyan, G, Pius, A and Apparao, B V. 1999**. Calcium requirement for minimizing fluoride toxicity. *Bulletin of the Chemical Society of Ethiopia,* Vol. 13 (1), 23-29.

114. **Kasyanenko, A, Sinyagovsky, G and Kovgan, N. 1981**. Medical geographical study of dental fluorosis prevalence in Poltava Oblast and measures of its prophylaxis. In: *Proceedings 50th Anniversary Poltava Medical Stomatological Institute Republican Scientific Conference.* (Poltava), 11.

115. **Khun, M. 2001a**. *Fluorine in the Environment of the Ziarska Kotlina Basin.* (Bratislava: HYDEKO-KV).

116. **Khun, M. 2001b**. *Contamination of the Environment by Fluorine in the Ziarska Kotlina Basin.* (Bratislava: HYDEKO-KV).

117. **Khun, M. 2001c**. *Fluorine - Environmental - Geochemical Data Profile.* (Bratislava: HYDEKO-KV).

118. **Kierdorf, U and Kierdorf, H. 2000**. Comparative analysis of dental fluorosis in roe deer (Capreolus capreolus) and red deer (Cervus elaphus): interdental variation and species differences. *Journal of Zoology,* Vol. 250 (1), 87-93.

119. **Kilham, P and Hecky, R. 1973**. Fluoride geochemical and ecological significance in East African waters and sediments. *Limnology and Oceanography,* Vol. 18 (6), 932-945.

120. **Kiritsy, M C, Levy, S M, Warren, J J, Guha-Chowdhury, N, Heilman, J R and Marshall, T. 1996**. Assessing fluoride concentrations of juices and juice-flavored drinks. *Journal of the American Dental Association,* Vol. 127 (7), 895-902.

121. **Korzh, A, Dyeduh, N and Shevchyenko, S. 1997**. *Osteoarthrosis.* (Kharkiv: Osnova).

122. **Kotsyubinksy, I, Filimonov, Y and Kazakova, R. 1989**. Dental caries prevalence and intensity maxillodental anomalies under conditions of fluoride deficit. In: *Proceedings of the 7th Ukrainian Republic Stomatologists Meeting - Complex Treatment and Prophylaxis of Stomatological Diseases.* (Kiev).

123. **Kozlov, E. 1972**. *Hydrogeological characteristics of Moldovian artesian basin.* (Lenningrad-Kishinev: LSU).

124. **Kozlov, E and Samarin, B. 1969**. *Hydrogeological Characteristics of the Upper Water-bearing Horizon of the Moldovan Artesian Basin.* 11977 (Leningrad-Kishinev: Earth Crust Institute).

125. **Krainov, S and Petrov, N. 1976**. Study of fluorine hydrochemistry in underground waters of Moldova. In: *Study of Hydrogeological and Engineering Geological Condition in the Territory of Moldova.* (Moscow: VSEGINGEO).

126. **Krishnamachari, K A. 1985**. Osteoporosis in fluoride toxicity. In:

Mills, C F, Bremner, I and Chesters, J K.(ed.) *Trace Elements in Man and Animals.* Vol. 5 (London: Commonwealth Agricultural Bureau), 267-270.
127. **Krishnamachari, K A. 1986a**. Fluorine. In: Mertz, W.(ed.) *Trace Elements in Human and Animal Nutrition*. Vol. 1 (London: Academic Press), 365-407.
128. **Krishnamachari, K A. 1986b**. Skeletal fluorosis in humans - a review of recent progress in the understanding of the disease. *Progress in Food and Nutrition Science,* Vol. 10 (3-4), 279-314.
129. **Kristinsson, I, Valdimarsson, O and Teingrimdottis, L. 1994**. Relation between calcium intake, grip strength and peak bone mineral density in the forearms of girls aged 13 and 15. *Journal of International Medicine,* Vol. 236 (4), 385-390.
130. **Krylov, S and Pyettsold, K. 1982**. Eruption of temporal teeth and fluorosis injury under high fluoride contents in drinking water. *Stomatology,* Vol. 61 (1), 75-77.
131. **Lahermo, P, Sandstrom, H and Malisa, E. 1991**. The occurrence and geochemistry of fluorides in natural waters in Finland and East Africa with reference to their geomedical implications. *Journal of Geochemical Exploration,* Vol. 41, 65-79.
132. **Lalumandier, J and Rozier, R. 1995**. The prevalence and risk factors of fluorosis among patients in a pediatric dental practice. *Paediatric Dentistry,* Vol. 17 (1), 19-25.
133. **Lappe, J, Recker, R and Weidenbusch, D. 1998**. Influence of activity level on patellar ultrasound transmission velocity in adolescents. *Osteoporosis International,* Vol. 8 (1), 39-46.
134. **Larsen, M J, Kir-Kegaard, E and Poulsens, S. 1987**. Patterns of dental fluorosis in a European country in relation to the fluoride content of drinking water. *Journal of Dental Research,* Vol. 66 (1), 10-12.
135. **Lehmann, R, Wapniarz, M, Hofmann, B, Pieper, B, Haubitz, I and Allolio, B. 1998**. Drinking water fluoridation: bone mineral density and hip fracture incidence. *Bone,* Vol. 22 (3), 273-278.
136. **Levine, R S, Beal, J F and Fleming, C M. 1989**. A photographically recorded assessment of enamel hypoplasia in fluoridated and non-fluoridated areas in England. *British Dental Journal,* Vol. 166 (7), 249-52.
137. **Levy, S M, Kiritsy, M C and Warren, J J. 1995a**. Sources of fluoride intake in children. *Journal of Public Health Dentistry,* Vol. 55 (1), 39-52.
138. **Levy, S M, Kohout, F J, Guha-Chowdhury, N, Kiritsy, M C, Heilman, J R and Wefel, J S. 1995b**. Infants' fluoride intake from drinking water alone, and from water added to formula, beverages, and food. *Journal of Dental Research,* Vol. 74 (7), 1399-407.
139. **Levy, S M, Kohout, F J, Kiritsy, M C, Heilman, J R and Wefel, J S. 1995c**. Infants' fluoride ingestion from water, supplements and dentifrice. *Journal of the American Dental Association,* Vol. 126 (12), 1625-32.
140. **Lewis, D W and Banting, D W. 1994**. Water fluoridation: current

effectiveness and dental fluorosis. *Community Dental Oral Epidemiology,* Vol. 22 (3), 153-8.
141. Li, C S, Gi, J C, Fan, J Y, Yin, W and Liang, X P. 1986. Relationships between ionic fluoride, total fluoride, calcium, phosphorus and magnesium in serum of fluorosis patients. *Fluoride,* Vol. 19 (4), 184-187.
142. Li, G and Ren, L. 1997. Effects of excess fluoride on bone turnover under conditions of diet with different calcium contents. *Chung Hua Ping Li Hsueh Tas Chih,* Vol. 26 (5), 277-280.
143. Li, Y, Liang, C K, Katz, B P, Niu, S, Cao, S and Stookey, G K. 1996. Effect of fluoride exposure and nutrition on skeletal fluorosis. *Journal of Dental Research,* Vol. 75 (SISI), 2699.
144. Liebe, P, Lorberer, A and Toth, G. 1984. Thermal Waters of Hungary. In: *Excursion Guide for the 27th International Geological Congress, Moscow, 1984.* (Moscow: IGC), 1 - 52.
145. Lloyd, T, Andon, M and Rollings, N. 1992. The effects of calcium supplementation on total body mineral density in adolescent females. *Journal of Bone Mineral Research,* Vol. 7 (Suppl 2), 176.
146. Lui, Y and Hua, Z W. 1991. Environmental characteristics of regional groundwater in relation to fluoride poisoning in North China. *Environmental Geology Water Science,* Vol. 18, 3-10.
147. Lukomsky, I. 1955. *Anti-caries Fluoridation of Teeth.* (Moscow: Meditsina).
148. Mabelya, L, Konig, K G and Van Palenstein-Helderman, W H. 1992. Dental fluorosis, altitude, and associated dietary factors (short communication). *Caries Research,* Vol. 26 (1), 65-7.
149. Mabelya, L, Van Palenstein-Helderman, W H, Van't Hof, M A and Konig, K G. 1997. Dental fluorosis and the use of a high fluoride-containing trona tenderizer (magadi). *Community Dental Oral Epidemiology,* Vol. 25 (2), 170-6.
150. Magaray, A, Boulton, T, Chatterton, B, Schultz, C, Nordin, B and Cockington, R. 1999. Bone growth from 11 to 17 years: relationships to growth, gender and changes with pubertal status including timing of menarche. *Acta Paediatrica,* Vol. 88 (2), 139-146.
151. Maksimenko, P, Skripnikova, T, Kozub, T, Vaslienko, V and Prihodko, M. 1988. Fluoride interaction on periodontal tissues and reactivity of organism under experiment. In: *Conference Proceedings - Scientific-technical Progress, Environmental Protection, Fundamental Problems of Medicine and Biology.* (Poltava), 57-58.
152. **Maksimenko, P, Skripnikova, T, Prosandyeyeva, G and Artyuh, V. 1987**. Prevalence of caries and periodontal diseases in residents of regions with low and increased fluoride content in drinking water. In: *Conference Proceedings - Scientific-technical Progress, Environmental Protection, Fundamental Problems of Medicine and Biology.* (Poltava).
153. Mankovska, B. 1980. The natural content of F, As, Pb and Cd in forest trees. *Biologica,* Vol. 35 (36), 489 - 496.

154. Mankovska, B. 1996. *Geochemical Atlas of Slovakia. Part - Biomass.* (Bratislava: GSSR, Lesnicky Vyskummy Ustav).
155. Marier, J R and Rose, D. 1971. *Environmental Fluoride.* (Ottawa: National Research Council of Canada).
156. Markert, B. 1992. Presence and significance of naturally occurring chemical elements of the periodic system in the plant organism and consequences for future investigations on inorganic chemistry in ecosystems. *Vegetatio,* Vol. 103, 1 - 30.
157. Markert, B. 1993. Interelement correlations detectable in plant samples based on data from reference materials and highly accurate research samples. *Fresenius Journal of Analytical Chemistry,* Vol. 345, 318-322.
158. Mascarenhas, A. 1999. Determinants of caries prevalence and severity in higher SES Indian adolescents. *Community Dental Health,* Vol. 16 (2), 107-113.
159. McGill, P. 1995. Endemic fluorosis. *Baillieres Clinical Rheumatology,* Vol. 9 (1), 75-81.
160. Melian, R, Myrlian, N, Gouriev, A, Moraru, C and Radstake, F. 1999. Groundwater quality and rural drinking-water supplies in the Republic of Moldova. *Hydrogeology Journal,* Vol. 7 (2), 188-196.
161. Milinarsky, A, Fischer, S, Giadrosich, V and Casanova, D. 1998. Bone mineral density by single photon X-ray absorptiometry in Chilean adolescents. *Journal of Rheumatology,* Vol. 25 (10), 2003-2008.
162. Ministry of the Environment. 1998. *The Evaluation of Ecological Sustainability of the Ziarska Kotlina Basin.* (Bratislava: Ministry of the Environment).
163. Misra, U K. 1992. Vitamin-D Deficiency and Fluorosis - Reply. *Fluoride,* Vol. 25 (4), 193-194.
164. Misra, U K, Gujral, R B, Sharma, V P and Bhargava, S K. 1992. Association of Vitamin-D Deficiency with Endemic Fluorosis in India. *Fluoride,* Vol. 25 (2), 65-70.
165. **Mithal, A and Godhole, M M. 1992**. Vitamin-D and endemic fluorosis. *Fluoride,* Vol. 25 (4), 191-192.
166. Mjengera, H. 1998. *Excess Fluoride in Potable Water in Tanzania and the Defluoridation Technology with Emphasis on the use of Polyaluminium Chloride and Magnesite.* (Tampere, Finland: Tampere University Publishers).
167. Mocik, A. 1986. *Minutes from Working Group for Standards.* (Bratislava: Centrum Podnej Urodnosti).
168. Moller, I. 1965. *Dental Fluorose of Caries.* (Copenhagen: Rodos Publ.).
169. Money, O V and Ivanov, V C. 1996. Monitoring of dental caries in children of Odessa. *Journal of Stomatology,* Vol. 5 (12), 379-383.
170. Morland, G, Reimann, C, Strand, T, Skarphagen, H, Banks, D, Bjorvatn, K, Hall, G and Siewers, U. 1997. The hydrogeochemistry of Norwegian bedrock ground-water - selected parameters (pH, F, Rn, U, Th, B, Na, Ca) in samples from Vestfold and Hordaland, Norway. *NGU-Bulletin,* Vol. 432, 103-117.

171. **Murthy, J, Anandavalli, T and Reddy, D. 1986**. Late responses in skeletal fluorosis. *Fluoride,* Vol. 19 (4), 181-183.
172. **Nanyaro, J, Aswathanarayana, U, Mungure, J and Lahermo, P. 1984**. A geochemical model for the abnormal fluoride concentrations in waters in parts of northern Tanzania. *Journal of African Earth Sciences,* Vol. 2 (2), 129-140.
173. **Nekrasova, H P. 1998**. Methodological approaches to relationships between water and health. In: *Abstracts of the International Science Conference.* (Odessa), 26-28.
174. **Nicholson, K. 1983**. Fluoride determination in geochemistry: errors in the electrode method of analysis. *Chemical Geology,* Vol. 38 (1-22).
175. **Nikolishyn, A. 1995**. *Dental Fluorosis in Poltava.* (Poltava: Honey Academy).
176. **Nikolishyn, A. 1999**. *Dental Fluorosis.* (Poltava).
177. **Notcutt, G and Davies, F. 2001**. Environmental accumulation of airborne fluorides in Romania. *Environmental Geochemistry and Health,* Vol. 23, 43-51.
178. **Nunn, J H, Ekanayake, L, Rugg-Gunn, A J and Saparamadu, K D. 1993**. Assessment of enamel opacities in children in Sri Lanka and England using a photographic method. *Community Dental Health,* Vol. 10 (2), 175-88.
179. **Okano, T. 1996**. Effects of essential trace elements on bone turn over in relation osteoporosis. *Nippon Rinsho,* Vol. 54 (1), 148-154.
180. **Okunyev, V, Smolyar, V and Lavrushenko, L. 1987**. *Pathogenesis, Prophylaxis and Treatment of Fluoride Intoxication.* (Kiev: Zdorovya).
181. **Ortiz, D, Castro, L, Turrubiartes, F, Milan, J and DiazBarriga, F. 1998**. Assessment of the exposure to fluoride from drinking water in Durango, Mexico, using a geographic information system. *Fluoride,* Vol. 31 (4), 183-187.
182. **Ovrutsky, G. 1962**. *Dental Fluorosis.* (Kazan).
183. **Ovrutsky, G, Redinov, I and Kisyelyov, A. 1985**. Fluoride influence on enameloblasts depending on non-specific resistability of organism. *Stomatology,* Vol. 64 (2), 12-14.
184. **Parkhurst, D. 1995**. *Users Guide to PHREEQC.* (Reston: United States Geological Survey), 95-4227.
185. **Pashayev, C. 1976**. Dental caries in hotspots of endemic fluorosis. In: *Proceedings of the 3rd Meeting of Russian Stomatologists.* (Volgograd), 110-113.
186. **Pashayev, C, Akhmyedov, R and Halifa-Zade, C. 1990**. Fluoride and other biogeochemical factors influence on microstrength of enamel and dentin. *Stomatology,* Vol. 69 (6), 10-12.
187. **Patrikyeyev, V. 1958**. Histological study of dental hard tissue injured by endemic fluorosis. *Stomatology,* Vol. 5, 19-21.
188. **Patrikyeyev, V. 1968**. *Clinical and Electronic-Microscope Studies of Dental Hard Tissues under Non-Caries Injuries.* (Moscow: Thesis Abstract).

189. **Pavlyenko, L, Nikolishyn, A and Shahova, T. 1987**. Structure of dental fluorosis in adolescents residing in different bio-geochemical provinces of Poltava Oblast. In: *Conference Proceedings - Scientific-technical Progress and Health of Human Beings.* Vol. (Poltava), 105.
190. **Pecsi, M. 1989**. *National Atlas of Hungary.* (Budapest: Kartografiai Vallalat).
191. **Pendrys, D G. 1987**. Development of a fluorosis risk index. *Journal of Dental Research,* Vol. 66 (SISI), 216.
192. **Pendrys, D G, Katz, R and Morse, D. 1994**. Risk factors for enamel fluorosis in a fluoridated population. *American Journal of Epidemiology,* Vol. 140, 461-471.
193. **Petakov, E and Poliakov, L. 1987**. *Experimental Investigation of Underground Mineralised Waters Defluorising Opportunity in One Region of Moldovian Republic with Electrodialisis Methods.* (Kishinev: Association of State Geologists).
194. **Petrovich, Y, Podorozhnaya, R, Dmitriyeva, L, Knavo, O and Vasyukova, O. 1995**. Glutamate and organic phosphates metabolic ferments under fluorosis. *Stomatology,* Vol. 74 (2), 26-28.
195. **Pickford, J. 1992**. *Water, Environment and Management.* (Kathmandu, Nepal: WEDC).
196. **Piper, A. 1944**. A graphic procedure in the geochemical interpretation of water analysis. *Transactions of the American Geophysical Union,* Vol. 25, 914-923.
197. **Politun, A. 1996**. *Epidemiological Peculiarities of Periodonatal Disease Development and their Prophylaxis under Conditions of Biogeochemical Fluoride and Iodine Deficit.* (Kiev: Ukrainian State Medical University).
198. **Posokhov, E V. 1965**. *Hydrochemistry.* (Rostov).
199. **Povoroznuk, V. 1998**. Structural-functional state of bone in women of different ages residing in endemic regions with high water fluoride content. *Osteoporosis International,* Vol. 8 (3), 34.
200. **Povoroznuk, V, Zhovinsky, E, Barhanel, I and Voloh, O. 2001a**. *Impact of increased fluoride concentrations in water on bone tissue functional state and teeth.* Ukrainian Medical Almanac Vol 1. (Kiev).
201. **Povoroznuk, V, Zhovinsky, E, Grygoreva, N, Vilensky, A and Bidenco, N. 2001b**. Impact of increased fluoride concentrations in water on bone tissue functional state, teeth, anthropometric parameters and physical development of teenagers. In: *Abstracts of the XI Congress of the Polish Osteoarthology Society and Polish Foundation of Osteoporosis.*(Krakow, Poland), 38.
202. **Radochina, S, Sollogub, E, Antonenko, A and Lutskina, Y. 1989**. Prevalence of maxillodental deformities in adolescents residing in climatic-geographic zones of Ukrainian Republic with reduced fluoride content in drinking water. *Stomatology.* 117-119.
203. **Raheb, J. 1995**. Water fluoridation, bone density and hip fractures: a review of recent literature. *Community Dental Oral Epidemiology,* Vol. 23 (5), 309-316.

204. **Rajagopal, R and Tobin, G. 1991**. Fluoride in drinking water: a survey of expert opinions. *Environmental Geochemistry and Health,* Vol. 13, 3-13.

205. **Rajyalakshmi, K and Rao, N V R. 1985**. Fluorosis in Nalgonda District in Relation to Chemical Characteristics of Potable Water and Staple Food. *Fluoride,* Vol. 18 (4), 198-203.

206. **Rapant, S, Vrana, K and Bodis, D. 1996**. *Geochemical Atlas of Slovakia - Part 1. Groundwater.* (Bratislava: Geological Survey of the Slovak Republic).

207. **Reddy, D R, Lahiri, K, Rao, N, Vedanayakam, H S, Ebenezer, L N and Mohan, S R. 1985**. Trial of magnesium compounds in the prevention of skeletal fluorosis - an experimental-study. *Fluoride,* Vol. 18 (3), 135-140.

208. **Reddy, K and Gloss, S. 1992**. Geochemical speciation as related to the mobility of F, Mo and Se in soil leachates. *Applied Geochemistry,* Vol. Supplementary Issue (2), 159-163.

209. **Redinov, I. 1981**. Fluoride, calcium, phosphorous content in surface layers of dental enamel under experimental fluorosis. In: *Conference Proceedings - 60th Anniversary of Tartar Republic Stomatological Society.* (Kazan), 34-35.

210. **Redinov, I. 1984**. Dental fluorosis development under different states of organisms resistability. *Kazan Medical Journal,* Vol. LXV (3), 220-221.

211. **Redinov, I. 1985**. *Non-specific Prophylaxis of Dental Fluorosis.* (Kazan: Abstract of Thesis).

212. **Reimann, C, Hall, G, Siewers, U, Bjorvatn, K, Morland, G, Skarphagen, H and Strand, T. 1996**. Radon, fluoride and 62 elements as determined by ICP-MS in 145 Norwegian hard rock groundwater samples. *The Science of the Total Environment,* Vol. 192, 1-19.

213. **Riordan, P J. 1989**. Guidelines for the use of dietary fluoride supplements in Australia. *Australian Dental Journal,* Vol. 34 (4), 359-62.

214. **Riordan, P J. 1993a**. Perceptions of dental fluorosis. *Journal of Dental Research,* Vol. 72 (9), 1268-74.

215. **Riordan, P J. 1993b**. Dental fluorosis, dental caries and fluoride exposure among 7-year-olds. *Caries Research,* Vol. 27 (1), 71-7.

216. **Riordan, P J. 1996**. The place of fluoride supplements in caries prevention today. *Australian Dental Journal,* Vol. 41 (5), 335-42.

217. **Rock, W P and Sabieha, A M. 1997**. The relationship between reported toothpaste usage in infancy and fluorosis of permanent incisors. *British Dental Journal,* Vol. 183 (5), 165-70.

218. **Rozier, R. 1999**. The prevalence and severity of enamel fluorosis in North American Adolescents. *Journal of Public Health Dentistry,* Vol. 59 (4), 239-246.

219. **Ruan, J and Wong, M H. 2001**. Accumulation of fluoride and aluminium related to different varieties of tea plant. *Environmental Geochemistry and Health,* Vol. 23, 53-63.

220. **RuggGunn, A J, AlMohammadi, S M and Butler, T J. 1997**. Effects of fluoride level in drinking water, nutritional status, and

socio-economic status on the prevalence of developmental defects of dental enamel in permanent teeth in Saudi 14-year-old boys. *Caries Research,* Vol. 31 (4), 259-267.

221. Rwenyonyi, C, Bjorvatn, K, Birkeland, J and Haugejorden, O. 1999. Altitude as a risk indicator of dental fluorosis in adolescents residing in areas with 0.5 and 2.5 mg fluoride per litre in drinking water. *Caries Research,* Vol. 33 (4), 267-274.

222. Rybakov, A and Baziyan, G. 1972. Dental state in adolescents residing in hotspots of endemic fluorosis. *Stomatology,* Vol. 51 (1), 42-48.

223. Sabeiha, A and Rock, W P. 1997. Relation between fluoride intake and enamel mottling. *Journal of Dental Research,* Vol. 76 (3040), 393.

224. Saether, O, Reimann, C, Hilmo, B and Taushani, E. 1995. Chemical composition of hard- and softrock groundwaters from central Norway with special consideration of fluoride and Norwegian drinking water limits. *Environmental Geology,* Vol. 26, 147-156.

225. Sampaio, F C, Vonder-Fehr, F R, Arneberg, P, Gigante, D P and Hatloy, A. 1999. Dental fluorosis and nutritional status of 6- to 11-year-old children living in rural areas of Paraiba, Brazil. *Caries Research,* Vol. 33 (1), 66-73.

226. Schamschula, R G, Duppenthaler, J L, Sugar, E, Un, P S, Toth, K and Barmes, D E. 1988a. Fluoride intake and utilization by Hungarian children: associations and interrelationships. *Acta Physiology Hungary,* Vol. 72 (2), 253-61.

227. Schamschula, R G, Sugar, E, Un, P S, Duppenthaler, J L, Toth, K and Barmes, D E. 1988c. Aluminium, calcium and magnesium content of Hungarian foods and dietary intakes by children aged 3.9 and 14 years. *Acta Physiology Hungary,* Vol. 72 (2), 237-51.

228. Schamschula, R G, Sugar, E, Un, P S, Toth, K, Barmes, D E and Adkins, B L. 1985. Physiological indicators of fluoride exposure and utilization: an epidemiological study. *Community Dental Oral Epidemiology,* Vol. 13 (2), 104-7.

229. **Schamschula, R G, Un, P S, Sugar, E, Duppenthaler, J L, Toth, K and Barmes, D E. 1988b**. Daily fluoride intake from the diet of Hungarian children in fluoride deficient and naturally fluoridated areas. *Acta Physiology Hungary,* Vol. 72 (2), 229-35.

230. Schamschula, R G, Un, P S, Sugar, E, Duppenthaler, J L, Toth, K and Barmes, D E. 1988d. The fluoride content of selected foods in relation to the fluoride concentration of water. *Acta Physiology Hungary,* Vol. 72 (2), 217-27.

231. Schuling, R, Andriessen, P, Frapporti, G, Kreulen, R, De Leeuw, J, Poorter, R, De Smeth, J, Vergouwen, L, Vriend, S, Zuurdeeg, B and Nijenhuis, I. 1994. *Introduction to Geochemistry.* (Utrecht, Netherlands: Institute of Earth Sciences).

232. Schunau, E. 1998. The development of the skeletal system in adolescents and the influence of muscular strength. *Hormone Research,* Vol. 49 (1), 27-31.

233. **Selwitz, R, Nowjack-Raymer, R, Kingman, A and Driscoll, W. 1995**. Prevalence of dental caries and dental fluorosis in areas with optimal and above-optimal water fluoride concentrations: a 10 year follow-up survey. *Journal of Public Health Dentistry,* Vol. 55 (2), 85-93.
234. **Selwitz, R, Nowjack-Raymer, R, Kingman, A and Driscoll, W. 1998**. Dental caries and dental fluorosis among school-age adolescents who were lifelong residents of communities having either low or optimal levels of fluoride in drinking water. *Journal of Public Health Dentistry,* Vol. 58 (1), 28-35.
235. **Seow, W K and Thomsett, M J. 1994**. Dental fluorosis as a complication of hereditary diabetes insipidus: studies of six affected patients. *Paediatric Dentistry,* Vol. 16 (2), 128-32.
236. **Sergio-Gomez, S, Weber, A and Torres, C. 1989**. Fluoride content of tea and amount ingested by children. *Odontologia Chilena,* Vol. 37 (2), 251-5.
237. **Shareaevskii, L and Borevskii, B. 1977**. *Regional Estimation of Underground Exploitation Resources in the Area between Dnister and Prut Rivers at 1/1/77.* (Kishinev: Association of State Geologists).
238. **Shupe, J L, Christofferson, P V, Olson, A E, Allred, E S and Hurst, R L. 1987**. Relationship of cheek tooth abrasion to fluoride-induced permanent incisor lesions in livestock. *American Journal of Veterinary Research,* Vol. 48 (10), 1498-503.
239. **Shylkina, L. 1997a**. Osteoarthrosis prevalence in residents of Buchatska fluoride province within the bounds of Poltava Oblast. *Orthorpedics, Traumatology and Prosthetics,* Vol. 4, 99-101.
240. **Shylkina, L. 1997b**. Results of fluoride hydrogeological region on prosthetic repair. *Orthorpedics, Traumatology and Prosthetics,* Vol. 4, 17-20.
241. **Silva, M and Reynolds, E C. 1996**. Fluoride content of infant formulae in Australia. *Australian Dental Journal,* Vol. 41 (1), 37-42.
242. **Siposs, Z and Toth, G. 1989**. Hydrogeology. In: Pecsi, M.(ed.) *National Atlas of Hungary.* (Budapest: Kartografiai Vallalat), 46-47.
243. **Skinner, C. 2000**. In praise of phosphates, or why vertebrates chose apatite to mineralise their skeletal elements. *International Geology Review,* Vol. 42, 232-240.
244. **Skripnikova, T, Maksimenko, P and Kozub, T. 1993**. Periodontal tissues and some indices of organism reactivity in animals using water with different fluoride concentrations. In: *Proceedings of the Scientific-practical Conference - Fluoride. Problems of Ecology, Biology, Medicine and Hygiene.* (Poltava), 79.
245. **Slangen, P.** *Zeolite Synthesis using Rapid Heating Methods, Towards Continuous Synthesis.* (Delft: Technical University).
246. **Slemenda, W, Reister, T and Hui, S. 1994**. Influence on skeletal mineralisation in adolescents: evidence for varying effects of sexual maturation and physical activity. *Journal Paediatrics,* Vol.

125 (2), 201-207.
247. **Smith, M, Lantz, E and Smith, H. 1931**. The cause of mottled enamel. *Science,* Vol. 74, 244.
248. **Smolyar, V. 1970**. Calcium-phosphorous balance under introduction of different amounts of fluoride. *Hygiene and Sanitation,* Vol. 12, 16-19.
249. **Smolyar, V. 1974**. Some aspects of skeletal mineralisation under long term exposure to different amounts of fluoride. *Hygiene and Sanitation,* Vol. 1, 17-20.
250. **Smolyar, V. 1989**. *Hypo- and Hypermicroelementoses.* (Kiev: Zdorovye).
251. **Sowers, M R, Wallace, R B and Lemke, J H. 1986**. The Relationship of Bone Mass and Fracture History to Fluoride and Calcium Intake - a Study of 3 Communities. *American Journal of Clinical Nutrition,* Vol. 44 (6), 889-898.
252. **Spuzyak, M and Sharmazanova, Y. 1997**. Osteopenia and traumatic skeletal injuries in adolescents. *Pharmaceutical Chemist,* Vol. 11, 23.
253. **StopFluoridation. 2000**. Posting Date. StopFluoridation. http://www.rvi.net/~fluoride/index.htm
254. **Susheela, A K. 1993**. *Health Aspects. Prevention and Control of Fluorosis in India.* (Delhi: NDHI National Drinking Water Mission).
255. **Susheela, A K. 1999**. Fluorosis management programme in India. *Current Science,* Vol. 77 (10), 1250-1256.
256. **Sutygina, A. 1989**. Inclination to periodontal injuries in adolescents under different fluoride concentrations in drinking water. In: *Clinical System in Stomatology.* (Kazan), 29-30.
257. **Tebbutt, T H Y. 1983**. *Relationship between Natural Water Quality and Health.* (Paris: UNESCO).
258. **Teotia, M, Teotia, S P S and Singh, K. 1998**. Endemic chronic fluoride toxicity and dietary calcium deficiency interaction syndromes of metabolic bone disease and deformities in India: year 2000. *Indian Journal of Paediatrics,* Vol. 65 (3), 371-381.
259. **Teotia, S P S. 1999**. Dental fluorosis. *National Medical Journal of India,* Vol. 12 (3), 96-98.
260. **Teotia, S P S and Teotia, M. 1994**. Dental-caries - a disorder of high fluoride and low dietary calcium Interactions - 30 years of personal research. *Fluoride,* Vol. 27 (2), 59-66.
261. **Teotia, S P S, Teotia, M and Singh, R. 1981**. Hydrogeochemical aspects of endemic fluorosis in India - an epidemiological study. *Fluoride,* Vol. 14 (2), 69-75.
262. **Todorashko, O. 1989**. Inclination to caries injuries in children of pre-school age depending on fluoride contents in drinking water. In: *Proceedings of the 7th Ukrainian Republic Stomatologists Meeting - Complex Treatment and Prophylaxis of Stomatological Diseases.* (Kiev), 329-330.
263. **Tole, M, Moturi, W and Davies, T. 1999**. The contributions of drinking water to dental fluorosis in Njoro Division, Nakuru District. In: *Geomedicine In Eastern and Southern Africa.* (Nairobi, Kenya).

264. **Toma, S, Kreidman, J, Vedina, O and Veliksar, S. 1999**. Some observations on fluoride problems in the Moldova Republic. *Fluoride,* Vol. 32 (2), 67-70.
265. **Tomlinson, A. 1998**. *Modern Zeolites, Structure, Function in Detergents and Petrochemicals.* (Switzerland: Trans Tech Publications).
266. **Toss, G. 1992**. Effect of calcium intake versus other life-style factors on bone mass. *Journal of International Medicine,* Vol. 231 (2), 181-186.
267. **Toth, G. 1989**. Mineral and Thermal Wells. In: M., P.(ed.) *National Atlas of Hungary.* (Budapest: Kartografiai Vallalat), 74.
268. **Toth, K and Sugar, E. 1978**. Fluoride content of food and the estimated daily intake from foods. *Acta Physiology Hungary,* Vol. 51 (4), 361-369.
269. **Tsitsishvili, G, Andronikashvili, T, Kirov, G and Filizova, L. 1992**. *Natural Zeolites.* (England: Ellis Horwood Ltd).
270. **US-EPA. 2000a**. Posting Date. Air Toxics Web-site. http:/www.epa.gov/ttnuatw1/hlthef/hydrogen.html.
271. **US-EPA. 2000b**.Posting Date. IRIS Databse. http://www.epa.gov/ngispgm3/iris/subst/00053.htm
272. **Van Palenstein-Helderman, W H, Mabelya, L, Van't Hof, M A and Konig, K G. 1997**. Two types of intraoral distribution of fluorotic enamel. *Community Dent Oral Epidemiology,* Vol. 25 (3), 251-5.
273. **Vanchanen, V V. 1997**. Dental caries in different biogeochemical regions of Ukraine. *Medical Business,* Vol. 3, 17-20.
274. **Vedina, O and Kreidman, J. 1999**. Fluoride distribution in burozems of Moldova. *Fluoride,* Vol. 32 (2), 71-73.
275. **Vorontsov, I. 1986**. *Regularities of adolescents physical development and methods of its evaluation.* (Leningrad: Medical Institute Publishing House).
276. **Voynar, A. 1960**. *Biological role of Microelements in Human and Animal Organism.* (Moscow: Vysshaya shokola).
277. **Vrana, K and Kusikova, S. 1998**. The use of hydrogeochemical methods to solve the ecological stability of land. In: *Proceedings of the 10th Hydrogeologicka Conference.* (Strad Pod Ralskem), 233-236.
278. **Vyeltishchyev, Y. 1995**. Ecopathology in childhood. *Paediatrics,* Vol. 4 (26-33).
279. **Vyesnina, L. 1993**. Correlation relationships of periodontal tissues functional state and erythrocytes under fluoride intoxication and other pathological states. In: *Proceedings of Conference - Problems of Ecology, Biology, Medicine and Hygiene.* (Poltava), 13-14.
280. **Warren, J J, Kanellis, M J and Levy, S M. 1999**. Fluorosis of the primary dentition: what does it mean for permanent teeth? *Journal of the American Dental Association,* Vol. 130 (3), 347-56.
281. **WEDC. 2000**. Posting Date. WEDC Conference Series. http://info.lboro.ac.uk/departments/cv/wedc/papers/contents.html
282. **Weeks, K J, Milsom, K M and Lennon, M A. 1993**. Enamel

defects in 4- to 5-year-old children in fluoridated and non-fluoridated parts of Cheshire, UK. *Caries Research,* Vol. 27 (4), 317-20.
283. **Weimann, E, Witzel, C, Schwidergall, S and Buhles, H. 1998**. Effects of high performance sports on puberty development of female and male gymnasts. *Wein Medizinische Wochenschrift,* Vol. 148 (10), 231-234.
284. **Whitford, G M. 1997**. Determinants and mechanisms of enamel fluorosis. *Ciba Foundation Symposium,* Vol. 205, 226-41; discussion 241-5.
285. **Whitford, G M. 1999**. Fluoride metabolism and excretion in adolescents. *Journal of Public Health Dentistry,* Vol. 59 (4), 224-228.
286. **WHO. 1984**. *Fluorine and Fluorides.* (Geneva: WHO).
287. **WHO. 1986**. *Appropriate Use of Fluorides for Human Health.* (Geneva: WHO).
288. **WHO. 1996a**. *Trace Elements in Human Nutrition and Health.* (Geneva: World Health Organisation).
289. **WHO. 1996b**. *Guidelines for Drinking Water Quality.* (Geneva: World Health Organisation).
290. **WHO. 2000a**. Posting Date. Fluoride in Drinking Water. http://www.who.int/environmental_information/Information_resources/htmdocs/Fluoride/fluoride.html
291. **WHO. 2000b**. Posting Date. Water and Sanitation - Fluoride. http://www.who.int/water_sanitation_health/GDWQ/Chemicals/fluoridefull.html
292. **Winston, A E, Nunez, A, Charig, A and Novack, S. 2000**. Effect of fluoride on calcium uptake from a remineralizing toothpaste. *Journal of Dental Research,* Vol. 79 (SISI), 1186.
293. **Woltgens, J H, Etty, E J, Nieuwland, W M and Lyaruu, D M. 1989**. Use of fluoride by young children and prevalence of mottled enamel. *Advances in Dental Research,* Vol. 3 (2), 177-82.
294. **Wong, M. 1991**. Clinical comparison of treatment for endemic dental fluorosis. *Journal of Endodontics,* Vol. 17 (7), 343-345.
295. **Wright, J T, Chen, S C, Hall, K I, Yamauchi, M and Bawden, J W. 1996**. Protein characterization of fluorosed human enamel. *Journal of Dental Research,* Vol. 75 (12), 1936-41.
296. **Yoder, K M, Mabelya, L, Robison, V A, Dunipace, A J, Brizendine, E J and Stookey, G K. 1998**. Severe dental fluorosis in a Tanzanian population consuming water with negligible fluoride concentration. *Community Dental Oral Epidemiology,* Vol. 26 (6), 382-93.
297. **Zaichick, V, Tsyb, A, Matveenko, E and Chernichenko, I. 1996**. Instrumental neutron activation analysis of essential and toxic elements in child and adolescent diets in the Chernobyl disaster territories of Kaluga Region. *The Science of the Total Environment,* Vol. 192 (3), 269-274.
298. **Zang, Z Y, Fan, J Y, Yen, W, Tian, J Y, Wang, J G, Li, X X and Wang, E L. 1996**. The effect of nutrition on the development of endemic osteomalacia in patients with skeletal fluorosis. *Fluoride,*

Vol. 29 (1), 20-24.
299. Zaydenshtein, A and Yashkova, T. 1978. Influence of small-dose fluoride on marginal parodondtium. *Kazan Medical Journal,* Vol. LIX (2), 10-11.
300. Zhang, B, Hong, M, Zhao, Y, Lin, X, Zhang, X and Dong, J. 2003. Distribution and risk assessment of fluoride in drinking water in the West Plain region of Jilin Province, China. *Environmental Geochemistry and Health,* Vol. 25 (4), 421-431.
301. Zhavoronkov, A. 1976. Histopathology of maxillodental system under experimental fluorosis. *Bulletin of Experimental Biology and Medicine,* Vol. LXXXII (12), 1506-1509.
302. Zhavoronkov, A and Avtsyn, A. 1989. Fluorosis and hypofluorosis. In: *Proceedings of All-Russia Symposium Microelements of Human Beings.* 96-98.
303. **Zheng, B S, Ding, Z H, Huang, R G, Zhu, J M, Yu, X Y, Wang, A M, Zhou, D X, Mao, D J and Su, H C. 1999**. Issues of health and disease relating to coal use in southwestern China. *International Journal of Coal Geology,* Vol. 40 (2-3), 119-132.
304. Zhovinsky, E. 1976a. *Fluorine in Sedimentary Rocks and Lithogenesis Problems in Moldova.* (Kiev: Minerals, Geochemistry and Physics Institute).
305. Zhovinsky, E. 1976b. Geochemistry of fluorine in Upper Proterozoic sedimentary and sedimentary-volcanogenic formations of the south-west of the Eastern-European platform. In: *Geochemistry of Sedimentary Rocks and Prognosis of Mineral Resources.* (Kiev: Naukova Dumka), 8.
306. Zhovinsky, E. 1977. Some issues of fluorine geochemistry of sedimentary-volcanogenic formations lithogenesis. In: *Proceedings of XI Congress of the Carpathian-Balkan Geological Association.* (Kiev: Naukova Dumka), 307-308.
307. **Zhovinsky, E. 1978**. Fluorine in Upper Proterozoic sedimentary and sedimentary-volcanogenic formations of the south-west of the Eastern-European platform. In: *Geochemistry of Sedimentary Rocks and Prognosis of Mineral Resources.* (Kiev: Naukova Dumka), 32-42.
308. Zhovinsky, E. 1979a. *Geochemistry of fluoride in sedimentary formations of southwestern East-European Platform.* (Kiev: Naukova Dumka).
309. Zhovinsky, E. 1979b. *Geochemistry of Elements in Sedimentary Thickness Lithogenesis in Moldova.* (Kiev: Minerals, Geochemistry and Physics Institute).
310. Zhovinsky, E. 1979c. Methods of epigenetic ore deposit exploration in sedimentary rocks (exemplified by fluorite-polymetallic ore deposits of Podoliya). In: *Ore-controlling Factors and Rare and Non-ferrous Metal Deposit Formation Conditions in Sedimentary Rocks.* (Moscow: Academy of Sciences of the USSR).
311. Zhovinsky, E. 1980a. Some issues of fluorite geochemistry of sedimentary-volcanogenic formations lithogenesis. In: *Lithology. Proceedings of XI Congress of Carpathian-Balkan Geological*

Association. (Kiev: Naukova Dumka), 307-308.
312. **Zhovinsky, E. 1980b**. Hydrogeochemical fluorite deposits exploration method. In: *Sedimentary Rocks and Ores.* (Kiev: Naukova Dumka), 111-118.
313. **Zhovinsky, E. 1980c**. *Geochemistry of Fluorine in Sedimentary and Sedimentary-volcanogenic Formations of the South-west of the Eastern-European platform.* (Kiev: Academy of Sciences of the Ukrainian SSR).
314. **Zhovinsky, E. 1981a**. *Determination of Fluorine Sorption and Lixiviation by Sedimentary Rocks in Moldova for Establishment of Underground Waters Defluorising Opportunity.* (Kiev: Minerals, Geochemistry and Physics Institute).
315. **Zhovinsky, E. 1981b**. Fluorine sources and fluorite formation in sedimentary formations of the south-west of the Eastern-European platform. In: *Composition, Genesis and Allocation of Sedimentary Rocks and Ores.* (Kiev: Naukova Dumka), 268-274.
316. **Zhovinsky, E. 1981c**. Geochemical fluorimetric exploration methods of fluorspar. In: *Fluorite of Ukraine.* (Kiev: Naukova Dumka), 55-65.
317. **Zhovinsky, E. 1982a**. Peculiarities of fluorine migration in natural landscapes. In: *Geochemistry of Landscapes for Natural Mineral Deposit Exploration and Environmental Protection.* (Novorossiysk).
318. **Zhovinsky, E. 1982b**. Fluorimetric exploration of fluorspar and other mineral resources. In: *Geochemical Exploration Methods for Natural Mineral Deposits. Thesis of Reports III of All-Soviet Conference.* Vol. B.6. (Moscow: Nauka), 28-30.
319. **Zhovinsky, E. 1982c**. *Geochemical Exploration Methods for Fluorite of the Bakhtyn Deposit Area.* (Kiev).
320. **Zhovinsky, E. 1983a**. Geochemical exploration methods for fluorite deposits. In: *Geochemistry and Ore Formation.* Vol. 11 (Moscow), 44-47.
321. **Zhovinsky, E. 1983b**. Significance of fluorine desorption mechanism for geochemical exploration for fluorspar. *Reports of the Academy of Sciences of the Ukrainian SSR,* Vol. 1, 7-9.
322. **Zhovinsky, E. 1985**. *Fluorimetric Exploration Methods.* (Kiev: Naukova Dumka).
323. **Zhovinsky, E. 1986**. Lithogenesis and fluorite formation. In: *Lithogenesis and Mineral Resources.* (Kiev: Naukova Dumka), 20-26.
324. **Zhovinsky, E. 1987**. Fluorimetric fluorspar and other mineral exploration methods. In: *Lithogeochemical Exploration Results Interpretation Methods.* (Moscow: Nauka).
325. **Zhovinsky, E. 1988**. Superimposed fluorine haloes (theory and practice of geochemical exploration). In: *Theory and Practice of Geochemical Exploration in Modern Conditions.* Vol. Book 4 (Moscow), 40-41.
326. **Zhovinsky, E. 1992**. Geochemical exploration for hidden ore deposits by superimposed haloes of halogens. In: *Abstracts of the 29th International Geological Congress, Session on New*

Exploration Methods for Hidden Ore Deposits. (Kyoto, Japan: IGC).

327. Zhovinsky, E. 1994a. Mobile forms of fluorine in the environment. In: *Abstracts of the 3rd International Symposium on Environmental Geochemistry.* (Krakow Poland), 462.

328. Zhovinsky, E. 1994b. Mobile forms of fluorine in the environment (soil and water). In: *Abstracts of the International Mineralogical Association 16th General Meeting.* (Pisa, Italy), 461.

329. Zhovinsky, E. 1994c. Mobile forms of fluorine in soils. In: *Proceeding of the XXth Conference of the International Society for Fluoride Research.* (China), 89.

330. Zhovinsky, E. 1994d. Determination of fluorine forms - indicators of endemic diseases in potable waters. In: *Proceedings of the XXth Conference of the International Society for Fluoride Research.* (China), 89.

331. Zhovinsky, E. 1995. Fluorine and flysch evolution in the Ukrainian Carpathians. In: *Abstracts of the CBGA XV Congress.* (Athens, Greece).

332. Zhovinsky, E. 2000. Exploration of mineral deposits by mobile forms of chemical elements. *Mineralogical Journal of Ukraine,* Vol. 22 (5/6), 26-29.

333. Zhovinsky, E and Dmytrenko, G. 2000a. New methods of geochemical mapping by mobile forms of chemical elements. In: *Abstracts of the 31st International Geological Congress - Geochemistry.* Vol. 14-4 (Rio de Janeiro, Brazil), 177.

334. Zhovinsky, E and Dmytrenko, G. 2000b. Mobile forms of fluorine in ecosystems and endemic diseases. In: *Abstracts of the 31st International Geological Congress - Environmental Geology.* Vol. 23-1 (Rio de Janeiro, Brazil), 219.

335. Zhovinsky, E, Dobrovolsky, Y and Ostrovska, G. 1981a. Kinetic study of fluorite dissolution in water and water solutions of salts. *Reports of the Academy of Sciences of the Ukrainian SSR,* Vol. 6 (3-6).

336. Zhovinsky, E, Dovgan, R and Melnichuk, E. 1984a. Fluorine - geochemical exploration indicator of fluorite and rare-metal mineralization in the west part of the Ukrainian Shield. *Reports of the Academy of Sciences of the Ukrainian SSR,* Vol. 2, 16-19.

337. Zhovinsky, E and Gamarnik , M. 1981. Quantitative X-ray diffraction phase analysis of fluorite in mixture with calcite and apatite. *Reports of the Academy of Sciences of the Ukrainian SSR,* Vol. 9, 3-6.

338. Zhovinsky, E and Ivanchenko, V. 1980. Interpretation of hydrogeochemical fluorite anomalies by the example of Dniester Region. *Reports of the Academy of Sciences of the Ukrainian SSR,* Vol. 6 (15-16).

339. Zhovinsky, E and Karpenko, A O. 1975. Dependence of hydration biotites from F content. *Reports of the Association of Science of the Ukrainian SSR,* Vol. 9, 780-782.

340. Zhovinsky, E, Kirillov, G and Otreshko, A. 1983a. *Geological Conditions of Allocation, Prognosis and Exploration Criteria of*

Fluorite Deposits in the Volnovakhsk Zone of the Ukrainian Shield. (Simferopol).

341. **Zhovinsky, E, Kolesnikova, R and Kuraeva, I. 1990**. *Kinetics of Fluorite Dissolution Processes in Organic Acid Solutions.* (Kiev: Naukova Dumka).

342. **Zhovinsky, E, Korzun, E and Kuraeva, I. 1984b**. *Fluorimetric Survey of Tectonic Activation Zone Segments of the Territory of the Moldavian SSSR.* (Kiev: Academy of Sciences of the Ukrainian SSR).

343. **Zhovinsky, E, Korzun, E and Kuraeva, I. 1985a**. *Fluorimetric Fluorspar Exploration within the Bakhtyn Ore-Prospect Area.* (Kiev: Academy of Sciences of the Ukrainian SSR).

344. **Zhovinsky, E, Korzun, E and Kuraeva, I. 1987**. Delineating tectonic fault zones in the territory of Moldavia by superposed fluorine haloes. *Reports of the Academy of Sciences of the Ukrainian SSR,* Vol. 8, 6-8.

345. **Zhovinsky, E and Kuraeva, I. 1986a**. Fluorine - mineral local prognosis and exploration indicators in various geochemical landscapes. In: *Geochemistry of Landscapes.* Vol. 45-48 (Novorossiysk: Rostov University).

346. **Zhovinsky, E and Kuraeva, I. 1986b**. Hydrogeochemical exploration for mineral resources by fluorine. In: *Thesis of Reports of All-Soviet Conference.* (Tomsk: Tomsk Political Institute), 85-86.

347. **Zhovinsky, E and Kuraeva, I. 1987a**. *Geochemistry of Fluorine (Applied Significance).* (Kiev: Naukova Dumka).

348. **Zhovinsky, E and Kuraeva, I. 1987b**. *Geochemistry of Fluoride.* (Kiev: Naukova Dumka).

349. **Zhovinsky, E and Kuraeva, I. 1990a**. Fluorine migration in conditions of technogenic pollution of natural environments. In: *Ways of Reducing Anthropogenic Impacts on Resources.* (Kiev: Znaniye), 30-31.

350. **Zhovinsky, E and Kuraeva, I. 1990b**. Fluorine in ecologo-geochemical systems of the hypergenesis zone. In: *Microelements in Biology and Their Application in Agriculture and Medicine.* (Samarkand).

351. **Zhovinsky, E and Kuraeva, I. 1991**. *Approbation, Improvement and Implementation of Geochemical Exploration Methods by Superimposed Fluorine Haloes.* (Kiev: Academy of Sciences of the Ukrainian SSSR).

352. **Zhovinsky, E and Kuraeva, I. 1996**. Kinetics of fluorine dissolution in the zone of hypergenesis. In: *Abstracts of the VI International Symposium on Experimental Mineralogy, Petrology and Geochemistry.* (Baureth, Germany).

353. **Zhovinsky, E, Kuraeva, I and Kolesnilova, R. 1993a**. Fluorite solubility in solutions of organic acids. In: *Mineralogical-Geochemical Fluorite Exploration Criteria.* (Kiev: Naukova Dumka), 72-86.

354. **Zhovinsky, E, Kuraeva, I, Krychenko, N, Shurpach, N and Kolyabina, I. 2001a**. Basic mobile forms of chemical elements in certain types of potable underground waters of Ukraine. *Mineralogical Journal of Ukraine,* Vol. 2/3, 68-70.

355. Zhovinsky, E, Kuraeva, I, Kryuchenko, N and Dmytrenko, G. 2001b. Geology-structural and geochemical conditions of formation of fluorine-bearing provinces of Ukraine. *Mineralogical Journal of Ukraine,* Vol. 5/6, 31-36.

356. Zhovinsky, E, Kuraeva, I and Manichev, V I. 1985b. *Geochemistry of Fluorine and Scientific Justification of Lithogeochemical Fluorspar Exploration Criteria in Ukraine.* (Kiev: Academy of Sciences of the Ukrainian SSR).

357. **Zhovinsky, E, Kuraeva, I and Ostrovskaya, G. 1989a**. Organic matter influence in fluorite dissolution kinetics. In: *Kinetics and Dynamics of Geochemical Processes.* (Chernogolovka).

358. Zhovinsky, E, Kuraeva, I and Ostrovskaya, G. 1993b. Fluorine sorption during halo formation. In: *Mineralogical-Geochemical Fluorite Exploration Criteria.* (Kiev: Naukova Dumka), 86-98.

359. Zhovinsky, E, Kuraeva, I and Stremovsky, O. 1986. Hydrogeochemical fluorine anomalies and their significance for fluorspar exploration in the zone of the Donbas and Axov Region. *Reports of the Academy of Sciences of the Ukrainian SSR,* Vol. 2 (3-6).

360. Zhovinsky, E and Kvasyuk, V I. 1980. *Hydrogeochemical exploration by fluorine with principles of thermodynamic analysis.* (Kiev).

361. Zhovinsky, E and Mamaev, I. 1982. *Report on the Results of Common Exploration for Fluorite in the Bakhtyn Deposit Area (the Central Dniester Region).* (Kiev).

362. Zhovinsky, E, Manichev, V and Kuraeva, I. 1988a. Indicator role of clay minerals in exogenous fluorine halo formation. In: *Composition and Properties of Clay Minerals.* (Novosibirsk).

363. Zhovinsky, E, Manichev, V and Kuraeva, I. 1988b. Efficiency of fluormetry and PF for polymetallic mineralization exploration. In: *Theory and Practice of Geochemical Exploration in Modern Conditions.* Vol. Book 4 (Moscow), 42.

364. Zhovinsky, E, Manichev, V and Kuraeva, I. 1989b. *Fluorimetric Survey of the Kirovograd Fluorite-bearing Zone.* (Kiev).

365. Zhovinsky, E and Manichev, V I. 1979. Geochemistry of fluorine flysch formation of the Eastern Ukrainian Carpathians Palaeogene. *Reports of the Academy of Sciences of the Ukraine SSR,* Vol. 3, 166-168.

366. Zhovinsky, E, Novikova, L and Kuraeva, I. 1984c. Fluorine adsorption and desorption by sedimentary rocks. In: *Sedimentary Rocks and Ores.* (Kiev: Naukova Dumka), 42.

367. Zhovinsky, E, Novikova, L and Zulfigarov, O. 1984d. Application of a new buffer system for potentiometric determination of fluoride-ions. *Journal of Analytical Chemistry,* Vol. 11, 6-9.

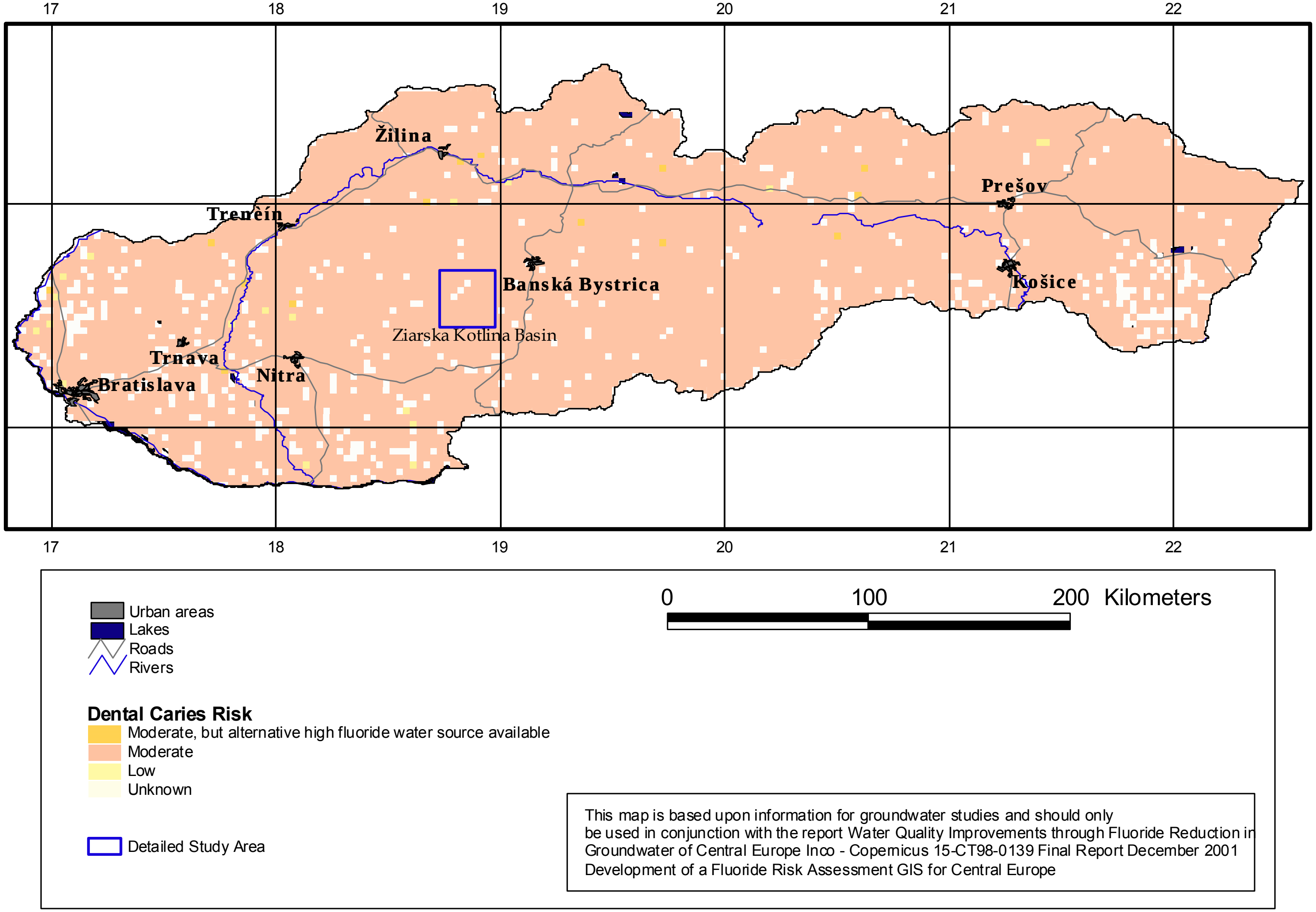
368. **Zhovinsky, E, Novikova, L and Zulfigarov, O. 1984e**. On fluorine migration in natural waters in the presence of organic matter. *Reports of the Academy of Sciences of the Ukrainian*

SSR, Vol. 7 (5-14).
369. **Zhovinsky, E, Novikova, L B and Askochenskaya, R M. 1983b**. Application of a new buffer system and extraction method for fluorine determination in environmental objects. In: *Methods of Analysis of Environmental Objects. Thesis of Reports of All-Soviet Conference.* (Moscow: Nauka).
370. **Zhovinsky, E and Ostrovska, G. 1996**. *Geochemical Methods for Exploration for Fluorite.* UA 10559A Bulletin 4 (Kiev).
371. **Zhovinsky, E and Povoroznuk, V. 1998**. Fluorine in water of Lvov region and relation with bone diseases. In: *Carpathian-Balkan Geological Association XVI Congress.* (Vienna: University of Austria).
372. **Zhovinsky, E, Rybalko, S and Fuzik, R. 1981b**. Electron-optical studies of fluorites of the Dniester Region in relation with problem of genesis. In: *Fluorite of Ukraine.* (Kiev: Naukova Dumka), 125-129.
373. **Zhovinsky, E and Stasiv, V P. 1975**. Geochemistry of fluorine of sedimentary formations of Galitsian plication area Ripheid and Kaledonide. In: *Proceedings of the 10th Congress Mineralogy, Geochemistry and Metallogeny.* Vol. Section IV (Bratislava: KBGA), 269-273.
374. **Zhovinsky, E and Stasiv, V P. 1976**. Regularities of fluorine distribution in concretionary formations of coal-bearing carbon of Lvov-Volyn basin. In: *Geochemistry of Sedimentary Rocks and Prognosis of Mineral Resources.* (Kiev: Naukova Dumka), 55-56.
375. **Zhovinsky, E and Stasiv, V P. 1979**. Conditions of fluorine accumulation in carbon sedimentary rocks of Lvov-Volyn basin. *Reports of the Academy of Sciences of the Ukrainian SSR,* Vol. 4, 253-255.
376. **Zhovinsky, E, Stulchikov, A and Ilovayska, S. 1983c**. Fluorine distribution in Pre-Cambrian sedimentary-volcanogenic formations of the Verkhivtsevo syncline. *Reports of the Academy of Sciences of the Ukrainian SSR,* Vol. 8, 28-30.
377. **Zhovinsky, E and Tkachuk, L G. 1976**. Thermodynamic analysis of the solution-rock system and its role when searching for fluorite. In: *Fluorite.* (Moscow: Nauka), 274-280.
378. **Zhovinsky, E and Tkachuk, L G. 1977**. Duration of epigenetic rock transformation determination by fluorine content in micas. *Reports of the Academy of Sciences of the Ukraine SSR,* Vol. 3, 217-220.
379. **Zhovinsky, E and Tkachuk , L G. 1980a**. Kaolinization duration determination by fluorine content in hydromicas exemplified by the Velykogadominetske deposit. *Reports of the Academy of Sciences of the Ukrainian SSR,* Vol. 7, 38-41.
380. **Zhovinsky, E and Tkachuk, L G. 1980b**. Fluorine and fluorite formation in sedimentary formations of the south-west of the Eastern-European platform. In: *Geochemistry of Platform and Geosynclinal Sedimentary Rocks of Phanerozoic and Upper Proterozoic Age.* (Moscow), 293-294.
381. **Zhovinsky, E Y, Manichev, V and Kuraeva, I. 1993c**.

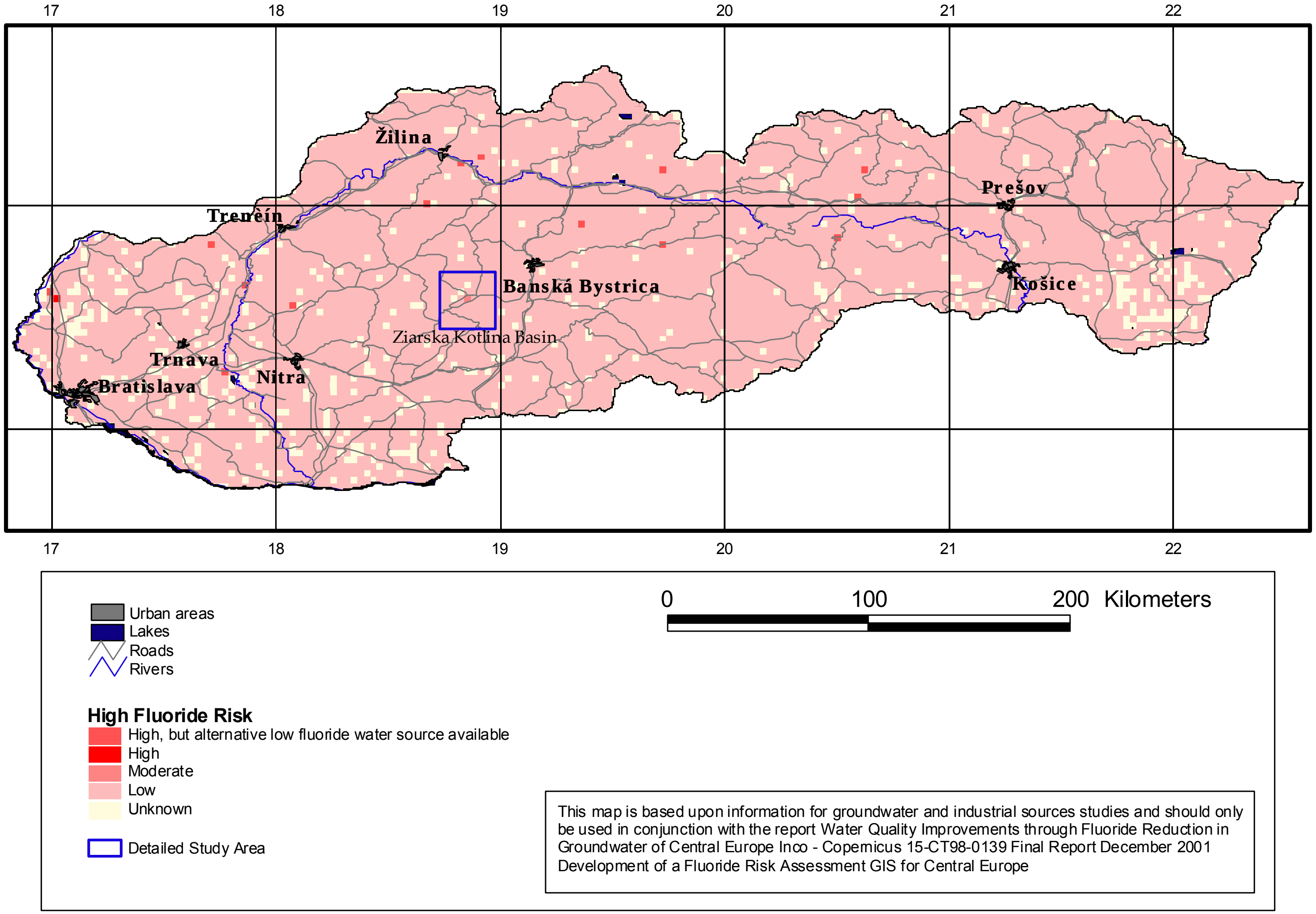
Mineralogical-geochemical peculiarities of the Vinozhsk and Bobrinets fluorite ore manifestations. In: *Mineralogical-Geochemical Fluorite Exploration Criteria.* (Kiev: Naukova Dumka), 147.

382. **Zhylenko, V and Dyeshchyuk, T. 1975**. Fluorosis of temporal teeth in adolescents residing in hotspots of increased fluoride content. In: *Proceedings of 7th All USSR Student Scientific Conference - Pathology of Digestive System.* (Donyetsk-Kharkiv), 134-135.

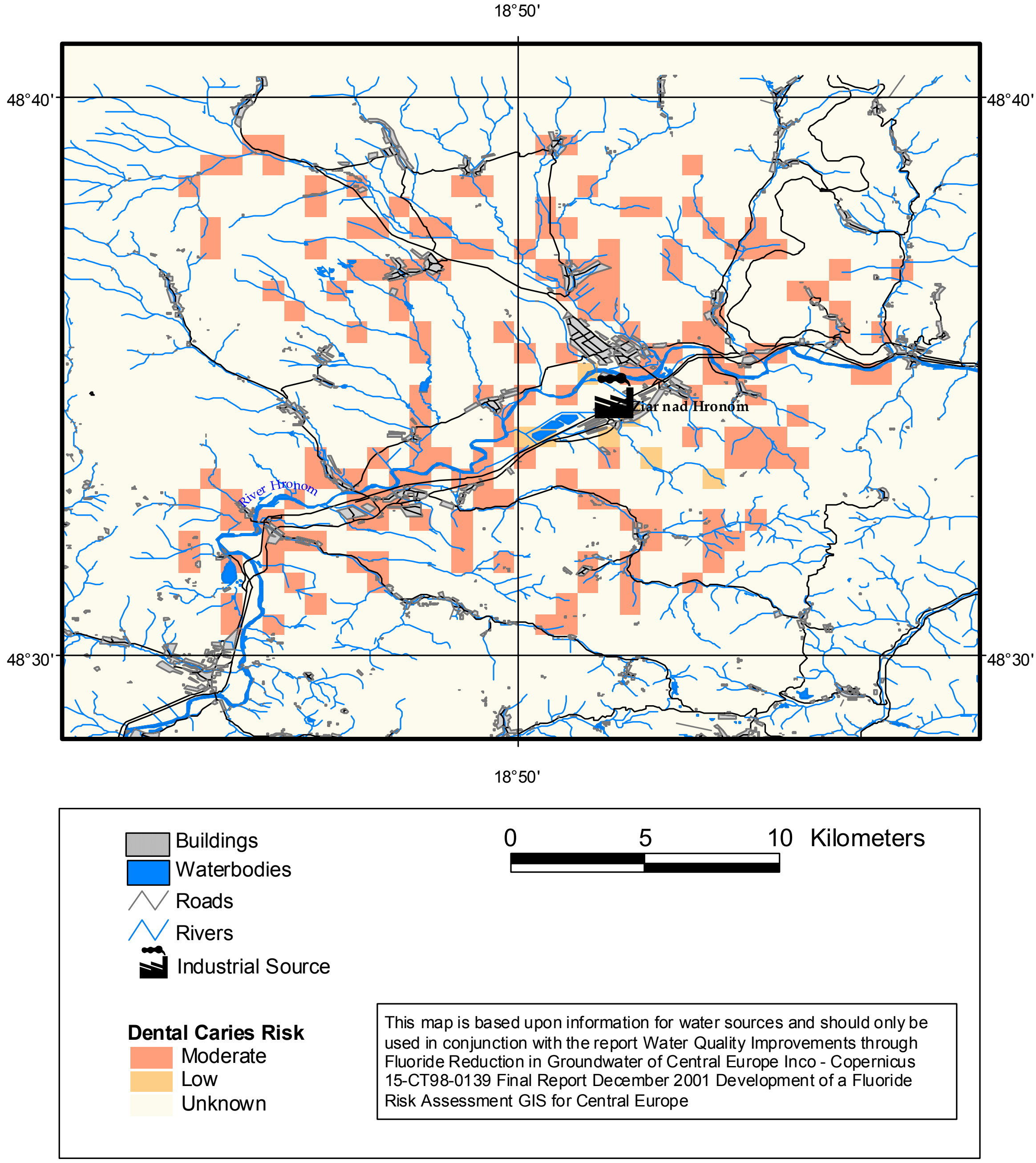
ANNEX 1. DENTAL CARIES RISK AVOIDANCE MAP OF SLOVAKIA



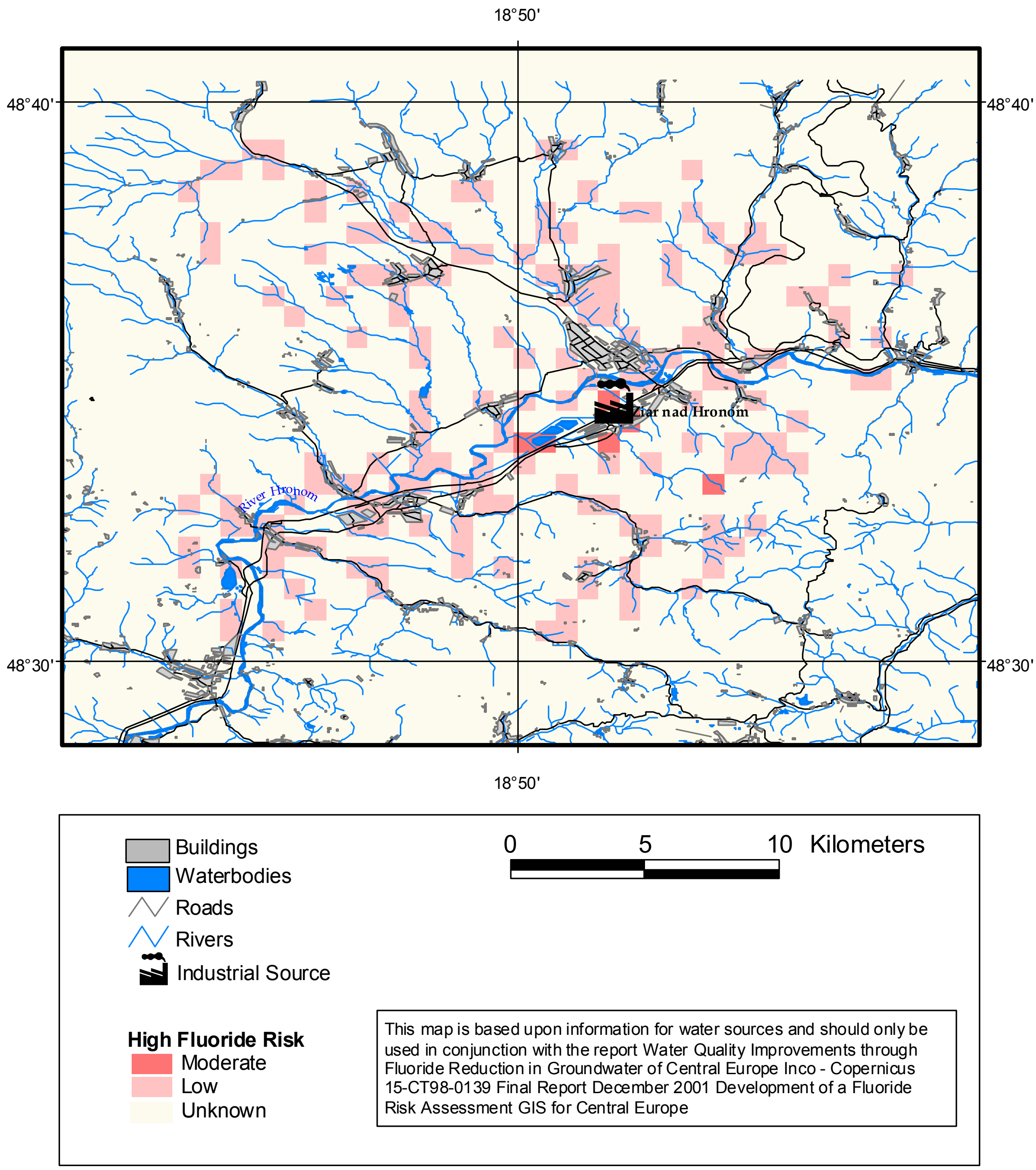
ANNEX 2. HIGH-FLUORIDE RISK AVOIDANCE MAP OF SLOVAKIA



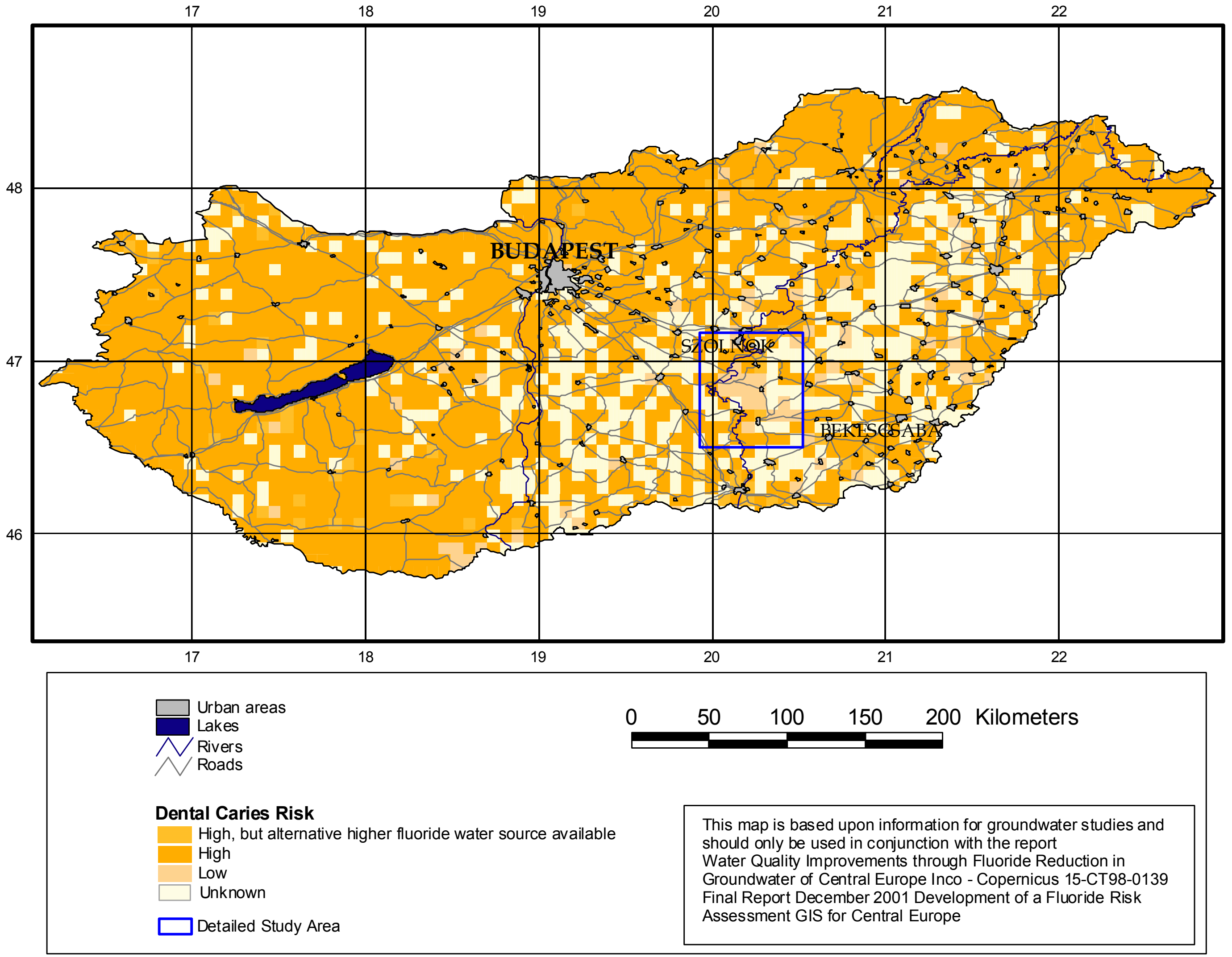
ANNEX 3. DENTAL CARIES RISK AVOIDANCE MAP OF THE ZIARSKA KOTLINA BASIN, SLOVAKIA



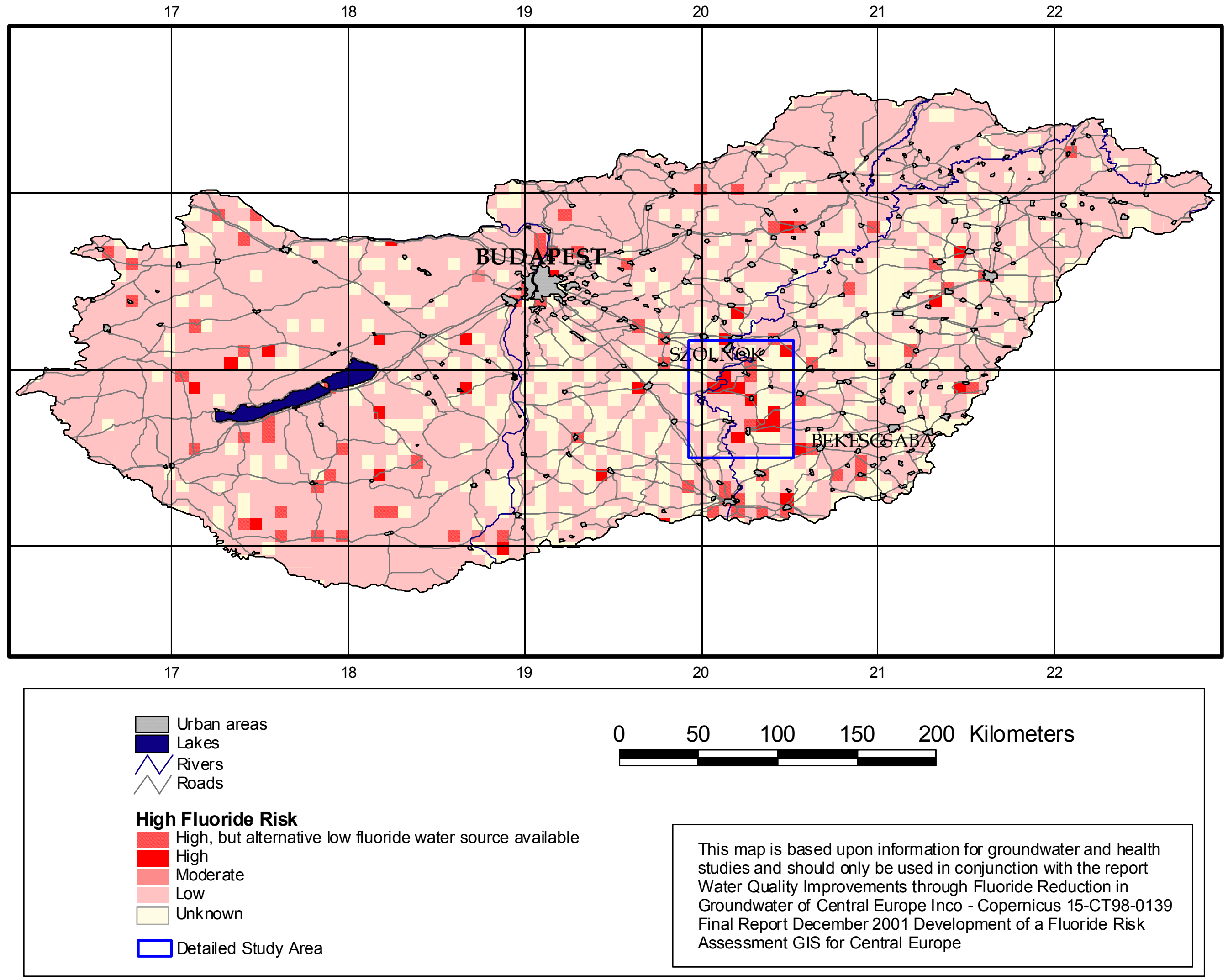
ANNEX 4. HIGH-FLUORIDE RISK AVOIDANCE MAP OF THE ZIARSKA KOTLINA BASIN, SLOVAKIA



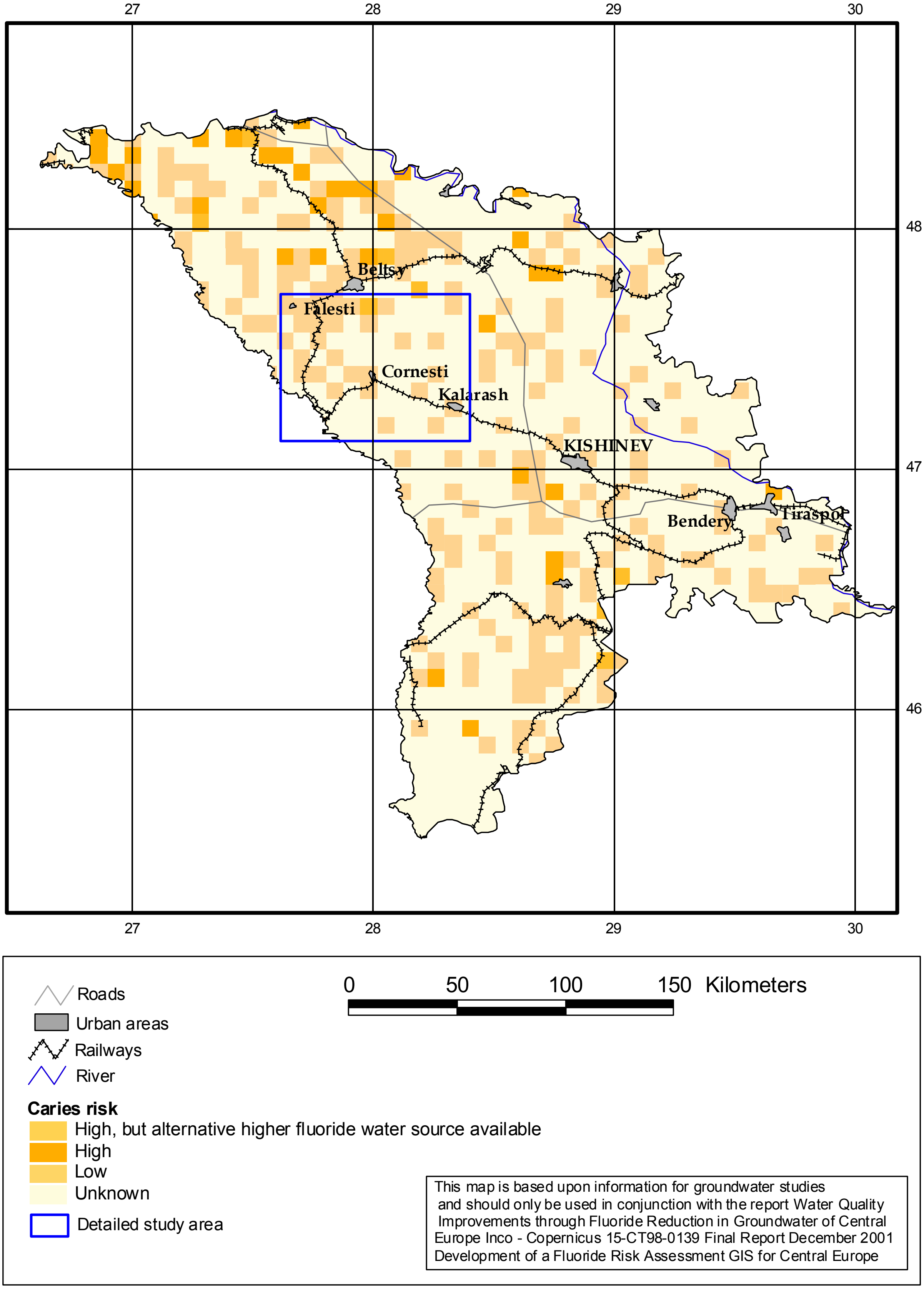
ANNEX 5. DENTAL CARIES RISK AVOIDANCE MAP OF HUNGARY



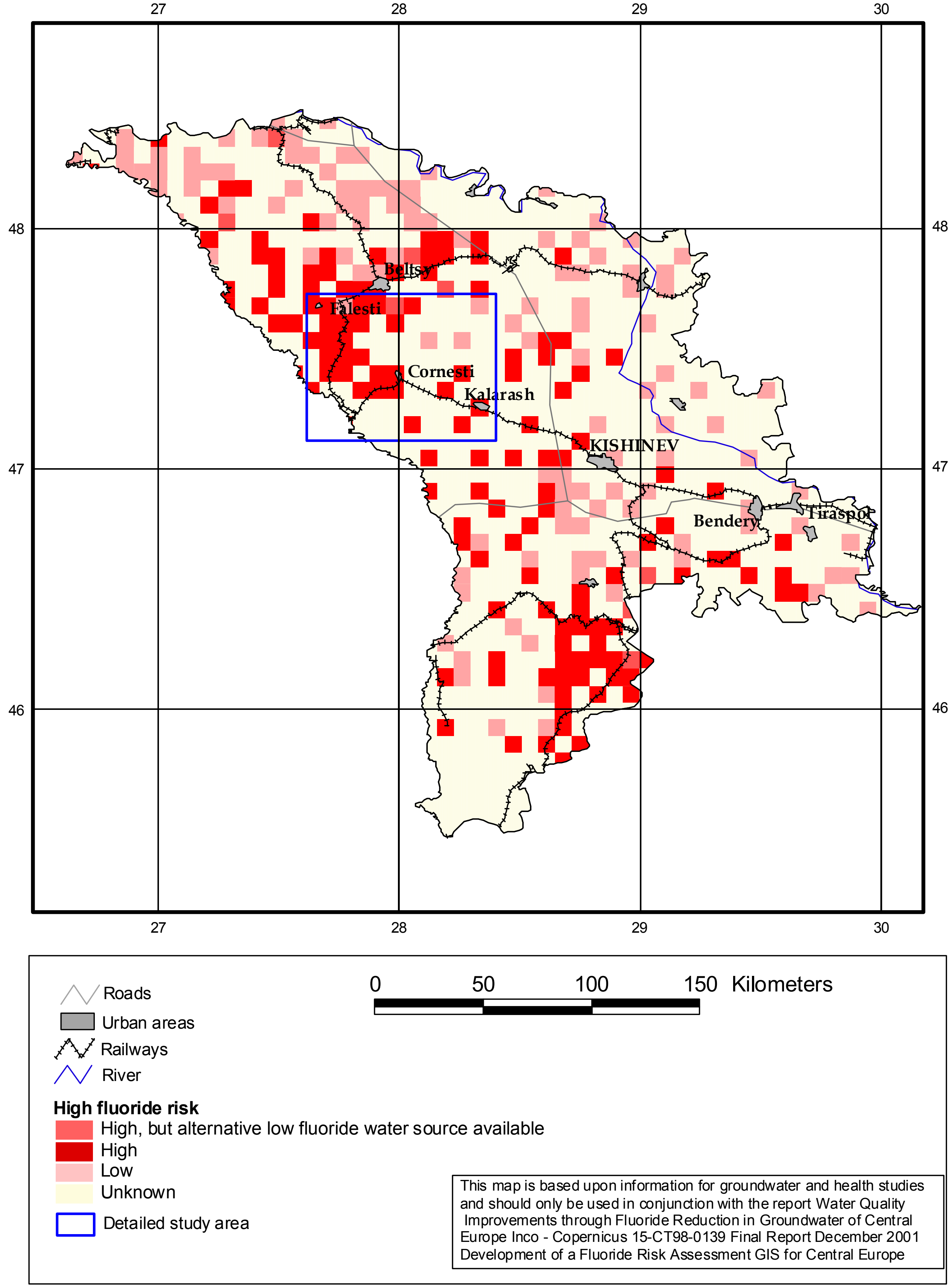
ANNEX 6. DENTAL CARIES RISK AVOIDANCE MAP OF HUNGARY



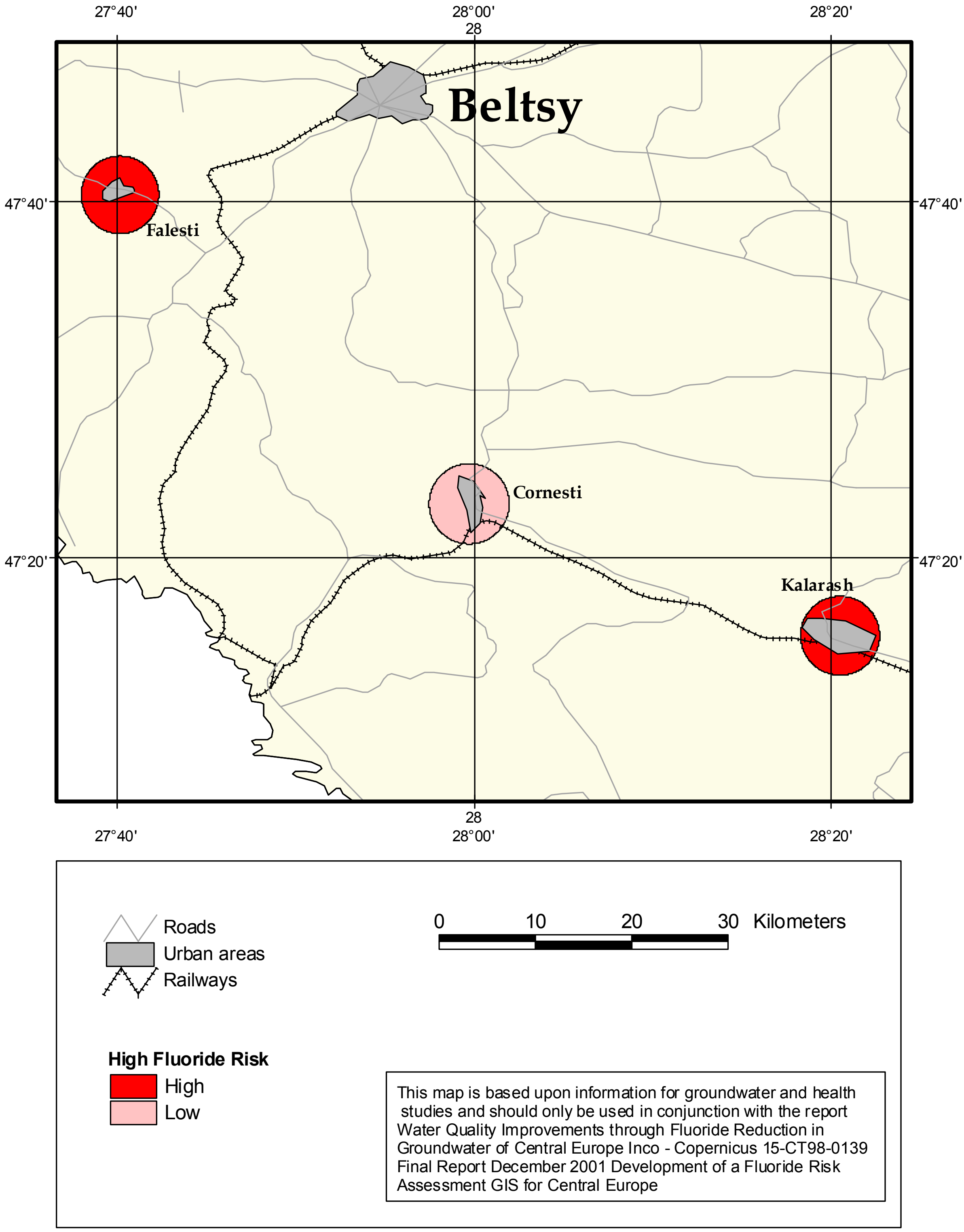
ANNEX 7. DENTAL CARIES RISK AVOIDANCE MAP OF MOLDOVA



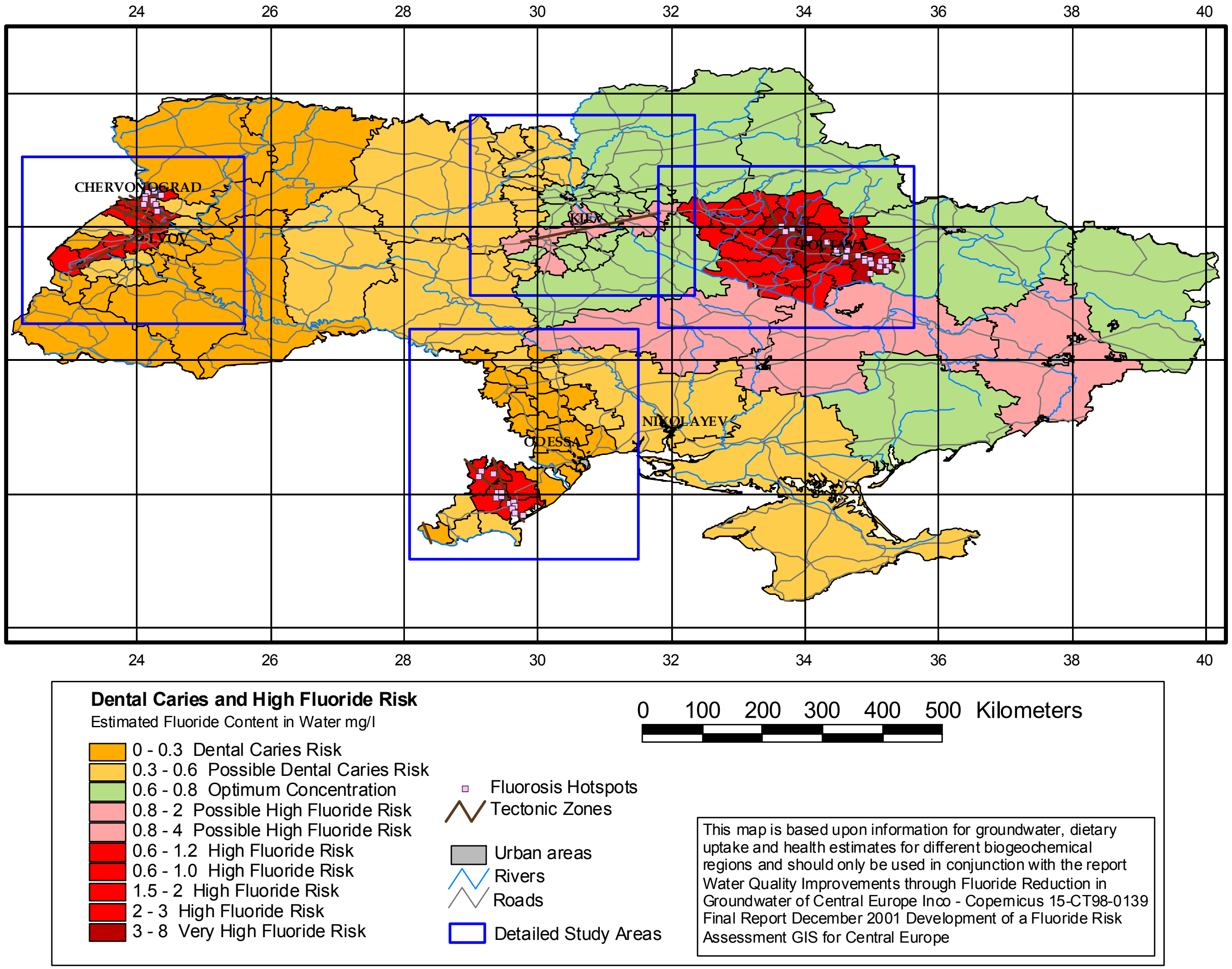
ANNEX 8. HIGH-FLUORIDE RISK AVOIDANCE MAP OF MOLDOVA



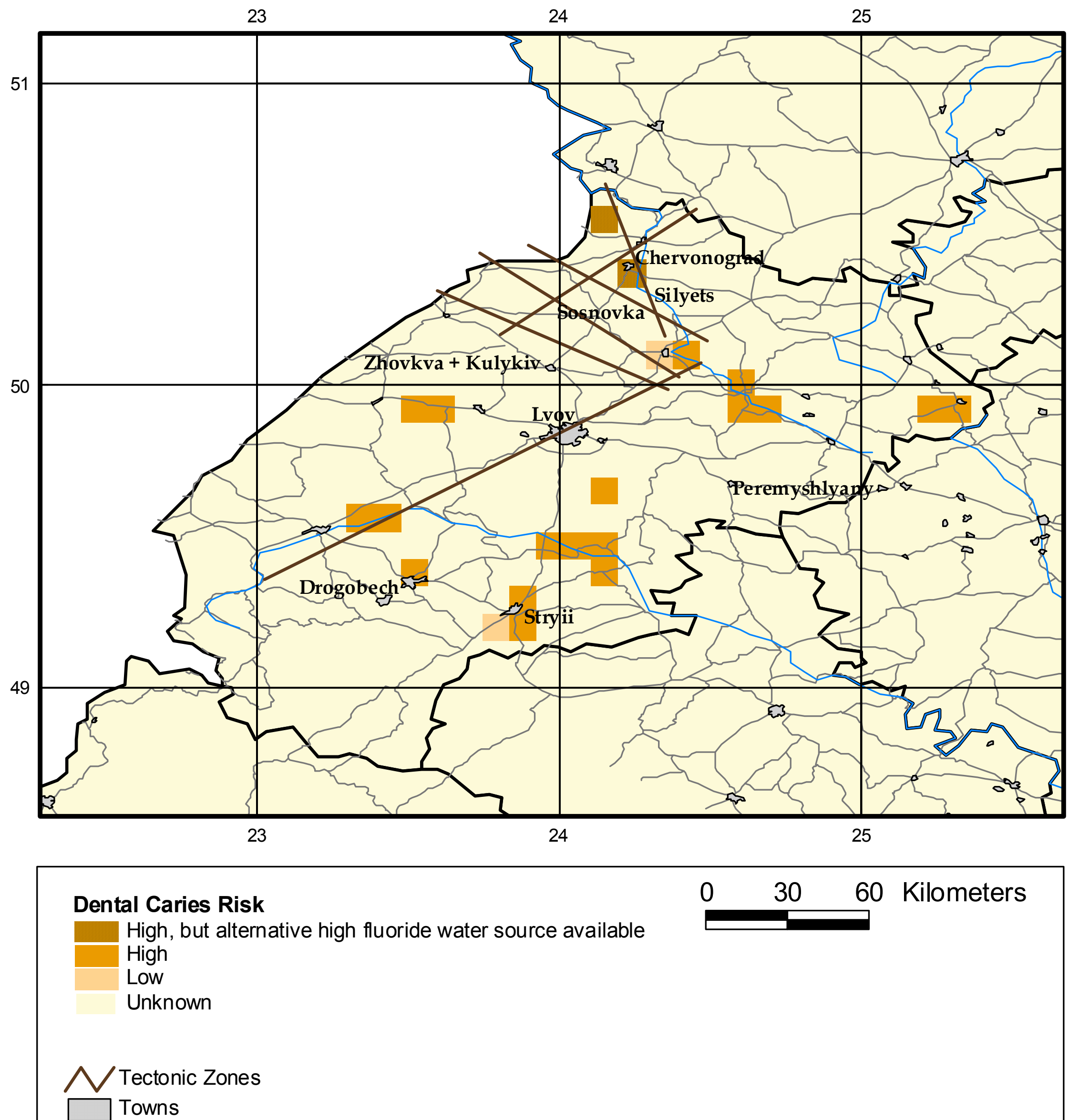
ANNEX 9. HIGH FLUORIDE RISK AVOIDANCE MAP OF FALESTI REGION, MOLDOVA



ANNEX 10. FLUORIDE RISK AVOIDANCE MAP OF UKRAINE

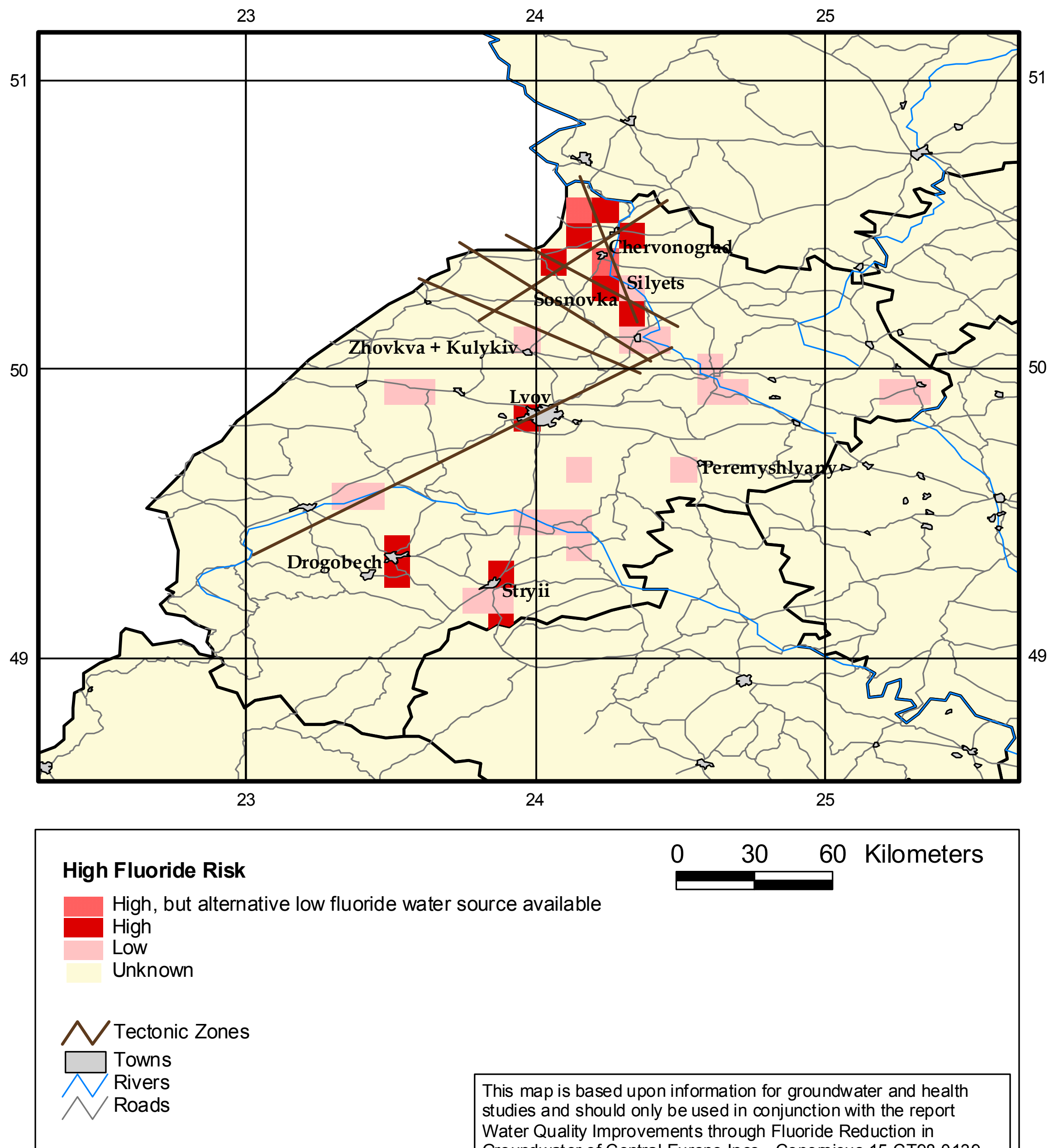


ANNEX 11. DENTAL CARIES RISK AVOIDANCE MAP OF LVOV REGION, UKRAINE



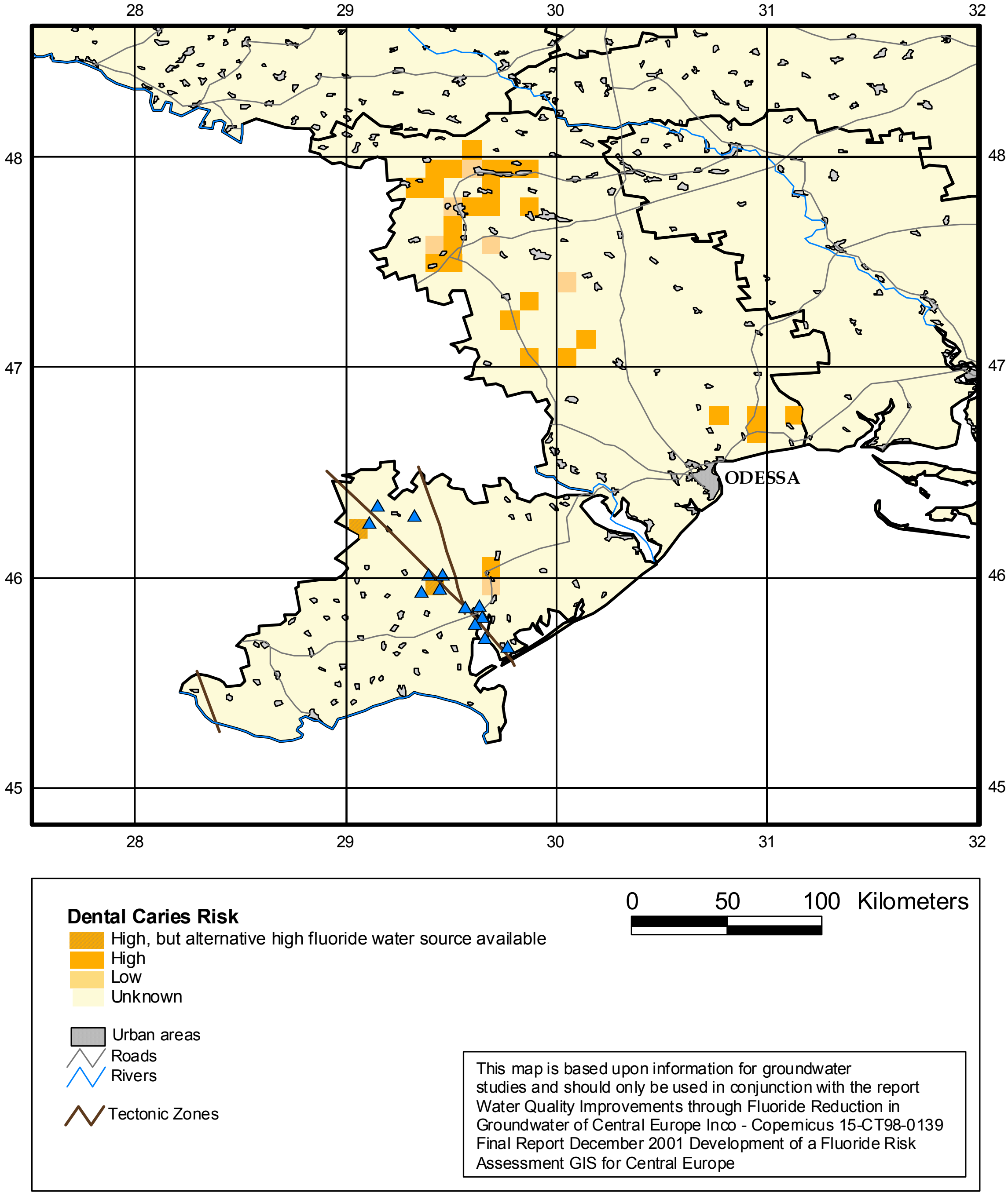
This map is based upon information for groundwater studies and should only be used in conjunction with the report Water Quality Improvements through Fluoride Reduction in Groundwater of Central Europe Inco - Copernicus 15-CT98-0139 Final Report December 2001 Development of a Fluoride Risk Assessment GIS for Central Europe

ANNEX 12. HIGH-FLUORIDE RISK AVOIDANCE MAP OF LVOV REGION, UKRAINE

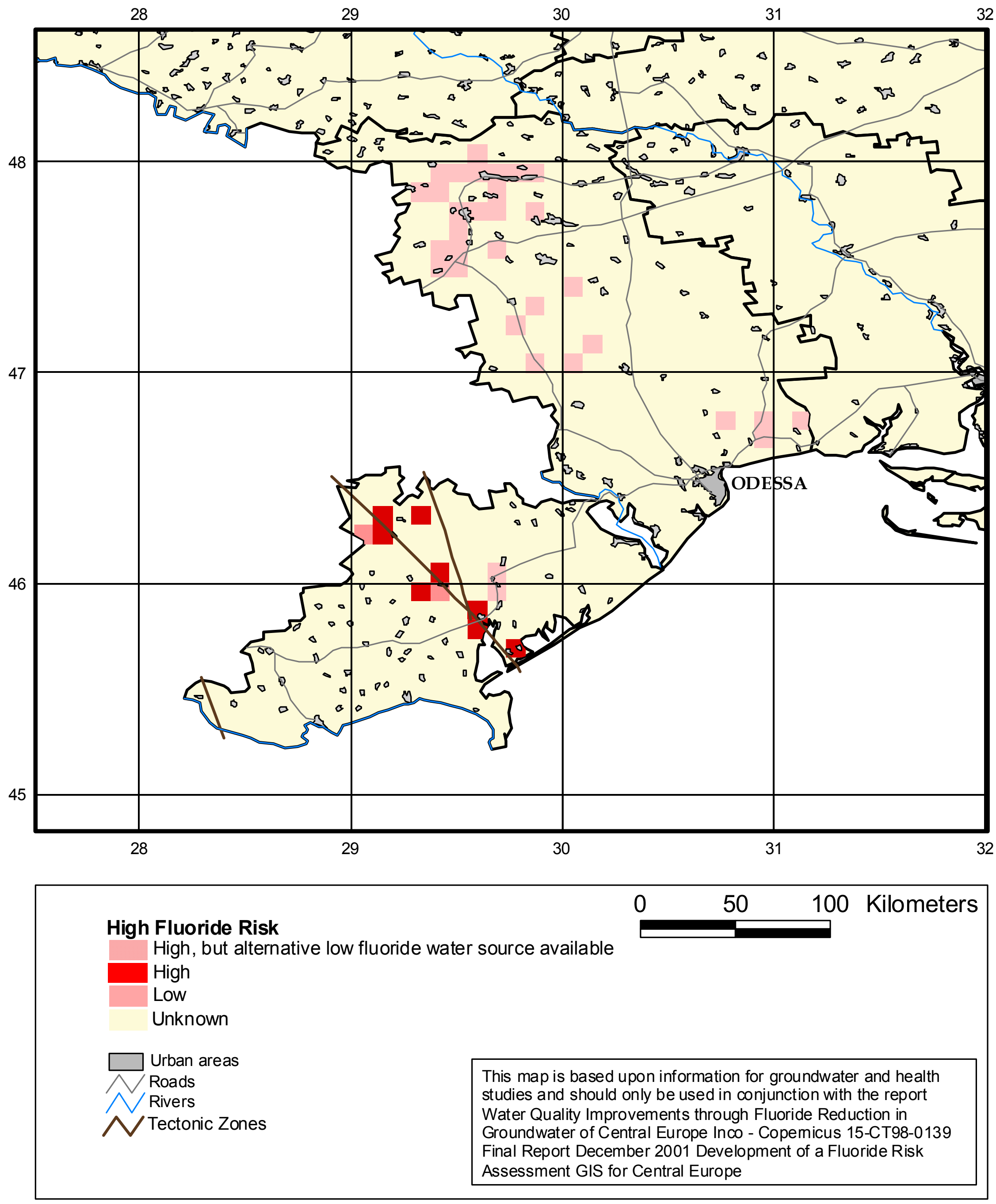


This map is based upon information for groundwater and health studies and should only be used in conjunction with the report Water Quality Improvements through Fluoride Reduction in Groundwater of Central Europe Inco - Copernicus 15-CT98-0139 Final Report December 2001 Development of a Fluoride Risk Assessment GIS for Central Europe

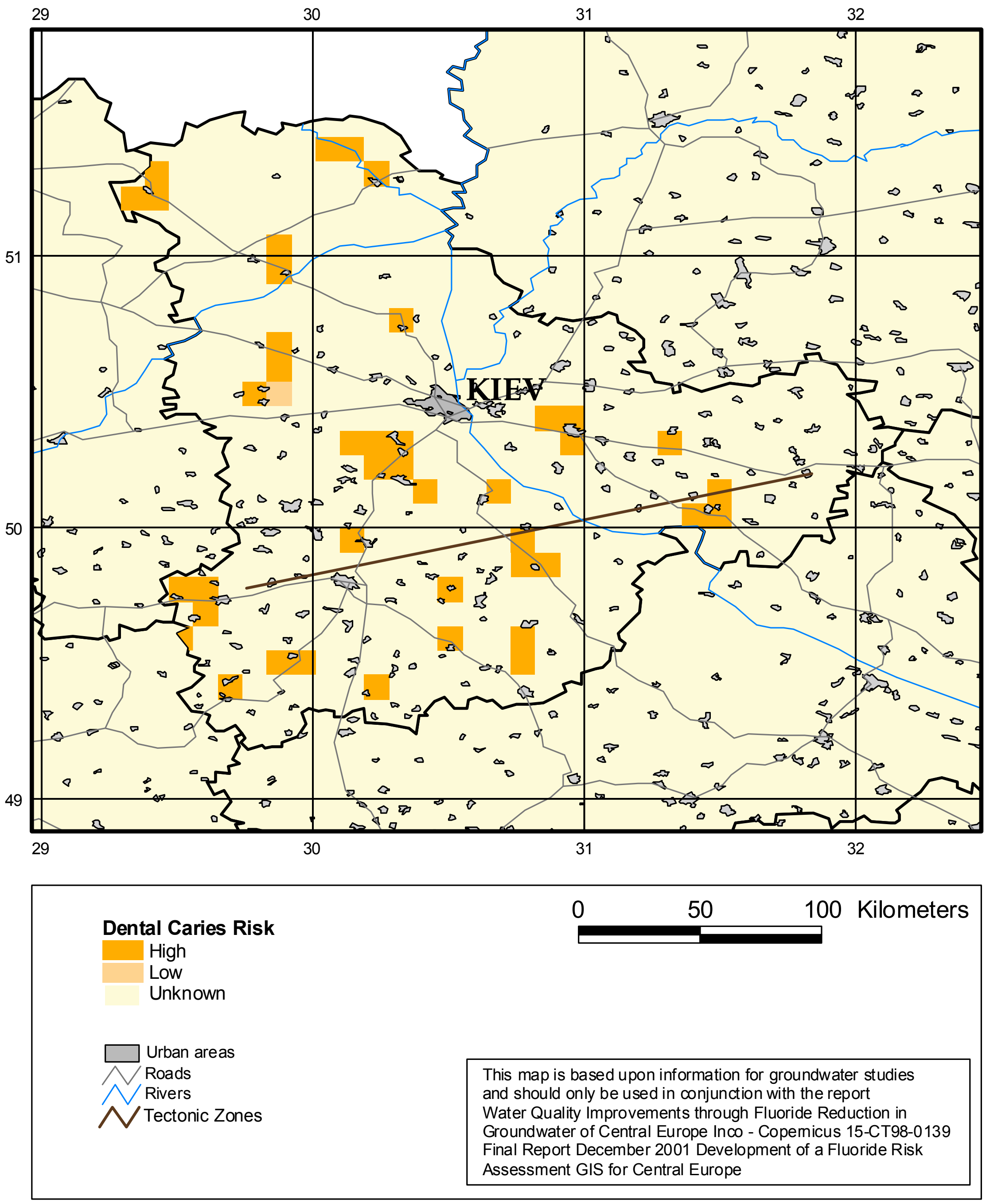
ANNEX 13. DENTAL CARIES RISK AVOIDANCE MAP OF ODESSA REGION, UKRAINE



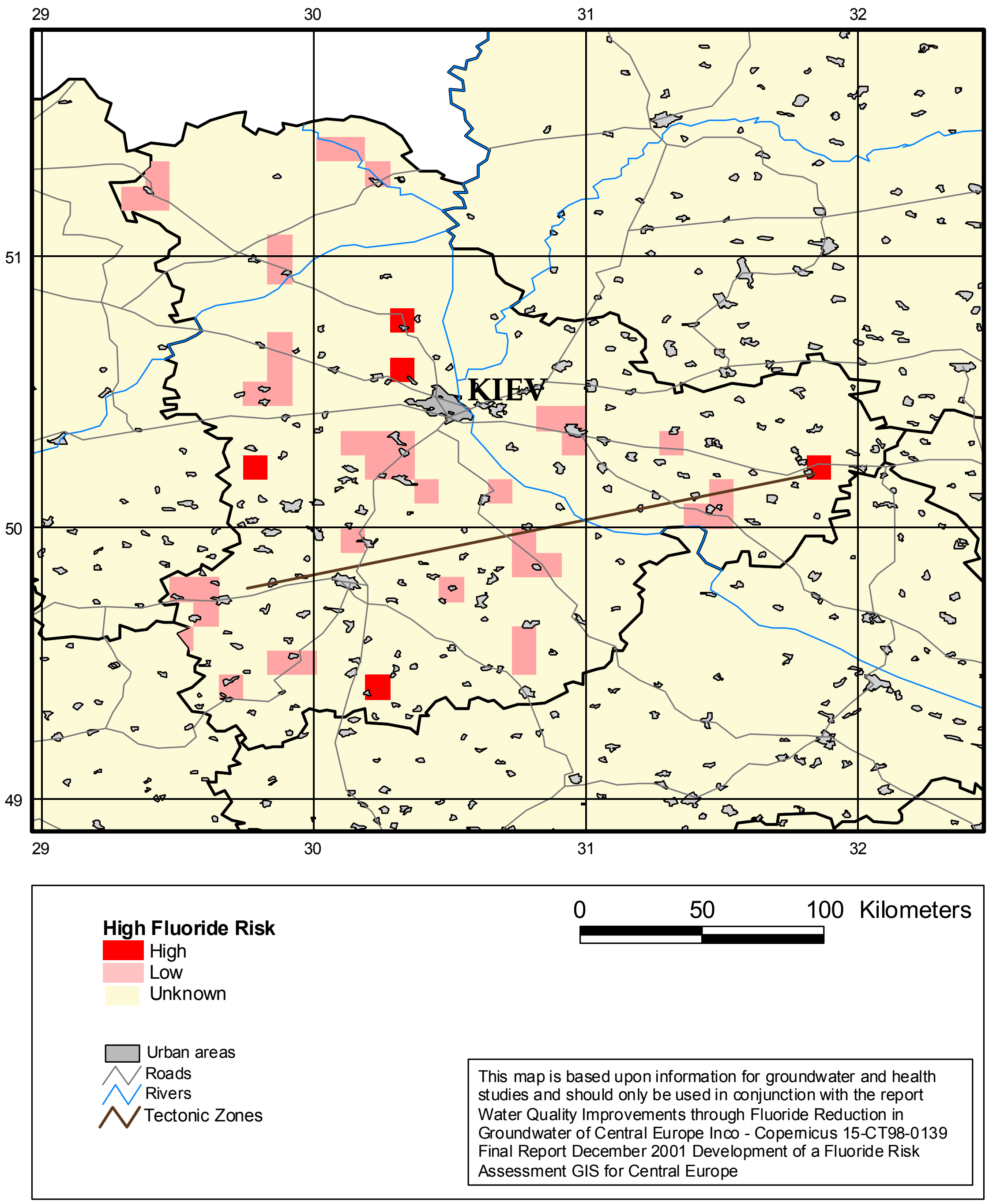
ANNEX 14. HIGH-FLUORIDE RISK AVOIDANCE MAP OF ODESSA REGION, UKRAINE



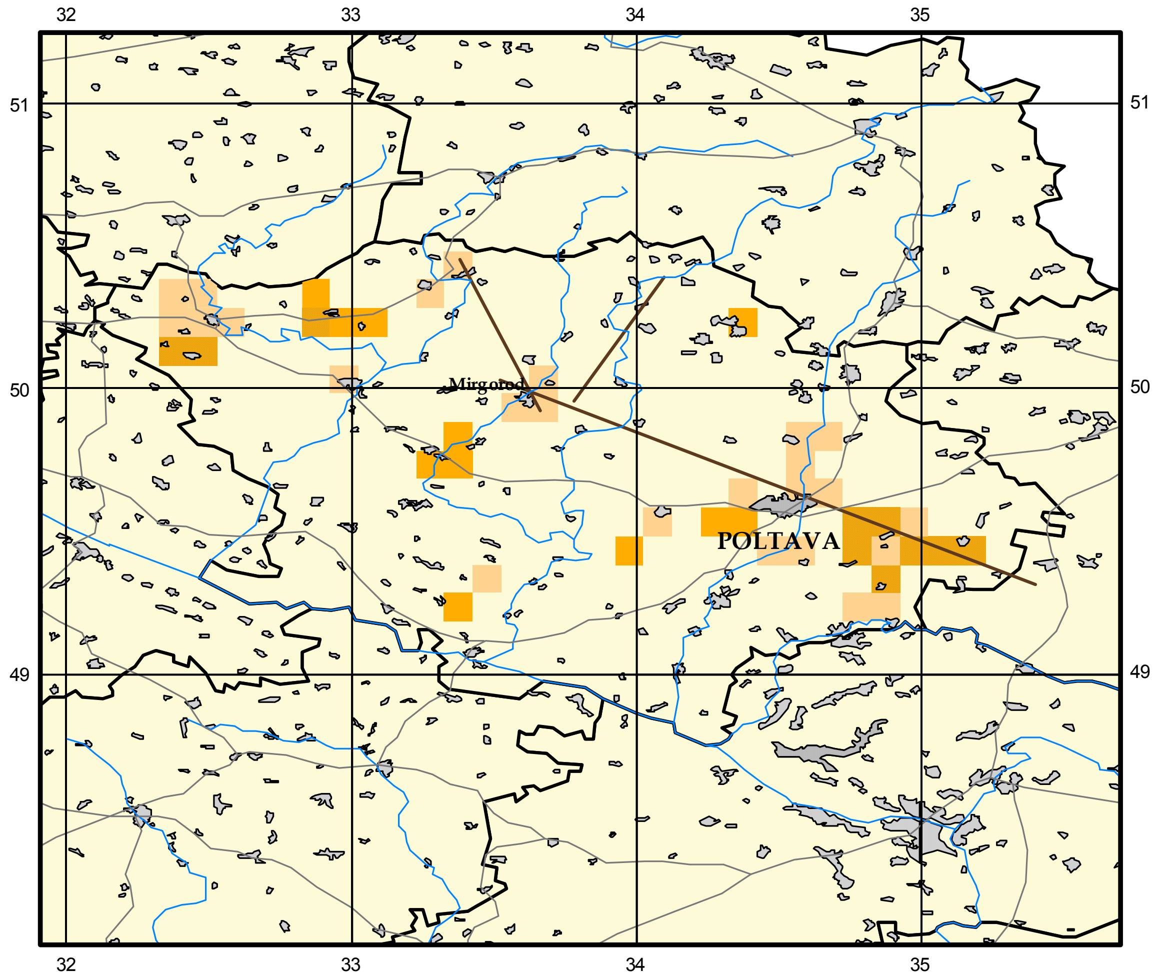
ANNEX 15. DENTAL CARIES RISK AVOIDANCE MAP OF KIEV REGION, UKRAINE



ANNEX 16. HIGH-FLUORIDE RISK AVOIDANCE MAP OF KIEV REGION, UKRAINE



ANNEX 17. DENTAL CARIES RISK AVOIDANCE MAP OF POLTAVA REGION, UKRAINE



Dental Caries Risk

- High, but alternative high fluoride water source available
- High
- Low
- Unknown

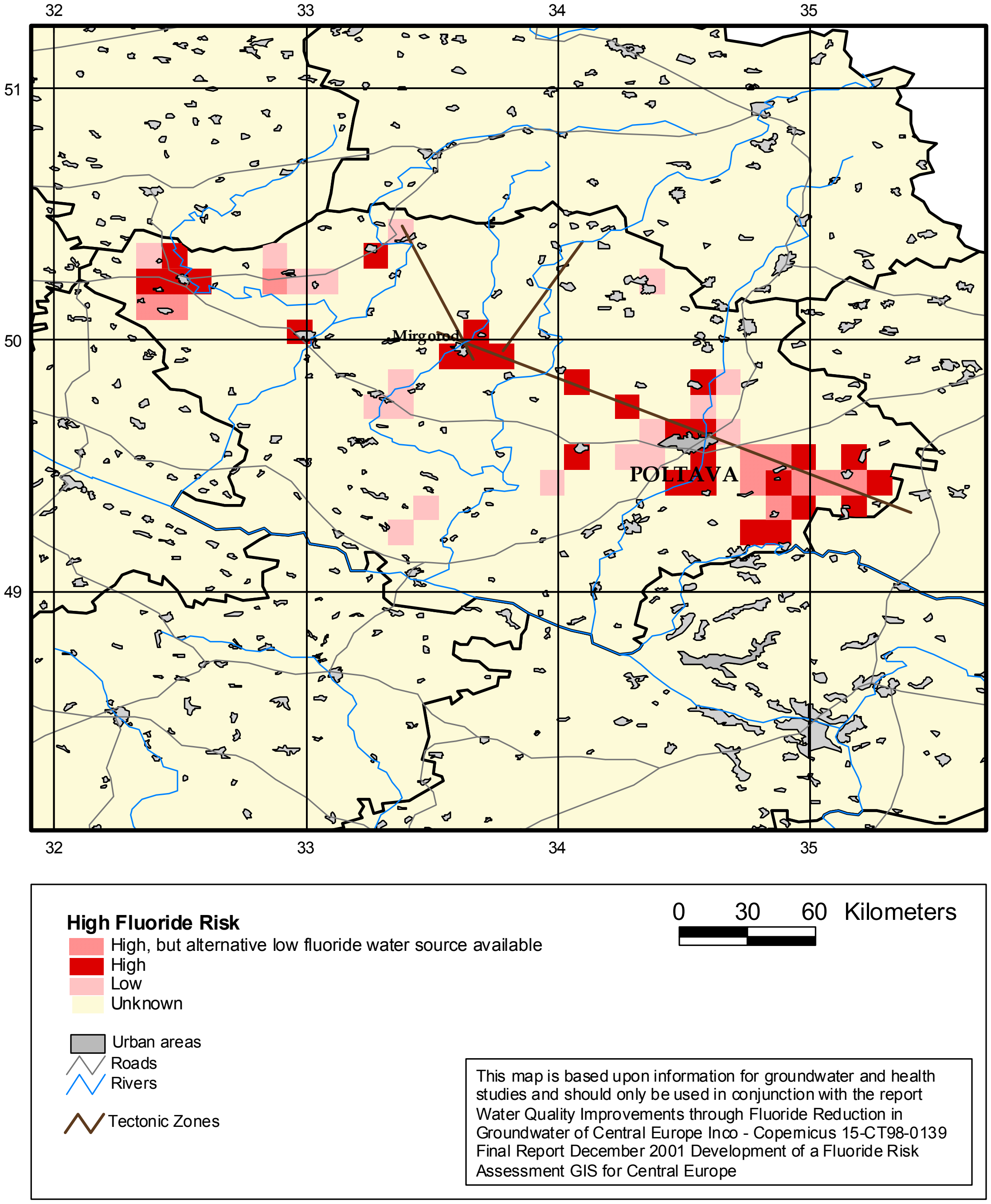
- Urban areas
- Roads
- Rivers

- Tectonic Zones

0 30 60 Kilometers

This map is based upon information for groundwater studies and should only be used in conjunction with the report Water Quality Improvements through Fluoride Reduction in Groundwater of Central Europe Inco - Copernicus 15-CT98-0139 Final Report December 2001 Development of a Fluoride Risk Assessment GIS for Central Europe

ANNEX 18. HIGH-FLUORIDE RISK AVOIDANCE MAP OF POLTAVA REGION, UKRAINE



ANNEX 19. HIGH-FLUORIDE RISK AVOIDANCE MAP OF CENTRAL EUROPE