CHAPTER 5
The impact of aquifer intensive use on groundwater quality

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ABSTRACT: Groundwater quality degradation owing to intensive aquifer exploitation is recorded in many countries. Recognition of the impact of intensive abstraction of aquifers is nearly almost based on hydraulic phenomena. However, subtle changes in the groundwater chemical composition caused by pumping may often be observed before becoming evident from groundwater level decline. Therefore, groundwater quality monitoring and vulnerability assessment should be implemented and targeted on the specific groundwater quality problem caused by intensive aquifer exploitation. Most often, groundwater quality is affected by saltwater intrusion into coastal aquifers, by the downward and upward influx of poor water quality from superposed and underlying aquifers into exploited aquifers or by the discharge of polluted surface water into phreatic aquifers. Presented case studies show the social, ecological and economic consequences of the uncontrolled intensive use of groundwater resources. The holistic concept reflecting a close connection between surface water and groundwater is emphasised in the policy and management of groundwater resource development, protection and quality conservation.

1 INTRODUCTION

Groundwater, a renewable and finite natural resource, vital for human life, for social and economic development and moreover a valuable component of the ecosystem, is vulnerable to natural and human impacts. Earlier, little attention was paid to the protection of groundwater quality, mainly because people were unaware of the threats to this hidden resource. The idea that the geological environment protects groundwater and that it is therefore not vulnerable to human activities prevailed for a very long time. This had serious and long-term consequences on many countries' groundwater quality.

Since the 1960s, there has been a growing interest in the need to protect groundwater quality and conceptual approach to groundwater protection has become an important element in national water planning, policy and management.

The holistic concept for water resource policy and management, as emphasised at the International Conference of Water and the Environment in Dublin (1992), significantly influenced the approach to development and protection of groundwater resources. This concept reflects the social, economic and ecological value of groundwater, the close connection between groundwater and surface water and the integrity of aquatic and terrestrial ecosystems. Moreover, it pays the same attention to both the quantitative and qualitative aspects of groundwater and it is based on a participatory approach involving scientists, planners, managers, policy and decision-makers, stakeholders and the general public. However, the holistic concept for water resource policy, planning and management has not been applied in many countries so far. There is an intrinsic and not always spelled out psychological problem related to the exploitation of groundwater. Since groundwater cannot generally be seen (as is the case of surface water) people do not feel much responsibility for this resource and its quality. Therefore, it is necessary to build institutional and technical capacities to promote an effective water resource management based on sustainable development and the protection of groundwater resources in general and groundwater quality conservation in particular (Fig. 1).

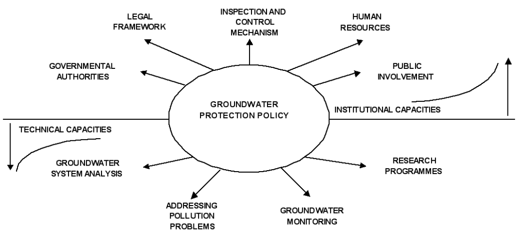

Figure 1. Institutional and technical capacities of groundwater protection policy and management.

Institutional capacity building includes: 1) the set-up of governmental institutions for performing the required administrative operation and for the co-ordination and implementation of a comprehensive water policy; 2) the establishment of a legal framework and regulatory statutes; transboundary aquifer development and protection call for the appointment of international principles and rules concerning shared groundwater; 3) the creation of governmental control mechanisms based on relevant legislation and water quality standards, on the *polluter pays principle* and on the implementation of repressive and stimulating financial instruments; 4) the recruiting of qualified, experienced, trained and motivated human resources; and 5) public awareness of and participation in water planning and policy based on intelligible information and public education programmes. In many countries, there is still a big gap in communication between policy and decision-makers and the general public.

Technical capacity includes mainly: 1) comprehensive groundwater system analysis based on the assumption that the groundwater system can be effectively protected when its properties are well understood and known; 2) identification and inventory of potential and existing human impacts on the groundwater system and evaluation of their nature and extent; 3) establishment and operation of groundwater monitoring systems to provide data for assessing the current state and forecasting trends in the groundwater system due to natural processes and human impacts in time and space; and 4) research concerning development, improvement and/or innovation of groundwater protection and quality conservation methods.

Groundwater policy and management are effective only if the above institutional and technical capacities are applied in a coherent manner. However, a certain degree of ignorance and uncertainty in terms of behaviour, properties and vulnerability of the groundwater system always has to be considered. The risk that human impact on the groundwater system cannot be predicted accurately always has to be considered.

2 CHEMICAL EVOLUTION AND COMPOSITION OF NATURAL GROUNDWATER

Groundwater contains a broad range of inorganic dissolved solids in various concentrations and a small amount of organic matter. Groundwater composition control:

- The properties of the soil and rock environment in which groundwater moves.
- Contact time and contact surface of groundwater with geological materials along the flow paths.
- The rate of geochemical (dissolution, precipitation, hydrolysis, adsorption, ion exchange, oxidation, reduction), physical (dispersion, advection, filtration, temperature), microbiological (microbial metabolism and decomposition, cell synthesis) processes passing in the soil-rock-groundwater system.
- The presence of dissolved gases, particularly carbon dioxide.
- The chemical composition of rain and snow, which infiltrate into the groundwater system.

There are differences in the lateral (recharge-discharge areas) and the vertical (shallow oxidation-deep reduction zones) scale of the groundwater system in the evolution of groundwater composition.

Generally, groundwater in recharge and shallow aquifers has a lower content of dissolved solids than groundwater in discharge areas and deeper aquifers. Increasing the content of total dissolved solids and anion evolution sequence $HCO_3^- \rightarrow SO_4^{2-} \rightarrow Cl^-$, expressing the change of oxidising conditions (shallow zone) into reducing (deep zone) are usually well visible in the groundwater system's vertical profile (Chebotarev 1955):

Travel along flow path $\longrightarrow$

$$HCO_3^- \rightarrow HCO_3^- + SO_4^{2-} \rightarrow SO_4^{2-} + HCO_3^- \rightarrow SO_4^{2-} + Cl^- \rightarrow Cl^- + SO_4^{2-} \rightarrow Cl^-$$

Increasing age $\rightarrow$

Based on Chebotarev's evolution sequence, Domenico (1972) specified three main zones in large and deep sedimentary basins, which correlate in a general way with depth. Mineral availability and molecular diffusion control the gradual changes in anion composition in groundwater in the above mentioned zones.

Active groundwater flushing, low temperature and short time contact of groundwater with rock materials are typical for the upper shallow and recharge zones. Groundwater is low in total dissolved solids and HCO_3^- is the major anion.

In deeper intermediate zones, temperature, pressure and time and space contact between groundwater and rocks gradually increase and groundwater flow velocity decreases. The concentration of dissolved solids increases downward and the major anion is sulphate.

However, in deep groundwater systems, where groundwater flushing is very small, chloride gradually becomes the dominant anion and groundwater is high in total dissolved solids.

There are also significant differences in the age of groundwater in the upper and lower zones. According to Freeze & Cherry (1979), in some sedimentary basins, groundwater in the upper zone may be years or tens of years old, whereas in deep basins, an age of hundreds or thousands of years is common. Saline, chloride rich water in the deep zone is usually very old, the ages may vary from thousands to millions of years. Such deep aquifers usually contain non-renewable fossil water.

The HCO_3^- content in groundwater is mostly derived from soil zone CO_2 and from the dissolution of calcite and dolomite, both present in rocks in large quantities. The origin of sulphate in groundwater depends on the presence of soluble sulphate bearing minerals (gypsum $CaSO_4 . 2H_2O$ and anhydrite $CaSO_4$). The high content of chloride in deep zones strongly depends on the time and space contact between groundwater and rocks rich in highly soluble chloride minerals of sedimentary origin, particularly halite NaCl and sylvite KCl.

A cation evolution sequence in the groundwater system similar to Chebotarev's sequence used for anions is difficult to identify because there is a large variation in the content of main cations. The presence of major cations (Ca^{2+}, Mg^{2+}, $Na^+ + K^+$) strongly depends on the solubility of minerals in groundwater and on the type, extent and velocity of the cation exchange processes. Moreover, Matthess (1982) defined the following geochemical zonation based on the characteristic cation:

$$Ca^{2+} \rightarrow Ca^{2+} + Mg^{2+} \rightarrow Na^+$$

Biological processes accelerate the extent and rate of geochemical processes and are particularly intensive near the ground in the soil-root-uppermost part of the unsaturated zone, where dissolved oxygen is usually available and serves for the respiration of organisms and the breakdown of organic matter. The biochemical processes affect a great capability of the soil to produce a large amount of inorganic and organic acids.

The formation of the groundwater chemical composition is a result of very complex geochemical and biological processes occurring in the soil-groundwater-rock system, whose description is not the objective of this article. However, these processes have to be carefully studied when groundwater quality changes and deterioration caused by intensive aquifer exploitation is observed.

3 NATURAL AND HUMAN IMPACT ON GROUNDWATER QUALITY

Groundwater quality (natural background) could be well known, when the extent of human impacts on groundwater is studied and assessed.

3.1 *Natural groundwater quality*

Groundwater quality in natural conditions is generally good with respect to its potability and use in agriculture and industry. However, in deep aquifers, aquifers adjacent to surface water bodies, or in low permeable rocks with a slow movement of groundwater and a long contact time, groundwater quality is often not suitable for the water supply or other particular uses. High concentrations of some constituents in natural groundwater could be hazardous for human health or not technically acceptable for use (incrustation or corrosion of wells and pipes).

3.1.1 *The impact of major constituents on groundwater quality*

The amount of total dissolved solids is a general indicator of groundwater suitability for drinking purposes and agriculture and industrial use. Water that contains more than 1 g/L of dissolved solids does not fulfil drinking water standards and could be corrosive to steel casing materials used in water well construction. When dissolved solids are high, water is also useless for irrigation and industrial purposes.

Among the major constituents, the origin of high contents of sodium, chloride and sulphate should be evaluated, because they degrade groundwater quality and make it unfit for drinking or other uses.

The highest concentration of sodium is found in groundwater in the vicinity of salt-bearing sediments and evaporates and sodium rich hydrolysates (argillites). According to Matthess (1982), the sodium content in groundwater in the Salado and Ruster formation (New Mexico, USA) reached 121 g/L. In the well located in the vicinity of sodium rich argillites, the content of Na^{+} in groundwater was 857 mg/L. However, usual sodium concentrations in groundwater are much lower (less than 20 mg/L).

Sources of high concentrations of chloride in groundwater (up to thousands of mg/L) are chloride-bearing sedimentary rocks, particularly evaporate deposits of marine and terrestrial origin and seawater intrusion affected coastal aquifers. Chloride waters are usually also high in sodium. However, chloride concentrations in natural groundwater are usually much lower. Groundwater contains mostly less than 100 mg/L Cl, which is the drinking water standard in many countries.

Sulphate in higher concentrations in natural groundwater is derived mainly from evaporates (gypsum, anhydride, potash salt deposits) and from metallic sulphide minerals. Drinking water standards limit permissible concentrations of sulphate in many countries to 250 mg/L. Drinking of high sulphate groundwater affects the gastrointestinal tract. Matthess (1982) stated that low or even zero sulphate concentrations are typical for groundwater in which microbiological reduction has been taking place.

3.1.2 *The impact of minor constituents on groundwater quality*

Natural groundwater quality is also frequently affected by the excessive content of minor constituents, particularly by iron, manganese, fluorine and iodine.

Iron content is common in groundwater. Drinking water standards in many countries tolerate an iron content within 0.3 mg/L. The amount of oxygen and pH control the form of iron in groundwater. Ferrous ions in great concentrations (1 to 10 mg/L and more) are present in reduced conditions only. In the presence of oxygen, ferrous ions (Fe^{2+}) are unstable and change to ferric ions (Fe^{3+}) and precipitate as ferric oxide and/or oxyhydroxides. The sudden change from ferrous to ferric ions occurs frequently during groundwater pumping. Groundwater aeration affects groundwater colour and leads to the incrustation of the well casing (particularly well screens) and water pipe distribution systems (especially in domestic water supplies). Special attention should be paid to methods of groundwater sampling, because ferric oxyhydroxides precipitate in the presence of air. Iron-bearing groundwaters also support the growth of iron bacteria. They may be introduced into production wells during drilling processes, through drilling fluids and their content frequently increases during pumping. Iron bacteria have a significant affect on well hydraulics.

Manganese concentration in groundwater is usually lower than iron. Chemical and biological processes leading to manganese precipitation are generally the same as in case of iron. However, manganese incrustations of a well construction and its surrounding natural rock materials are harder to remove than those from iron. Monitoring electrochemical corrosion and microbial presence and activity (particularly sulphate reducing bacteria) is desirable.

Fluoride content is usually lower than 1 mg/L in natural groundwater. Drinking water standards in many countries set a maximum limit of permissible fluoride concentrations of 1.5 mg/L.

Sources of fluoride in groundwater are fluoride-bearing minerals in igneous and metamorphic rocks, resistant sedimentary rocks, micas and volcanic ash. Fluoride in excessive concentrations (above 4 mg/L) in drinking water is dangerous, because it causes mottling of tooth enamel (children) and skeletal effects (adults).

Iodine is very necessary for human health. Higher concentrations of iodine in groundwater are recorded particularly in coastal aquifers and in the sediments of marine origin. However, groundwater use as a source of drinking water in many high mountain regions shows an iodine deficiency (less than 1 μg/L), which causes goitre.

3.1.3 *The impact of trace elements on groundwater quality*

Trace elements occur in natural groundwater in a very low concentration. However, several trace constituents in a high content are observed in acid groundwater in the vicinity of ore-bearing deposits. Copper, zinc, cadmium, mercury, lead, arsenic and aluminium should be mentioned, among others. The occurrence of arsenic in drinking groundwater is well-known as a serious social-health problem in several countries in Asia and in several parts of South and North America. Arsenic release into groundwater due to oxidation of arsenic-rich sulphide ores (particularly the dissolution of arsenic arsenopyrite) could also be derived from volcanic rocks and geothermal systems (Fetter 1993). High concentrations of arsenic (5 mg/L) had been reported from shallow vulnerable aquifers developed in the alluvial deposits of the Ganges-Brahmaputra-Meghna river system in West Bengal in India and Bangladesh. Groundwater is used in these regions as a source of drinking water for tens of million people. Long-term use of drinking water with arsenic concentrations highly exceeding WHO recommended limits 10 μg/L can lead to serious health problems (cancer, skin disorders).

A boron content of more than 1 mg/L in groundwater used for irrigation (often in arid and semi-arid areas in the vicinity of evaporate) is harmful for plant growth.

3.2 *Human impact on groundwater quality*

Groundwater quality deterioration and pollution as a consequence of human impact on the groundwater system is a serious worldwide social, economic and environmental problem. Groundwater pollution is understood to be a process whereby, due to human impacts, water gradually or suddenly changes its natural physical, chemical or biological composition and ceases to meet the criteria and standards set for drinking water, irrigation and other purposes. If it contains hazardous or toxic compounds, it becomes dangerous for people and water and terrestrial ecosystems.

Groundwater quality degradation or pollution owing to intensive use of aquifers is recorded. Most often, groundwater quality is affected by saltwater intrusion caused by excessive exploitation of coastal aquifers. The intrusion of poor quality water from shallow polluted aquifers to deeper aquifers or the upward influx of highly mineralised water from deep aquifers, both caused by the disturbance of the hydraulic gradient between groundwater bodies, and other examples of groundwater quality degradation by excessive pumping of groundwater, are described by Koussis *et al.* (this volume). There is no direct relation between intensive groundwater abstraction and pollution accidents. However, the lateral movement of pollutants along the flow path towards the depression cone of pumping wells is often observed.

Various criteria are used to classify groundwater pollution. The commonly used classification system based on the extent and source of pollution is used in the following description of pollution sources.

3.2.1 *Point pollution sources*

The most frequent point pollution sources with an impact on groundwater quality are industrial sites, mining areas and uncontrolled waste disposal sites. According to EEA (1995), the potential pollution of groundwater by point sources does not cover more than 1% of the European territory. However, point pollution sources mostly occur close to municipal areas or rural settlements and have serious impacts on the quality of public or domestic groundwater supplies. Oil products, heavy metals and various organic compounds are the most prominent pollutants of the groundwater system.

The impact of point pollution sources on groundwater quality mostly has a site-specific extent only. However, when pollution is not timely identified and the pollution plume reaches the groundwater table and moves through the saturated zone, groundwater pollution could be detected at a considerable distance (several hundred metres or even kilometres) from the pollution source. The pollution of public groundwater supplies due to the impact of point pollution sources located far from water supply wells is well known in several countries. In many cases, water supply systems have to be abandoned because groundwater pollution is irreversible.

a) *The impact of industrial effluents on groundwater quality*

Sources of industrial pollution are uncontrolled leaks from poorly designated and improperly located ponds, lagoons, pits, basins or ditches, which serve for disposal liquid or solid industrial wastes, many of them hazardous. Production of industrial wastes is enormous. The OECD (1993) estimates that the worldwide annual amount of industrial wastes is 2,100 million tons and about 338 million tons are hazardous wastes with a content of metallic compounds, halogenated solvents, cyanides, phenols and other toxic pollutants.

Metal plating techniques mostly produce acid wastes with hexavalent chromium, cadmium, lead, zinc and other metals, cyanides, phenols, oils, benzene, thiosulphate, etc. The tannery industry's wastes are rich in dissolved chloride, sulphide and chromium; the textile industry's wastes contain heavy metals, dyes and organochloride compounds; petrochemical and fat processing industries produce various kinds of oil wastes. The pulp and paper industry waste contains organic matter, chlorinated organic substances and toxins. Chemical and pharmaceutical industries generate a wide range of hazardous organic and inorganic wastes that are extremely dangerous for groundwater quality.

Petroleum products (gasoline, petroleum, kerosene, diesel fuel, oil, lubricants and emulsions) belong among the broadest point pollution sources of groundwater. Petroleum spillages are reported particularly during the operation and handling (oil refineries, oil processing plants, filling stations), storage and transport of oil. The taste and odour of groundwater polluted by petroleum products make water unfit for drinking purposes before the product concentration becomes a health risk (aromatic and oliphatic hydrocarbons in a concentration lower than 10 μg/L and in drinking water treated with chlorine already in a concentration of 1 μg/L).

Migration and transformation processes of petroleum products in the unsaturated and saturated zone depend on the nature of the rock-groundwater system and physical and chemical properties and the quantity of the petroleum product discharged. Oil hydrocarbons in a gaseous or liquid stage are generally well detectable by remote sensing and other monitoring systems still in the unsaturated zone.

Gravity, viscosity, density, solubility, sorption ability, microbial processes and emulsification control the degree and rate of vertical penetration and lateral spreading of oil hydrocarbons in the groundwater system. Viscosity and density affect the degree and rate of oil product penetration and migrations in the subsurface. Light nonaqueous phase liquids (LNAPL), whose viscosity is higher and density lower than water (gasoline, kerosene, diesel-fuel, light oils), flow on the immiscible phase on the groundwater table when they reach the saturated zone. Dense nonaqueous phase liquids (DNAPL), with viscosity lower and density higher than water (asphalt, heavy oils, lubricants), penetrate the deeper parts of the aquifer and accumulate at its bottom. Lateral migration of LNAPL is controlled by the groundwater flow gradient. DNAPL movement follows the slope of the underlying impermeable strata of the aquifer. Selective sorption occurs during the percolation of petroleum products in the groundwater system (non-polar compounds, for example, fall in the sequence olefin → aromatics → cyclanes → alkanes). The study of sorption processes helps to predict the duration and intensity of oil hydrocarbon pollution and the time necessary for the remediation of polluted groundwater. Evaporation of petroleum products is another important indicator of the underground extent of groundwater pollution. Petroleum products in a gaseous phase spread in the unsaturated zone by diffusion and are well detectable by monitoring the soil. Microbial processes have a significant influence on the rate of degradation of petroleum products. Biodegradation processes are much more intensive in aerobic conditions, however they also occur in an anaerobic environment. Free oxygen, nutrients, carbon and temperature conditions control the rate of microbial processes. Various micro-organisms accelerate the breakdown of oil hydrocarbons and are used in the remediation of polluted groundwater.

b) *The impact of mining on groundwater quality*

Uncontrolled leakages of wastewater from ore washing and dressing facilities, coal preparation and other post-extraction processing of mining material, uncontrolled leakages from tailings, piles, evaporation ponds and further disposal sites of extracted mine materials and excessive pumping of mine waters, produce a wide range of impacts on groundwater quality.

Mine waters are mostly very acid (pH $\leq$ 4) and contain various kinds of mobile soluble anion complexes of heavy metals released by the oxidation processes of metal sulphides, particularly present in ore bearing deposits. Iron sulphide (pyrite) is frequently present in coal, which in an air-water environment oxidises and forms ferrous sulphate and sulphuric acid. Aluminium, manganese, calcium, sodium, which along with iron and sulphate are potential pollutants of groundwater, are produced in high concentrations by the secondary reaction of sulphuric acid. Brine discharge from salt potash and iron mines contains a high content of dissolved salts. Groundwater saline pollution by oil brines is usual in all oil fields.

Lowering of groundwater levels in mining areas by water abstraction creates suitable conditions for oxidation processes in unsaturated zones, whose intensity controls temperature, pH and Eh. Dissolved oxygen in percolation water drifts down to the groundwater table and supports chemical interactions in the groundwater-rock system.

Groundwater pumping in mines located in coastal areas disturbs the equilibrium between the freshwater-saline water interface, which leads to uncontrolled saline intrusion and aquifer salinization.

c) *The impact of radioactive wastes on groundwater quality*

Wastewater leakage from uranium mines, land disposal of radioactive wastes and tailings from milling are the most risky activities with respect to the potential impact on groundwater quality.

In situ leach mining technology of uranium sedimentary deposits is based on the injection of a leach solution (acid or alkaline) into the uranium formation and the removal of the enriched solution by pumping production wells. During the leach mining process, groundwater is polluted by chemicals present in the leaching solution and by radionuclides and must be treated. A serious impact occurs when polluted groundwater flows outside of the mining field through the hydraulic barrier formed by the production wells. Such groundwater pollution has been recorded in the Czech Republic, where, in the past, uranium reached sediments were mining by the acid leaching system. A large cretaceous aquifer used for several municipal water supplies was polluted by uranium and sulphates.

Uranium mining produces a large amount of wastes with a content of uranium, thorium, radium and radon gas. Released ^{226}Ra poses a risk to the aquatic system because of the long time of half-life and high radiation. Reactor waste with a high content of acid water rich in nitrates, aluminium and a wide range of radionuclides of different half-life and type of radiation also poses a significant potential threat to groundwater quality.

d) *The impact of uncontrolled waste disposal sites on groundwater quality*

Uncontrolled waste disposal sites, often with an unknown composition of disposed wastes, improperly located (in permeable sediments above shallow aquifers, in the proximity of surface water bodies), poorly constructed (without liners and other techniques to prevent uncontrolled leaks) and without operation of water, gas and leakage monitoring systems, are significant potential pollution sources of groundwater. The impact of landfills on groundwater quality studied by Knoll (1969) demonstrated a significant long-term increase in organic substances, sulphate and chlorine in the aquifer below the landfill after 40 years of refuse disposal. Organochlorine compounds and other organic solvents and residues, heavy metals, pigments, oil hydrocarbons, phenols and other hazardous substances could be present in an elevated concentration in leakages from abandoned or poorly constructed waste disposal sites. Cases of groundwater quality deterioration by uncontrolled pollutant migration under landfills are well known in many parts of the world. Groundwater abstraction sites located in the range of influence of disposal sites should be protected against release pollutants spreading in a groundwater flow field, by the hydraulic barrier located between the pollution source and the water abstraction place.

3.2.2 *Multipoint pollution of groundwater*

Urban and rural areas are significant sources of multipoint and heterogeneous pollution of groundwater. Insufficient handling, treatment and management of household wastes and wastewater, industrial effluents, uncontrolled waste disposal sites, rain and melt waters and salt water intrusion in coastal areas are the main sources of multipoint pollution of municipal groundwater (Jackson *et al*. 1980, Matthess 1982, Vrba 1985, RIVM 1992).

Dissolved organic compounds (chloride, sulphate, nutrients –nitrogen and phosphate), pathogenic micro-organisms' (bacteria and viruses) trace elements and various types of household surfactants present in urban wastewater are the most potential threats to groundwater quality. However, uncontrolled leaks from urban industrial and commercial facilities are also significant potential sources of groundwater pollution by heavy metals, organic chemicals, immiscible organic fluids and phenols.

In rural areas the most frequent sources of groundwater pollution are unsewered sanitation systems (latrines, cesspools or septic tanks), which may cause degradation of groundwater quality in domestic and public water supply wells. Pathogenic micro-organisms, chloride, nitrate, ammonia, household detergents and disinfectants are the main pollutants of groundwater in rural settlements and are the cause of infections, illnesses and the mortality of the rural population in many developing countries.

3.2.3 *Non-point pollution sources*

The only widely occurring groundwater pollutant that is reported with respect to non-point or diffuse pollution is nitrate originating from organic and inorganic fertilisers applied to arable land. However, the pollution of groundwater by pesticides and groundwater quality degradation as a consequence of irrigation return flow are also recognised as a serious diffuse pollution problem in a large number of countries.

a) *The impact of fertilisers on groundwater quality*

The intensification of agricultural production with the aim of assuring the food supply and increasing *per capita* food consumption for expanding, and in several regions of the world, malnourished populations creates a serious impact on the quality of water resources. In Europe and the USA, groundwater quality is much more affected by diffuse nitrate pollution than in other continents. In several areas with intensive farming activities, nitrate levels in shallow aquifers are above 50 mg/L. According to Stanners & Bourdeau (1995), the nitrate content reaches the European Union target value (25 mg/L) in 87%, and the drinking water standard (50 mg/L) in 22% of shallow aquifers under agricultural soil in Europe. In the USA, particularly in the mid-continental Corn Belt, where nearly 60% of the nitrogen fertilisers of the whole United States are applied, high aquifer nitrate pollution (150 mg/L NO_3-N) can be found in many regions (Hallberg 1989, Spalding & Exner 1991). An NO_3-N content of 40 to 60 mg/L is also reported in groundwater in several irrigated valleys in California and other irrigated areas of the USA (Keeney 1986). However, high contents of nitrate in shallow wells are mostly a consequence of poor well construction and the location of wells in the proximity of animal corrals and cattle feeding areas. A high nitrate content is observed mainly in shallow phreatic aquifers under well-drained thin and/or sandy soils.

Nitrate pollution of groundwater in rural areas in developing countries is mostly affected by point pollution sources. The quality of groundwater in public and domestic wells is affected by their poor construction, being located close to pollution sources (septic tanks, latrines, animal slurry dumps) or by excrements surrounding some water supply wells used as a watering place for animals. The high content of nitrate and coliform bacteria in groundwater in many rural wells can lead to serious health hazards.

Potassium and phosphate compounds are derived from fertilisers and liquid and solid animal wastes. Due to their lower solubility and mobility, absorption in clay minerals and use in the biological cycle, they accumulate in the soil and in the upper part of the unsaturated zone and their impact on groundwater quality is not usual.

However, groundwater phosphate pollution conditions may arise in agricultural regions with a large livestock concentration and a high manure production. The application of 300 kg/ha/yr and more phosphate may affect groundwater quality.

Metals, such as cadmium, copper, nickel, molybdenum and chromium derived from certain inorganic fertilisers accumulate in the soil and affect its fertility, but they are not recorded in elevated concentrations in groundwater.

Sustainable management of groundwater quality in agricultural areas requires keeping dynamic stability of the soil organic matter in which the nitrogen pool is substantially larger than nitrogen input through agricultural activities. The high priority task is the restriction of the processes that lead to the mineralization of organic nitrogen, as mineralised nitrogen (as soluble nitrate) is washed out from the soil-root zone into the groundwater system. The nitrogen and carbon balance is essential for gaining insight into the physical, chemical and biological processes that take place in the soil-unsaturated zone and which control the amount of nitrogen leached into the saturated zone. The perturbation of the organic carbon and nitrogen balance in soil particularly occurs when the traditional crop rotation is replaced by monocultures. The content of $N\text{-}NO_3$ is usually higher in the unsaturated zone than in the aquifer. Short-term cyclic changes in the nitrate content in groundwater depend mainly on seasonal climatic conditions during the year. The long-term increasing trend of the nitrate content in groundwater reflects the farming impact. Observation in many agricultural regions proved nitrate vertical zonality in the groundwater system. Monitoring nitrate distribution in the vertical profile of the unsaturated and saturated zone is important when preventive measures of groundwater protection and conditions of aquifer sustainable exploitation have to be defined.

Due to the great areal extent of diffuse nitrate pollution, applying subsurface clean-up techniques is ineffective. Control measures depend above all on the steps taken in the agricultural sector (selecting suitable crops, designating a sowing rotation system, selecting suitable kinds of fertilisers and determining how much, when and how they are applied, selecting suitable cultivation techniques, especially tillage). In the sphere of groundwater management, control measures can be focused on symptomatic actions only, not eliminating the causes of groundwater pollution.

There is no direct relation between intensive groundwater exploitation and groundwater diffuse pollution in agricultural regions. However, protecting groundwater public supplies leads to the consecutive reduction of human activities in protection zones established around abstraction wells. Crop and root crop farming should be limited and controlled, particularly in recharge and vulnerable areas of the groundwater supply source. The objective evaluation of farmers' interests and the allocation of benefits and costs between the agricultural and water sectors are the key factors in the strategy of effective utilisation of soil and water resources in the groundwater protection zones.

b) *The impact of pesticides on groundwater quality*

For several decades, the aquatic system has been exposed to the impact of various types of pesticides widely used in agriculture throughout the world. In Europe, according to the model calculation of RIVM-the Netherlands (Boesten & van der Linden 1991), the pesticide standard of drinking water is exceeded more than ten times in 20% to 25% of the agricultural areas in EU countries. In the USA, systematic monitoring of pesticides in groundwater has been reported since the beginning of the 1980s. Aldicarb, atrazine, ethylene dibromide and other kinds of pesticides have been found in many wells in California, Florida, Hawaii and other states of the USA.

Groundwater vulnerability to pesticides is high in shallow phreatic aquifers below coarse or light textured sandy soil with high moisture and a low content of organic matter. Pesticides are mainly organic compounds and can be divided into ionic and non-ionic groups (Vrba & Romijn 1986). Ionic pesticides are mostly more soluble than non-ionic ones and in solution may be fixed in the soil or the unsaturated zone by soil organisms and by absorption to organic matter or clay. A special future of microbial metabolism and biodegradation has to be kept in mind in the process of broken-down pesticides. There are differences in the persistence of various groups of pesticides in the soil. In general, the most resistant are toxic organochlorine insecticides, which were used without any limitations even in the 1950s. Priority should be given to rapidly degradable types of pesticides (predators, hormone stimulators, pheromones, etc.), using the synergic effects of the pesticide mixture and so reduce their potential adverse affect on groundwater quality.

c) *The impact of irrigation return flow on groundwater quality*

Groundwater quality deterioration of areal extent as a consequence of irrigation return flow is recognised in many countries, particularly in semi-arid and arid zones. The increase in the content of dissolved solids in groundwater occurs in areas with over-irrigated soil without relevant drainage, which leads to the groundwater level rising and to an increase in evapotranspiration. By repeated irrigation, leached salts from the soil are transported to the underlying aquifers and groundwater quality deteriorates. Irrigation by water rich in nutrients is a source of a high content of nitrate in groundwater aquifers below sandy soils. In arid areas, desert soils contain a high amount of natural salts, which are leached by irrigated water and penetrate and degrade the groundwater quality of shallow vulnerable aquifers.

3.2.4 *The impact of line pollution sources on groundwater quality*

Uncontrolled leaks of various pollutants during road and railway transport and from municipal and rural sewerage networks, oil and gas pipelines and polluted surface streams are the main potential line pollution sources of groundwater.

Polluted runoff water from road surfaces (oil hydrocarbons, various salts applied in several countries in the winter season), soil and groundwater acidification by transport emissions and particularly spills of various substances due to road accidents, can have an immediate effect on groundwater quality in areas where roads are crossing vulnerable areas of aquifers. In many countries, the law bans the transport of oil and other hazardous material on roads located in water supply protection zones. Spills of liquid chemicals transported by tankers and released by train accidents have similar consequences on groundwater quality.

Uncontrolled leaks of waste and ballast water from defective municipal and rural sewerage networks are risky for shallow phreatic aquifers frequently used as the drinking water supply source. Seepage losses of wastewater from channels discharging household liquid wastes from rural and urban settlements in less developed countries have similar impacts on groundwater quality. Microbial pathogens and synthetic surfactants are the most frequent pollutants of groundwater.

Accidental spills and uncontrolled leaks of petroleum products and liquid gas from buried pipelines are recorded in many countries and are a source of groundwater pollution by oil hydrocarbons, propane, butane and other petrochemicals.

3.2.5 *The impact of atmospheric pollution sources on groundwater quality*

Acid atmospheric emissions (sulphur dioxide: SO_2 and nitrogen oxides: NO_X) are transported hundreds of kilometres across countries and their chemically converted products (sulphuric and nitric acids) are potential sources of regional transboundary acidification of the soil and water bodies. Their influence on groundwater quality (lowering pH values, increasing the content of aluminium sulphates and heavy metals) has been recognised in several industrial regions in Europe (Holmberg 1987, EEA 1995).

4 GROUNDWATER QUALITY MONITORING

Groundwater quality monitoring plays an important role in the policy of groundwater protection and quality conservation and effectively supports sustainable groundwater quality management. It provides a valuable base for assessing the current state of and forecasting trends in groundwater quality and helps to clarify and analyse the extent of natural processes and human impacts on the groundwater system in time and space. Credible and accurate groundwater quality data should be available and readily accessible through data management systems to planners, regulators, decision- and policymakers and managers. The data should also help to increase active public participation in the process of groundwater quality protection.

Groundwater quality monitoring programmes operate at international and national levels (background monitoring) and on regional and local levels (specific monitoring). The objectives of each of the above programmes govern the design of monitoring networks, the construction of monitoring wells, the frequency and methods of measurement and sampling and the number of variables to be measured and analysed. Regional and local monitoring networks should observe changes in groundwater quality owing to intensive exploitation.

Existing monitoring strategies tend to focus attention primarily on identifying and controlling the consequences of groundwater quality deterioration and not on the preventive protection of groundwater quality. An early warning monitoring strategy is therefore needed, which detects groundwater quality problems before massive groundwater quality degradation occurs. This strategy supports sustainable groundwater quality management and protection policies and helps to identify human impacts when they are still controllable.

Early warning monitoring, an integral part of groundwater quality monitoring programmes, is broad in nature, has different objectives, requires a progressive and gradual approach and covers both short-term and long-term policies. The early warning groundwater quality monitoring strategy supports:

- Evaluation of the chemical composition and evolution of natural groundwater.
- Identification of new groundwater pollution risks.
- Problem solution at a controllable and manageable stage.
- Decision-making, considering potential risks, conflicts and competitive factors between social and health implications, sustainable economic development and a groundwater quality protection activity.

Early warning groundwater quality monitoring also plays an important role in identifying changes in groundwater quality caused by intensive aquifer abstraction. Monitoring should be focused, among others, on the early detection of saltwater intrusion into coastal aquifers, the intrusion of poor quality surface water into adjacent aquifers, the penetration of contaminants into the groundwater system from point and non-point pollution sources and from irrigation return flow, the lateral movement of a pollution plume to the abstraction wells, the upward penetration of highly mineralised water from underlying aquifers into exploited superposed aquifers and on changes in the groundwater quality of public supplies.

Different approaches must be applied for early warning groundwater monitoring according to the specific characteristic of the groundwater system studied. Various monitoring methods that facilitate the early detection of changes in groundwater quality have to be implemented, mainly: remote sensing methods, soil gas surveys and deep profiling of the unsaturated zone and saturated aquifers through specially located and designed monitoring wells.

Groundwater quality early warning monitoring systems will alert managers about groundwater quality deterioration at an early stage, thus allowing them a sustainable operation and protection of the aquifer system. Early warning monitoring systems of public water supplies include production wells or springs and monitoring wells located in protection zones that usually cover vulnerable and recharge areas of the water supply source.

Early warning groundwater quality monitoring is not only technically demanding, but also a financially expensive process in terms of capital, installation, operation and maintenance costs. However, the implementation of a early warning groundwater monitoring strategy is many times less expensive than the costs related to aquifer remediation and investments needed to overcome social and ecological damages of groundwater pollution.

5 GROUNDWATER VULNERABILITY ASSESSMENT

Assessment of groundwater vulnerability based on relevant monitoring data is an important step in the evaluation of the impact of intensive aquifer exploitation on groundwater quality.

The concept of groundwater vulnerability is based on the assumption that: 1) all groundwater is vulnerable to various degrees to natural and human impacts; and 2) the physical environment provides some level of protection of the groundwater system. Vulnerability of groundwater is a relative, non-measurable, dimensionless property. The accuracy of vulnerability assessment depends particularly on the amount, quality and representativity of available data.

There are various definitions of groundwater vulnerability. However, many authors have considered vulnerability as an intrinsic property of a groundwater system that depends on the sensitivity (ability) of that system to cope with both natural and human impacts. Intrinsic (or natural) vulnerability depends solely on geological and hydrogeological attributes. The specific vulnerability of the groundwater system is mostly assessed in terms of the risk of the system becoming exposed to contaminant loading.

Groundwater intrinsic vulnerability attributes of primary importance are recharge (usually expressed as annual net recharge), soil (particularly texture, structure, thickness, and the content of organic matter and clay minerals), unsaturated zone (thickness, lithology, and vertical permeability), and saturated zone (permeability, hydraulic conductivity, and transmissivity).

The main parameter in the assessment of specific groundwater vulnerability is the attenuation capacity of the soil, unsaturated zone and saturated aquifer with respect to the properties of a particular contaminant or a group of contaminants.

When assessing groundwater vulnerability, different weights and rating may be assigned to the attributes, according to their importance for the vulnerability assessment. Weighting and rating methods developed by various authors usually give a high rating to the soil and unsaturated zone.

Vulnerability assessment mostly concerns the uppermost aquifers (first aquifer under the ground). Assessment of deeper aquifers is less frequent. Groundwater vulnerability is usually expressed and depicted on vulnerability maps. Vrba & Zaporozec (1994) give an overview of the methods of groundwater vulnerability assessment and mapping.

The assessment of specific vulnerability to pollution is particularly important in cases of shallow, phreatic and intensively exploited aquifers. The assessment of the vulnerability of deeper semi-confined or confined intensively exploited aquifers should concern changes in groundwater quality. Various isotopes (^{2}H, ^{3}H, ^{14}C, ^{18}O) and their multiple application should be used to assess changes in the age, origin and flow paths of the groundwater system, as important attributes of groundwater vulnerability. Groundwater level decline, base flow change and variations in the age and origin of groundwater will be important indicators of groundwater vulnerability to intensive exploitation.

Aquifers with a limited thickness and areal extent and low storage capacity are the most vulnerable to excessive pumping. In arid and semi-arid areas, the response of aquifers to intensive groundwater abstraction, which is a structural characteristic, could be much more significant than aquifer sensitivity to variable recharge. Such sensitivity, if combined with the risk of drought that affects the groundwater system and its *resistance* to drought, could be assessed, classified and mapped. It is a useful concept for planning water supply projects, since it indicates the reliability of the resource (Khouri 1993).

6 THE IMPACT OF THE INTENSIVE USE OF AQUIFERS ON GROUNDWATER QUALITY

To recognise and assess the response of aquifers to intensive exploitation, available background data about groundwater quality must be evaluated before aquifer abstraction is initiated. Such data should be compared against future changes in groundwater composition caused by pumping and interpreted in a compatible manner with groundwater level depletion or other aquifer hydraulic responses. However, such groundwater quality data are not always available or are scarce, because a relevant groundwater monitoring system was not established.

Recognition of the impact of intensive abstraction of aquifers is nearly always based on hydraulic phenomena. However, subtle changes in the groundwater chemical composition caused by pumping may often be observed before becoming evident from groundwater level decline. Therefore, groundwater quality monitoring should be implemented and targeted on the specific groundwater quality problem caused by intensive aquifer exploitation, land use changes, pollution impact or well failure. Specific chemical variables relevant to human impact should be identified and analysed. Well construction, sampling methods and frequency and the whole groundwater quality monitoring programme must be adapted with respect to various scenarios of groundwater quality degradation. In the following text, the effects of the intensive use of aquifers will be described and their consequences on groundwater quality evaluated.

6.1 *Seawater intrusion into coastal aquifers*

Seawater intrusion into coastal aquifers is the most frequent manifestation of groundwater quality deterioration caused by the intensive exploitation of groundwater resources. However, the risk of groundwater saline intrusion in coastal zones also depends on location of abstraction wells, technical aspects of well construction (well screen location) and depths and/or hydrogeological conditions (hydraulic gradient, groundwater flow direction, aquifer geometry and properties).

A significant proportion of the world's population (nearly 70%) lives in heavily urbanised coastal zones, where water resource requirements of drinking water supplies, industry, agriculture and tourism are extremely high. However, sustainable water resource management is often lacking or underestimated. Mismanagement of coastal aquifers leads to a disturbance of the equilibrium between the fresh, brackish and salt water interface and consequently to the spreading of groundwater salinization into inland regions far from the coast.

6.1.1 *Saltwater-freshwater interface*

The saltwater-freshwater interface in coastal unconfined aquifers under hydrostatic conditions has been expressed by Ghyben (1888) and Herzberg (1901) by the equation

$$hs = \frac{df}{ds - df} \; hf \qquad (1)$$

where *hs* = distance below mean sea level at the freshwater/saltwater interface; *hf* = distance from the groundwater table to mean sea level; *ds* = density of saltwater (1.025 g/cm^3); *df* = density of freshwater (1 g/cm^3).

When the groundwater table is lowered 1 m, then the relationship between hs and hf is

$$hs = \frac{1}{1.025 - 1} \; hf = 40 \; hf \qquad (2)$$

and the saltwater interface will move 40 m upwards. Thus the freshwater-saltwater system is very sensitive to groundwater withdrawal, even if the lowering of the groundwater head is small.

However, when the groundwater head goes up and allows discharge to the sea and there are conditions of steady-state groundwater flow into the sea, Hubbert's concept (1940), based on groundwater flow net, should be applied.

A numerical technique for calculating the transient position of the saltwater front in a confined coastal aquifer considering dispersion was presented by Pinder & Cooper (1970).

The salt-fresh water interface is not a sharp contact, but mixing brackish water forms a transitional zone between both water bodies. The thickness of the diffuse zone of brackish water determines the exact position of the interface, particularly when the diffusion zone, controlled by the dispersion of the aquifer system, is extensive. Tidal fluctuations, stream flow changes and the volume of groundwater flow towards the seashore affect the equilibrium of the fresh-salt water interface in coastal zones. However, their influence is much lower than the human impact caused by groundwater intensive exploitation.

Seawater chemical composition significantly affects groundwater quality when the state of equilibrium between these two water bodies of different densities is disturbed.

The salt content of seawater is approximately 35 g/kg and varies in coastal seawaters. The average concentration of major dissolved solids in seawater is shown in Table 1. Chloride, a major component of seawater, is primarily an indicator of seawater intrusion into the coastal groundwater system (when there are no other sources of saline contamination). The seawater pH is determined by the system $CaCO_3$-CO_2-H_2O and is close to 8 (Matthess 1982). Revelle (1941) proposed the chloride-bicarbonate ratio as a good indicator to recognise seawater intrusion into coastal aquifers. A low calcium-magnesium ratio may also help to identify saltwater intrusion into coastal groundwater.

Table 1. Average composition of seawater in mg/kg, after Culkin (1965) and Turekian (1969).

Ion	Concentration (mg/kg)
Cl	19,350 – 19,400
Na	10,760 – 10,800
SO_4	2,712
Mg	1,290 – 1,295
Ca	410 – 413
K	387 – 392
Br	67
B	4 – 4.45
F	1 – 1.3

6.1.2 *Some examples of saline intrusion into coastal aquifers*

Serious groundwater quality problems caused by seawater intrusion are reported by many regions throughout the world.

In China, particularly in the coastal zones of Shandong, Hebei and Liaoning provinces, seawater intrusion causes significant aquifer quality deterioration. Thousands of hectares of fertile farmland was damaged and many pumping wells became useless.

In the cities of Longkow and Laizhou, in Shandong province, the total saline water intrusion area reached 360 km^2 and the groundwater table drop reached 10 m.b.s.l. More than 2,000 wells were abandoned because excessive penetration of saline water occurred or groundwater table declined below the bottom of the wells (Xueyu & Longcang 1992). In shallow aquifers developed along the coastal zone of Laizhou bay, the seawater intrusion increased up to 40 km^2/yr during the 1980s. Groundwater salinity grew from 0.45 g/L to 5.25 g/L in one decade and the average chloride content reached 3–4 g/L (Jichun *et al.* 1992). Groundwater salinization led to shortages of groundwater resources used for drinking and irrigation purposes and significantly affected province economy, particularly agricultural production.

Excessive groundwater pumping has also caused aquifer salinization in the littoral area of the North plain of Hebei province. The groundwater chemical composition changed from the HCO_3-Ca type to the Cl-Na type in one decade (Dehong & Zhengzhou 1992).

Numerous places of lateral seawater intrusion into coastal aquifers are also reported in Vietnam. At Ho Chi Minh city, for example, the withdrawal of groundwater was 80,000 m^3/d at the beginning of the 1960s and saline intrusion was not identified. However, when the pumping rate reached 160,000 m^3/d and the water table was lowered to 4–11 m (end of the 1960s), seawater intrusion extended over 75% of the city area.

Seawater intrusion is also reported in several countries in Central and South America.

Aquifer overexploitation has resulted in saline intrusion for distances up to 25 km from the coast in Northern Mexico (Foster 1991). Many production wells polluted by saline water were abandoned and agricultural production was significantly affected.

Excessive exploitation of shallow aquifers developed in fluvial deposits in the northern part of the coast plateau of Falcón state (Venezuela) has led to groundwater tables falling up to 22.5 m.b.s.l. Related lateral penetration of saline water has resulted in the sharp increase of TDS (3,500 mg/L), chloride (1,500 mg/L) and Cl/HCO_3 ratio from 1 to 15 (Alvarado 1991).

Lateral seawater intrusion caused by excessive pumping of the coastal Puelche aquifer in the Mar del Plata municipal area (Argentina) is reflected in the high salinity (20 g/L) of groundwater. The saltwater coastline extended 75 m/yr into the continent as a result of mismanagement of the groundwater supply system and 15 water supply wells have had to be abandoned (Auge 1991).

Groundwater quality deterioration as a result of intrusion of saltwater is also a serious problem in many European regions, especially along the Mediterranean, Baltic and Black Sea coasts.

Seawater intrusion into coastal karstic aquifers has been recorded in the Apulia peninsula in Southern Italy (Grassi & Tadolini 1991). More than 80,000 wells were drilled in an anisotropic carbonate formation with markedly different rates of permeability, variable yield (5–50 L/s) and drawdown (1–130 m). Due to excessive groundwater pumping, saline intrusion has extended from the coastal belt to the whole territory of the southern part of the peninsula and groundwater salinity reached 10–15 g/L.

Guimerá & Candela (1991) described increases of up to 40% of seawater presence in the coastal detrital Maresme aquifer located north of Barcelona (Spain) from 1989 to 1999. Electrical conductivity reached more than 40,000 µS/cm in this small, highly vulnerable aquifer. The extension and intensity of seawater intrusion is related to industrial and municipal uncontrolled groundwater abstraction.

The consequences of the excessive exploitation of the Baix Llobregat aquifers (Spain) have been studied by means of environmental isotope techniques (Iríbar *et al.* 1991). These small and highly permeable alluvial and delta aquifers are exploited for urban water supply and irrigation (since the late 19th century) and industry (since 1920). Environmental isotope studies combined with chloride data have documented that seawater intrusion occurred as a result of excessive pumping affecting the groundwater quality of 30% of the area of delta aquifers.

6.1.3 *The sustainable management of coastal groundwater resources*

Several methods should be applied to control seawater intrusion and to manage coastal groundwater resource quality in a sustainable manner. The most effective and economically reasonable method of groundwater quality improvement is the reduction of the groundwater pumping rate, based on the calculation of the maximum permissible drawdown of the groundwater table, which still excludes seawater intrusion. Other methods, such as the construction of underground barriers, the artificial recharge of aquifers through infiltration wells, channels or galleries, hydraulic barriers caused by pumping from wells located parallel to the coastline, or the relocation of pumping wells, are less effective and financially more demanding techniques in the improvement of groundwater quality.

Implementing all the above-mentioned methods of groundwater quality restoration is a costly, long-term and technically demanding process and often water supply wells have to be abandoned temporarily or permanently.

The design of the early warning groundwater monitoring system, located between the coast and groundwater supply wells, supports the detection of saline intrusion into coastal aquifers when problem solution is still at a controllable and manageable stage. The design of monitoring wells has to make it possible to obtain water samples within particular depth intervals in an aquifer. The best method of identifying the fresh-salt water interface is electrical logging carried out in monitoring wells.

6.2 *The impact of the surface water-groundwater interface on groundwater quality*

Many shallow alluvial aquifers are hydraulically and hydrologically connected with surface water bodies. Hydraulic gradients between surface water and groundwater control the possibility of bank infiltration of surface water to the adjacent aquifers and *vice versa*. In natural conditions, surface water flow comes from a mixture of surface runoff and groundwater inflow. Stream flow response to specific precipitation events reflects short- and long-term seasonal fluctuations and changes in the hydraulic head of surface water and groundwater bodies. During long dry periods, surface flow depends almost exclusively on groundwater. Under such so-called base flow conditions, the water quality in the stream reflects the quality of the underlying aquifers.

Uncontrolled abstraction of shallow aquifers in the vicinity of the surface water body disturbs the natural surface water-groundwater interface and creates conditions, when the depression zone reaches the stream and surface water is induced into the aquifer. The transformation of gaining stream to losing stream provoked by the change in the hydraulic gradient may have serious environmental, social and economic consequences, particularly when surface water is polluted. However, the penetration of polluted surface water into underlying aquifers may occur far from the pollution source, where the river is a losing stream and the conditions of surface water infiltration are set in. A similar hydraulic situation occurs when, in gaining stream, groundwater is polluted far from the place of discharge into the surface water body. Surface waters chemically and biologically purify when they penetrate into fluvial deposits. However, due to the low attenuation capacity of fluvial materials (mostly gravels and sands) and the short resident time of groundwater, high permeable alluvial deposits are usually unable to retain or remove some specific pollutants and exploited aquifers become long-term polluted.

Surface water pollution through the discharge of a phreatic glacial aquifer contaminated by hexavalent chromium, cadmium and copper in Long Island, New York (USA) was described by Ku (1980). The source of pollution is metal plating waste disposed in waste basins which penetrated through the unsaturated zone into the saturated aquifer. From there, the pollution plume (1,310 m long, 300 m wide and 21 m thick) moved a distance of 1,300 m along the flow path towards the local creek where a part seeps into the stream and the remainder flows down gradient beneath the stream. The calculated groundwater velocity was approximately 168 m/yr. A detailed hydrogeological and hydrochemical investigation, sampling of vertical aquifer profile and the implementation of a two-dimensional groundwater mass transport model indicated that, with complete cessation of all pollutant discharges, it would take 7 to 11 years for the plume, whose upper surface is less than 3 m below the water table, to move out of the polluted area and discharge in a surface stream or migrate under the creek. According to the model, chromium acts as a conservative ion. Analysed core samples of aquifer material indicated an average concentration of chromium of 7.5 mg/kg and of cadmium of 1.1 mg/kg. The adsorption occurred on hydrous iron oxide coatings of the aquifer sandy material.

6.3 *The downward and upward influx of poor quality groundwater from superposed and underlying aquifers into an exploited aquifer*

The impact of the downward or upward influx of groundwater from shallow and deep aquifers on the exploited aquifer owing to the disturbance of the hydraulic gradient is reflected in the change in quality of pumping groundwater. For shallow groundwater is typical pollution. Higher mineralization and an elevated temperature are typical for deep groundwater.

Shallow aquifers are mostly phreatic, vulnerable to human impact and therefore groundwater quality is often degraded. The most typical pollutants are nitrate in agricultural areas and oil hydrocarbons, chlorinated hydrocarbons and other organic chemicals and heavy metals in industrial and municipal areas. Pollutant transport in the groundwater system is a complicated process, which particularly depends on rock media properties (granular, fractured, karstic). In granular media, dispersion of contaminant salts, affected by aquifer heterogeneity and anisotropy, hydraulic conductivity and the distance of pollutant migration, mainly control the solute transport. Spatial distribution, types and aperture of the fissures control solute transport in fractured media. However, fissured rocks should also have primary porosity (sandstones). Solute transport in these double porosity rocks should be carefully studied, because water in fissures is not usually in equilibrium with water in the pores of the rock matrix. In addition, the degree of diffusion varies. Matrix diffusion is much more important in fissured porous rocks, while in opened large fissures pollutant transport occurred without diffusion. Secondary mineral coatings on the fissures surface and on the adjacent porous matrix also significantly affect the solute transport process. Oxides or carbonates, which coat the fractures, may modify the fracture diffusion process because they create a zone of different reactive properties, porosities and diffusion compared with the adjacent porous matrix. As a result of big differences between fracture and matrix water velocities, the chemical equilibrium of groundwater in fractured rock media is usually not attained.

Pollutants of groundwater have a different density, viscosity and solubility and therefore immiscible displacement processes and multiphase flow prevail in solute transport in the groundwater system. Mobility and transport rates of pollutants and their attenuation in the groundwater system are also affected by various physical (dispersion, filtration and rate of gas movement), chemical (dissolution, hydrolysis, precipitation, adsorption, ion exchange, oxidation, reduction) and microbial (metabolism, cell synthesis, respiration) processes. The intensity of such processes depends very much on the properties of a particular contaminant (especially on its reactivity) and on the groundwater composition. A comprehensive investigation is therefore needed to clarify and assess hydrogeological and hydrochemical conditions and define sustainable management of groundwater quality of the exploited aquifer affected by downward influx of poor quality water from shallow aquifer.

Groundwater from deeper aquifers is not usually polluted. However, it is mostly more mineralised and of a higher temperature. Their chemical equilibrium is disturbed when mixture of deep water with water from an exploited aquifer occurs. According to the low of mass action, water tends to achieve a new equilibrium. However, changes in hydraulic and physical (temperature, pressure) conditions occurring in the exploited aquifer make it impossible to attain a new chemical equilibrium.

The solubility of minerals depends on the space and time contact of groundwater as it moves along its flow paths in the aquifer system. The physical, chemical and biological processes described above affect groundwater composition and quality. The chemical type of water and rate of mineralization reflect the rock medium composition in which groundwater moves. The volume of deep groundwater discharged into the exploited aquifer affects the formation of the chemical composition of abstracted groundwater. There are all kinds of possible scenarios when groundwater from an exploited aquifer mixes with groundwater from an underlying aquifer: groundwater quality improves, deteriorates or will have a similar quality.

The task of exploited aquifer groundwater management is to minimise the impact of poor quality water from superposed and underlying aquifers on the exploited aquifer.

The following case studies describe the relation between exploited aquifers and groundwater quality in superposed and underlying aquifers.

Travi & Faye (1991) studied hydrological and hydrochemical conditions of the downward influx of groundwater with high fluoride concentrations from Eocene aquifers in Western Senegal. The authors linked the origin of fluoride with the phosphatic root zone with a high content of fluoride, magnesium and sodium. Measurements of piezometric levels, combined with geochemical and isotope studies and F-diffusion modelling, demonstrated that fluoride mineralization and contamination of exploited Palaeocene aquifers occur by percolation from the upper level Eocene aquifers through the phosphatic roof zone. However, the upward influx of groundwater with an elevated content of boron from a deep Maastrichtian aquifer into superposed Palaeocene aquifers has also been confirmed by geochemical and isotopic studies. Research revealed that groundwater in Palaeocene aquifers is always in the saturated and over saturated stage with respect to calcite and dolomite, and Ca^{2+} and Mg^{2+} activities are not modified. The calculation of the chemical equilibrium based on the extreme value of ionic strength showed fluoride contents ranging between 3–4 mg/L. The fluoride mineralization will be lower in the unconfined part of the aquifer because of the influence of dilution by precipitation water in the rainy season.

The upward influx of poor quality groundwater into the shallow aquifer owing to large groundwater decline in the south-eastern part of the Hebei plain in China was described by Xiulan *et al.* (1992). The drawdown of the groundwater level by intensive pumping reached 20–30 m and extended to an area of 10,000 km^2. Groundwater quality dramatically decreases, because the deep aquifer contains water with a high concentration of fluorine. The groundwater with a fluorine content over 2 mg/L (up to 8 mg/L) covers 17,000 km^2. Another problem is high alkalinity of deep water used for irrigation. Alkaline water affected both crop growth and soil structure and the decrease in the crop yield is reported over a large agricultural area.

6.4 *Groundwater quality degradation by lateral movement of the pollution plume*

The lateral movement of various kinds of pollutants owing to intensive aquifer exploitation with successive impact on groundwater quality is registered in many countries. Therefore, the general protection of groundwater resources and comprehensive protection of water supply systems should be an integral part of water protection policy.

The general protection of groundwater resources calls for: 1) intensification, listing and control of the existing and potential pollution sources; 2) establishment and operation of a groundwater quality monitoring system; 3) determination and implementation of protective measures assisted by a relevant legislation; and 4) determination of the aquifer safe yield to sustain groundwater quality and to control pollutants spreading in the aquifer.

Comprehensive protection of groundwater supply systems should be based on the delineation of protection zones (I and II degree) and the establishment of a specific management plan of groundwater resource quality and land use activities in the protection zones. Determining the maximum rate of the withdrawal of water supply wells, controlling groundwater levels, the extent of the depression cone and calculating the delay time, are important attributes of groundwater protection and quality conservation.

However, groundwater quality protection against pollution migration due to intensive aquifer exploitation is always a very complex task. Complex investigation, mapping, monitoring and modelling of climatic, geological and hydrogeological conditions and the study of pollution transport and transformation processes in the groundwater system, with respect to pollution origin and properties are needed to identify the groundwater pollution risk and to specify the threats to which the groundwater system is exposed.

The following examples of pollution of the groundwater supply system of two big European cities by lateral movement of chlorinated hydrocarbons and oil hydrocarbons are given.

Beretta *et al.* (1992) described the excessive exploitation of aquifers in the Milan urban area in Italy, where a decrease in the groundwater level of about 15 m has been recorded in the last 40 years. The regional extent of the lowering groundwater table affected infiltration from surface streams into the shallow aquifer and leakage from this aquifer into the hydraulically connected underlying aquifer. The depression cone of a number of water supply wells reached about 100 km^2. Many point pollution sources are present in the highly industrialised Milan area. The movement of halogenated hydrocarbons, identified as the main pollutants, towards the depression cone in the town centre has been registered. About 30% of existing wells are polluted and their exploitation must be stopped. An improvement in groundwater quality in the Milan urban area indicates the need for a sustainable water resource management. The reduction of groundwater pumping from the two principal aquifers, the redistribution of abstraction wells and the exploitation of a partially confined deeper aquifer, at present not much used, have been proposed.

The lateral movement of hydrocarbons and the pollution of the groundwater supply system of Bratislava, the capital city of Slovakia, are described by Elek (1980). The refinery has been located in the upstream part of the Danube island at a distance of 3 km from Bratislava waterworks (the upstream part of the same island), designated with a capacity of 1.2 m^3/s. The thickness of quaternary deposits on the Danube island area varies between 11–50 m. The average hydraulic conductivity of the shallow phreatic aquifer is 5.4×10^{-3} m/s. The groundwater table is 5 to 7 m below the ground. The first signs of groundwater pollution by oil hydrocarbons were observed at a distance of 2 km from the refinery after 10 years of operation. After 15 years of refinery operation, the dissolved and emulsified petroleum derivatives have polluted groundwater over 20 km^3. The thickness of the oil layer below the pollution source attained several metres. The content of oil hydrocarbons in water supply wells reached 0.45 mg/L. After field investigation, monitoring and implementation of mathematical simulation models describing pollutant transport and transformation processes in the polluted aquifer, the hydraulic barrier perpendicular to the direction of groundwater flow has been chosen, with the scope to protect the water supply system and at the same time to remediate polluted groundwater. The hydraulic barrier formed by 22 wells located in two rows is about 1 km long, A total rate of pumping was between 500–700 L/s. The calculated groundwater drawdown by pumping created a coherent hydraulic barrier as a result of interaction between the individual drawdown cones. The total depression cone of pumping wells extended over a 1.5 km^2 area in the direction of natural groundwater flow. During the first two years of remediation pumping, approximately 30,000 m^3 of petroleum were removed from the surface of the groundwater table, the annual rate later stabilised at 10,000 m^3. In connection with two physically and chemically different fluids (water and oil) and groundwater level fluctuation, the relevant construction of remediation wells of the hydraulic barrier has been designated.

6.5 *The impact of intensive aquifer exploitation on groundwater quality in arid and semi-arid regions*

Special attention should be paid to groundwater quality deterioration in arid and semi-arid regions. Groundwater quality in such regions is very sensitive and vulnerable to both natural and human impacts. However, it is usually difficult to differentiate the magnitude of the above-mentioned impacts.

The amount and mode of natural recharge from precipitation and from *wadi* flow, indirect recharge through irrigation return flow and decline in groundwater table related to aquifer intensive exploitation, control groundwater quality in desert and semi-desert regions. Natural recharge in these regions is generally low, since the potential evaporation significantly exceeds the rates of precipitation. According to Khouri (1989), many aquifers are independent of present arid climatic conditions (precipitation < 100 mm/yr), because recent recharge is negligible. Aquifers were recharged during the humid episodes of the Quaternary period.

In natural conditions, the vulnerability of groundwater in arid regions is usually low, because the amount of percolating water is small and downward migration of potential contaminants in the unsaturated zone is slow. Their long-term residence time in the soil-unsaturated zone supports contaminant attenuation before they attain the groundwater table. However, the soil's function as a natural protective filter on the retardation and attenuation of contaminants is not significant in arid zones, since the soil layer is usually poorly developed.

Curiously, the decline in groundwater levels due to pumping also has a positive influence on groundwater quality. The larger distance from the ground to the groundwater table prolongs contaminant movement downwards and creates conditions for contaminant attenuation in the unsaturated zone. In arid climatic conditions, the uncontrolled surface spill of some organic chemicals might be released to the atmosphere due to their volatility and their potential impact on groundwater quality is reduced.

Groundwater quality deterioration has become a serious problem in arid lands under irrigated agriculture. The return flow of irrigated water in arid climatic conditions forms a significant indirect recharge (Llamas *et al.* 1992) and contributes to the growing salinity of the soil and degradates the groundwater quality of underlying shallow aquifers.

7 CONCLUSIONS

Aquifer intensive exploitation affects groundwater quality on various levels. Integrated policy and management of groundwater resource sustainable development is therefore a very urgent task in the process of groundwater quality protection. The objective of the policy of groundwater quality protection should be: 1) based on relevant legislation; 2) integrated with the remaining components of the hydrogeological cycle; 3) coordinated with land use activities and industrial development; 4) based on the value of groundwater resources, their availability, vulnerability and water supply requirements; 5) linked to social policy; and 6) attentive to cultural and historical traditions of the society. The assessment of competitive factors and their hierarchical screening is needed in the policy and management of groundwater resource quality, with the aim of finding a balance between sustainable groundwater development, environmentally sound groundwater protection, economic development and potential social and health implications.

REFERENCES

Alvarado, J. 1991. Sobreexplotación del acuífero en Venezuela. In *Proceedings of IAH XXIII International Congress, Aquifer Overexploitation*. Canary Islands, Spain: 407–410.

Auge, M.P. 1991. Sobreexplotación del acuífero Puelche en la Plata, Argentina. In *Proceedings of IAH XXIII International Congress, Aquifer Overexploitation*. Canary Islands, Spain: 411–416.

Beretta, G.P.; Pagotto, A.; Vandini, R. & Zanni, S. 1992. Aquifer overexploitation in the Po plain: Hydrogeological, geotechnical and hydrochemical aspects. *IAH Selected Papers on Aquifer Overexploitation*. Vol. 3, Ver. H. Heise: 115–130.

Boesten, J.J.T.I. & van der Linden, A.M.A. 1991. Modeling the influence of sorption and transformation on pesticide leaching and persistence. *Journal of Environmental quality* (20): 425–435.

Chebotarev, I.I. 1955. Metamorphism of Natural Waters in the Crust of Weathering. *Geochim. Cosmochim. Acta*, 8. London, New York: 23–48, 137–170, 198–212.

Culkin, F. 1965. The mayor constituents of sea water. In J.P. Riley & G. Skirrow (*eds.). Chemical Oceanography,* Vol. 1. Academic Press, London: 121–161.

Dehong, S. & Zhengzhou, Y. 1992. The effect of groundwater development on ecological environment. In *Proceedings of Int. Work*. Beijing, China: 10–14. Seismological Press.

Domenico, P.A. 1972. *Concepts and models in groundwater hydrology*. Mc Graw-Hill, New York.

EEA 1995. *Europe's Environment*. European Environment Agency. Copenhagen: 676 pp.

Elek, T. 1980. Hydrocarbon contamination of an alluvial aquifer beneath an oil refinery, Czechoslovakia. In *Aquifer contamination and protection,* UNESCO-IHP, Paris: 318–328.

Fetter, C.W. 1993. *Contaminant hydrogeology*. MacMillan, New York: 458 pp.

Foster, S.S.D. 1991. Unsustainable development and irrational exploitation of groundwater resources in developing nations –an overview. In *Proceedings of IAH XXIII International Congress, Aquifer Overexploitation.* Canary Islands, Spain: 385–401.

Freeze, R.A. & Cherry, J.A. 1979. *Groundwater*. Prentice-Hall Inc.: 604 pp.

Ghyben, W.B. 1888. Nota in verband met de voorgenomen putboring nabij Amsterdam. *Tijdschrift van Let Koninklijk*. Ins. van Ing.

Grassi, D. & Tadolini, T. 1991. The effects of karstic groundwater overdrafting in Apulia (Southern Italy). In *Proceedings of IAH XXIII International Congress, Aquifer Overexploitation*. Canary Islands, Spain: 523–526.

Guimerá, J. & Candela, L. 1991. Quality variability of groundwater resources in the Maresme coastal aquifer, Barcelona, Spain. In *Proceedings of IAH XXIII Inter-*

national Congress, Aquifer Overexploitation. Canary Islands, Spain: 520–530.

Hallberg, G.R. 1989. Nitrate and Groundwater in the United States. In R.F. Foll (ed.). *Nitrogen, Management and Groundwater Protection*. Elsevier, Rotterdam: 35.

Herzberg, A. 1901. Die Wasserversorgung einiger Nordseebader. *J. Gasbeleucht. Wasserversorg*. 44: 478–487.

Holmberg, M. 1987. Assessing Aquifer Sensitivity to Acid deposition. In *Proceeding and Information No. 38 Vulnerability of soil and groundwater pollutants*. TNO, RIVM, The Hague: 373–380.

Hubbert, M.K. 1940. The theory of groundwater motion *J. Geol*. 48: 785–994.

Iríbar, V.; Manzano, M. & Custodio, E. 1991. Evaluation of overexploitation effects in the Baix Llobregat aquifers by means of environmental isotope techniques. In *Proceedings of IAH XXIII International Congress, Aquifer Overexploitation*. Canary Islands, Spain: 535–538.

Jackson, R.E. *et al.* 1980. *Aquifer Contamination and Protection*. UNESCO IHP Programme: 440 pp.

Jichun, W.; Yuqun, X. & Zhihui, Z. 1992. Groundwater development and sea water intrusion in Laizhou Bay. In *Proceedings of Int. Work*. Beijing, China: 178–184. Seismological Press.

Keeney, D.R. 1986. Sources of Nitrate to Groundwater. *Critical Review in Environ. Control* 16: 257–335.

Khouri, J. 1989. Development in hydrological mapping of the Arab region: A contribution to hydrogeological mapping in arid zones. *Mem. of the International Symposium on Hydrogeological. Maps as Tools for Economic and Social Development*, Hanover, Germany, May 30–June 2: 358–368.

Khouri, J. 1993. Impacts of intensive development of deep groundwater in the great basins of SSO and Arab regions. *Sahara and Sahel Observatory (SSO) Publ*., Paris, France: 101 pp.

Knoll, K.H. 1969. Hygienissche Bedeutung Natürlicher Selbstreinigungsvorgänge für die Grundwasser Beschaffenheit in Bereich von Abfalldeponien. *Müll Abfall*: 35–41.

Ku, H. 1980. Groundwater Contamination by Metal-Plating Wastes, Long Island, New York, USA. In *Aquifer Contamination and Protection*, UNESCO-IHP: 310–317.

Llamas, R.; Back, W. & Margat, J. 1992. Groundwater use: Equilibrium between social benefits and potential environmental costs. *Applied Hydrogeology* 2/92: 3–14.

Matthess, G. 1982. *The properties of groundwater*. John Wiley, New York: 406 pp.

OECD 1993. *Environmental Data Compendium 1993*. Organisation for Economic Cooperation and Development, Paris.

Pinder, G.F. & Cooper, H.H. 1970. A numerical technique for calculating the transient position of the saltwater front. *Water resources res*. 6: 875–882.

Revelle, R. 1941. Criteria for recognition of sea water in ground water. *Am. Geophys. Union Trans.,* Vol. 22: 593–597.

RIVM 1992. *The environment in Europe: A global perspective*. Report no. 481505001: 119 pp.

Spalding, R.F. & Exner, M.E. 1991. Nitrate Contamination in the Contiguous United States. In *Nitrate Contamination*, NATO ASI Series G, Vol. 30: 13–48.

Stanners, D. & Bourdeau, P. 1995. *Europe's Environment*. European Environment Agency, Copenhagen: 676 pp.

Travi, Y. & Faye, A. 1991. Fluoride in Palaeocene aquifer in Senegal: an example of contamination of a confined aquifer by its roof zone, aggravated by an intensive exploitation. In *Proceedings of IAH XXIII International Congress, Aquifer Overexploitation*. Canary Islands, Spain: 171–174.

Turekian, K.K 1969. The oceans, streams, and atmosphere. In K.H. Wedepohl (ed.). *Handbook of Geochemistry,* Vol. 1. Berlin, Heidelberg, New York, Springer: 297–323.

Vrba, J. 1985. Impact of domestic and industrial wastes and agricultural activities on groundwater quality. In *Memories of the 18th Congress. Hydrogeology in the Service of Man*. Vol. XVIII, Part I: 91–117.

Vrba, J. & Romijn, E. 1986. *Impacts of agricultural activities on groundwater*. Int. cont. of hydrog. 5, Ver. H. Heise: 332.

Vrba, J. & Zaporozec, A. 1994. *Guidebook on mapping groundwater vulnerability*. Inter. contr. to hydrog. 16, Ver. H. Heise: 131.

Xiulan, Z.; Ningsheng, Ch. & Yizhong, Z. 1992. Research on the effect of development of deep groundwater on the environment. In *Proceedings of Int. Work*., Beijing, China: 97–102. Seismological Press.

Xueyu, L. & Longcang, S. 1992. Aquifer overexploitation and environmental effects. In *Proceedings of Int. Work*., Beijing, China: 6–10. Seismological Press.